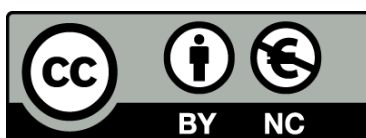




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Study of transition metal carbide catalysts of group 5 in the RWGS reaction

Arturo Javier Pajares Rojas



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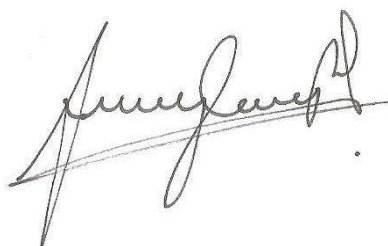
Study of transition metal carbide catalysts of group 5 in the RWGS reaction

Memòria presentada per optar al grau de doctor per
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Programa de doctorat en Nanociències

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SUMMARY

Nowadays there is a growing interest in the capture and utilization of CO₂ because of the increase of its concentration in the atmosphere. Captured CO₂ can be recycled through different processes to obtain several value-added products, such as fuels. Current processes for the production of synthetic fuel and of some other products use syngas, a mixture of CO and H₂ of varying composition, as feedstock. Syngas can be obtained by the catalytic reduction of CO₂ to CO using an excess of H₂ through the reverse water gas shift (RWGS) reaction. The RWGS reaction is endothermic and to reach appropriate conversion values, needs high temperature and the presence of a catalyst. Suitable catalysts should present not only high activity and selectivity, but also a good stability and low cost. In this context, transition metal carbides (TMCs) have been proposed as a good alternative to conventional catalysts to be used in the RWGS reaction. Theoretical and experimental investigations have shown that molybdenum carbide presents good catalytic behavior in the RWGS reaction. However, very few investigations about the use of TMCs of group 5 as catalysts in this reaction have been reported.

The main objective of this work is the study of the CO₂ reduction to CO under RWGS conditions over catalysts based on transition metal carbides of group 5 (G5TMC=VC, NbC and TaC). Additionally, some of these materials have been tested as catalysts in the methanol steam reforming (MSR). The catalysts have been characterized before and after reaction by means of different techniques, such as, X-ray diffraction, N₂ adsorption-desorption isotherms, Raman spectroscopy, X-ray photoelectron spectroscopy, H₂-temperature programmed reduction, scanning and transmission electron microscopy, and precession electron diffraction. In addition, studies of CO₂ adsorption and reactivity have been carried out using thermogravimetry, calorimetry and in-situ diffuse reflectance infrared spectroscopy.

The preparation of bulk and, γ -Al₂O₃-, TiO₂-, SBA-15-, SiO₂-, CeO₂-, ZrO₂- and activated carbon-supported catalysts, based on G5TMC has been performed avoiding the use of carburizing methods. A sol-gel method using 4,5-

dicyanoimidazole as carbon source, metal chloride and alkoxide as metal precursors, and different thermal treatments has been developed. The use of metal alkoxides resulted in the preparation of bulk G5TMCs with smaller crystallite size compared to that obtained when metal chloride was used. Moreover, for metal alkoxide precursors, a decrease of the crystallite size of G5TMC was observed when the 4,5-dicyanoimidazole/metal precursor molar ratio was increased. An increase of the temperature of treatment led to a higher crystallite size of the G5TMCs. For supported vanadium carbide catalysts, VC_x with different crystallite sizes were obtained as a function of the support and/or method of preparation used.

The catalysts were tested under RWGS conditions, $CO_2/H_2=1/3$ in the 573-873 K range. The catalysts based on vanadium carbide were active and highly CO selective, reaching values of CO selectivity near to 100% above 773 K. The samples based on niobium carbide and tantalum carbide were inactive under the experimental conditions used.

For bulk vanadium carbide catalysts, the coexistence of two different phases, VC (stoichiometric), and V_8C_7 (C deficient) was determined. The presence of a higher amount of V_8C_7 phase was related with a smaller VC_x crystallite size and a higher CO_2 adsorption energy. The catalyst, which presented a higher presence of V_8C_7 , showed a better catalytic behavior in all the temperature range studied.

The experimental results obtained in this work have been interpreted in the light of theoretical studies performed in the group of Prof. Illas (University of Barcelona) in a frame of a collaborative research. The dissociative adsorption of CO_2 to $CO+O$ over G5TMC is proposed; a subsequent surface oxy-carbide species formation and CO release would take place. The presence of C vacancies in vanadium carbide catalysts allows the reactants to absorb more strongly, lowering the energy barrier for both H_2 and CO_2 dissociation steps. VC-based catalysts with smaller VC_x crystallite size, showed lower activation energy in the RWGS reaction under the conditions used.

Supported vanadium carbide catalysts produced a higher amount of CO per mol of V than the corresponding bulk catalyst. VC/Al_2O_3 , VC/SiO_2 and VC/AC ,

which had the smallest crystallite sizes of VC_x phase showed the best catalytic behavior in the RWGS reaction.

Some catalysts have been tested in the RWGS during 4 days, showing a high stability under the reaction conditions used.

Finally, several bulk and supported G5TMC catalysts were tested under MSR conditions (CH₃OH/H₂O=1/1, 573-723 K). CH₄ was the main product found when vanadium carbide catalysts were used; this is related with the methanol decomposition. On the other hand, for niobium carbide and tantalum carbide catalysts, HCHO was the main product, which could be formed via methanol dehydrogenation. After MSR catalytic tests, the characterization of used catalysts revealed a high S_{BET} reduction and the presence of abundant carbon deposits, which is associated with the high deactivation of the catalysts observed under the reaction conditions used.

RESUMEN

El aumento de la concentración de CO_2 en la atmósfera en los últimos años ha provocado un gran interés en los aspectos relacionados con su captura y posterior utilización. Una vez capturado el CO_2 , este se podría utilizar como fuente de carbono y por tanto reciclar a través de diferentes procesos para obtener diversos productos de interés, como combustibles. Los procesos mejor establecidos actualmente para la producción de combustibles sintéticos y otros productos de valor añadido, utilizan como fuente de partida el gas de síntesis, una mezcla de CO e H_2 de composición variable. El gas de síntesis puede obtenerse mediante la reducción catalítica del CO_2 a CO , usando un exceso de H_2 , a través de la reacción inversa de desplazamiento de agua (*RWGS por sus siglas en inglés*). Esta reacción es endotérmica y necesita temperaturas elevadas para alcanzar valores de conversión adecuados en presencia de un catalizador. Los catalizadores necesarios para llevarla a cabo deben presentar una actividad y selectividad elevada, pero también gran estabilidad y evidentemente ser de bajo costo. En este contexto, los carburos de metales de transición (CMT) podrían ser una alternativa a los catalizadores convencionales para su utilización en la reacción de RWGS. En los últimos años se han reportado estudios experimentales y teóricos mostrando las capacidades catalíticas en la RWGS de catalizadores basados en carburo de molibdeno. Sin embargo, hasta el momento, apenas se han estudiado en este proceso catalizadores basados en CMT del grupo 5 (CMTG5=VC, NbC y TaC).

El principal objetivo de este trabajo es el estudio de catalizadores basados en CMTG5 (VC, NbC and TaC) en la reducción selectiva de CO_2 a CO bajo condiciones de RWGS. Adicionalmente, algunos de estos materiales se han probado como catalizadores en el reformado de metanol con vapor (*MSR por sus siglas en inglés*). Los catalizadores se han caracterizado adecuadamente antes y después de su uso en reacción mediante una diversidad de técnicas físico-químicas como, difracción de rayos X, isoterma de adsorción-desorción de N_2 , espectroscopia Raman, espectroscopia fotoelectrónica de rayos X, reducción a temperatura programada con H_2 , microscopia electrónica de barrido

y de transmisión y difracción electrónica en modo precesión. Asimismo, se han llevado a cabo estudios de adsorción y reactividad de CO₂ mediante termogravimetría, calorimetría y espectroscopia infrarroja en modo reflectancia difusa *in situ*.

La preparación de los catalizadores basados en CMTG5, máscicos y utilizando diferentes soportes (γ -Al₂O₃, TiO₂, SBA-15, SiO₂, CeO₂, ZrO₂ y carbón activo (AC)), se ha realizado evitando los procesos convencionales de carburización. A tal efecto, se ha desarrollado un método sol-gel, usando 4,5-dicyanoimidazole como fuente de carbono, el correspondiente cloruro o alcóxido como precursores metálicos y diversos tratamientos térmicos. El uso de un alcóxido metálico como precursor conllevó la preparación de CMTG5 con un tamaño de cristalito más pequeño que el obtenido cuando se utilizó el correspondiente cloruro. Además, se observó una disminución del tamaño de cristalito de los CMTG5 cuando se incrementó la relación molar 4,5-dicyanoimidazole/alcóxido metálico. Un incremento de la temperatura de tratamiento resultó también en un aumento del tamaño de cristalito de los CMTG5. En los catalizadores soportados de carburo de vanadio, se obtuvieron diferentes tamaños de cristalito de la fase VC_x soportada en función del soporte y/o el método de preparación utilizado.

Se han ensayado los diferentes materiales bajo condiciones de RWGS, CO₂/H₂=1/3 en el rango de 573-873 K. Los catalizadores basados en carburo de vanadio fueron activos y altamente selectivos a CO alcanzando valores cercanos al 100% a partir de 773 K. Los materiales basados en carburo de niobio y carburo de tántalo fueron inactivos bajo las condiciones experimentales usadas.

En los catalizadores de carburo de vanadio másico se pudo determinar la coexistencia de dos fases, una estequiométrica VC, y otra deficiente en C, V₈C₇. La presencia de una mayor cantidad de la fase V₈C₇ se relaciona con el menor tamaño de cristalito y se refleja en una mayor energía de adsorción de CO₂. El catalizador que presentó mayor presencia de la fase V₈C₇ mostró el mejor comportamiento catalítico en todo el rango de temperatura estudiado.

Los resultados experimentales obtenidos en este trabajo se han podido interpretar adecuadamente en base a estudios teóricos llevados a cabo en el

grupo del Prof. F. Illas (Universidad de Barcelona) en el marco de una colaboración de investigación. Se propone que tiene lugar una adsorción disociativa de CO_2 a $\text{CO} + \text{O}$ sobre los CMTG5, con la posterior formación de especies oxi-carburo superficiales y la liberación de CO . La existencia de vacantes de C en los catalizadores basados en carburo de vanadio permite que los reactantes se adsorban más fuertemente, reduciendo la barrera energética de disociación de H_2 y CO_2 . Estos resultados se manifiestan en el mejor comportamiento catalítico de los catalizadores basados en VC_x con menor tamaño de cristalito, que presentan las menores energías de activación para la reacción de RWGS bajo las condiciones estudiadas.

Todos los catalizadores soportados de carburo de vanadio produjeron una mayor cantidad de CO por mol de V que el catalizador másico correspondiente. Los catalizadores $\text{VC}/\text{Al}_2\text{O}_3$, VC/SiO_2 y VC/AC , que presentaron los menores tamaños de cristalito de la fase VC_x mostraron el mejor comportamiento catalítico.

Algunos catalizadores se ensayaron en la RWGS durante 4 días, mostrando una elevada estabilidad bajo las condiciones de reacción utilizadas.

Finalmente, diversos catalizadores másicos y soportados de CMTG5 se ensayaron bajo condiciones de MSR, $\text{CH}_3\text{OH}/\text{H}_2\text{O}=1/1$ en el rango de 573-723 K, obteniéndose diferentes productos. Con los catalizadores de carburo de vanadio se obtuvo como producto mayoritario CH_4 , el cual se asocia con la descomposición de metanol. Por otra parte, con los catalizadores de carburo de niobio y carburo de tántalo, se obtuvo mayoritariamente HCHO , que se formaría vía la deshidrogenación de metanol. La caracterización de los catalizadores usados reveló una gran reducción del área superficial S_{BET} y la presencia de abundantes depósitos carbonosos, lo que se asocia con la elevada desactivación observada bajo las condiciones de reacción utilizadas.

Study of transition metal carbides catalysts of group 5 in the RWGS reaction

Contents

Chapter 1: Introduction.....	15
1.1. CO ₂ current scenery: emission and utilization.....	17
1.2. The reverse water gas shift (RWGS) reaction.....	21
1.3. Transition metal carbides (TMCs).....	26
1.3.1. TMCs in the RWGS reaction.....	29
1.3.2. TMCs in the methanol steam reforming (MSR) reaction.....	32
1.4. Objectives and structure of the Thesis.....	36
1.5. References.....	37
Chapter 2: Experimental.....	51
2.1. Characterization techniques	53
2.1.1. Powder X-ray diffraction.....	53
2.1.2. N ₂ adsorption-desorption isotherms	54
2.1.3. Raman spectroscopy.....	55
2.1.4. H ₂ -Temperature programmed reduction.....	56
2.1.5. X-ray photoelectron spectroscopy.....	56
2.1.6. Thermogravimetry-differential scanning calorimetry.....	57
2.1.7. Scanning electron microscopy.....	59
2.1.8. Transmission electron microscopy and precession electron diffraction.....	59
2.1.9. Chemisorption of CO ₂ , CO and CO ₂ +H ₂ studied by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).....	61
2.1.10. Inductively-coupled plasma atomic emission spectrometry.....	63
2.2. Reaction systems.....	63
2.2.1. RWGS reaction system.....	63
2.2.2. MSR reaction system.....	67
2.3. References.....	69

Chapter 3: Transition metal carbides of group 5 in the RWGS reaction.....	73
3.1. Study of the preparation of bulk G5TMC catalysts.....	76
3.2. Bulk G5TMC catalysts in the RWGS reaction.....	89
3.2.1. Characterization of bulk G5TMC catalysts.....	89
3.2.2. Catalytic behavior of G5TMC catalysts in the RWGS reaction....	114
3.3. References	125
Chapter 4: Supported transition metal carbides of group 5 in the RWGS reaction.....	131
4.1. G5TMC/Al ₂ O ₃ catalysts.....	134
4.1.1. Preparation of G5TMC/Al ₂ O ₃ catalysts.....	134
4.1.2. Characterization of G5TMC/Al ₂ O ₃ catalysts.....	134
4.1.3. Catalytic behavior of G5TMC/Al ₂ O ₃ catalysts in the RWGS reaction.....	149
4.2. Supported VC catalysts.....	157
4.2.1. Preparation of supported VC catalysts.....	157
4.2.2. Characterization of supported VC catalysts.....	157
4.2.3. Catalytic behavior of supported VC catalysts in the RWGS reaction.....	172
4.3. References	181
Chapter 5: Transition metal carbides of group 5 in the MSR reaction.....	187
5.1. Preparation of catalysts.....	190
5.2. Characterization and catalytic behavior in the MSR reaction.....	190
5.2.1. Bulk G5TMC catalysts.....	190
5.2.2. Supported VC catalysts.....	205
5.3. References	220
Chapter 6: Conclusions.....	225
Annex I: Preparation and characterization of Mo_xC and WC_{1-x} catalysts...	231
Annex II: Preparation details of G5TMC used as catalysts in the RWGS and MSR reaction.....	235
Annex III: XPS profiles of supported VC used as catalysts in the RWGS reaction.....	237

CHAPTER 1

INTRODUCTION

1.1. CO₂ Current scenery: emission and utilization

Climate change is one of the most pressing challenges in the world nowadays. Greenhouse gases such as CO₂, NO_x, CH₄, CFCs and others have increased global temperature approximately 1°C since pre-industrial times [1]. Global atmospheric emissions and greenhouse gases concentrations are used to calculate the radiative forcing from 1979 [2,3]. Radiative forcing is defined as the change of solar radiation, which is trapped by the atmosphere and remains near Earth. When the radiative forcing is less than zero, a cooling effect occurs, but when is higher a warming effect is produced. Figure 1.1 shows the constant increase of this parameter along time in the last decades [2,3].

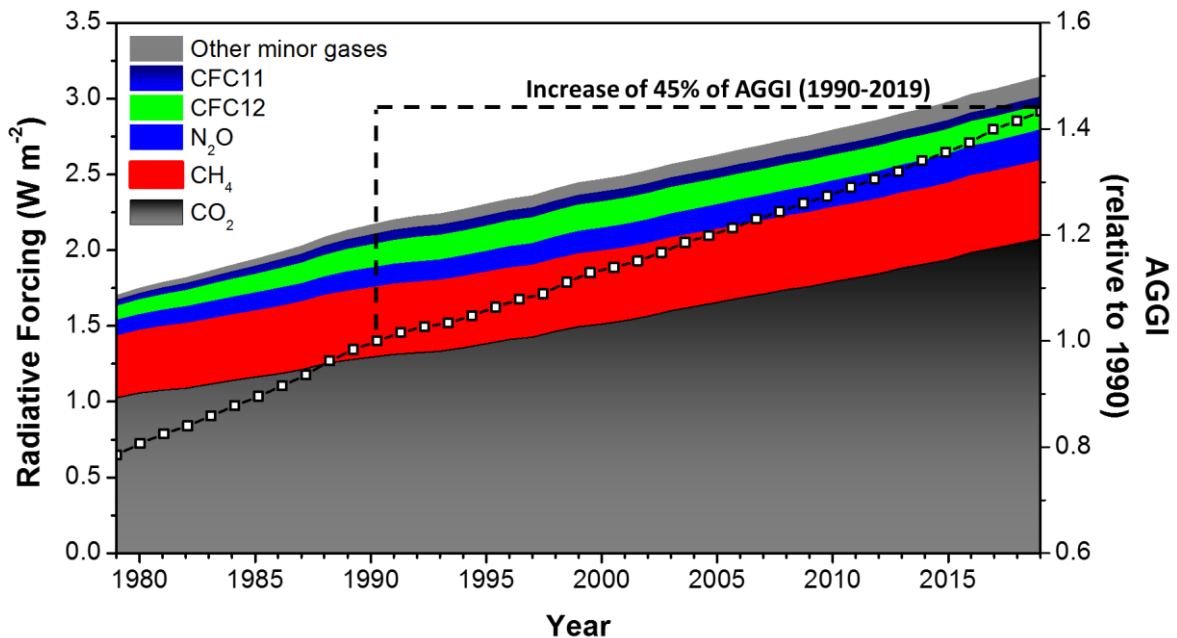


Figure 1.1. Contribution of all major human-produced greenhouse gases to radiative forcing (left vertical axis) and AGGI (right vertical axis). Data obtained from NOAA [2,5].

Figure 1.1 also shows the variation of the Annual Greenhouse Gas Index (AGGI), which is the value of the total radiative forcing normalized to the year 1990. As it can be seen, the total radiative forcing has increased a 45% since 1990 [4].

Nowadays, the increase of carbon dioxide emissions in the atmosphere contributes about a 65% to the radiative forcing (Figure 1.1).

Solar radiation passes largely unhindered through the atmosphere, heating the Earth's surface. In turn, energy is re-emitted as infrared, much of which is absorbed by CO₂ and water vapor in the atmosphere. Despite CO₂ is less abundant and less influential than water vapor as greenhouse gas, it absorbs wavelengths of radiation that water vapor does not. On the other hand, CO₂ absorbs less heat per molecule than other greenhouse gases, such as, CH₄ or N₂O. However, it is more abundant and it remains in the atmosphere for a longer time.

According to the State of the Climate report from the National Oceanic and Atmospheric Administration (NOAA) and the American Meteorological Society, the global growth rate of atmospheric carbon dioxide concentration was roughly 0.6 ppm per year in the 1960s. However, in the last decade (2010-2019) the growth rate was about 2.3 ppm per year. The global atmospheric carbon dioxide concentration was 410 ppm in 2019, a new record was achieved. That is an increase of 2.5 ppm from 2018 to 2019, similar to the increase of 2.4 ppm between 2017 to 2018 [2,5].

Furthermore, carbon dioxide is important in the Earth system, because it dissolves into the ocean lowering the ocean's pH. Since the Industrial Revolution, the pH of the oceans has dropped from 8.21 to 8.10. This drop in pH is called ocean acidification [5]; a drop of 0.1 may not seem much, but being the pH a logarithmic scale, a change of 0.1 is an increase of ~30% in [H⁺].

Carbon capture and sequestration (CCS) may offer a rapid response to the global challenge of reducing greenhouse gas emissions, by capturing CO₂ from power plants or industrial processes and subsequently underground injection into depleted oil and gas reservoirs or saline aquifers (via soil carbon sequestration techniques) (Figure 1.2). However, carbon capture and utilization (CCU) is receiving more interest from the scientific community because can result in the use of the captured CO₂ for the production of other substances or marketable products with higher economic value, either directly or after conversion (Figure 1.2).

For several decades, CO₂ has been used directly in food and drink industry as preservative or carbonating agent, respectively. Moreover, CO₂ has been used in oil and gas industry, in processes of crude oil (Enhanced Oil Recovery) and gas extraction (Enhanced Coal Bed Methane). Lastly, CO₂ has been considered to be used in geothermal fields for power generation (Enhanced Geothermal Systems) [6,7].

Current applications for the CO₂ conversion are the production of organic compounds such as urea, salicylic acid and organic carbonates; inorganic carbonates (MgCO₃, CaCO₃, etc.) are also produced. A potential and attractive route for the use of CO₂ is its fixation and subsequent conversion into valuable commodities or fuels. The use of CO₂ as oxidant (oxidative dehydrogenation) or for the production of syngas (H₂+CO), hydrocarbons and oxygenates compounds, as well as for the polycarbonates or polyurethanes production are promising applications.

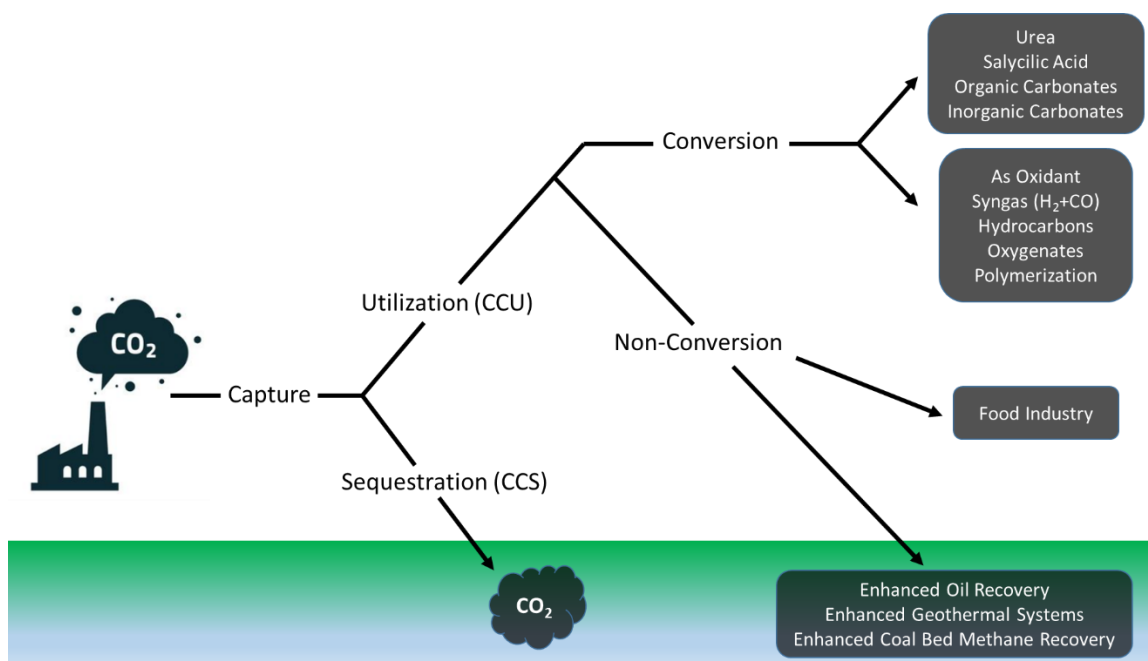


Figure 1.2. Possible routes for carbon dioxide capture and utilization [6-8].

CO₂ utilization technologies can convert CO₂ through chemical, biological, photo-assisted and electrochemical processes into carbon-based products [8-12].

An overview of the different possibilities and routes for CO₂ conversion to fuels is shown in Figure 1.3. Various products (methanol, DME, methane, formic acid, higher hydrocarbons, etc.) can be produced from CO₂ and H₂ [10].

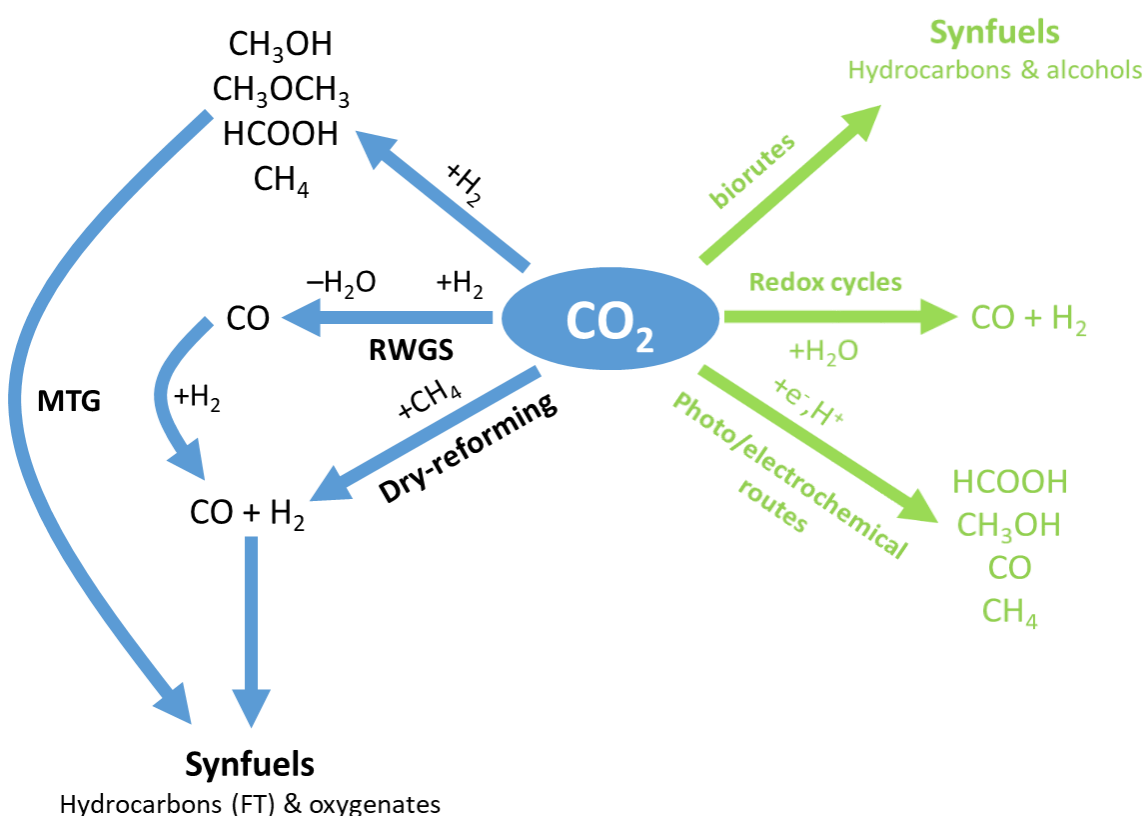


Figure 1.3. Possible routes for the CO₂ conversion to fuels.

Syngas can be obtained by the reduction of CO₂ to CO using an excess of H₂ through the reverse water gas shift (RWGS) reaction and after water separation: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$.

Although, syngas can be also produced by reaction of CO₂ and hydrocarbons, particularly CH₄ (so-called dry-reforming), it needs more severe reaction conditions and the use of a fossil fuel as raw material. The RWGS

reaction route using H₂ coming from a renewable source (water electrolysis) can be a good alternative for the syngas generation.

The syngas can be used as feedstock for its transformation into fuels such as methanol/DME, or hydrocarbons via Fischer-Tropsch. The subsequent transformation of methanol can result in gasoline (Methanol to gasoline, MTG); diesel can be obtained *via* hydrocracking of the alkanes produced in the FT process.

Other possibilities of CO₂ reduction include (i) bioroutes, for example the CO₂ reduction to CO under visible light has been reported using a hybrid enzyme-TiO₂ system [13,14], (ii) the use of metal oxides-based redox cycles and concentrated solar energy for the conversion of CO₂ and H₂O into H₂ and CO [15,16] and (iii) photo and electro-catalytic reduction of CO₂ [17-20]. However, these routes are still far in terms of application.

1.2. The reverse water gas shift (RWGS) reaction

The RWGS reaction is an equilibrium limited and endothermic reaction (eq. 1.1) [21].

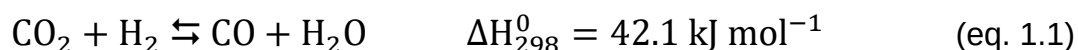


Figure 1.4 shows the CO₂ conversion plots in the temperature range of 373-1073 K at 0.1 MPa and using different CO₂/H₂ molar ratios (1/1, 1/2 and 1/3). CO₂ conversion enhances when the temperature increases and an excess of H₂ is used.

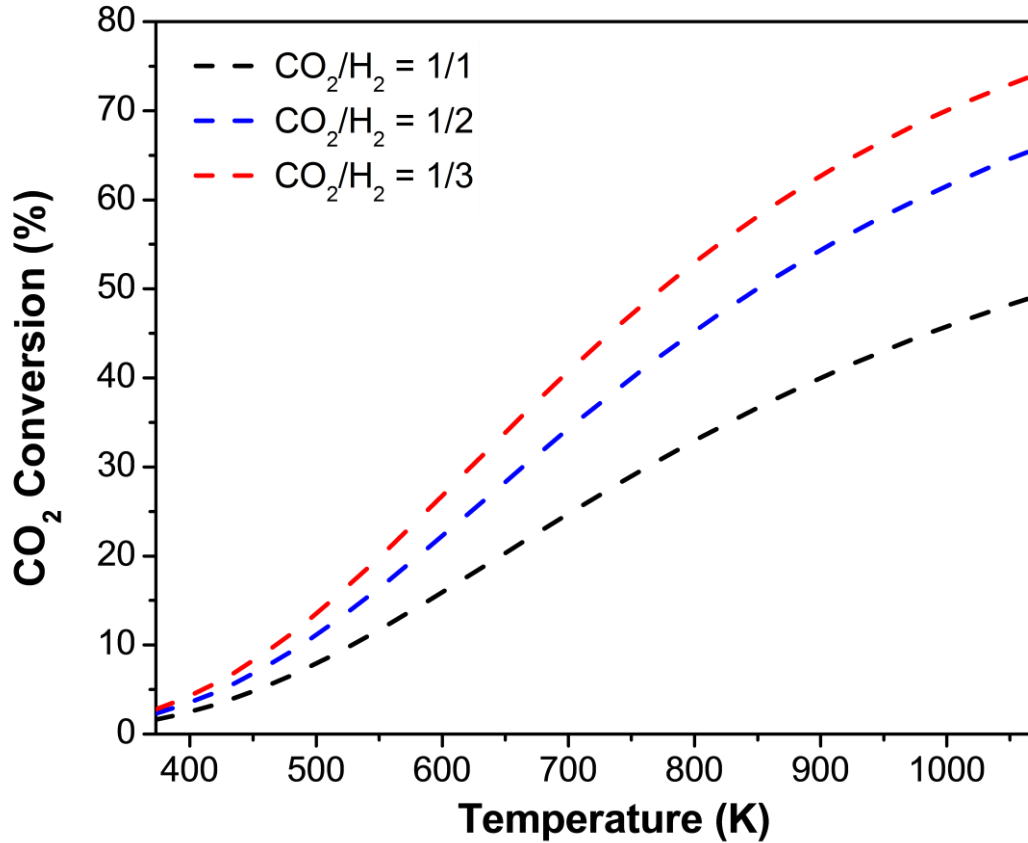


Figure 1.4. CO₂ equilibrium conversion in the RWGS reaction at different CO₂/H₂ molar ratios (1/1, 1/2 and 1/3), P=0.1 MPa and T=373-1073 K.

Under RWGS conditions, secondary reactions, such as methanation (eq. 1.2) and Sabatier (eq. 1.3) reactions can also take place.

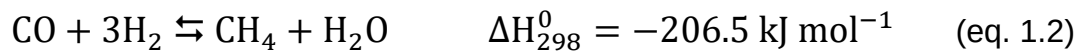


Figure 1.5 shows the equilibrium composition for a CO₂/H₂=1/3 molar ratio at 0.1 MPa and a temperature range of 373 to 1273 K. Methane formation is favored at low temperatures; at temperatures higher than 973 K only traces of CH₄ can be detected [21]. Moreover, it is important to mention that an increase in pressure favors the CH₄ formation.

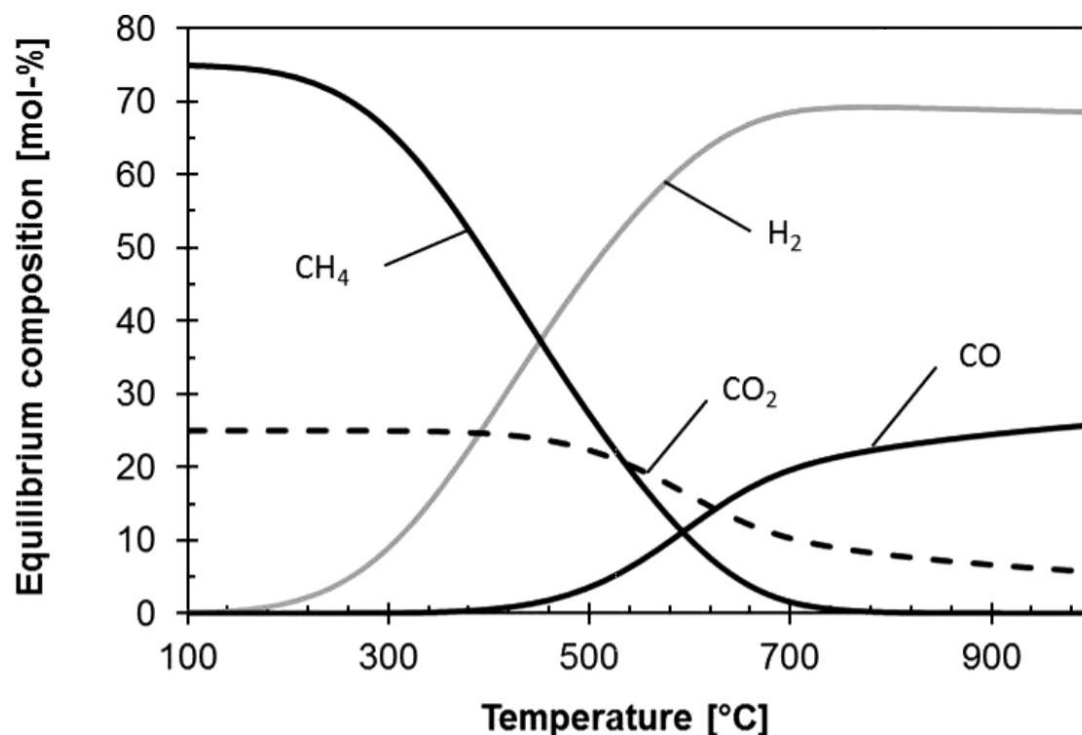


Figure 1.5. Equilibrium composition under RWGS conditions at 0.1 MPa and CO_2/H_2 molar ratio of 1/3. Taken from Ref 22.

Representative catalysts employed in the RWGS reaction are detailed in Table 1.1 [23,24]. Some of the catalysts listed are based on noble metals of group 9 and 10, such as Pt, Pd and Rh. Catalysts based on Cu, Co or Ni have also been studied due to their low cost and earth-abundance. However, the stability of this kind of materials is limited by deactivation. The excessive surface hydroxyl species formation caused by the large amount of water produced under reaction conditions favors sintering. Moreover, the presence of pollutants containing sulphur in the feedstock could transform the active sites by poisoning [23,25,26].

Table 1.1. Catalytic behavior of representative catalysts used in the RWGS reaction.

Catalyst	Temp. (K)	Pres. (MPa)	H₂:CO₂ ratio	CO₂ Conv. (%)	CO Selec. (%)	Ref.
Pd/Al ₂ O ₃	533	0.1	1:1	N/A	78	[27]
Pd/CeO ₂ /γ-Al ₂ O ₃	533	0.1	1:1	N/A	87	[27]
Pd/La ₂ O ₃ /γ-Al ₂ O ₃	533	0.1	1:1	N/A	70	[27]
Pt/TiO ₂	673	-	1.4:1	~30	N/A	[28]
Pt/Al ₂ O ₃	673	-	1.4:1	~30	N/A	[28]
PtCo/CeO ₂	573	0.1	3:1	3.3	71.0	[29]
PtCo/γ-Al ₂ O ₃	573	0.1	3:1	5.1	89.4	[29]
Pt-Co/MCF17	473 - 673	0.55	3:1	~5	~99	[30]
Rh/TiO ₂	543	2	1:1	7.9	14.5	[31]
Rh-Fe/TiO ₂	543	2	1:1	9.2	28.4	[31]
Rh/SiO ₂	473	5	3:1	0.52	88.1	[32]
Cu/Al ₂ O ₃	773	-	1:9	~60	N/A	[33]
Cu-Ni/γ-Al ₂ O ₃	873	0.1	1:1	28.7	79.7	[34]
Cu-Fe/SiO ₂	873	0.1	1:1	15	N/A	[35]
Cu/K/SiO ₂	873	0.1	1:1	12.8	N/A	[36]
NiO/CeO ₂	973	0.1	1:1	~40	~100	[37]
NiO/SBA-15	673	0.1	1:1	5	100	[38]
NiO/SBA-15	1173	0.1	1:1	55	100	[38]
Ni/CeO ₂	1023	0.1	1:1	40	100	[39]
Co/MCF-17	473 - 573	0.55	3:1	~5	~90	[30]
Co/γ-Al ₂ O ₃	573	0.1	3:1	3.8	67.0	[29]
Co/CeO ₂	573	0.1	3:1	3.8	39.4	[29]
CeO ₂ -Ga ₂ O ₃	773	0.1	1:1	11.0	N/A	[40]
Li/RhY (Li:Rh=0)	523	3	1:1	24.1	0.3	[41]
Li/RhY (Li:Rh=3)	523	3	3:1	12.0	3.7	[41]
Li/RhY (Li:Rh=7)	523	3	3:1	11.1	27.6	[41]
Li/RhY (Li:Rh=10)	523	3	3:1	13.1	86.6	[41]

Data taken from Ref 23 and Ref 24

Different reaction pathways have been proposed for the CO formation through the RWGS reaction over metals. One of them is the redox mechanism,

which has been observed in CuO/ZnO/Al₂O₃, Cu/ZrO₂ and Cu/ZnO systems, in which CO₂ oxidizes Cu⁰ to generate CO and copper (I) oxide species while H₂ reduces the copper (I) oxide species and forms H₂O (Figure 1.6) [42-44].

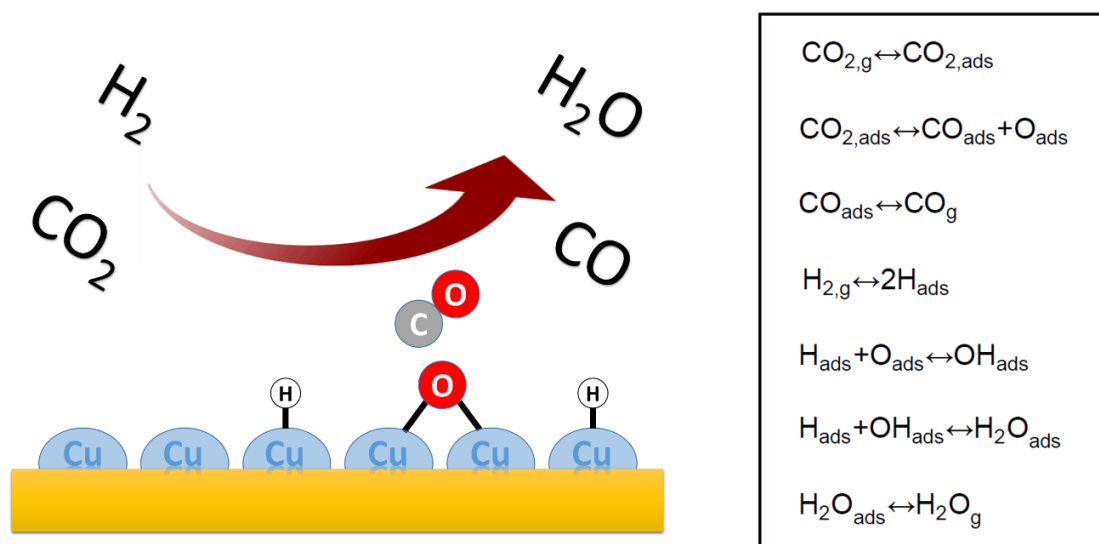


Figure 1.6. Redox mechanism on Cu surface under RWGS reaction conditions.

The other widely accepted pathway is through formate intermediate in which CO₂ is first hydrogenated into formate followed by cleavage of one C-O bond and the OH formation, which forms subsequently H₂O (Figure 1.7). This mechanism has also been proposed for Cu-based catalysts, such as ZnO/Cu and Cu/K/SiO₂ systems [45-48].

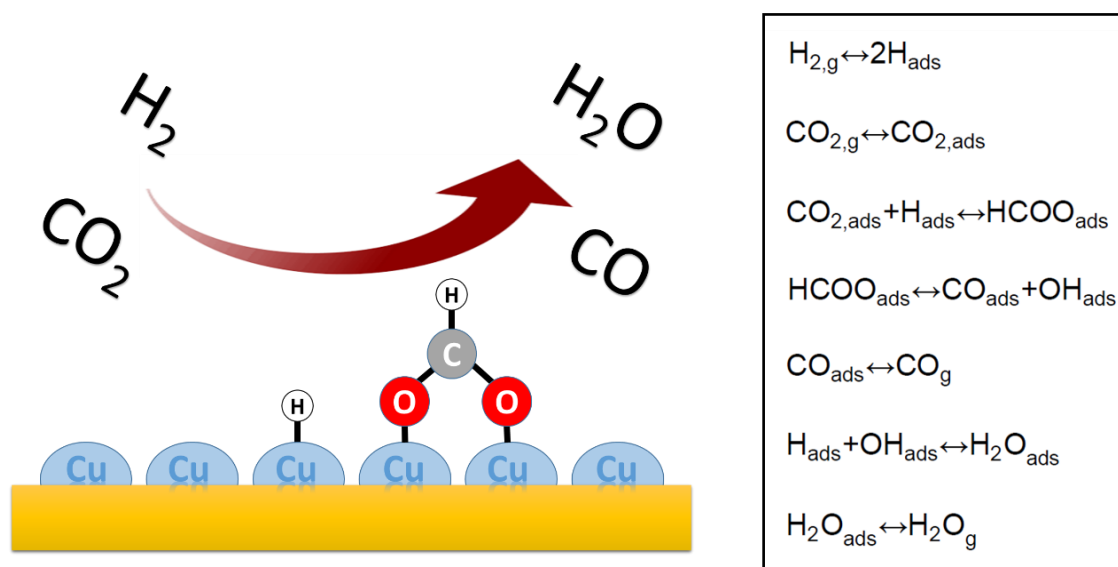


Figure 1.7. Formate formation mechanism on Cu surface under RWGS reaction conditions.

On the other hand, a main role in the RWGS of several supports such as CeO_2 has been demonstrated [49]. For Pt/CeO_2 , the presence of surface vacancies is related with the main route of CO formation through surface carbonate species. The main role of Pt in this case would be activate H_2 , which react with a surface O^{2-} to form H_2O and an oxygen vacancy on CeO_2 [49].

Due to the high cost of the noble metals and the thermal and poisoning deactivation of Cu-based catalysts, transition metal carbides (TMCs) have received major attention by researchers as alternative to conventional catalysts for the RWGS reaction [23,24].

1.3. Transition metal carbides (TMCs)

Transition metals from groups 4-10 can form TMCs except for metals of the second and third row of groups 9-10 (Rh, Ir, Pd and Pt). The TMCs reported nowadays are listed in Table 1.2 [50-57]. TMCs show a great strength and durability and can be used under extreme conditions of pressure and/or temperature [58]. TMCs present good mechanical properties (hardness, strength, durability), which are typical of ceramics, and simultaneously electrical

conductivity (or even superconductivity). In some cases, TMCs show catalytic activity and magnetic properties [58-60].

Table 1.2. Different transition metal carbides and their positions in the periodic table.

Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10
TiC _{1-x} Ti ₂ C Ti ₃ C ₂	V ₂ C V ₄ C ₃ V ₆ C ₅ V ₈ C ₇ VC	Cr ₂₃ C ₆ Cr ₇ C ₆ Cr ₃ C ₂	Mn ₂₃ C ₆ Mn ₁₅ C ₄ Mn ₃ C Mn ₅ C ₂ Mn ₇ C ₃	Fe ₃ C Fe ₇ C ₃ Fe ₂ C	Co ₃ C Co ₂ C	Ni ₃ C
ZrC _{1-x} Zr ₃ C ₂	Nb ₂ C Nb ₃ C ₂ NbC Nb ₄ C ₃	Mo ₂ C Mo ₃ C ₂ MoC _{1-x} MoC	TcC(*)	RuC(*)	-	-
HfC _{1-x} Hf ₃ C ₂	Ta ₂ C Ta ₃ C ₂ TaC Ta ₄ C ₃	W ₂ C WC _{1-x} WC	ReC Re ₂₋₄ C	OsC(*)	-	-

(*) Under debate.

TMCs of groups 4-6 are the most thermodynamically stable. This can be related to the force of TM-C bonds that increases from right to left in a period and from up to down in a group of the periodic table [61,62]. For instance, Hugosson et al [63] showed by theoretical calculations that the formation of a C vacancy in ZrC costs 0.8 eV at 0 K, meanwhile in NbC only 0.6 eV.

The classical synthesis of these materials uses strong synthetic conditions (high temperature, high pressure, strong reducing agents, etc.). One of the ways to produce TMC is via solid state reaction of the parental metals under inert or reducing atmosphere (H₂) by heating up to ~2273 K, and using pure carbon (coal or graphite) as carbon source [51]. The carbothermal reduction is a well-known procedure (solid-gas reaction), where the corresponding metal oxide under a hydrocarbon-containing stream (CH₄, C₂H₄, C₂H₆) and/or CO, reacts to obtain the

TMC, but usually this method produces impurities, low surface area and often non-crystalline products [51,52,60].

More recent routes involve more friendly methods, which avoid the use of extreme conditions through the use of suitable carbon precursors, such as: biopolymers, urea, sugars, etc [64-68]. The use of these methods allows minimizing the heat treatment by decreasing reaction temperature and heating time resulting in an increase of porosity and/or surface area of the final product and favors the preparation process scalability. An increase of porosity and/or surface area of TMCs might improve their catalytic performance, which, together with their lower cost, can make these materials a feasible alternative to expensive and often scarce noble metal catalysts.

The study of the bonding and electronic properties of TMCs and the comparison with those of the corresponding parental metals is especially interesting. Levi and Boudart discovered the similarities of the electronic and catalytic properties of WC with those of Pt in different reactions, such as the formation of water from its components at room temperature and in some hydrocarbon isomerization reactions. Another characteristic of WC found was its ability to dissociate H_2 in presence of H_2O . This ability was demonstrated by the catalytic reduction of WO_3 to H_xWO_3 by wet H_2 in presence of WC below 673 K. However, in general WC activity found was much lower than that of Pt [69].

Since this early work [69], TMCs have shown good performances as catalysts in some reaction such as hydrogenation reactions [70,71], Fischer-Tropsch synthesis [72,73], hydrocarbon isomerization [74], CH_4 dry reforming [75], electrolytic oxygen and hydrogen evolution [76,77], and others.

However, literature about the use of TMCs as catalysts is relatively scarce compared to their corresponding metal oxides.

1.3.1. TMCs in the RWGS reaction

Both, the CO₂ activation and the H₂ dissociation over different TMC single crystals have been theoretically studied.

Many theoretical investigations have been carried out on MoC (cubic) and Mo₂C (hexagonal) phases, which are the most studied carbides [78-80]. Posada-Pérez et al [81] observed that the ratio Mo:C often plays a key role in the surface chemistry and catalytic behavior of the corresponding carbide. Moreover, the study of the CO₂ uptake and activation over different TMCs(001), such as, VC, TiC, ZrC, HfC, NbC and TaC have been performed by DFT calculations, demonstrating the high potential of these materials even at low temperature [82].

Theoretical investigations demonstrated the high performance of Mo₂C(001), MoC(001) and TiC(001) for H₂ dissociation due to the high interaction of these materials with H₂ on both top-M and top-C adsorption sites [83,84]. Prats et al [85] demonstrated that TMCs(001) of group 4 and δ -MoC(001) are better candidates for hydrogenation reactions than TMCs(001) of group 5. Among TMCs(001) of group 5, the only H₂ dissociated state is observed on top-M site in TaC.

The effect on the H₂ dissociation of different TMC(001) surfaces used as supports has also been studied. Florez et al [86] studied the H₂ dissociation on Au₄ nanoclusters supported over different TMCs. They observed a better H₂ dissociation over Au/TiC(001) and Au/ZrC(001), than over Au/MoC(001) and Au/VC(001). They suggested that H₂ dissociation leads to an H atom directly interacting with the Au₄ cluster while the second H atom is transferred to the support in Au/TiC(001) and Au/ZrC(001), however, both H atoms only interact with the Au₄ cluster in Au/MoC(001) and Au/VC(001) cases.

Investigations concerning the reaction mechanism of RWGS over Mo₂C confirmed the dissociative adsorption of CO₂ resulting in the CO and O formation by producing the corresponding oxy-carbide species, subsequently the hydrogenation of this surface oxy-carbide species results in Mo₂C and H₂O formation [78,79,87-89]. This mechanism is similar to the redox mechanism proposed for Cu-based catalysts [42-44] (Figure 1.6). The HCOO formation was less favored than CO+O formation according to the authors [78,79,87-89].

Tominaga et al [79] used a cluster of Mo_4C_2 as model catalyst to describe the reaction pathways for CO_2 reduction over Mo_2C using DFT calculations. The mechanism via the dissociative CO_2 adsorption is favored over the Mo_4C_2 model catalyst (Figure 1.9). Additionally, they observed that the HCOO formation is not favored in the CO_2 reduction over Mo_4C_2 model due to the activation energy required for HCOO formation ($119.9 \text{ kJ mol}^{-1}$) is higher than that necessary for the formation of $\text{CO}+\text{OH}$ (59.4 kJ mol^{-1}) (Figure 1.10).

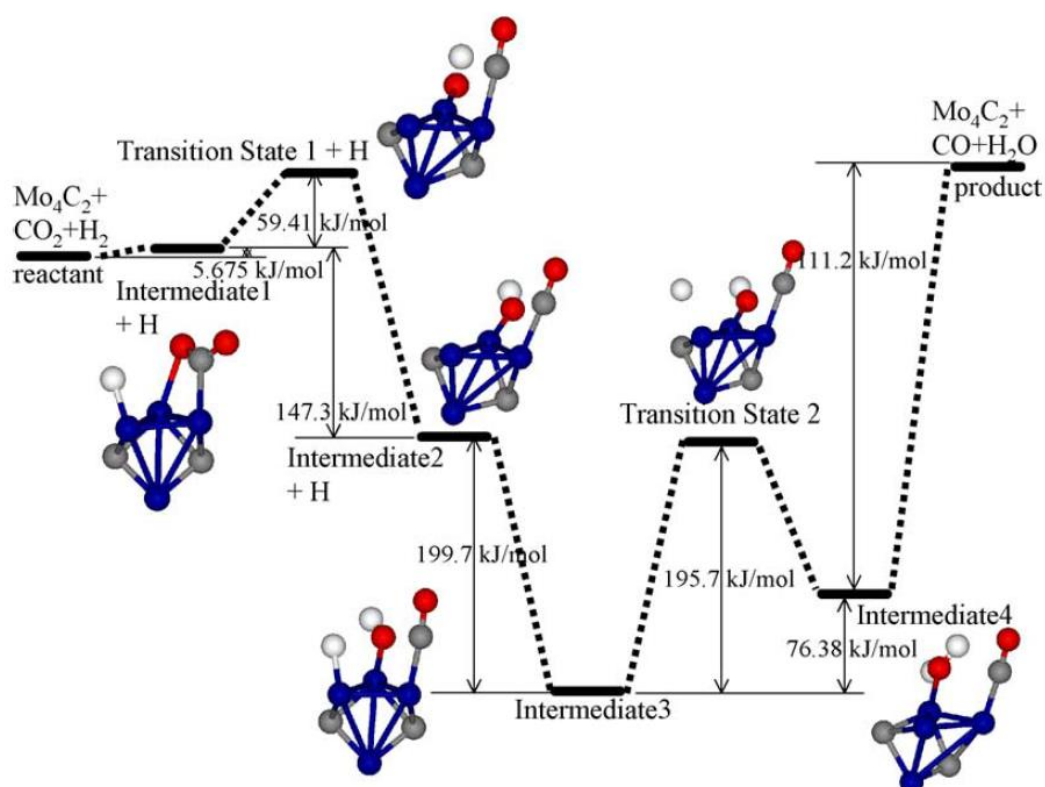


Figure 1.9. DFT potential energy plot for Mo_4C_2 model catalyst in the RWGS reaction via dissociative CO_2 adsorption. Mo:blue. O:red. C:gray. H:white. Taken with permission from Ref 79.

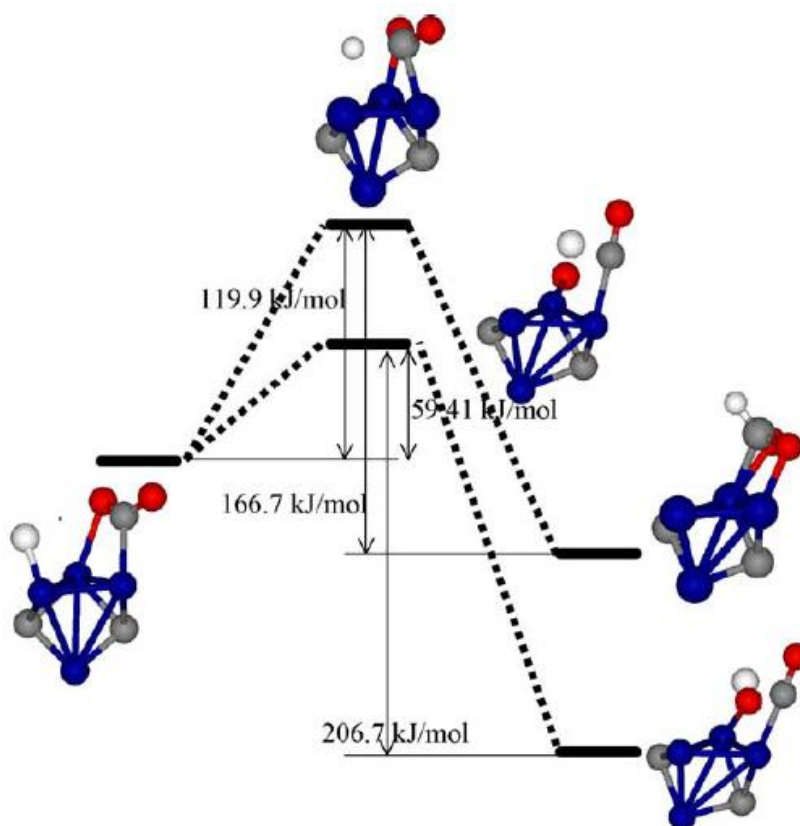


Figure 1.10. DFT estimates for formation of HCOO or CO + OH on Mo₄C₂ model catalyst. Mo:blue. O:red. C:gray. H:white. Taken with permission from Ref 79.

In the same investigation, they compared the Mo₄C₂ model with its parent metal, Mo (Mo₄ cluster as model catalyst) for the same reaction. Mo₄C₂ cluster showed a lower activation energy than that of the Mo₄ cluster in the formation of CO+H₂O. This demonstrated the better catalytic activity of Mo₂C than Mo metal. This was verified in an experimental study of CO₂ hydrogenation reaction at 573 K and atmospheric pressure, where Mo₂C produced 0.847 $\mu\text{molCO g}^{-1} \text{s}^{-1}$, and Mo metal only 0.0325 $\mu\text{molCO g}^{-1} \text{s}^{-1}$ [90].

Few experimental investigations about the use of TMCs as catalysts in the RWGS have been reported. Porosoff et al [91] tested commercial and non-commercial polycrystalline-TMCs of groups 4-6 (TiC, ZrC, NbC, TaC, Mo₂C and WC) in the RWGS reaction resulting that Mo₂C was the most active. Liu et al [87] reported a combination of experiments and DFT calculations on the behavior of Mo₂C in the RWGS reaction, showing a high activity and CO selectivity of this

material. The use of VC as catalyst has not been reported in the RWGS reaction so far.

The effect of different promoters onto TMCs has also been studied. The addition of K to $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ improved the CO selectivity and the stability of the catalyst [89]. A similar effect was observed when K was added to WC used in the RWGS reaction [92]. Zhang et al [93] reported the effect of Cs and Cu addition over Mo_2C , enhancing also the stability and selectivity to CO.

The addition of Co onto Mo_2C improved CO_2 conversion and CO selectivity at 573 K compared to solely Mo_2C . Additionally the Co/ Mo_2C system showed a better catalytic performance when it was compared to Pt-Co and Pd-Ni bimetallic NPs supported on CeO_2 [29].

The study of supported Mo_xC catalysts in the RWGS reaction has also been reported. Different Mo_xC phases were successfully supported over Al_2O_3 , SiO_2 and TiO_2 and exhibited a higher CO production than the bulk Mo_2C catalyst [89,94,95]. However, to our knowledge, supported TMCs of group 5 have not yet been studied in the RWGS.

1.3.2. TMCs in the methanol steam reforming (MSR) reaction

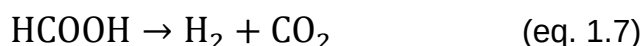
Hydrogen is considered a clean energy carrier for a near future. The production of electrical power using H_2 as raw material is nowadays a mature and environmentally friendly technology. However, the H_2 production, storage and transport are important drawbacks for the use of H_2 in the present energy context [96]. Even though steam reforming of CH_4 is the main process currently used in industrial hydrogen production, the reforming of other energy-carriers such as methanol or ethanol has been proposed [97-100]. Methanol is the simplest alcohol and possesses several advantages for hydrogen production: it is biodegradable, liquid at atmospheric conditions and has a high hydrogen to carbon ratio. Moreover, the absence of strong C-C bonds facilitates its reforming at lower temperatures (473-573 K) compared to ethanol, which is reformed around 673 K, and also compared to methane, which is reformed above 773 K. MSR is an endothermic reaction (eq. 1.4):



The most common catalysts for MSR are Cu- and Pd-based ones [101-104]. Cu-based catalysts are highly active and H₂ selective; however, they present low thermal stability and sintering at temperatures above 573 K. Moreover, they are easily deactivated by coke formation and/or the presence of contaminants that can be present in the feedstock [105-107].

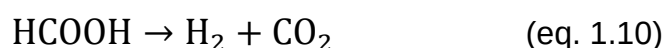
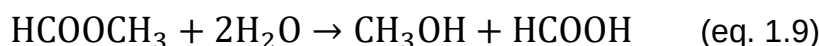
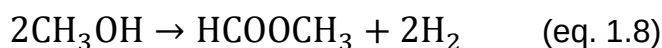
Two reaction pathways for MSR reaction have been proposed in the literature so far [108]: *i) Formaldehyde intermediate* and *ii) Methyl-formate intermediate*

- i) Formaldehyde intermediate:* This is the main mechanism accepted, which consist in the methanol dehydrogenation to formaldehyde (eq. 1.5) followed by the formation of HCOOH (eq. 1.6) and its subsequent decomposition to H₂ and CO₂ (eq. 1.7).



Takezawa et al [109] found that HCHO was involved as intermediate in the MSR reaction over supported Cu and group 8 (Ni, Rh, Pd and Pt) metal catalysts. Moreover, other authors verified the presence of formaldehyde in the MSR reaction over zirconia-containing Cu-Zn-Al and Cu/ZnO catalysts [110,111]. DFT calculations also indicated the HCHO formation over Cu(111) and Pd(111) surfaces [112].

- ii) *Methyl-formate intermediate*: The other accepted mechanism consists in the methanol dehydrogenation to methyl formate (eq. 1.8) followed by HCOOH formation (eq. 1.9), which decomposes into H₂ and CO₂ (eq. 1.10).



Yi et al [113] observed the methyl formate formation over Au/CeO₂ surface via *in-situ* temperature programmed surface reaction approach. Lin et al [114] used density functional theory to investigate the role of methyl formate in MSR on PdZn alloy, showing that methyl formate should be formed by a reaction between formaldehyde and methoxy species.

Regarding the use of TMCs in MSR reaction. The reaction of water and methanol on TMC surfaces have been studied [115]. Some experimental investigations in the methanol decomposition over TMC single crystals have been carried out as described below.

Hwu et al examined and compared the decomposition of CH₃OH on carbide-modified metallic single crystals, C/Mo(110), C/W(110) and C/W(111) [116-118]. HREELS experiments revealed that methoxy (CH₃O) is produced as intermediate on all three surfaces. The formation of CO and H₂, and the total decomposition of CH₃OH to atomic C and O (onto surface) were found in all cases. However, CH₄ production was only found on C/W(110) and C/W(111).

On the other hand, a high selectivity to CH₄ is observed when methanol decomposition is carried out over C/V(110) and C/Ti(0001) single crystals [119]. The total decomposition to atomic C and O is the main pathway and CH₄ is the only gas phase product in both surfaces. This could be associated to the strong

V-O and Ti-O bonds, which promotes the C-O bond scission of the surface methoxy intermediate, resulting in CH₄ formation.

Over ZrC(111), NbC(111) and TiC(111) single crystals, methanol is dissociated to methoxy, subsequently into atomic species (C, H and O atoms) at room temperature. However, over ZrC(100), NbC(100) and TiC(100) only molecular CH₃OH adsorption takes place [120-122].

For Mo₂C(100) single crystal, the addition of K also favored the CH₄ formation after CH₃OH adsorption. In this case, the presence of K could help to break the C-O bond of surface methoxy species [123].

Among bulk TMCs, only polycrystalline (hcp-Mo₂C) based catalysts have been studied so far in the decomposition of methanol and the MSR reaction [124,125]. In the MSR reaction, the catalytic activity was improved when Mo₂C was supported on carbon nanotubes, ZrO₂, Al₂O₃ and carbon Norit compared to solely Mo₂C [126,127].

Additionally, (M=Pt, Fe, Co and Ni)-Mo₂C, prepared by in-situ carburization of metal-doped molybdenum, showed a higher methanol conversion and hydrogen yield than bulk Mo₂C. Among the different metals, Pt-doped Mo₂C showed the highest catalytic activity and H₂ selectivity; Pt doped Mo₂C also showed a long-time stability in the range of temperature of 473-673 K [128].

Cao et al [129] studied the intermediate species generated during MSR reaction over metal-doped Mo₂C by temperature programmed surface reaction (TPSR). They found different intermediate species formed depending on the metal used. At low temperature (<453 K), the MSR reaction over Cu-Mo₂C proceeds through HCOOH intermediate pathway (eq. 1.5-1.7). At temperature higher than 453 K, the MSR reaction over hcp-Mo₂C and (Cu,Ni,Pt)-modified Mo₂C proceeds through the methyl formate intermediate pathway (eq. 1.8-1.10). Additionally to CO₂ and H₂ production, byproducts such as CH₄ and CO were obtained in all cases. Over hcp-Mo₂C, the rate of H₂O dissociation is high, producing MoO_x. H₂O acts as oxidant reactant here, producing a low rate of methanol adsorption and dissociation, leading to the catalyst deactivation. However, the addition of a suitable Ni amount over Mo₂C accelerates the rate of methanol activation, resulting in more reduced species such as CO, which could

reduce the MoO_x ; the better balance in the oxidation-reduction rate is related with the higher stability of the catalyst [129]. Ni-doped Mo_2C showed a higher stability than Fe-doped and Co-doped Mo_2C [130].

1.4. Objectives and structure of the Thesis

The main objective of this work is the study of the CO_2 reduction to CO under RWGS conditions over catalysts based on transition metal carbides of group 5 (G5TMC=VC, NbC and TaC). Additionally, some of these materials have been explored as catalysts in the MSR reaction.

To carry out this purpose, the following specific objectives are proposed:

- Study of the preparation of bulk and supported G5TMC-based catalysts using a novel sol-gel method; analysis of their characteristics.
- Study of the new catalysts prepared in the RWGS and their use in the MSR reaction.
- Analysis of the catalytic behavior of vanadium carbides in the RWGS in the light of the presence of carbon vacancies.

The Thesis is structured in 6 chapters as follows:

The Chapter 1, includes a brief review of the state of the art for the materials and reactions involved in this thesis.

In Chapter 2, the characterization techniques and the reaction systems (RWGS and MSR) used are described.

In Chapter 3, the preparation and characterization of G5TMCs (VC, NbC and TaC) are described and the use of G5TMC as catalysts for the RWGS reaction is studied. Moreover, the effect in the RWGS of the presence of carbon vacancies in vanadium carbide catalysts and an *in-situ* DRIFTS study are included.

In Chapter 4, the preparation, characterization and the catalytic behavior of VC, NbC and TaC supported on Al_2O_3 catalysts for the RWGS reaction are

displayed. A series of supported VC catalysts and their behaviors in the RWGS reaction are also studied.

In Chapter 5, bulk and supported TMCs of group 5 are explored as catalysts in the MSR reaction.

Finally, Chapter 6 presents the main conclusions of the work.

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CHAPTER 2

EXPERIMENTAL

In this chapter, the main characterization techniques used to determine the physicochemical properties of the materials prepared in this work are detailed. Additionally, the reaction systems, to carry out the RWGS and MSR, are also presented. All characterization techniques were performed in the Scientific and Technological Centers of the University of Barcelona (CCiTUB), Catalonia Institute for Energy Research (IREC) and Materials and Catalysis (MATCAT) group at UB. Some procedures are detailed in the Handbook of instrumental techniques from CCiTUB [1]. The catalytic tests (RWGS and MSR reactions) were performed at the MATCAT group and IREC.

2.1. Characterization techniques

2.1.1. Powder X-ray diffraction

Powder X-ray diffraction (XRD) was used to obtain information about the crystalline structure of the materials and the estimation of the crystallite size, which was calculated using the Debye-Scherrer equation [2,3]:

$$d = \frac{K \cdot \lambda}{b \cos \theta} \quad (\text{eq. 2.1})$$

d is the mean size of the crystallite; K is a dimensionless shape factor, with a value close to unity, but varies with the actual shape of the crystallite, in this work we take $K=1$; λ is the X-ray wavelength; b is the line broadening at the half of the maximum intensity (FWHM) due to particle size; θ is the Bragg angle, expressed in radians.

The value of b can be obtained from [2,4,5]:

$$b = \sqrt{(B^2 - \beta^2)} \quad (\text{eq. 2.2})$$

Where B is the FWHM of the measured peak of the corresponding phase, and β is the FWHM due to all other causes (correction factor). If $\beta < \frac{1}{5}B$ or for large crystallite sizes (>100 nm) it can be neglected [5].

X-ray powder diffraction characterization was carried out using a Panalytical X'pert Pro diffractometer, with a Ge (111) primary monochromator, using Cu $K\alpha$ radiation, $\lambda=1.5406$ Å and an applied voltage and current of 45 kV and 40 mA, respectively. Scanned 2θ range was measured from 4-100° with a step size of 0.017° and a time of measuring of 50 second per step. The powder samples were normally pressed with a glass plate to obtain a flat surface, cylindrical standard sample holders of 16 mm of diameter and 2.5 or 1.5 mm of height were used [1].

2.1.2. N₂ adsorption-desorption isotherms

Physisorption of N₂ is widely applied for the measurement of the specific surface area of porous materials by means of the Brunauer-Emmett-Teller (BET) equation [6,7]:

$$\frac{p}{v(p^0-p)} = \frac{1}{v_m c} + \frac{(c-1)}{v_m c} \cdot \frac{p}{p^0} \quad (\text{eq. 2.3})$$

Where, p and p^0 are the equilibrium and the saturation pressure, respectively, of adsorbates at the temperature of adsorption, v is the volume of the adsorbed gas at relative pressure p/p^0 , v_m is the volume of the gas adsorbed when a monolayer is formed, and c is the BET constant, which is described as follows:

$$c = \exp\left(\frac{E_1-E_L}{RT}\right) \quad (\text{eq. 2.4})$$

E_1 and E_L are the heat of adsorption for the first and the second and higher layers, respectively. The calculated specific surface (S_{BET}) is:

$$S_{BET} = \frac{\sigma_m \cdot n_m \cdot N_A}{m} \quad (\text{eq. 2.5}) \quad \text{and} \quad n_m = \frac{v_m \cdot \rho}{M_m} \quad (\text{eq. 2.6})$$

Where:

σ_m : Cross-sectional area occupied for one molecule adsorbed (0.162 nm² for N₂)

n_m : Number of moles of the adsorbed gas when a monolayer is formed

N_A : Avogadro constant

ρ : Density of adsorbed gas (N₂)

M_m : Molecular mass of the adsorbate

m : Mass of adsorbent

N₂ adsorption-desorption isotherms of the samples were recorded using a Micromeritics Tristar II instrument at 77 K. Prior to measurement, samples were outgassed overnight at 523 K under N₂ flow. The BET surface area was measured by multi-point BET. Pore volume and pore size distributions were determined using the Barrett-Halenda-Joyner (BJH) method [8].

2.1.3. Raman spectroscopy

In this work Raman spectroscopy was used to determine the presence of oxide species [9] and carbonaceous deposits on the samples [10,11]. The Raman spectra were collected using a Jobin-Tvon LabRam HR 800 instrument, with an optical Olympus BXFM microscope, a 532 nm laser and a CCD detector. The laser power was limited to 0.75 mW to reduce laser-heating effects during spectra acquisition in a spot of 15x15 µm of sample.

2.1.4. H₂-Temperature programmed reduction

H₂ temperature programmed reduction (H₂-TPR) is a characterization technique which is used to study the reducibility properties of materials [12,13].

The sample is submitted to a programmed temperature rise while a reducing gas mixture (~10%vol H₂ in inert gas) is flowed through. This technique was employed particularly to identify the metal oxide species present in TMCs-based catalysts.

H₂-TPR experiments were performed using a Micromeritics AutoChem II 2920 chemisorption apparatus. Approximately, 100 mg of sample were placed in a U-shape quartz tube reactor. The sample was pretreated at 363 K under He and then, exposed to a H₂/Ar (12%v/v) flow. Afterwards, the temperature was increased up to 1073 K (10 K min⁻¹). A thermal conductivity detector (TCD) was used to determine the H₂ consumption.

2.1.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique based on the photoelectric effect that can identify elements on the surface of the material. A monochromatic beam of X-rays radiation hits the sample producing an emission of electrons. The kinetic energies of the emitted electrons are measured by means of an energy analyzer. The binding energy (BE) of the electron emitted can be deduced from [14,15],

$$BE = h\nu - E_k - \phi \quad (\text{eq. 2.7})$$

Where:

E_k : Kinetic energy of the emitted electrons

ϕ : Work function of the spectrometer

$h\nu$: Energy of the incident X-ray

The atomic concentration of the element “x” on the surface of samples is obtained as follows [14]:

$$C_x = \frac{I_x/S_x}{\sum_{i=1}^n I_i/S_i} \quad (\text{eq. 2.8})$$

Where:

C_x : Atomic concentration of the element x

I_i : Area of the peak of the element i

S_i : Atomic sensitivity factor of the element i

XPS analysis was carried out using a Perkin Elmer PHI-5500 Multitechnique System (Physical Electronics) equipped with an Al X-ray source ($h\nu=1486.6$ eV and 350 W). Samples were kept in an ultra-high vacuum chamber ($5 \cdot 10^{-9}$ - $2 \cdot 10^{-8}$ Torr) during acquisition. The BE values were referred to C 1s at 284.8 eV, attributed to adventitious carbon, which was previously determined using Au as reference ($4f_{7/2}$ peak at 84.0 eV).

2.1.6. Thermogravimetry-differential scanning calorimetry

A thermogravimetry-differential scanning calorimetry (TG-DSC) equipment was used to study the CO₂ adsorption onto the catalysts and the reactivity of catalysts under CO₂ atmosphere. The differential scanning calorimetry system consists in two cells, one contains the sample under study and the second cell serves as reference (Platinum cell was used as reference). The two cells are maintained at the same conditions during the measurement. Figure 2.1 shows a schematic of the DSC system.

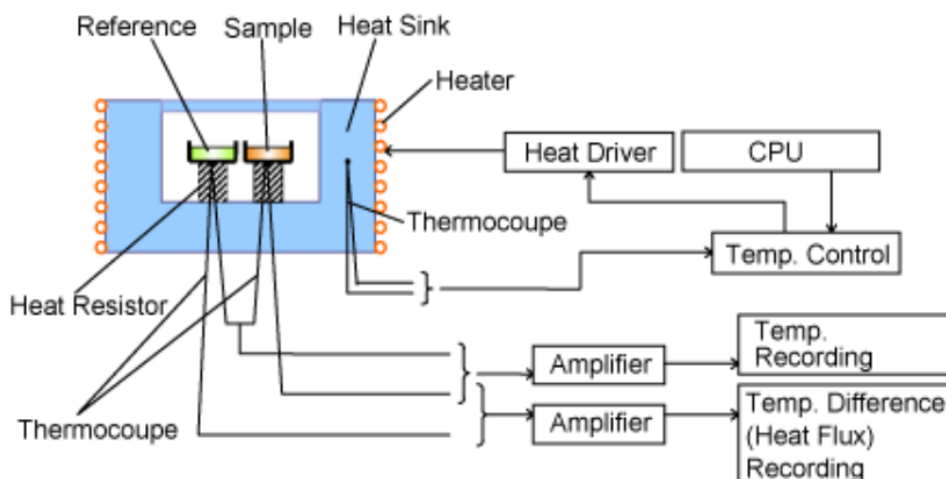


Figure 2.1. Schematic of DSC instrument.

The adsorption of a gas, in this case CO_2 , on the sample produces a heat exchange and a variation in the weight of the sample. The values of heat flow and the variation of weight of the samples are recorded by the system which is coupled to a balance.

For CO_2 adsorption experiments, approximately 100 mg of sample were firstly dried in Ar flow at 353 K, afterwards the sample was heated up to 823 K (10 K min^{-1}) under flowing H_2/Ar (10 %v/v), after 3h at 823 K, the sample was cooled down to 303 K for CO_2 chemisorption. The exothermic peak corresponding to CO_2 adsorption was integrated to provide the total enthalpy of adsorption. The mean adsorption energy was calculated by considering the total amount of adsorbed CO_2 .

For CO_2 reactivity studies, the samples (~100 mg) were heated up to 873 K at 10 K min^{-1} under a flow of CO_2/Ar (10%v/v), then the samples were kept for 3h at 873 K, finally the samples were cooled down at room temperature. The outlet flow was on-line analyzed by mass spectrometry (MS) to determine the presence of CO.

The measurements were carried out in a Sensys Evo TG-DSC instrument (SETARAM), equipped with a 3D thermal flow sensor and a Pfeifer mass spectrometer.

2.1.7. Scanning electron microscopy

The scanning electron microscopy (SEM) was used for determining the morphology of samples.

The SEM analysis was complemented with energy-dispersive X-ray (EDX) spectroscopy, which allowed the determination of the distribution and/or quantification of elements in the samples.

SEM analysis was performed on a JEOL J-7100F scanning electron microscope, equipped with an EDX detector, under an accelerating voltage up to 20 kV. The EDX analysis was operated with an Oxford Instrument INCA at an acquisition time of 60 s.

2.1.8. Transmission electron microscopy and precession electron diffraction

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HR-TEM) were used to obtain images and structural information of the materials.

Electron diffraction (ED) was used to obtain crystallographic structural information of the materials, resulting from the interaction between electrons and crystalline materials, which produces a pattern of rings or spots that allows to characterize the structure of the sample.

Precession electron diffraction (PED) is an inverted hollow cone illumination technique for electron diffraction pattern collections under quasi-kinematical conditions (Figure 2.2A). A tilted incident electron beam rotates around the central axis of the microscope generating a PED pattern formed by the integration over a collection of diffraction conditions. The transmitted beam is then re-centered using additional group of deflecting coils located below the sample. The two tilts (upper and lower) are synchronized with a dedicated hardware unit (ASTAR from NanoMEGAS) that allows rotation speeds of several hundred hertz.

PED guarantees a better resolution and non-incorrect data collection of the sample [16]. Figure 2.2B shows an unprocessed and precessed electron diffraction patterns acquisition in a particular case of mayenite [1].

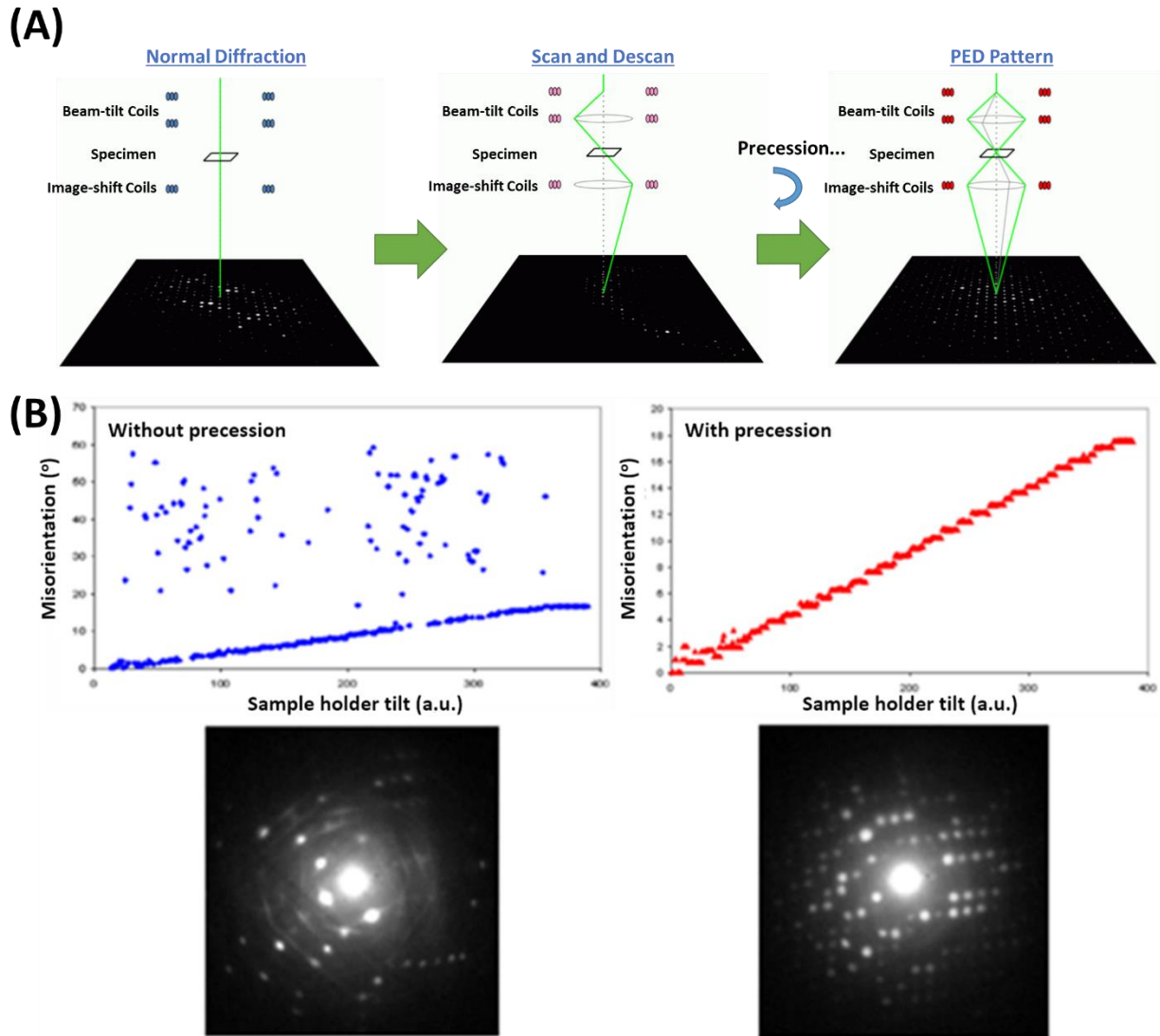


Figure 2.2. Schematic of PED technique and the influence of precession in data acquisition: (A) Geometry of electron beam in precession electron diffraction; (B) Orientation values for mayenite (100) nanocrystal obtained without precession (left) and with precession (right). Ref 1 and Ref 16.

This technique can provide the identification of crystal structures of nanoparticles. In this context, PED was used in this work to distinguish two cubic phases of vanadium carbide (VC and V_8C_7) (Chapter 3).

The PED pattern recognition analysis was carried out using a commercial ASTARTM technique [17-19]. PED mapping was acquired using a step size of 5-10 nm and operating at 100 Hz. 5 frames per second and a precession angle of 1° were used. PED patterns were recorded using an ultrafast external camera (Stingray F-046 Allied Visions) for the crystal phase mapping construction.

TEM and HRTEM images and the PED pattern recognition analysis of samples were performed in a JEOL J2010F transmission electron microscope with an accelerating voltage up to 200 kV.

In some experiments an EDX detector was used to identify the elements present in the samples. EDX analysis was carried out using an Oxford Instruments INCA x-sight, with Si (Li) detector coupled to a Scanning Transmission Electron Microscopy (STEM) system. The STEM images were obtained with a JEOL JEM-2100 LaB6 transmission electron microscope operated at 200 kV, using the high angle annular dark field detector. The beam size was about 15 nm.

2.1.9. Chemisorption of CO₂, CO and CO₂+H₂ studied by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS technique was performed to study the behavior of catalysts in front of probe molecules, such as, CO₂, CO and a mixture of CO₂/H₂=1/3.

A Bruker VERTEX 70 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector and a Harrick Scientific HVC-DRP-4 DRIFTS catalytic chamber with ZnSe windows and a thermocouple for temperature measurement and control were used.

Figure 2.3 shows a scheme of the Harrick Scientific HVC-DRP-4 reaction chamber.

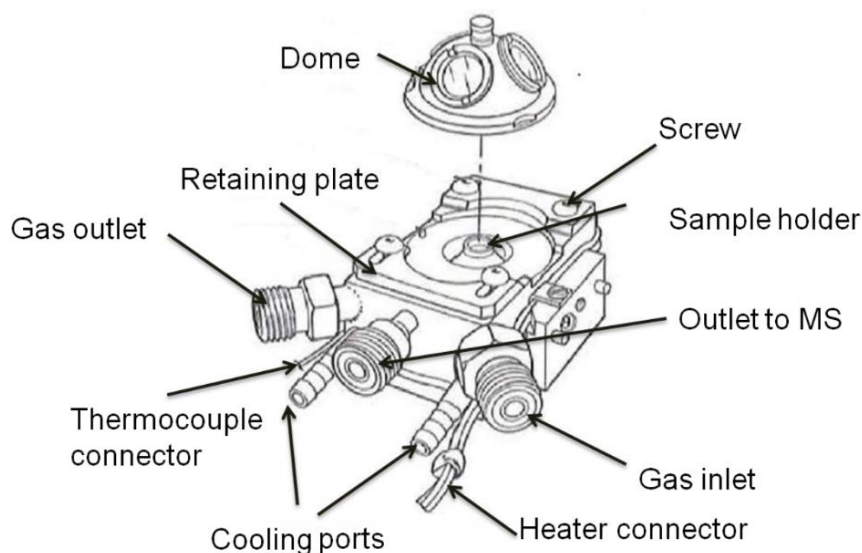


Figure 2.3. Harrick Scientific HVC-DRP-4 reaction chamber.

The outlet of the chamber was connected on-line with a ThermoStar GSD320T1 mass spectrometer.

Approximately 30 mg of sample was deposited on the sample holder of the reaction chamber. The chamber was purged with He flow before measurements.

For adsorption experiments, the sample was firstly treated *in situ* in the DRIFTS cell under He flow (20 mL min^{-1}) up to 573 K for 30 min, then the flow switched to H_2 for 1 h. After H_2 treatment, the sample was cooled down to 308 K under He flow and a background spectrum was recorded at this step.

Afterwards 20 mL min^{-1} of CO_2/He (10% v/v) or CO/He (10% v/v) mixture were introduced at 303 K and contacted with the sample for 30 min. 20 and 6 mL min^{-1} were used for CO_2/He (10% v/v) and H_2 , respectively to achieve the desired mixture of $\text{CO}_2/\text{H}_2=1/3$. Then the flow was switched to He and the final spectrum was recorded at 308 K.

The spectra were recorded at a spectral resolution of 4 cm^{-1} by collecting 256 scans in the range of $4000\text{-}650 \text{ cm}^{-1}$ every 5 minutes.

2.1.10. Inductively-coupled plasma atomic emission spectrometry

Inductively-coupled plasma atomic emission spectrometry (ICP-AES) is an analytical technique used for chemical analysis of the samples [19]. ICP-AES was used for analyzing supported VC samples.

Prior to the analysis, solid samples (~50 mg) were digested by the solutions shown in Table 2.1.

Table 2.1. Mixture of solutions used for digesting supported VC catalysts.

Sample	Solution
VC/ZrO ₂	4mL HNO ₃ + 3mL H ₂ SO ₄ + 0.5g NH ₄ F + 1mL HF
VC/CeO ₂	5mL HNO ₃ + 3mL H ₂ SO ₄ + 0.5g NH ₄ Cl
VC/Al ₂ O ₃	4mL HNO ₃ + 1mL HCl + 3mL H ₃ PO ₄
VC/AC ¹	7mL HNO ₃ + 1mL HCl
VC/TiO ₂ and VC/SiO ₂	6mL HNO ₃ + 1mL HCl + 1mL HF

⁽¹⁾AC is activated carbon

In all cases, the solution obtained after digesting was placed in a Teflon reactor for a microwave-assisted treatment at 483 K. Afterwards, the solution was cooled down up to room temperature and diluted with water (HPLC grade) up to 50 mL. The resultant solution was analyzed by ICP-AES.

The ICP-AES measurements were performed using a Perkin Elmer Optima 3200 RL apparatus.

2.2. Reaction systems

2.2.1. RWGS reaction system

The RWGS catalytic tests were performed using a Microactivity-Reference unit (PID Eng&Tec) (Figure 2.4). The system consists of a fixed-bed tubular reactor, with the catalyst bed placed inside upon a porous plate. The flow inside

the reactor is up-down, whereby the reactant mixture is fed through the upper part of the reactor and the reaction products are obtained through the lower part.

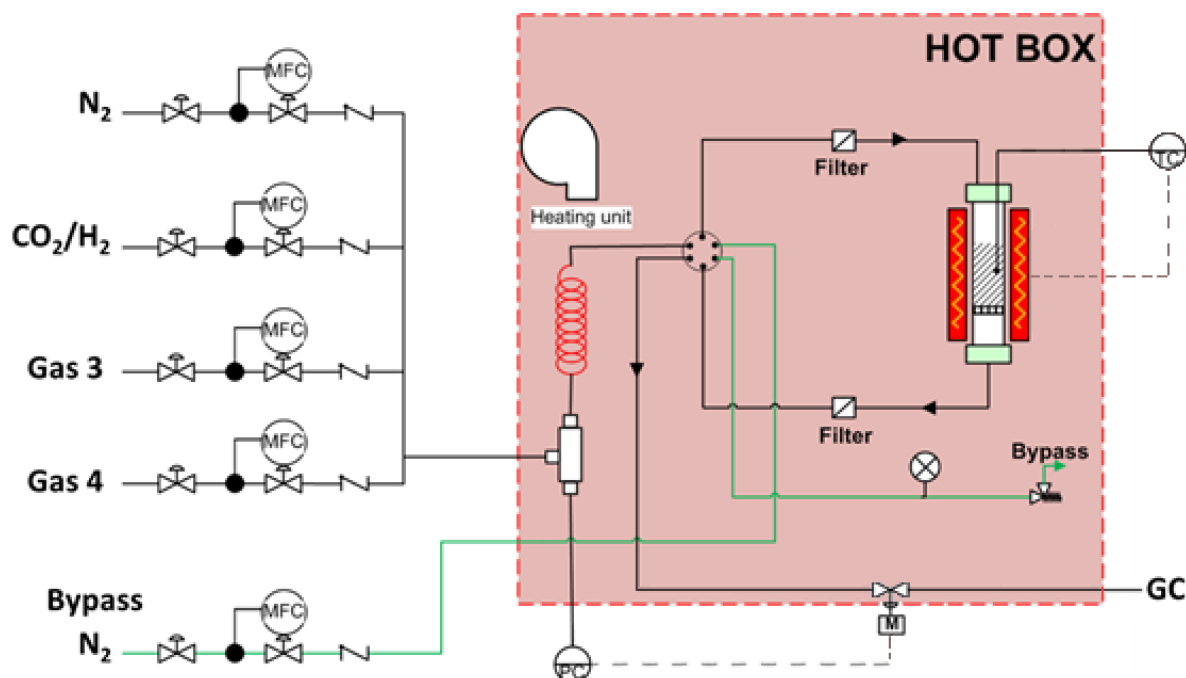


Figure 2.4. Scheme of the RWGS reaction system.

The reactant mixture of CO_2/H_2 (1/3, $\geq 99.99\%$) was mixed with N_2 ($\geq 99.999\%$), to achieve a molar ratio of $\text{CO}_2/\text{H}_2/\text{N}_2 = 1/3/1$, which was controlled by means of mass flow controllers (MFCs). In order to stop the product flowing back through the lines, the MFCs were protected with check-valves fitted with Kalretz elastomer seals (elastomeric Teflon). The flow was introduced into the hot box system that includes an electric forced convection heater that allows keeping the system at 453 K to avoid possible condensations. Once the gases have been preheated, they were fed into the reactor downwards contacting with the catalyst after passing by a 6-port valve. The valve is operated by remote pneumatic control and allows the flow passage of reactant mixture or auxiliary gas (N_2) through the reactor. Two 10 μm sintered filters made of 316 stainless steel are attached at the inlet and outlet of the reactor to protect the valves from possible finely-separated catalyst particles. The outlet of the reactor flows direct to the pressure control system, consisting of a servo positioned micrometric

regulating valve, which is in the hot box and provides a continuous and constant flow of gases at the outlet.

The outlet flow was directed out of the hot box through a thermostated transfer line for subsequent on-line measurement by means of a gas chromatograph.

Figure 2.5 shows the inside view of the Microactivity-Reference Unit, in which the RWGS reaction was carried out.

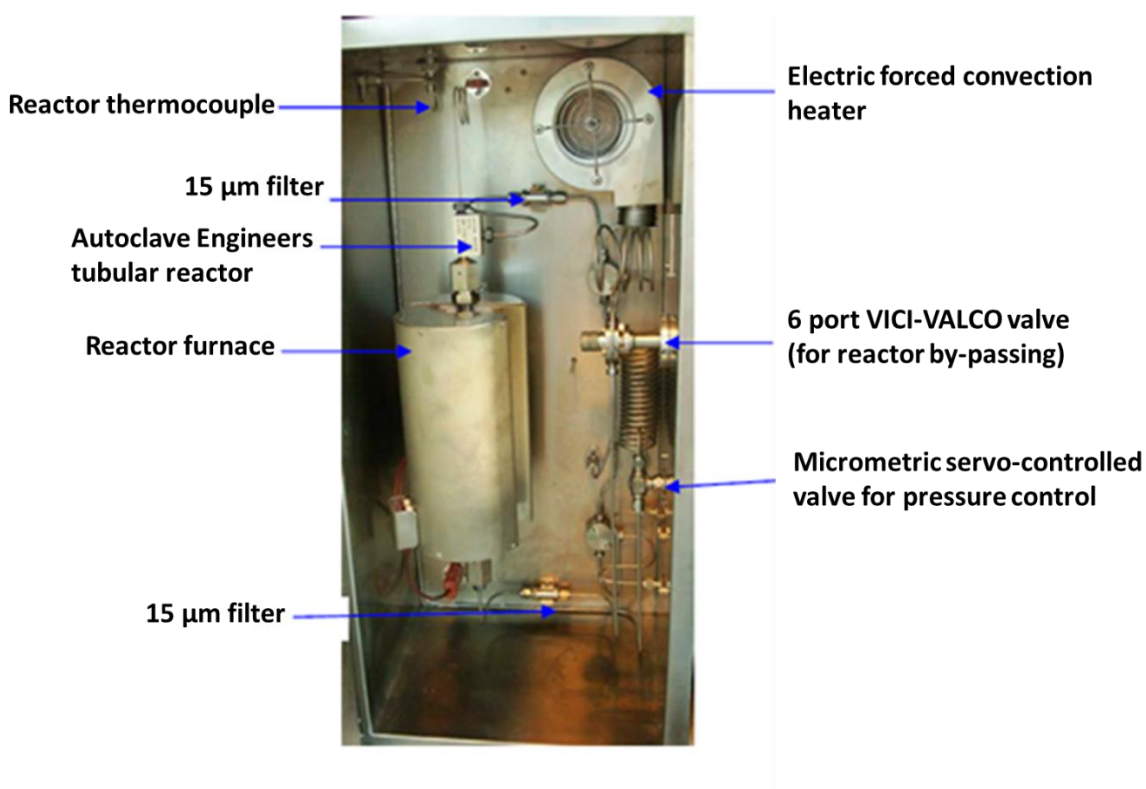


Figure 2.5. Inside view of Microactivity-Reference Unit

A tubular fixed bed reactor (316-L stainless steel, 305 mm long and 9 mm i.d.) with a thermocouple (K-type) in direct contact with the catalytic bed was utilized.

150 mg or 300 mg of catalyst (powder) were diluted with SiC to have a catalytic bed of 1mL. The sample was crushed with a mortar and sieved with a stainless steel mesh, 0.177 mm, prior catalytic tests. All tests were carried out at

a Gas Hourly Space Velocity (GHSV) of 3000 h⁻¹ at 0.1 MPa at increasing temperature. The catalysts were kept 1.5 or 2.5 h at each temperature. Each temperature change was reached in 10 min. The first measurement was taken after 30 min at each temperature. The range of reaction temperature analyzed varies according to the set of experiments.

The products were analyzed online with a Varian 450-GC equipped with a thermal conductivity detector (TCD) and two flame ionization detectors (FID). The TCD channel is equipped with a Mol.Sieve 13X column (1.5 m), and Ar as carrier (Sample loop: 1 mL). The FID channels used He as carrier and are equipped with Hayesep Q (0.5 m) (Sample loop: 1 mL) and CP-Sil5 CB (25 m) columns (Sample loop: 250 µL). To quantify CO and CO₂, a methanizer is incorporated into the chromatograph, where takes places the CO and CO₂ conversion into CH₄, then CH₄ is quantified in a FID channel.

The CO₂ conversion (X_{CO_2}) and the selectivity to the i products (S_i) were defined as follows:

$$X_{CO_2}(\%) = \left(1 - \frac{(C_{CO_2})_{outlet}}{(C_{CO_2})_{outlet} + \sum(C_i)_{outlet}}\right) \cdot 100 \quad (\text{eq. 2.9})$$

$$S_i(\%) = \frac{(C_i)_{outlet}}{\sum(C_i)_{outlet}} \cdot 100 \quad (\text{eq. 2.10})$$

Where:

C_i : Molar concentration of the i product (CO or CH₄).

C_{CO_2} : Molar concentration of CO₂.

X_{CO_2} and S_i were obtained by the average of 2-4 different analyses at each temperature.

2.2.2. MSR reaction system

The MSR catalytic tests were performed using a Microactivity-Reference unit (PID Eng&Tech) (Figure 2.6), similar to that used for RWGS tests described above but equipped with a GILSON liquid pump. The pump was used to inject a reactant mixture $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 1/1$ (molar ratio) at constant flow and atmospheric pressure. The pre-heated liquid mixture (473 K) was mixed with N_2 (>99.999%), that was added to reach a GHSV of 2500 h^{-1} . The gaseous mixture, $\text{H}_2\text{O}/\text{CH}_3\text{OH}/\text{N}_2=1/1/1.2$ (molar ratio), was flowed through the tubular reactor at atmospheric pressure. Afterwards, a liquid-gas separator fitted with a level sensor allowed the condensation of vapors at the outlet of the system, working at 277 K. The hot box was maintained at 453 K during the whole MSR reaction tests.

300 mg of catalyst (powder) were diluted in a catalytic bed of 1 mL with SiC. The sample was crushed with a mortar and sieved with a stainless steel mesh, 0.177 mm, prior catalytic tests. All tests were carried out at 573-723 K, 0.1 MPa and a GHSV of 2500 h^{-1} . Each temperature change was reached in 10 min. The first measurement was taken after 30 min at each temperature. The catalysts were kept for 1.5 h at each temperature.

The gaseous products were analyzed online employing a Varian 4900 micro-GC equipped with three channels with micro TCDs and M5A (10 m, Ar as carrier), PPQ (10 m, He as carrier) and 5CB (8 m, He as carrier) columns, respectively. A sample loop of 10 μL was used in all three channels.

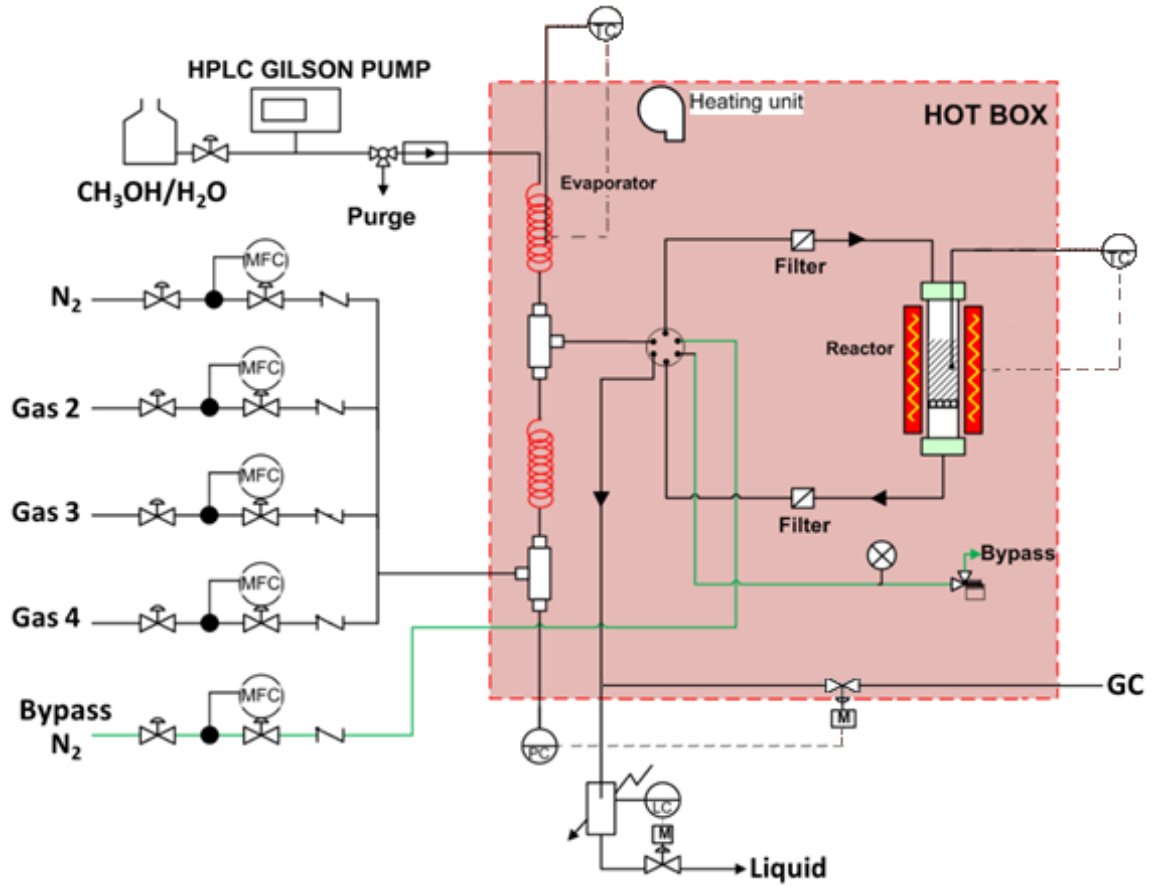


Figure 2.6. Scheme of the MSR reaction system.

The CH_3OH conversion ($X_{\text{CH}_3\text{OH}}$) was defined as:

$$X_{\text{CH}_3\text{OH}}(\%) = \frac{\sum a_i (\eta_i)_{\text{outlet}}}{(\eta_{\text{CH}_3\text{OH}})_{\text{inlet}}} \cdot 100 \quad (\text{eq. 2.11})$$

Where:

a_i : Number of carbon atoms per molecule of the product i (CH_4 , CO , CO_2 , HCHO , C_2H_4 and C_2H_6).

η_i : Number of moles of the product i (CH_4 , CO , CO_2 , HCHO , C_2H_4 and C_2H_6).

$\eta_{\text{CH}_3\text{OH}}$: Number of moles of methanol.

The product distribution is given as molar fraction (Y_i) of products obtained:

$$Y_i(\%) = \frac{(C_i)_{outlet}}{\sum(C_i)_{outlet}} \cdot 100 \quad (\text{eq. 2.12})$$

Where, C_i is the concentration of the product i .

The selectivity to carbon compounds (S_i) is obtained as:

$$S_i(\%) = \frac{a_i \cdot (n_i)_{outlet}}{\sum a_i \cdot (n_i)_{outlet}} \cdot 100 \quad (\text{eq. 2.13})$$

2.3. References

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CHAPTER 3

TRANSITION METAL CARBIDES OF GROUP 5 IN THE RWGS REACTION

In this chapter, a study of the preparation, characterization and catalytic behavior of bulk G5TMC (VC-1, VC-2, VC-1_1623, NbC-1 and TaC-1) catalysts in the RWGS reaction at 573-873 K and atmospheric pressure is presented. Characterization of samples before and after reaction was performed by means of XRD, BET surface area, Raman, XPS, H₂-TPR and TEM techniques. Moreover, thermogravimetric and calorimetric analysis and *in-situ* DRIFTS experiments were performed of CO₂ adsorption and reaction. Theoretical investigations carried out in the group of Prof. F. Illas were used to interpret the experimental results.

VC samples were active in the RWGS under the reaction conditions used; meanwhile NbC-1 and TaC-1 were not. The coexistence of two different vanadium carbide phases in VC samples, stoichiometric VC and V₈C₇ (being C deficient), was observed through precession electron diffraction technique. The presence of more stoichiometric VC phase in vanadium carbide samples was reflected in a lower CO₂ adsorption heat and poorer catalytic behavior. The sample containing more V₈C₇ phase showed a higher CO₂ conversion, CO selectivity and a lower apparent activation energy, this sample also presented a good stability over long-time test.

DFT calculations confirmed that C vacancies in V₈C₇ are responsible for the observed catalytic behavior, allowing reactants to absorb more strongly, and lowering the energy barrier for both H₂ and CO₂ dissociation steps on the surface. Moreover, a reaction pathway for the RWGS reaction over VC systems is proposed.

3.1. Study of the preparation of bulk G5TMC catalysts

Common methods of preparation of VC, NbC and TaC are based on carbothermal reduction process or on the use of a mixture of H₂ and carburizing agents (CO, CH₄, C₂H₆) at high temperature (up to ~2273 K) and the corresponding metal oxides [1-3]. The use of other reducing agents, such as Mg, have also been reported employing lower temperature of treatment but using autoclave reactors (high pressure) [4-7]. In this process, Mg, MO_x and the carbon source are treated in an autoclave reactor under inert atmosphere, when the temperature increases Mg reduces the MO_x to highly active metal while the carbon precursor used is converted to carbon, the latter is deposited on the surface of the metal to form the corresponding TMC.

Few number of papers deals with sol-gel methods for the preparation of VC, NbC and TaC [8-10]. Zhao et al [8] prepared V₈C₇ nanoparticles using NH₄VO₃ and a mixture of glucose and urea as vanadium and carbon sources, respectively; after a treatment at 1323 K under Ar, crystallite sizes of ~80 nm were obtained. Preiss et al [9] prepared NbC and TaC using Nb(OC₂H₅)₅ and Ta(OC₂H₅)₅ as niobium and tantalum precursors and a carbonaceous gel formed by coal tar, sucrose and ethanol; then the mixture was treated at 1673 K under Ar obtaining crystallite sizes of ~50 nm in both cases.

In this thesis a new sol-gel method for the preparation of G5TMCs is developed.

Bulk G5TMCs here presented were prepared using 4,5-dicyanoimidazole (*Manchester Organics* 97%) as carbon source and metal chloride or alkoxide as metal precursors. The use of 4,5-dicyanoimidazole as carbon source was inspired in the work of Giordano et al [10] for the preparation of Cr₃C₂.

Modifying the “carbon source/metal precursor” molar ratio (R) and/or the temperature of thermal treatment, catalysts with different characteristics such as crystallite size and/or specific surface area were obtained.

Figure 3.1 shows the general procedure of G5TMC preparation.

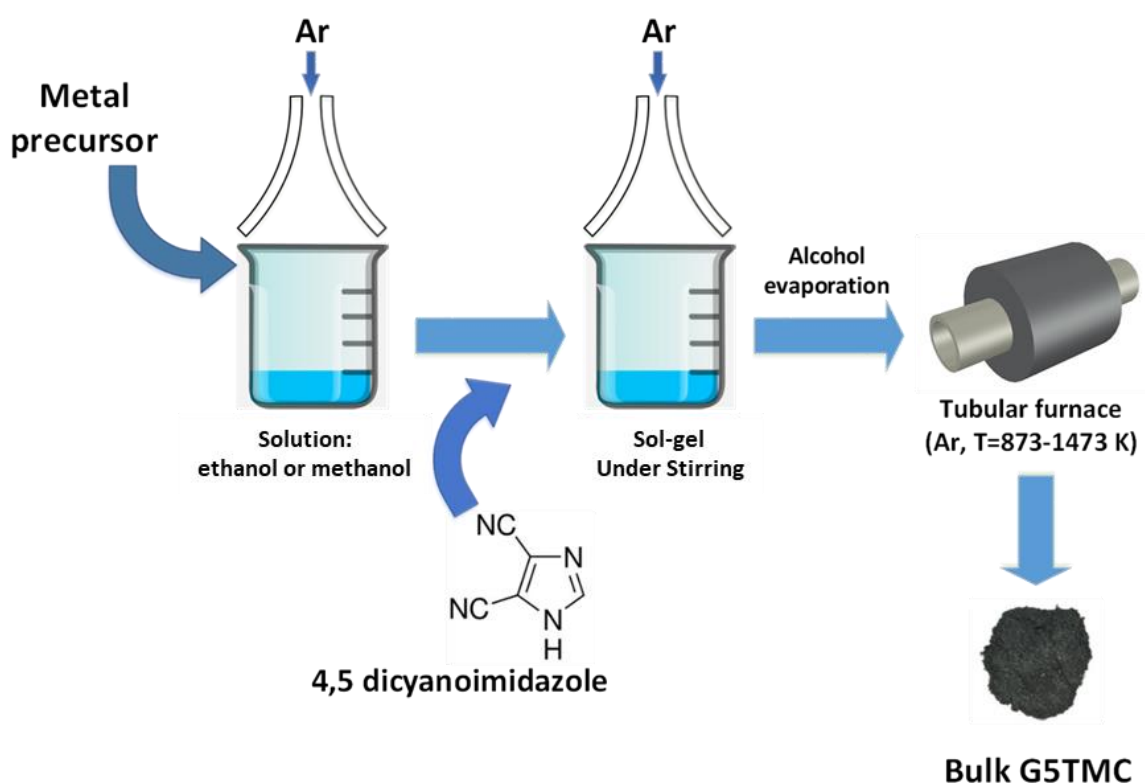


Figure 3.1. Schematic of bulk G5TMC preparation.

For the preparation of the samples, 4,5-dicyanoimidazole was added under stirring to an alcoholic solution (ethanol or methanol) containing the metal precursor under a flow of Ar to avoid hydrolyzation. Then the alcohol was evaporated forming a gel, which was placed into a tubular furnace at the set temperature (2.5 K min^{-1}) under Ar for 5 h.

The study of the preparation of G5TMC samples is given bellow:

Vanadium Carbide

The study of the preparation of vanadium carbide has been carried out using two different vanadium precursors: $\text{VO}(\text{isopropoxide})_3$ (*Alfa Aesar*, 96%) and VOCl_3 (*Alfa Aesar*, 99%).

The preparation using $\text{VO}(\text{isopropoxide})_3$ as vanadium precursor was performed by varying the 4,5-dicyanoimidazole/ $\text{VO}(\text{isopropoxide})_3$ molar ratio

(R), $R=0.25, 0.5, 0.8, 1, 1.35, 1.5$ and 2 , and using a treatment temperature of 1373 K . XRD analysis indicated that for $R<1$, vanadium carbide and nitride phases were formed as shown in Figure 3.2. EDX spectroscopy verified the presence of N on samples prepared with a $R<1$. For a $R=1$ no N was detected (Figure 3.3).

For $R\geq 1$, only peaks corresponding to cubic V_8C_7 and/or VC are observed (Figure 3.2). The presence of cubic V_8C_7 and/or VC phases cannot be distinguished by XRD; the most intense peaks of both phases are located at the same positions ($2\theta=37.4, 43.4, 63.1, 75.6$ and 79.7°); V_8C_7 presents additional peaks with very low intensity. This can be observed in the reference XRD patterns of VC and V_8C_7 phases shown in Figure 3.2.

Figure 3.4 shows the crystallite sizes of VC_x phases calculated from XRD of the different samples as a function of the R used in the preparation. When R was increased up to 1.35 , a decrease of the VC_x crystallite size was observed, and then the crystallite size remained almost constant with the increase of R. We propose the formation of a “*templating network*” during the synthesis, which would avoid the sintering of VC_x nanoparticles. This *templating network* would be the responsible for the decrease of crystallite size when R increases up to 1.35 . However, the increase of R could lead to a carbon excess in the final product (with $R=1$, the weight of sample was 15% higher than the theoretical value).

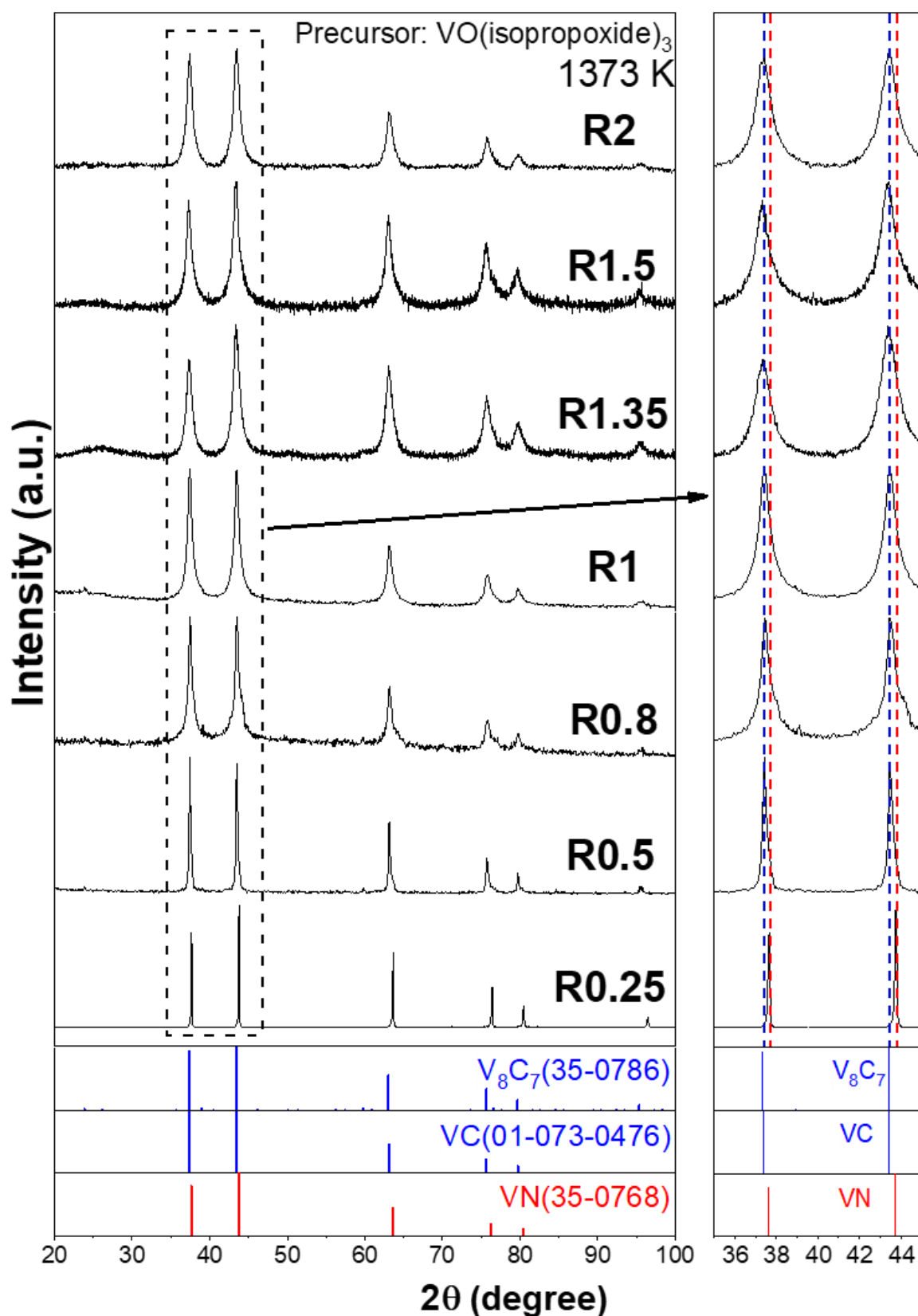


Figure 3.2. XRD patterns of VC samples prepared using $\text{VO}(\text{isopropoxide})_3$ and different 4,5-dicyanoimidazole/ $\text{VO}(\text{isopropoxide})_3$ molar ratios (R). Treatment temperature: 1373 K.

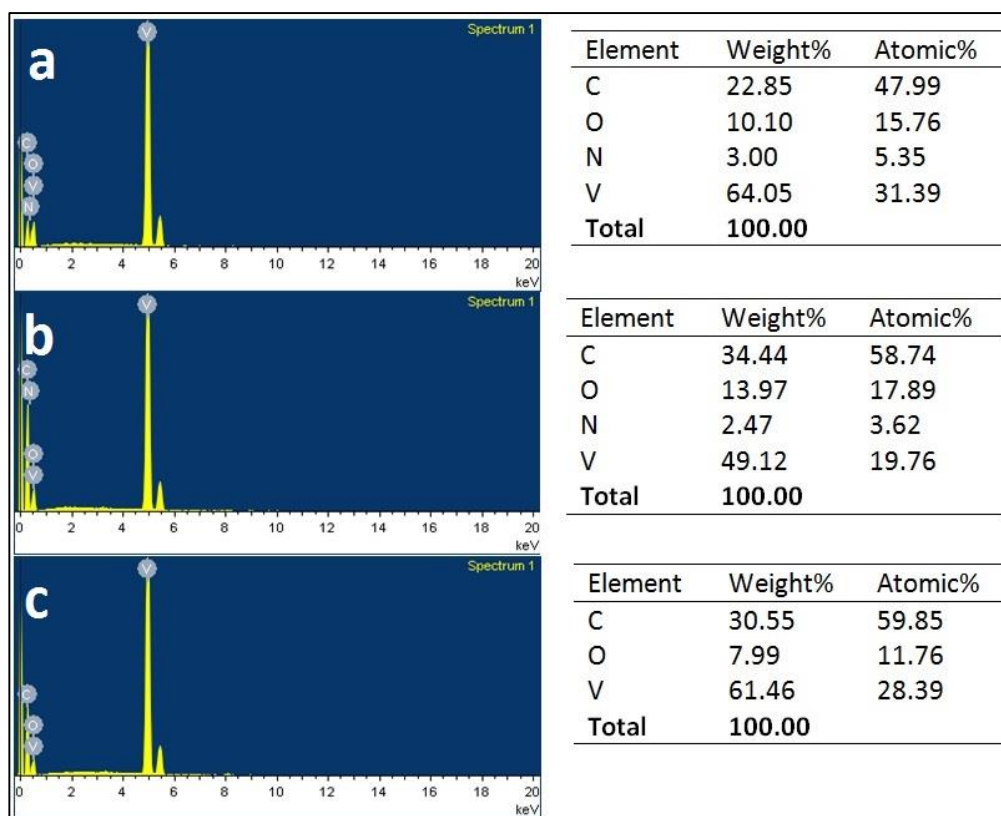


Figure 3.3. EDX spectra of VC samples prepared using VO(isopropoxide)₃ and different 4,5-dicyanoimidazole/VO(isopropoxide)₃ molar ratios (R) (a) R=0.5; (b) R=0.8 and (c) R=1. Treatment temperature: 1373 K.

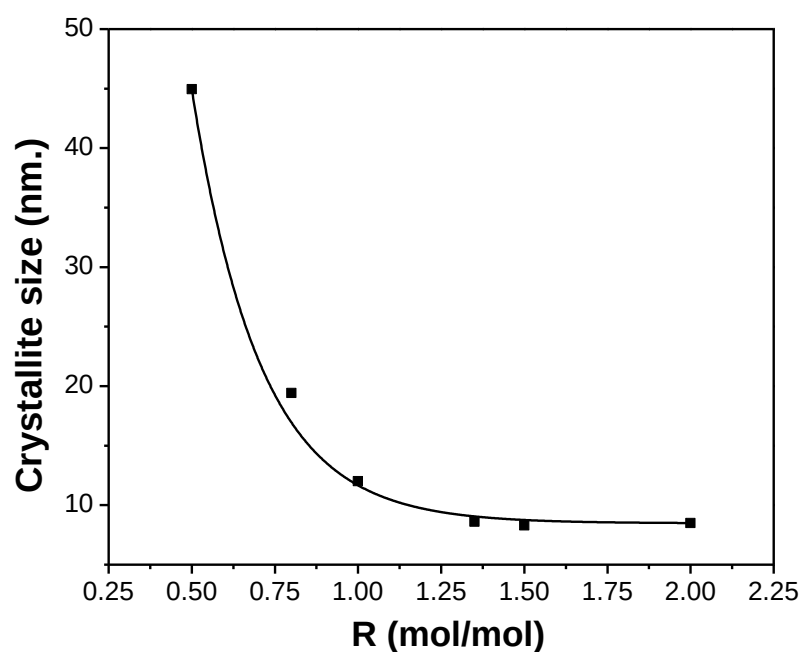


Figure 3.4. Plot of crystallite size of VC_x phase calculated by XRD as a function of the 4,5-dicyanoimidazole/VO(isopropoxide)₃ molar ratio (R) used in the preparation. Treatment temperature: 1373 K.

The effect of the temperature in the preparation of vanadium carbide was also studied. Two more samples were prepared with a $R=1$ and treated at 1273 and 1473 K. The corresponding XRD patterns are shown in Figure 3.5. In all cases, peaks characteristics of cubic VC_x phase were found and the absence of crystalline VO_x was determined.

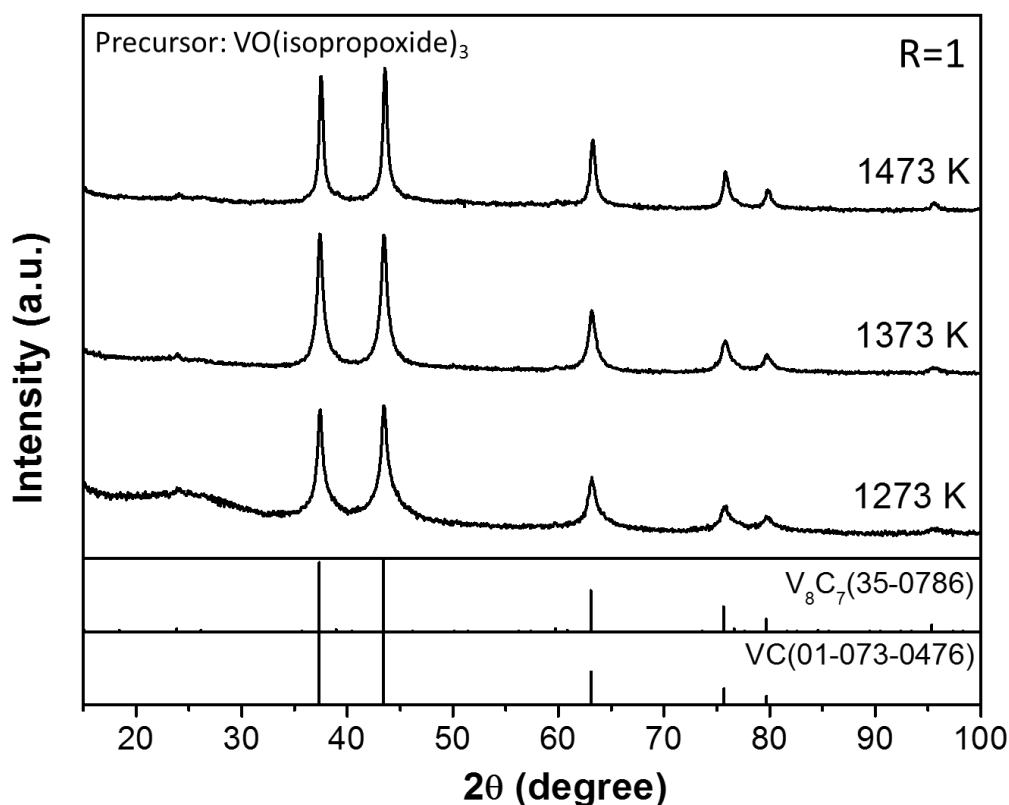


Figure 3.5. XRD patterns of VC samples prepared using $VO(\text{isopropoxide})_3$, 4,5-dicyanoimidazole/ $VO(\text{isopropoxide})_3=1$ (molar ratio) and different treatment temperatures.

The low intensity and broad peak at $2\theta=26^\circ$ for the sample treated at 1273 K might be attributed to residual carbon.

The crystallite size of VC_x phases increased with the increase of temperature. Crystallite sizes of 8, 11 and 15 nm were determined from XRD patterns for samples prepared at 1273, 1373 and 1473 K, respectively.

With this background, we studied the preparation of VC samples using VOCl_3 as vanadium precursor. Three VC_x samples varying the 4,5-dicyanoimidazole/ VOCl_3 molar ratio (R), $R=1$, 1.35 and 1.5 were prepared with a treatment temperature of 1373 K. The corresponding XRD patterns are shown in Figure 3.6. Only peaks characteristics of VC_x phase (VC and/or V_8C_7) were observed.

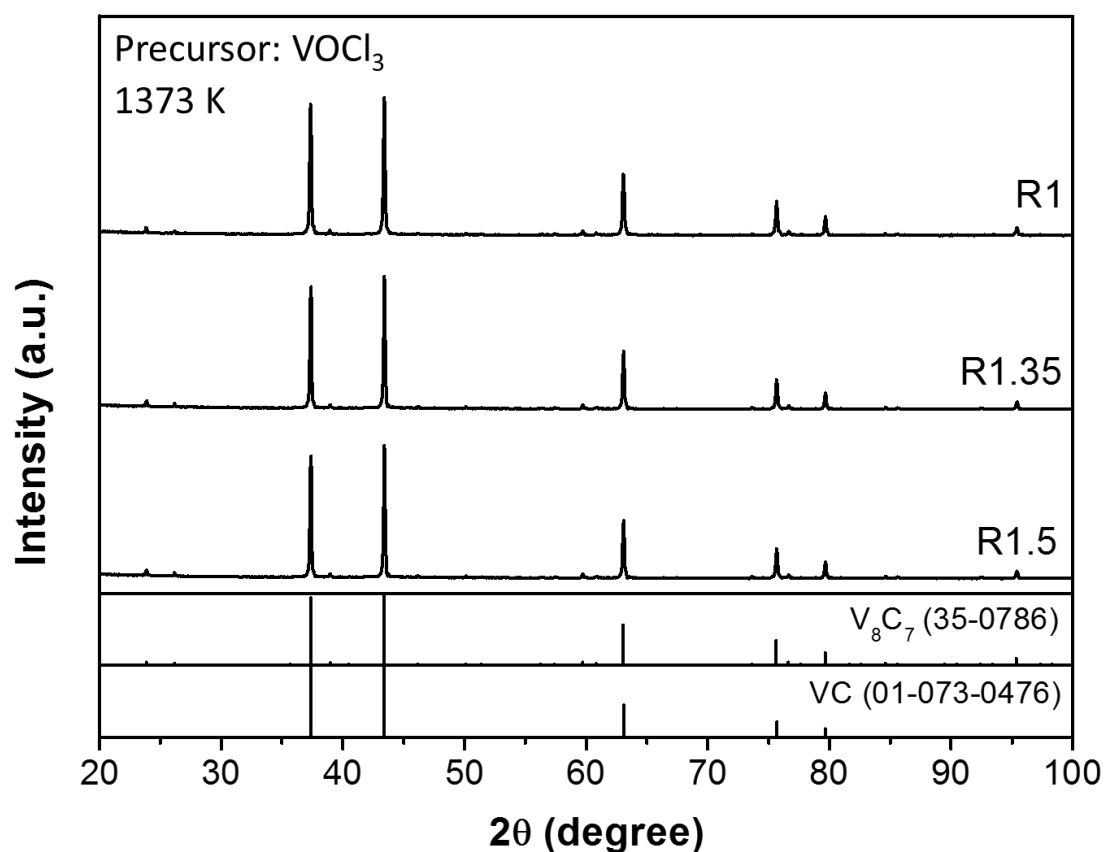


Figure 3.6. XRD patterns of VC samples prepared using VOCl_3 , different 4,5-dicyanoimidazole/ VOCl_3 molar ratios (R) and a treatment temperature of 1373 K.

In all cases the crystallite size was about 64 nm, which was much higher than that obtained when $\text{VO}(\text{isopropoxide})_3$ was used as vanadium precursor (11 nm for the sample prepared with $R=1$ and a treatment temperature of 1373 K)

Niobium carbide

The study of the preparation of niobium carbide has been carried out using NbCl_5 (*Alfa Aesar*, 99%) and $\text{Nb}(\text{OC}_2\text{H}_5)_5$ (*Alfa Aesar*, 99.95%) as niobium precursors.

When NbCl_5 was used, three samples with 4,5-dicyanoimidazole/ NbCl_5 molar ratio ($R=1, 2$ and 6) and treatment temperature of 1073 K were prepared. The XRD patterns are shown in Figure 3.7.

In all cases, XRD patterns show broad peaks at $2\theta=35.2, 41.8, 59.1, 70.9$ and 74.3° tentatively assigned to the presence of cubic $\text{NbC}_x\text{N}_{1-x}$ phase because these peaks are located between the peaks of cubic NbC and NbN. Additionally, peaks corresponding to NbO_2 (tetragonal phase) are observed for $R=1$. For $R=6$, the broad peak at $2\theta=26^\circ$ is associated to rather amorphous carbon deposits, related with the high amount of carbon precursor used in this preparation.

In order to synthesize NbC, a new sample with $R=2$ and a treatment temperature of 1373 K was prepared. The corresponding XRD pattern (Figure 3.7) only shows diffraction peaks characteristics of NbC; the determined crystallite size was 10 nm .

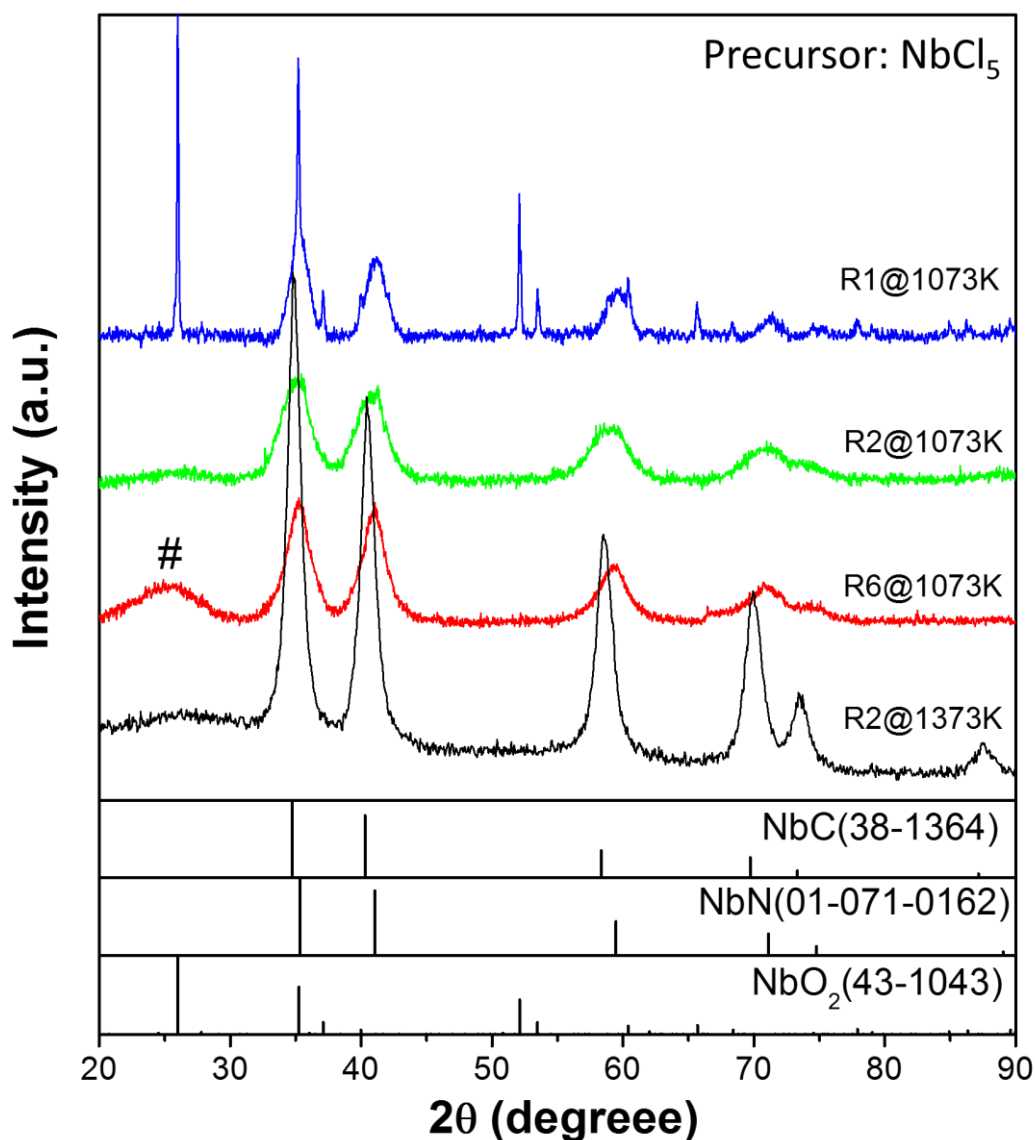


Figure 3.7. XRD patterns of NbC samples prepared using NbCl_5 , different 4,5-dicyanoimidazole/ NbCl_5 molar ratios (R) and treatment temperatures. (They are indicated in the name of samples). #Amorphous carbon.

When $\text{Nb}(\text{OC}_2\text{H}_5)_5$ was used as niobium precursor, three samples were prepared using 4,5-dicyanoimidazole/ $\text{Nb}(\text{OC}_2\text{H}_5)_5$ molar ratios ($R=1$, 1.5 and 2) and a treatment temperature of 1373 K. Their XRD patterns are shown in Figure 3.8. Peaks at $2\theta=34.7$, 40.3 , 57.3 , 69.7 , 73.3 , 87.1 and 97.4° correspond well with the presence of cubic NbC phase in all three cases.

An increase of the crystallite size of NbC was observed when the R was decreased. Crystallite sizes of 4, 6 and 16 nm were obtained for $R=2$, $R=1.5$ and

$R=1$, respectively. The very low intensity peaks at $2\theta=22.6^\circ$, 26.0° and 28.3° in the XRD corresponding to the catalysts prepared with $R=1$ could be related with the presence of Nb_2O_5 (orthorhombic phase) and NbO_2 (tetragonal phase). These peaks disappeared when the temperature of treatment was increased at 1473 K (Figure 3.8). Likewise, the increase of the treatment temperature also resulted in an increase of the determined crystallite size of NbC (20 nm).

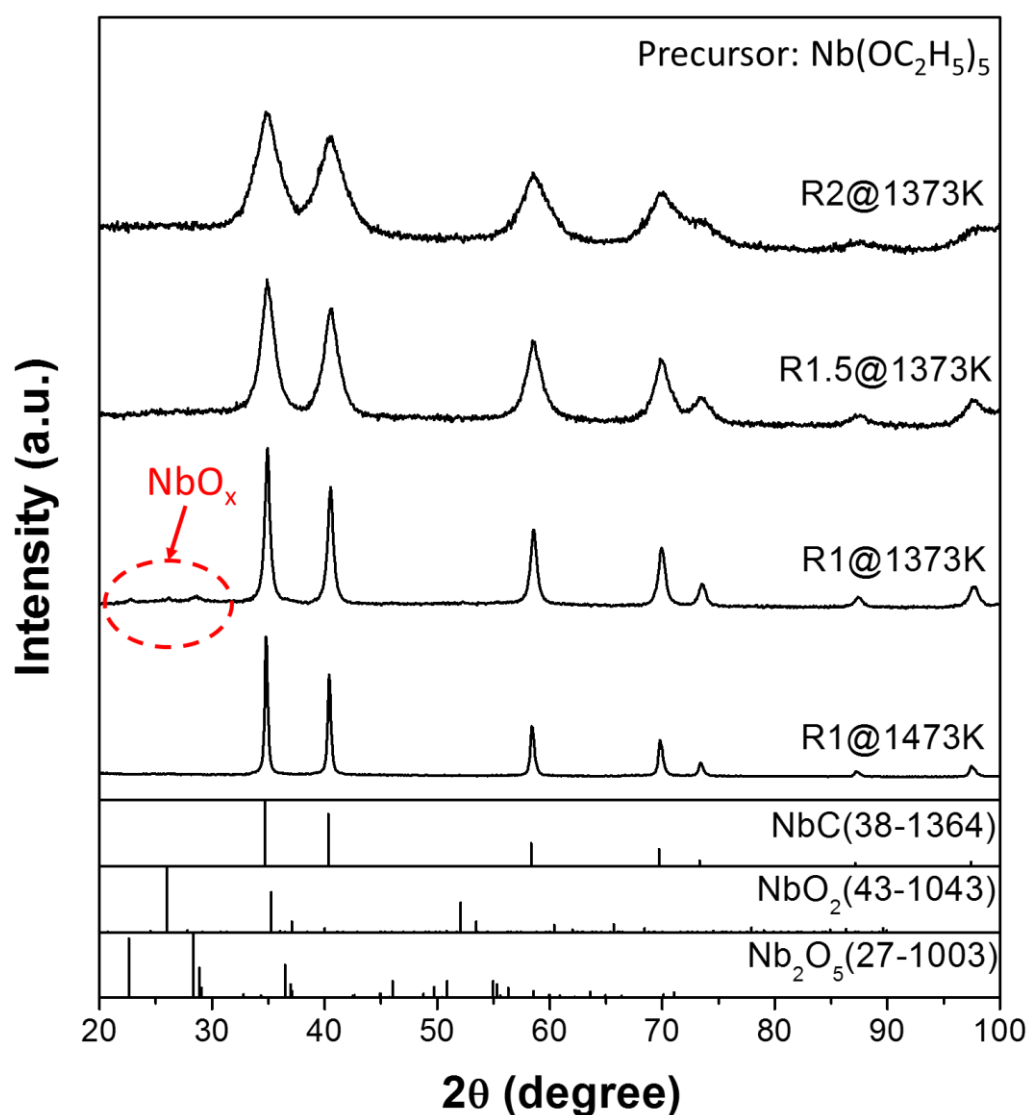


Figure 3.8. XRD patterns of NbC samples prepared using $\text{Nb}(\text{OC}_2\text{H}_5)_5$, different 4,5 dicyanoimidazole/ $\text{Nb}(\text{OC}_2\text{H}_5)_5$ molar ratios (R) and treatment temperatures. (They are indicated in the name of samples).

Tantalum carbide

The preparation of TaC was studied using TaCl₅ (*Alfa Aesar*, 99.8%) and Ta(OC₂H₅)₅ (*Sigma Aldrich*, 99.98%) as tantalum precursors. When TaCl₅ was used, methanol was employed as solvent because of the low solubility of TaCl₅ in ethanol.

The preparation of TaC using TaCl₅ was performed using different 4,5-dicyanoimidazole/TaCl₅ molar ratios (R) and treatment temperatures (T). The XRD patterns of TaC samples prepared are shown in Figure 3.9.

The sample prepared with the lowest treatment temperature (R3@1073K) showed broad diffraction peaks at $2\theta=35.2, 41.1, 59.5, 71.2$ and 75.8° assigned to cubic TaC_xN_{1-x} phase, the broad peak at $2\theta=26^\circ$ is referred to the presence of amorphous carbon. When the temperature of treatment was increased up to 1423 K a unique phase of TaC was obtained (Figure 3.9). As it was in the case of the preparation of VC and NbC a decrease of R used in the preparation produced an increase of crystallite size. Crystallite sizes of 9, 10 and 11 nm were calculated for R3@1423K, R2.5@1423K and R2@1423K, respectively.

The same behavior was found in the samples prepared at 1473 K. The crystallite size of R2@1473 K and R1.75@1473K were 17 and 22 nm, respectively. On the other hand, when the crystallite size of samples R2@1423K (11 nm) and R2@1473K (17 nm) are compared, it can be seen that an increase in the treatment temperature produced an increase in the crystallite size.

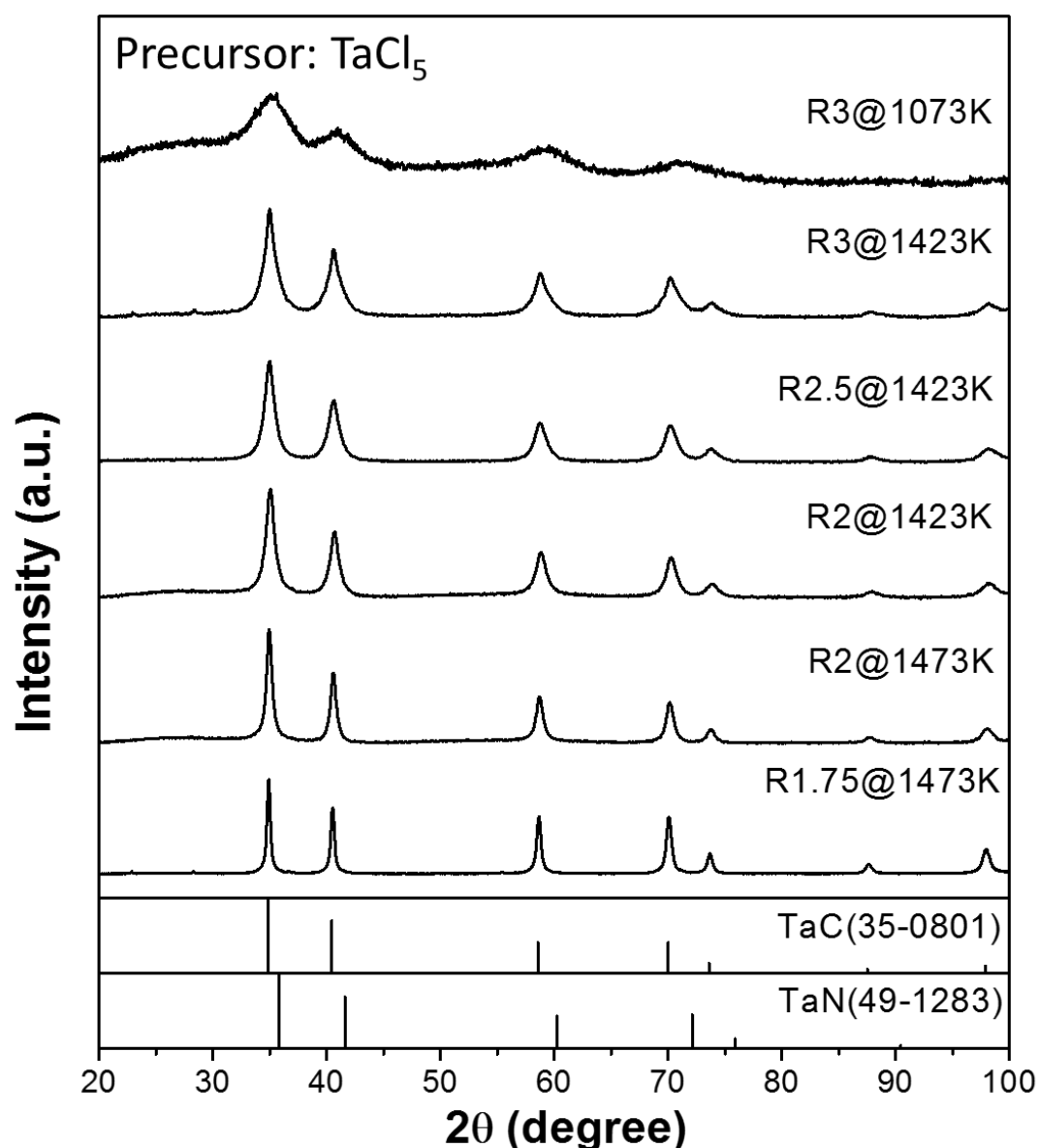


Figure 3.9. XRD patterns of TaC prepared using TaCl_5 , different 4,5-dicyanoimidazole/ TaCl_5 molar ratios (R) and treatment temperatures. (They are indicated in the name of samples).

When $\text{Ta}(\text{OC}_2\text{H}_5)_5$ was used as tantalum precursor, three samples were prepared using 4,5-dicyanoimidazole/ $\text{Ta}(\text{OC}_2\text{H}_5)_5$ molar ratios $R=2$, 2.5 and 3 and a treatment temperature of 1423 K. The XRD patterns of samples are shown in Figure 3.10. Diffraction peaks at $2\theta=34.9$, 40.5, 58.5, 70.0, 73.6, 87.5 and 97.9° correspond to the presence of cubic TaC phase in all three samples.

In this case, also an increase of the crystallite size of TaC was observed when R was decreased. Crystallite sizes of 3, 5 and 7 nm were obtained for R=3, R=2.5 and R=2, respectively.

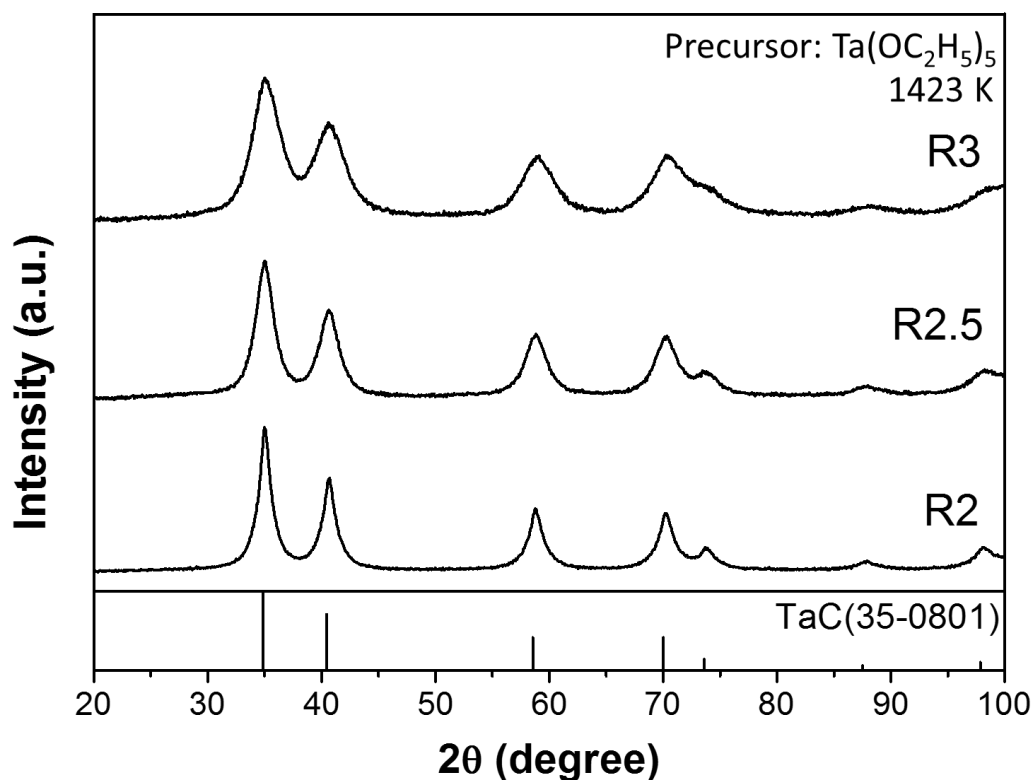


Figure 3.10. XRD patterns of TaC prepared using $\text{Ta}(\text{OC}_2\text{H}_5)_5$, different 4,5-dicyanoimidazole/ $\text{Ta}(\text{OC}_2\text{H}_5)_5$ molar ratios (R) and a treatment temperature of 1423 K.

In general, the use of metal alkoxide as metal precursor resulted in the preparation of bulk G5TMCs with a smaller crystallite size compared to those obtained when metal chloride was used.

The procedure described above has been extended for the preparation of other TMCs such as Mo_xC (hexagonal Mo_2C and cubic MoC) and cubic WC_{1-x} , and has been detailed in two recent publications [11,12]. In these two publications the catalytic behavior of Mo_xC in the RWGS and that of $\text{WC}_{1-x}/\text{TiO}_2$ in the photocatalytic H_2 production from ethanol_(aq) are reported, being a collaboration

work in our research group. The preparation and characterization of Mo_xC and WC_{1-x} are described in ANNEX I.

3.2. Bulk G5TMC catalysts in the RWGS reaction

3.2.1. Characterization of bulk G5TMC catalysts

Among all the G5TMC bulk catalysts described above, we chose those that appear in Table 3.1 to be tested in the RWGS reaction. Part of VC-1 sample was thermally treated up to 1623 K (catalysts named VC-1_1623), to observe the influence of the temperature on the characteristics and the catalytic behavior in the RWGS reaction. The specific preparation of these catalysts is given in the ANNEX II.

Table 3.1. Synthesis conditions of G5TMC samples.

Catalyst	Metal Precursor	Solvent	R ⁽¹⁾	Temperature (K)
VC-1	VOCl_3	Ethanol	1	1373
VC-2	$\text{VO}(\text{isopropoxide})_3$	Ethanol	1.35	1373
VC-1_1623	VC-1 treated up to 1623 K			
NbC-1	$\text{Nb}(\text{OC}_2\text{H}_5)_5$	Ethanol	1	1473
TaC-1	TaCl_5	Methanol	1.75	1473

⁽¹⁾R:4,5-dicyanoimidazole/metal precursor molar ratio.

In all cases, catalysts were exposed to ambient without passivation; a detrimental effect of passivation with O_2 had been reported for alumina-supported molybdenum carbide catalysts used in the CO_2 hydrogenation [13].

XRD patterns of vanadium carbide samples are shown in Figure 3.11. Characteristics peaks at $2\theta=37.4$, 43.4 , 63.0 , 75.6 and 79.7° , corresponding to cubic V_8C_7 (JCPDS 35-0786) and/or VC (JCPDS 01-073-0476) phases are observed. Precession Electron Diffraction-pattern recognition (PED-ASTAR)

technique was used to identify the presence of these two phases, which will be discussed later.

XRD patterns of NbC-1 and TaC-1 samples are shown in Figure 3.12. For NbC-1 sample, the peaks at $2\theta=34.7$, 40.3 , 57.3 , 69.7 , 73.3 , 87.1 and 97.4° are assigned to cubic NbC phase (JCPDS 38-1364). For TaC-1 sample, peaks at $2\theta=34.9$, 40.5 , 58.5 , 70.0 , 73.6 , 87.5 and 97.9° are attributed to the presence of cubic TaC phase (JCPDS 35-0801).

As stated above, nitrogen or oxygen substitution in lattice sites (C replacement), as well as metal vacancies, would affect the peak intensities and would shift the peak positions usually to a lower angle associated to the lattice expansion [14,15]. For the chosen samples, pure TMCs phases were obtained in all cases and no crystalline metal oxides were observed.

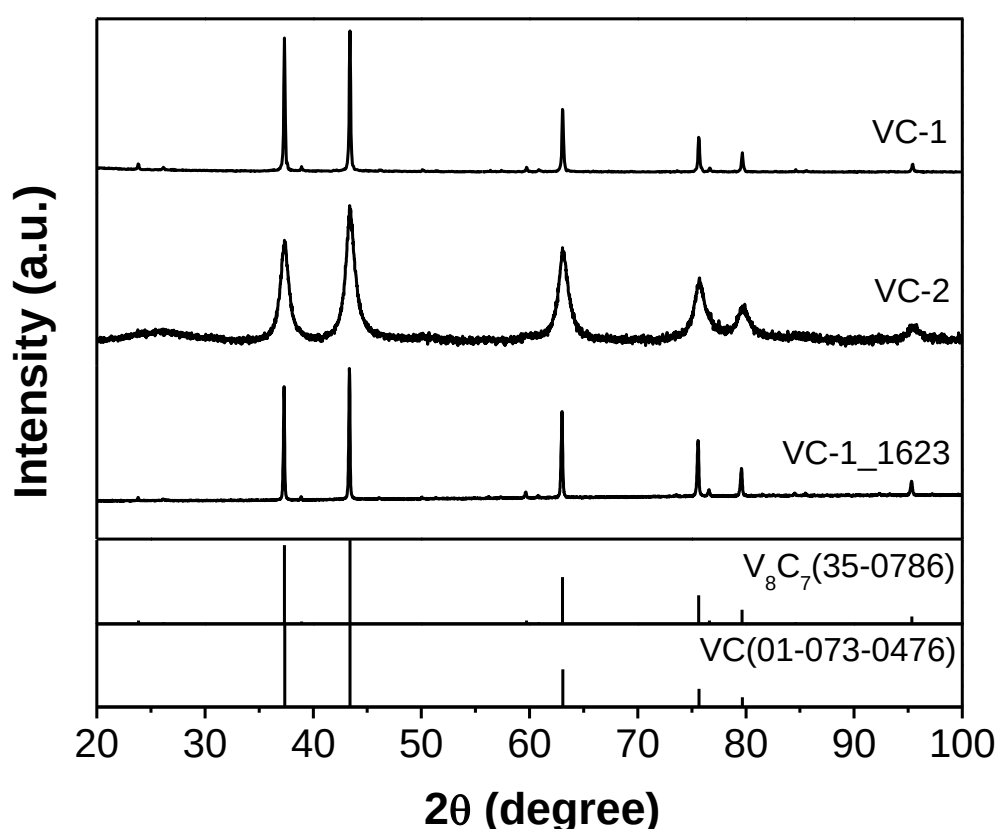


Figure 3.11. XRD patterns of VC catalysts.

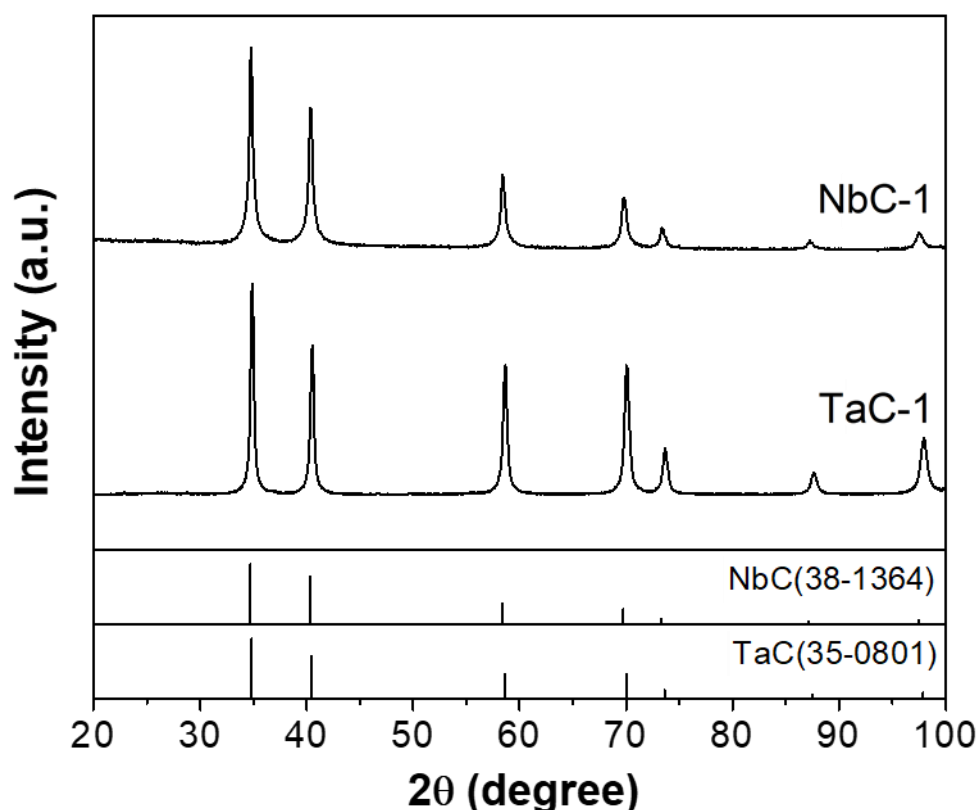


Figure 3.12. XRD patterns of NbC-1 and TaC-1 catalysts.

Table 3.2 shows the crystallite sizes of catalysts determined from XRD analysis. As observed, different crystallite sizes were obtained according to the method used in VC preparation. VC-2, which was prepared using $\text{VO}(\text{isopropoxide})_3$ as vanadium precursor, showed the smallest crystallite size (8 nm), meanwhile VC-1, which was prepared using VOCl_3 , showed a crystallite size of 64 nm. After heating VC-1 up to 1623 K (VC-1_1623) a slight increase in the VC crystallite size was observed (Table 3.2). NbC-1 and TaC-1 samples showed a similar crystallite size of 20 and 22 nm, respectively (Table 3.2).

VC samples displayed high BET surface areas, which could be related to the presence of residual carbon from the preparation (Table 3.2). Surprisingly, an increase of BET surface area resulted when VC-1 was heated in Ar up to 1623 K (VC-1_1623) (Table 3.2).

Table 3.2. Crystallite size (XRD) and BET surface area of G5TMC samples.

Catalyst	Crystallite size (nm)	S_{BET} ($m^2 g^{-1}$)
VC-1	64	204
VC-2	8	315
VC-1_1623	70	503
NbC-1	20	45
TaC-1	22	51

The VC samples, specifically VC-1 and VC-2, were further characterized by TEM-EDX, PED, Raman, H_2 -TPR and XPS techniques, because they showed a relevant catalytic behavior in the RWGS reaction compared to the other samples.

The TEM and HRTEM analysis (Figures 3.13A and 3.14A) confirmed the presence of higher VC_x particles in VC-1 (mean size of 64.1 nm, Figure 3.13C) than in VC-2 (mean size of 7.0 nm, Figure 3.14C). In both cases, these results are in agreement with those calculated by XRD (Table 3.2).

STEM-EDX analysis showed a homogeneous dispersion of vanadium throughout the samples (Figures 3.13B and 3.14B).

VC-1 and VC-2 samples were further characterized with spot electron diffraction-pattern recognition (PED-ASTAR) to verify the coexistence of V_8C_7 and VC cubic phases.

The best fitting indexation, to V_8C_7 or VC, was used to obtain a reliable nanoscale phase mapping (Figures 3.15 and 3.16). In general, from PED-ASTAR analysis a major presence of stoichiometric VC phase can be deduced in VC-1 (Figure 3.15). On the other hand, for VC-2, most of the analyzed zones showed a better fitting indexation when the presence of V_8C_7 phase is assumed (Figure 3.16). As stated above VC-1_1623 was obtained after heating VC-1 at 1623 K. A major presence of VC phase in VC-1_1623 could be assumed because the phase transition $V_8C_7 \rightarrow VC$ is favored with the increase of temperature [16].

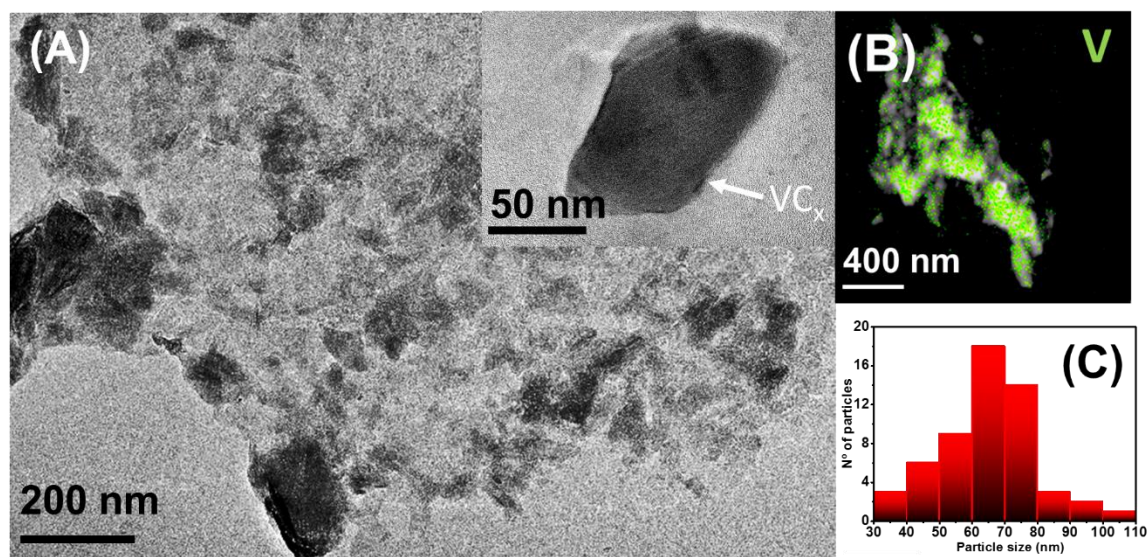


Figure 3.13. Characterization of VC-1: A) TEM and HRTEM images; B) STEM image and vanadium EDX mapping combination; C) Particle size distribution

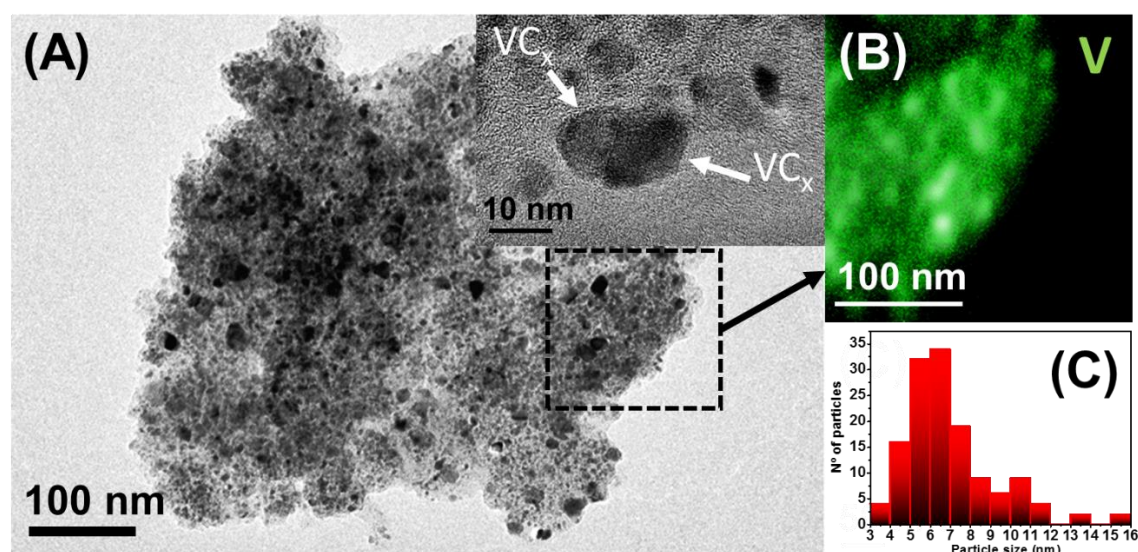


Figure 3.14. Characterization of VC-2: A) TEM and HRTEM images; B) STEM image and vanadium EDX mapping combination; C) Particle size distribution

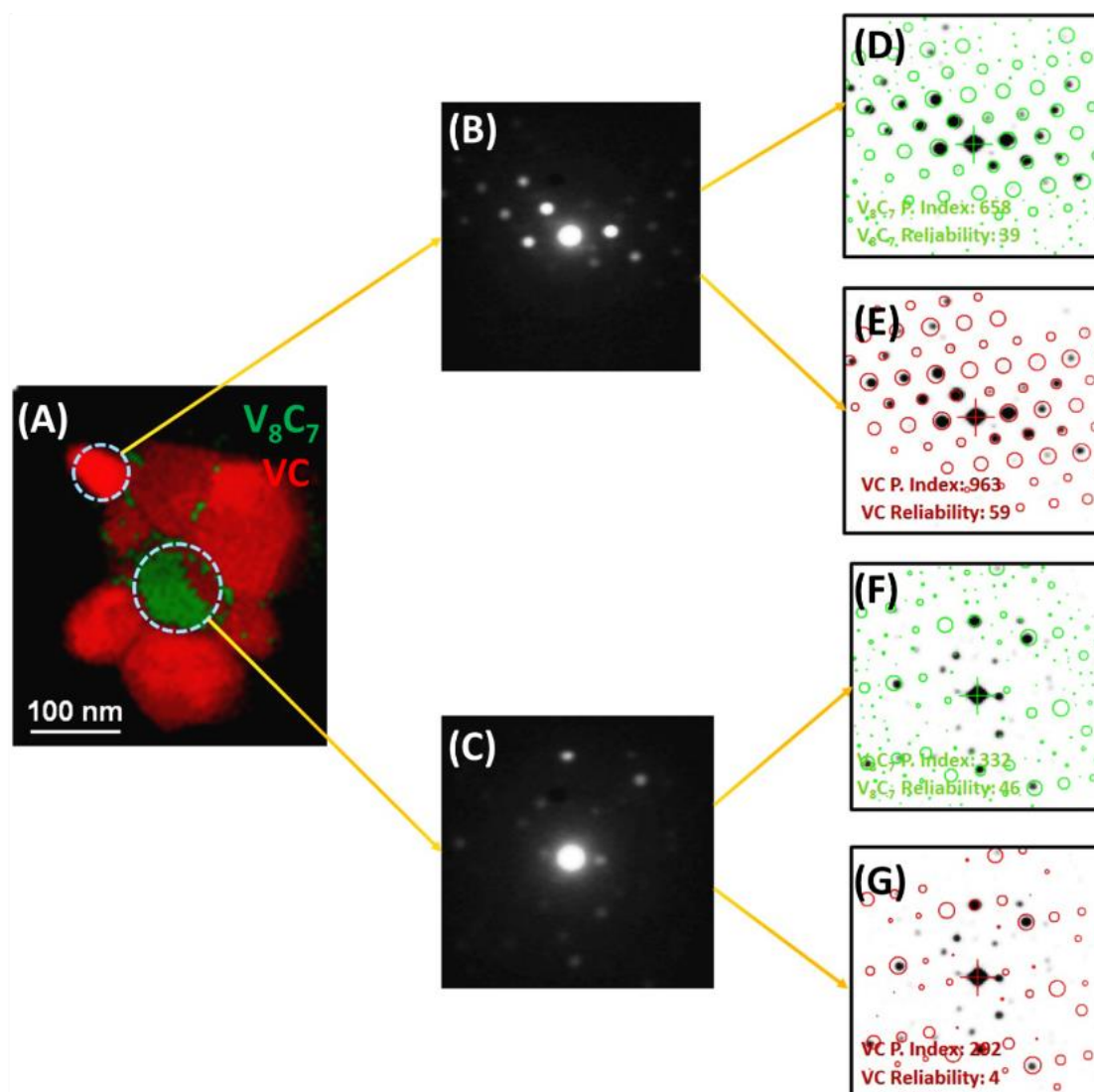


Figure 3.15. Precession Electron Diffraction (PED)-ASTAR characterization of VC-1: A) VC_x phase mapping obtained according with the best fitting indexation; B) and C) ED patterns of different zones; D) and F) Indexation of the corresponding ED pattern according to V₈C₇; E) and G) Indexation of the corresponding ED pattern according to VC.

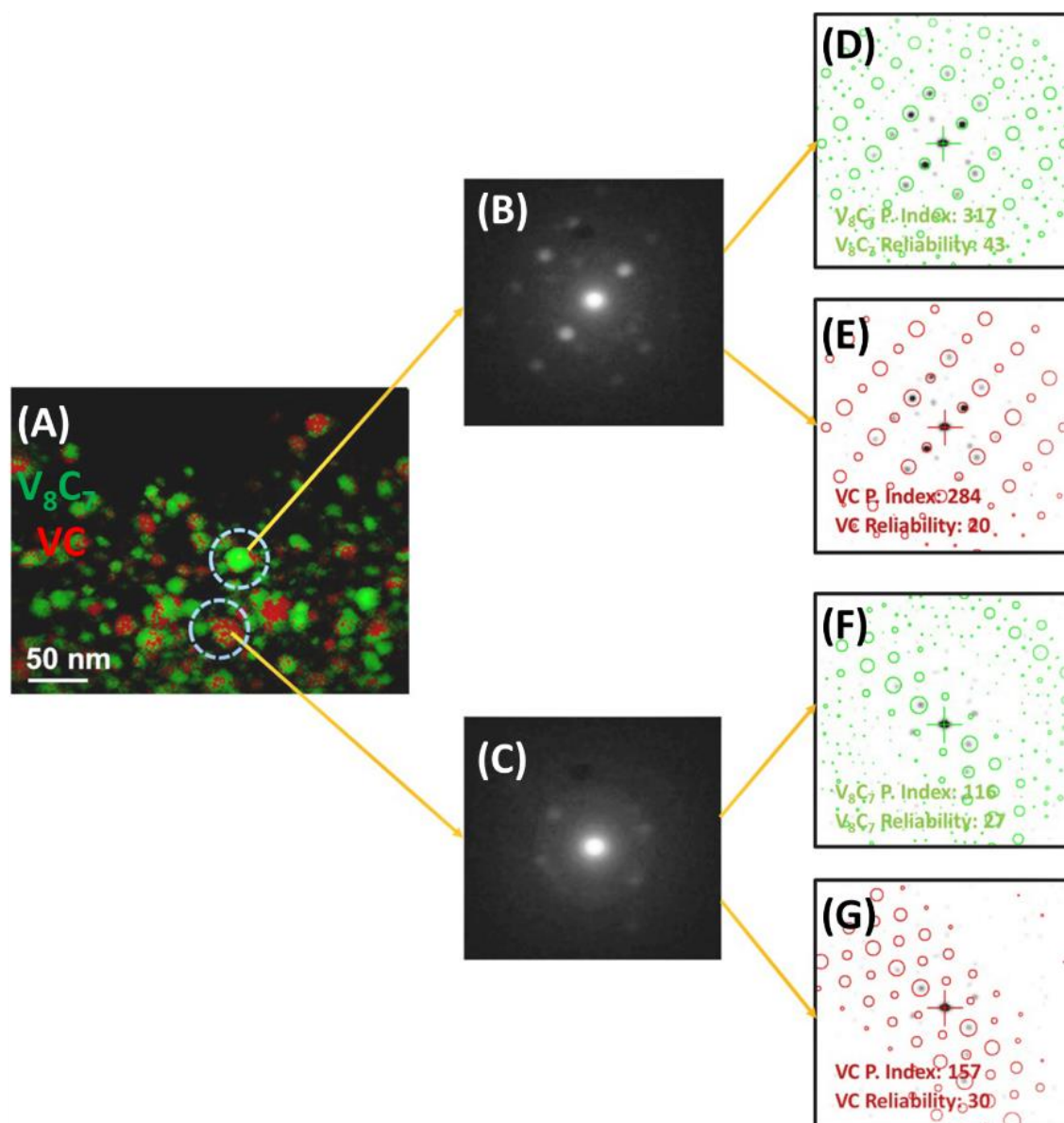


Figure 3.16. PED-ASTAR characterization of VC-2: A) VC_x phase mapping obtained according with the best fitting indexation; B) and C) ED patterns of different zones; D) and F) indexation of the corresponding ED pattern according to V_8C_7 ; E) and G) indexation of the corresponding ED pattern according to VC.

VC-1 and VC-2 showed low intensity Raman bands centered at 1358 cm^{-1} and 1595 cm^{-1} (Figure 3.17), assigned to the presence of residual amorphous carbon formed during the preparation. Moreover, VC-1 shows several bands in the $100\text{--}1100\text{ cm}^{-1}$ region related to surface oxy-vanadium species, likely formed when the samples were exposed to ambient [17-19]. The low intensity band at

991 cm^{-1} could indicate the presence of a very low amount of crystalline V_2O_5 [20-22]. VC-2 showed much lower intense Raman bands in the 100-1100 cm^{-1} region than VC-1 (Figure 3.17), which would indicate a lower amount of surface oxy-vanadium species.

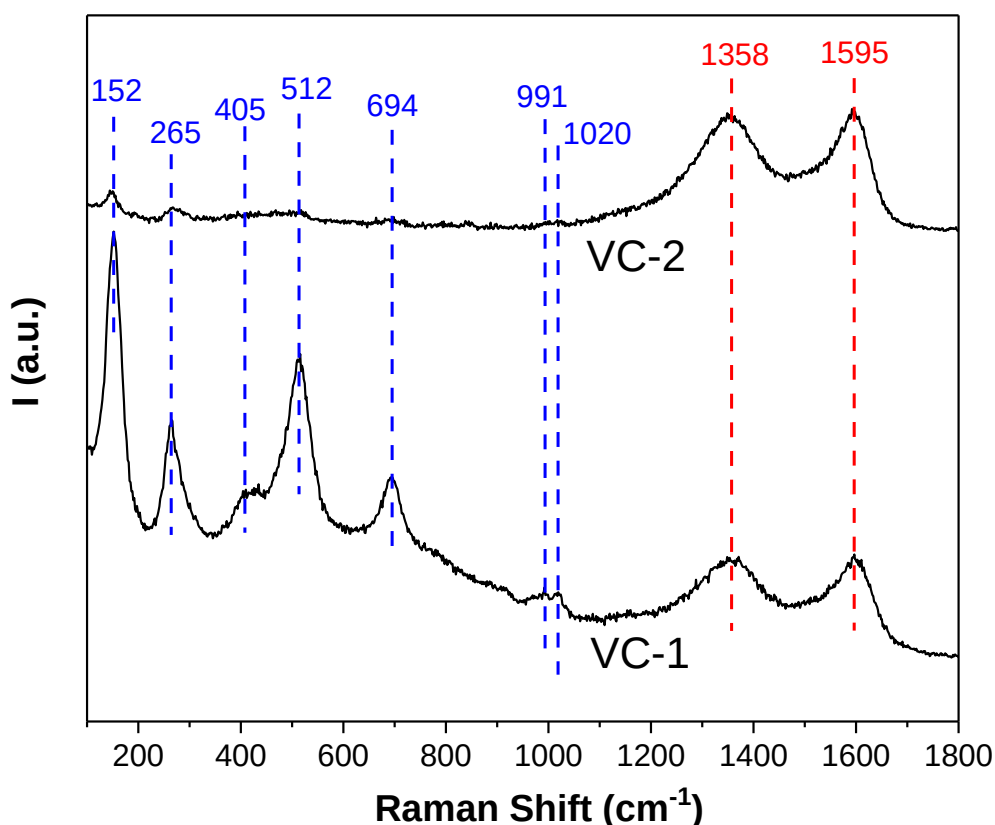


Figure 3.17. Raman spectra of VC-1 and VC-2 catalysts.

H_2 -TPR experiments were carried out in VC catalysts to verify the presence VO_x species in the samples.

The H_2 -TPR profile of VC-1 (Figure 3.18) indicates a small H_2 consumption at 743 K ($0.77 \text{ mmol H}_2 \text{ g}_{\text{cat}}^{-1}$), attributed to the reduction of mono-or polymeric oxy-vanadium (V) species because the reduction of amorphous V_2O_5 take place at ~ 852 K and that of crystalline V_2O_5 at higher temperatures [21,23]. The low H_2 consumption ($0.41 \text{ mmol H}_2 \text{ g}_{\text{cat}}^{-1}$) of VC-2 at 528 K can be associated to the reduction of vanadium oxy-carbide species as has been proposed for MoC_x systems [24]. The higher H_2 consumption observed for VC-1 than for VC-2 is

consistent with the larger presence of oxy-vanadium species in VC-1, as deduced from Raman spectroscopy analysis.

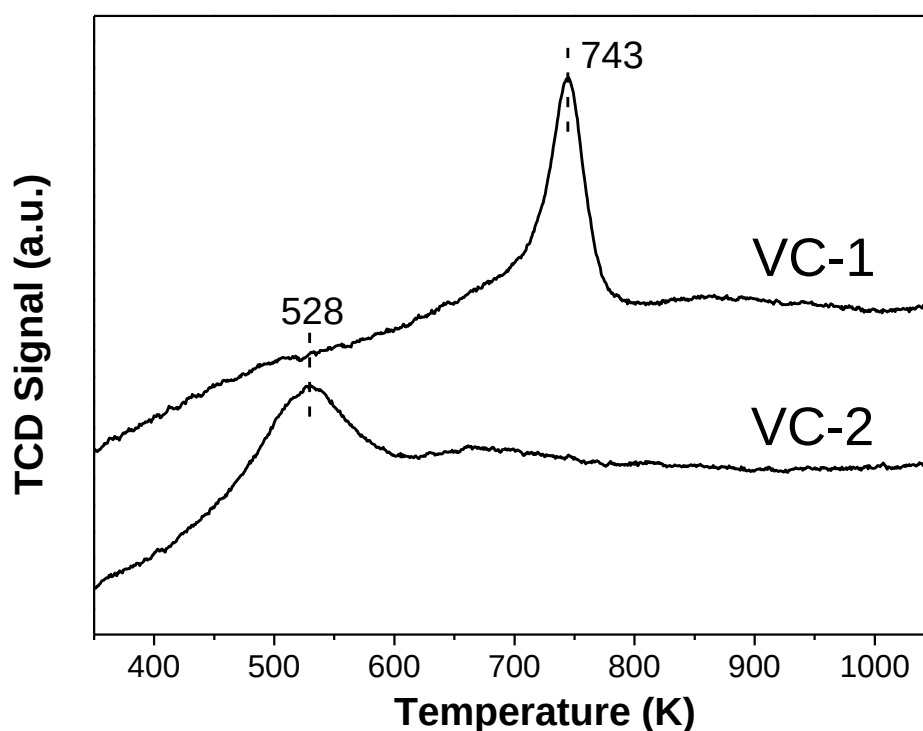


Figure 3.18. H₂-Temperature Programmed Reduction (H₂-TPR) profiles of VC-1 and VC-2 catalysts.

XPS was performed for the surface analysis of the VC catalysts. Figure 3.19 shows the V 2*p* and C 1*s* core level spectra.

The V 2*p* spectra were deconvoluted into 3 doublets (V 2*p*_{3/2} - V 2*p*_{1/2}), keeping an intensity ratio V 2*p*_{3/2}/V 2*p*_{1/2}=2/1 and a spin-orbital splitting of 7.6 eV (Figure 3.19). The corresponding V 2*p*_{3/2} components centered at 513.6-513.8 eV are assigned to V-C bonds in VC_x [25], and V 2*p*_{3/2} bands at higher BE (514.5-514.9 eV, and 516.5-517.3 eV) indicate the presence of different types of Vⁿ⁺-O species [25-27].

The C 1*s* spectra of both VC-1 and VC-2 samples are shown in Figure 3.19. The features at 282.9-283.0 eV are attributed to C-V bonds in VC_x [26,28]. The broad peak at 284.8 eV corresponding to C-C bonds can be associated to carbon

deposits formed during preparation, and the shoulders at BE higher than 284.8 eV are related to the presence of C-O, C=O and O=C-O groups [29-31].

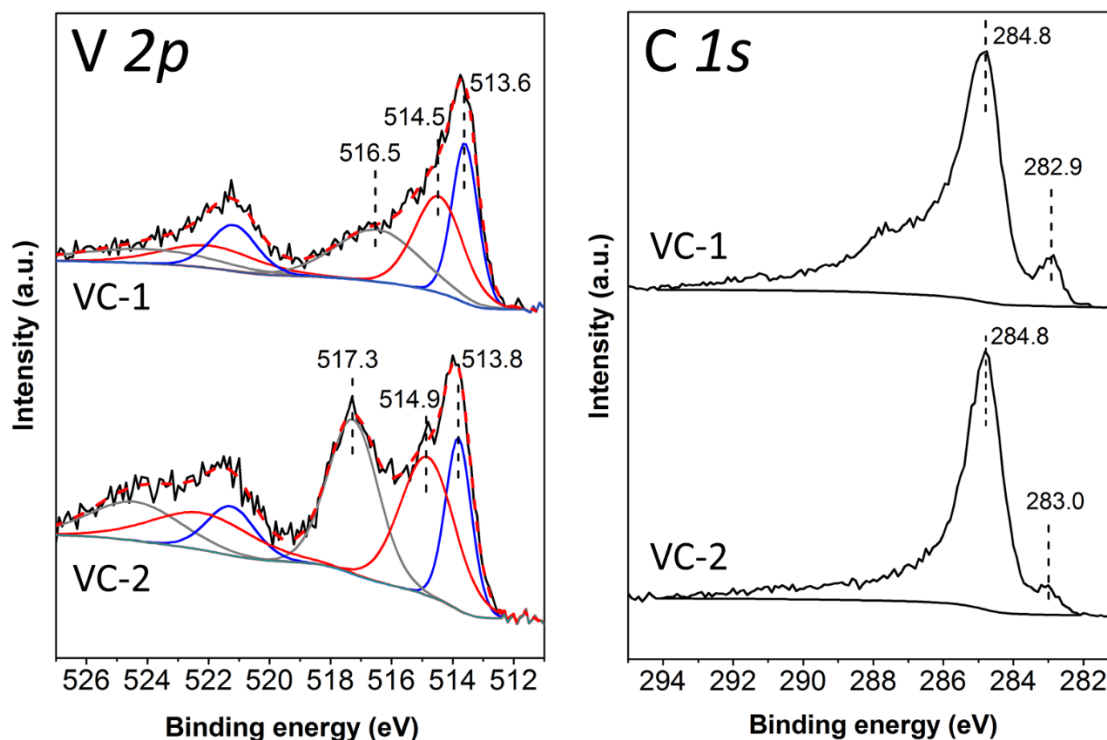


Figure 3.19. XPS profiles of V 2p and C 1s levels of VC-1 and VC-2 catalysts.

Wide O 1s peaks were found (Figure 3.20). The component at lower BE (530.0-530.4 eV) is assigned to oxy-species of vanadium and that at 531.3-531.5 eV to OH and/or oxy-carbide species; components at higher BE are attributed to different O-C bonded species [24,25,32].

XPS signals related to the presence of N-containing species were not found (Figure 3.20), indicating that N coming from the 4,5-dicyanoimidazole, used as carbon precursor, was eliminated during the VC_x preparation.

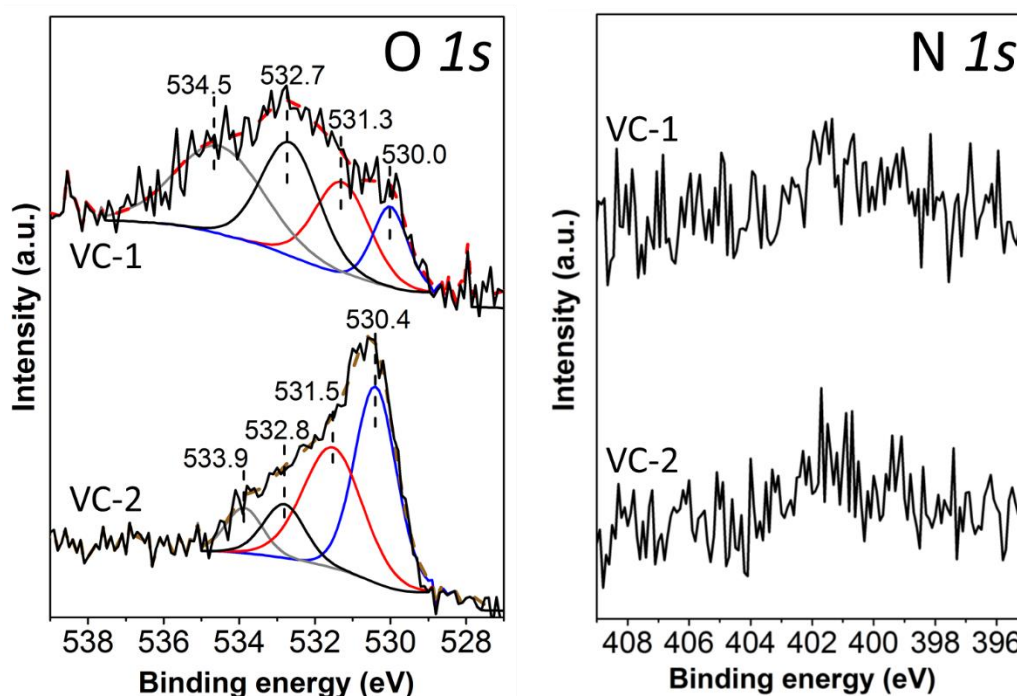


Figure 3.20. XPS profiles of O 1s and N 1s levels of VC-1 and VC-2 catalysts.

Taking into account that one of the determining steps in the RWGS reaction is the CO₂ adsorption, several experimental studies related to the CO₂ adsorption over G5TMCs were performed. Theoretical studies of CO₂ adsorption carried out by the group of Prof. F. Illas (University of Barcelona) in the frame of a collaboration, resulted in very good agreement with the experimental results obtained, which correlate well with the structural and surface characteristics and catalytic behavior in the RWGS reaction [33,34].

Thermogravimetric and calorimetric experiments of CO₂ adsorption were carried out with the prepared G5TMCs. Table 3.3 shows the results of adsorbed CO₂ and CO₂ adsorption heat values obtained.

Table 3.3. Amount of adsorbed CO₂ and CO₂ adsorption heat values on G5TMC samples.

Catalyst	Adsorbed CO ₂ ($\mu\text{gCO}_2 \text{ mg}_{\text{cat}}^{-1}$)	CO ₂ adsorption heat	
		eV	kJ mol^{-1}
VC-1	5.94	-0.25	-24.4
VC-2	7.40	-0.54	-52.5
VC-1_1623	5.52	-0.22	-21.3
NbC-1	0.89	-1.02	-98.7
TaC-1	0.91	-0.94	-90.8

Among the VC catalysts, VC-2 showed a higher CO₂ adsorption heat (-0.54 eV) than VC-1 (-0.25 eV) and VC-1_1623 (-0.22 eV). Furthermore, the amount of adsorbed CO₂ on VC-2 (7.40 $\mu\text{gCO}_2 \text{ mg}_{\text{cat}}^{-1}$) was slightly higher than that adsorbed on VC-1 (5.94 $\mu\text{gCO}_2 \text{ mg}_{\text{cat}}^{-1}$) and VC-1_1623 (5.52 $\mu\text{gCO}_2 \text{ mg}_{\text{cat}}^{-1}$). According with DFT calculations summarized below, the higher CO₂ adsorption heat of VC-2 can be associated to the higher amount of V₈C₇ present on the sample, compared to the other two catalysts.

It is necessary to recall here that a major presence of V₈C₇ in VC-2 and of stoichiometric VC in VC-1 was determined by PED-ASTAR analysis.

Following, a summary of the model used for DFT calculations is given [33]. Only the TMC(001) surface was considered, being the most stable one [35,36]. TMC(001) surface slab model used consists of a R45°(2 $\sqrt{2}$ ×2 $\sqrt{2}$) surface unit cell. The TMC(001) surface slab models were built with 4 atomic layers, each layer containing 8 TM and 8 C atoms.

For vanadium carbide, two (001) surface models were built, one corresponding to stoichiometric VC and another corresponding to V₈C₇. The VC(001) surface model which consist in a total of 32V and 32C atoms was labelled VC, whereas the second system corresponding to VC(001) model with a surface C vacancy, labelled VC-vac, was constructed to model the V₈C₇(001) phase. Basically, the only difference among these vanadium carbide bulk

structures arises from the presence of extra and ordered C vacancies in $V_8C_7(001)$ compared to $VC(001)$.

The experimental values of CO_2 adsorption heat on VC-2 (-0.54 eV), VC-1 (-0.25 eV) and VC-1_1623 (-0.22 eV) (Table 3.3) agree quite well with the DFT estimates of -0.85 and -0.18 eV for VC-vac and VC models, respectively (Table 3.4).

On the other hand, NbC-1 and TaC-1 samples displayed higher CO_2 adsorption heat values than VC catalysts. However, the amount of adsorbed CO_2 on NbC-1 and TaC-1 was much lower than on VC catalysts (Table 3.3).

DFT calculations also showed a higher CO_2 adsorption heat values on NbC and TaC with respect to VC samples (Table 3.4). However, the slightly stronger CO_2 adsorption heat value for NbC-1 (-1.02 eV) compared to TaC-1 (-0.94 eV) determined experimentally is not followed by DFT calculations (-0.87 for NbC and -1.21 eV for TaC), although the gap can be simply explained by the DFT accuracy of 0.1-0.2 eV [33,34].

Table 3.4. CO_2 adsorption heat values of $G5TMC(001)$ surface models calculated by DFT calculations. Taken from Ref 33,34 and 37.

CO_2 adsorption heat values (eV)	
VC-vac	-0.85
VC	-0.18
NbC	-0.87
TaC	-1.21

In separate thermogravimetric analysis (TGA) experiments, the reactivity of VC-1, VC-2, NbC-1 and TaC-1 with CO_2 at 873 K was followed for 3 h (Figure 3.21 and 3.22). When CO_2 was contacted with samples at 873 K, an exothermic process took place and the weight of samples increased in all cases.

For VC-1 and VC-2 the simultaneous on-line analysis of the gases evolved was carried out by MS and the production of CO was evidenced. The CO production decreased along time.

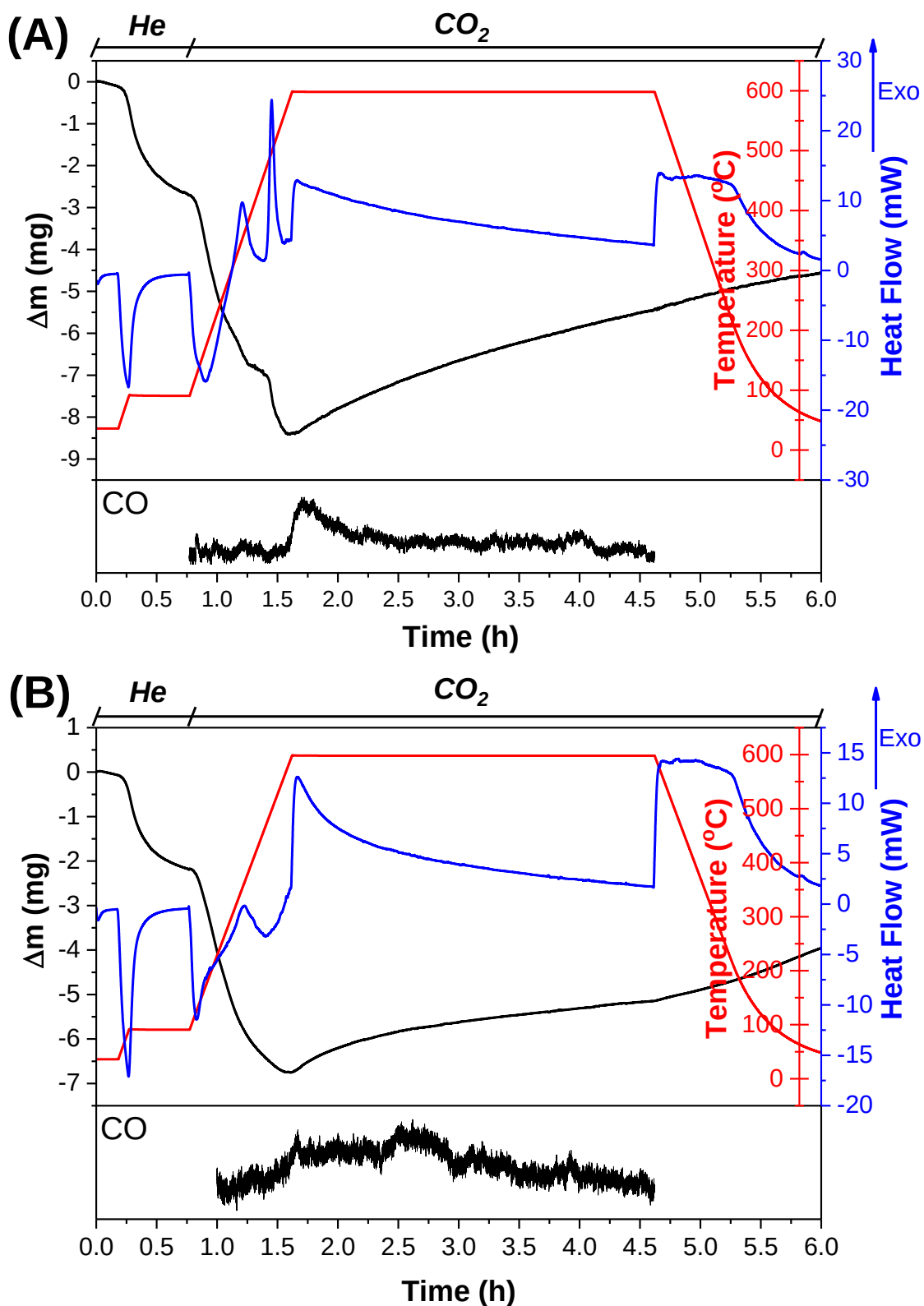


Figure 3.21. CO_2 reaction with catalysts followed by TGA-MS: A) VC-1, initial mass = 91.5 mg; B) VC-2, initial mass = 90.6 mg. Mass loss (black line); Heat Flow (blue line); T (red line). On the bottom part, released CO MS-profile.

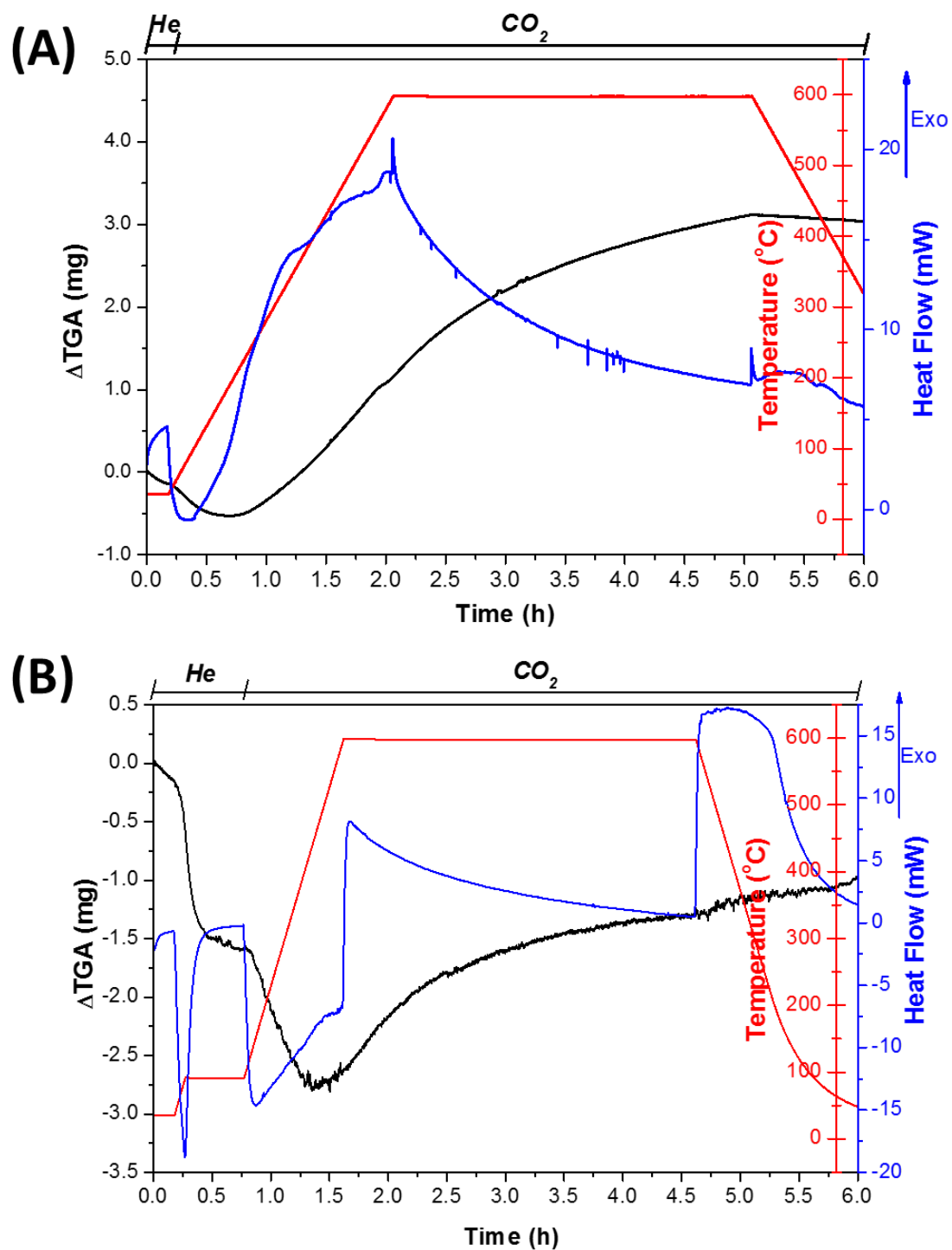


Figure 3.22. CO₂ reaction with catalysts followed by TGA: A) NbC-1, initial mass = 112.2 mg; B) TaC-1, initial mass = 177.9 mg. Mass loss (black line); Heat Flow (blue line); T (red line).

The XRD patterns after the CO₂ reactivity experiments at 873 K, carried out in TGA, indicated the formation of crystalline metal oxides in VC-1, VC-2 and NbC-1 (Figure 3.23 and 3.24).

For VC-1, the formation of rhombohedral V₂O₃ is clearly observed, and the small diffraction peaks at $2\theta=27.5$ and 28.1° would indicate the presence of monoclinic VO₂ (Figure 3.23). For VC-2, the very low intensity XRD peaks at $2\theta=27.5$ and 28.1° would be related with the presence of a small amount of monoclinic VO₂ with a poor crystallinity (Figure 3.23). For NbC-1, the very low intensity peaks at $2\theta=22.6$, 28.4 and 36.6° indicated the presence of a small amount of orthorhombic Nb₂O₅ (Figure 3.24). No peaks attributed to crystalline TaO_x were detected in TaC-1 (Figure 3.24). This could be related to the higher resistance to oxidation of TaC compared to NbC and VC systems [9,38].

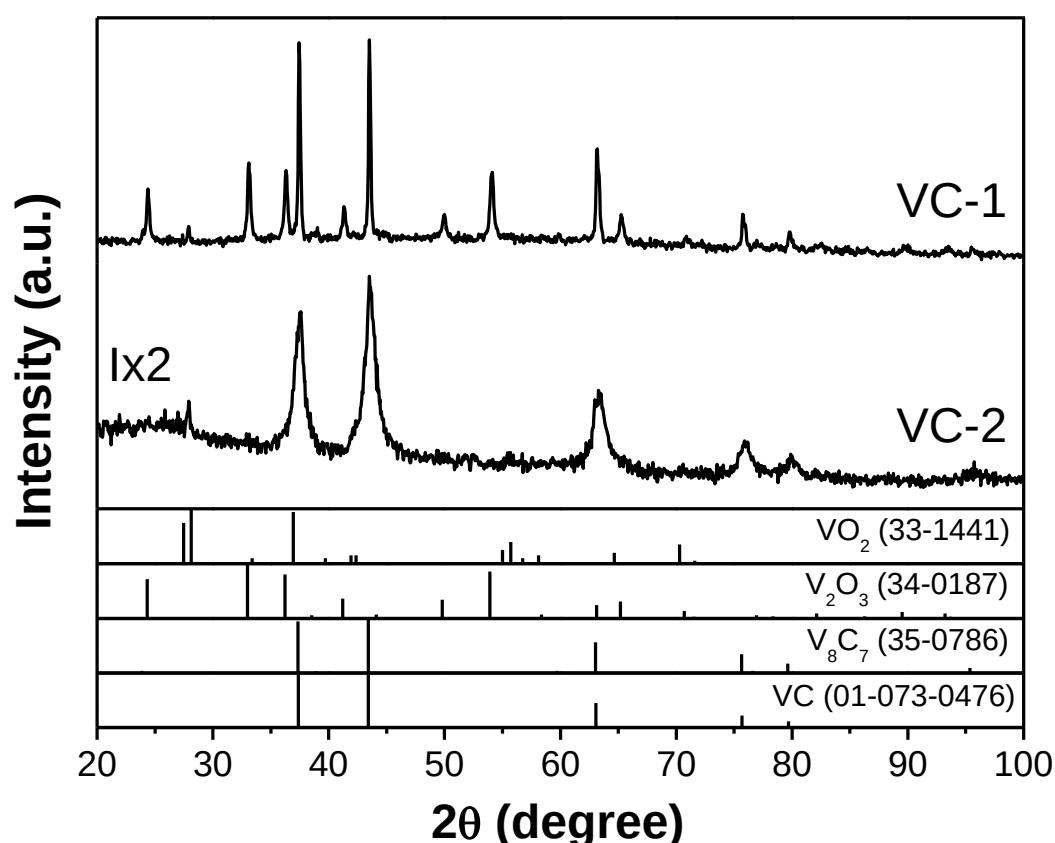


Figure 3.23. XRD patterns of VC samples after CO₂ reaction up to 873 K carried out in TGA experiments.

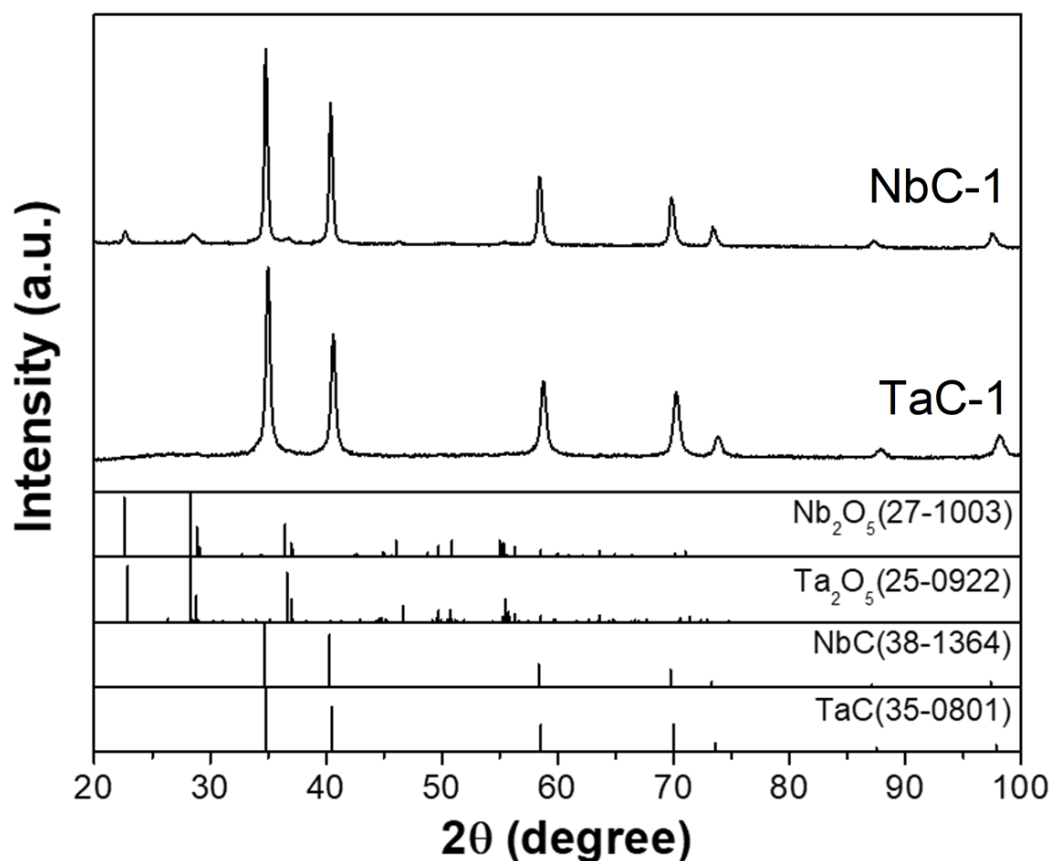


Figure 3.24. XRD patterns of NbC-1 and TaC-1 samples after CO₂ reaction up to 873 K carried out in TGA experiments.

In addition to the described TGA experiments and in order to quantify the CO released, the samples were studied under CO₂ atmosphere at 873 K for 140 min in the reaction system, as described in Chapter 2. The formation of CO is observed in all cases. Figure 3.25 shows the evolution of CO from the reactor effluent and CO₂ conversion along time. The amount of CO produced on VC-2, 2913 mmolCO kg_{cat}⁻¹, was higher than that on VC-1, 2112 mmolCO kg_{cat}⁻¹, and VC-1_1623, 1980 mmolCO kg_{cat}⁻¹. Moreover, NbC-1 and TaC-1 only produced 271 and 226 mmolCO kg_{cat}⁻¹, respectively. A high decrease in CO production is observed at the first minutes of reaction in all cases (Figure 3.25).

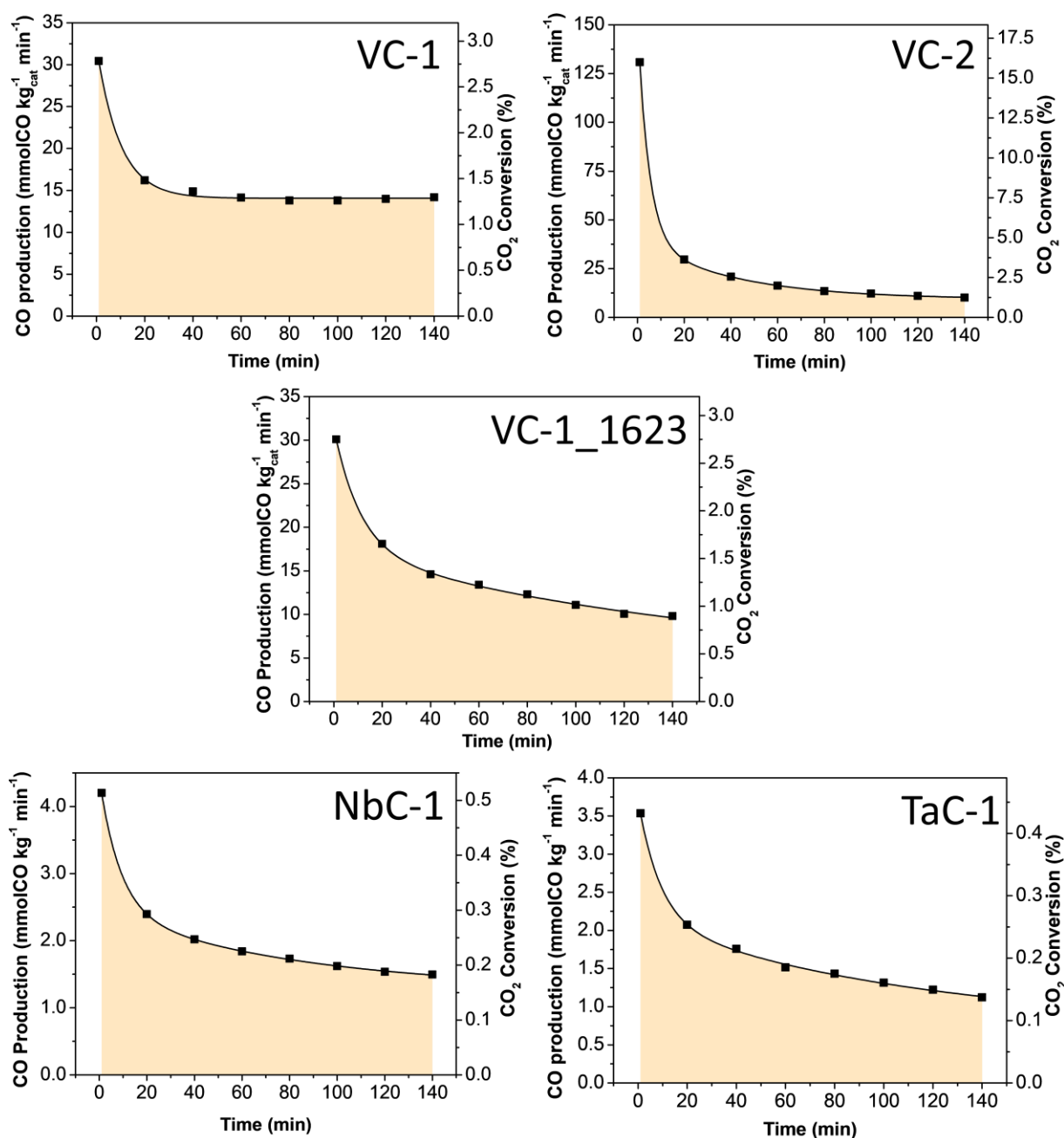


Figure 3.25. CO₂ conversion and CO production when CO₂ was flowed through bulk G5TMC catalysts at 873 K during 140 min. Reaction conditions: $m_{\text{cat}}=150$ mg, GHSV=3000 h⁻¹ and P=0.1 MPa.

From these results, a dissociative CO₂ adsorption on G5TMCs via the C-O scission could be proposed; a subsequent surface oxy-carbide species formation and CO release would take place. To gain deep knowledge of this process, *in-situ* DRIFTS experiments with on-line MS analysis were performed over VC-2,

VC-1_1623, NbC-1 and TaC-1 according to the experimental procedure described in Chapter 2. VC-1_1623 was chosen due to the possible major presence of stoichiometric VC phase compared to VC-1.

Figure 3.26A (spectra a and b) shows the *in-situ* DRIFT spectra for CO₂ adsorption on VC-1_1623 and VC-2 samples in the 2100-1800 cm⁻¹ range, where the stretching vibrations of coordinated CO are expected. Although the intensities of bands are very low, it is possible to discern different adsorptions related to different coordinated species on the surface.

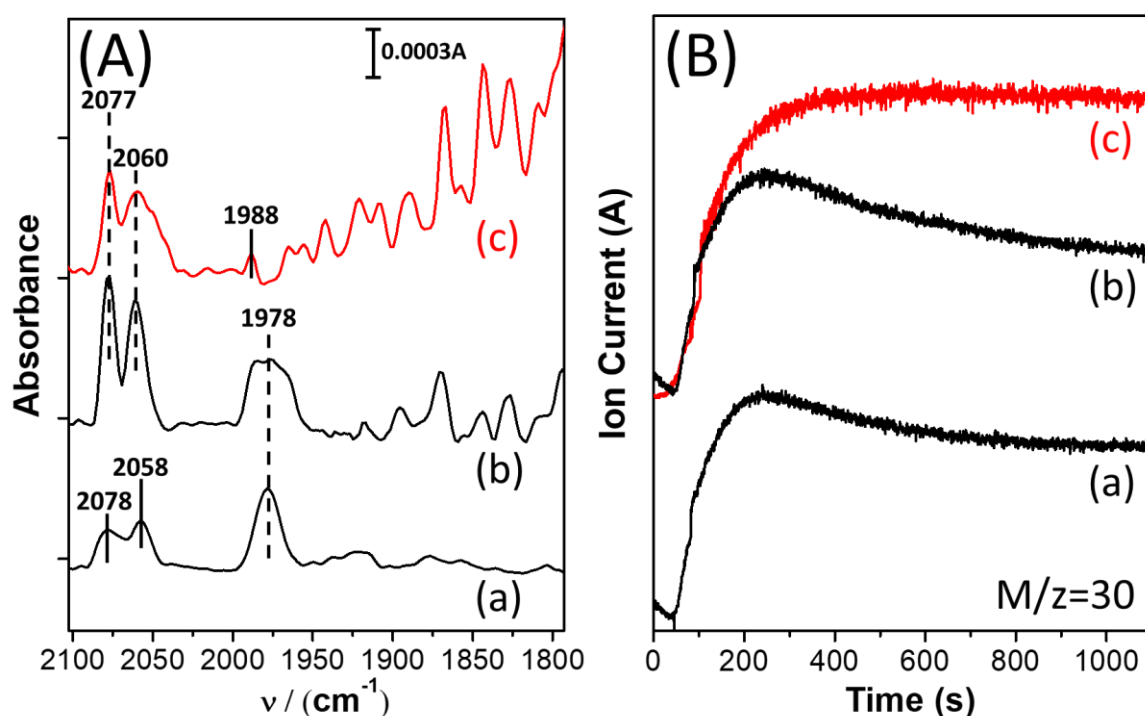


Figure 3.26. DRIFT spectra (A) and CO MS profile (B) of a) CO₂ adsorption over VC-1_1623; b) CO₂ adsorption over VC-2; c) CO₂/H₂=1/3 adsorption over VC-2. T=308 K.

Bands at 2078-2058 cm⁻¹ and 1978 cm⁻¹ can be associated to coordinated CO. Moreover, CO release was followed by MS analysis (Figure 3.26B). Initially, when CO₂ was contacted with the samples, CO was detected, after 200 s the CO signal decreased along time in both vanadium carbide samples (see profiles a and b). This might be associated to the decrease of active sites, which are

responsible for the CO₂ dissociation, and are continuously converted into oxy-carbide species.

To help to analyze the infrared results, a theoretical study has been carried out in the group of Prof. Illas [34]. The simulated IR spectra have been obtained from vibrational analysis of different possible coordinated species. Details from the DFT procedure are found elsewhere [32].

Table 3.5 summarizes the calculated infrared vibrational modes of chemisorbed CO₂, CO and O species, from the simulated model, on the most stable surface (001), of VC, VC with C vacancies (VC-vac) and VOC. IR simulation over VOC was performed because it is well known that TMC usually exhibit the presence in some extension of oxy-carbide species [17-19], which might also be related with the CO₂ adsorption and surface adsorbed CO species formation. Thus, as can be seen, the bands at 2078-2058 cm⁻¹ agree with those expected for C-O stretching vibration of linear coordinated CO on surface sites of stoichiometric VC. Meanwhile, the band at lower wavenumber (1978 cm⁻¹) could be reasonably assigned to the C-O stretching of coordinated CO on surface oxy-carbide species, which could be already present or formed during the CO₂ adsorption. This indicates that both VC-1_1623 and VC-2 catalysts expose in some extension common surface sites.

Table 3.5. Simulated IR vibrational modes (cm⁻¹) in the 2200-700 cm⁻¹ range of adsorbed CO₂ or coadsorbed CO+O species on VC, VC-vac and VOC surfaces [34].

Surface	CO ₂	CO+O
VC	O-C-O symmetric stretching: 1173 O-C-O bending: 759	C-O stretching: 2064 C _{slab} -O stretching: 840
VC-vac	C-O stretching: 1322 O-C-O bending: 722	C-O stretching: 1508
VOC		C-O stretching: 1983 V _{slab} -O stretching: 885

After about 20 min, the CO₂ flow was switched to He in order to remove possible physisorbed species. The corresponding DRIFT spectra of VC-2 and VC-1_1623 registered in the wavenumber range of 2200-800 cm⁻¹ are shown in Figure 3.27. The above discussed bands, now centered at 2069 and 1977 cm⁻¹, are still visible; this indicates that chemisorbed CO species remained. Moreover, a well-defined band at 1538 cm⁻¹ was visible for VC-2 sample but not for VC-1_1623. Following the simulated IR calculations, one could ascribe this band to the C-O stretching of coordinated CO on surface sites of the VC-vac model (Table 3.5). VC-2 catalyst exhibits a surface with more C vacancies (V₈C₇) than VC-1_1623. To verify the assignation of the IR bands discussed above, a separate CO adsorption experiment was carried out on VC-2 sample. After CO adsorption and further He flushing, the spectrum c in Figure 3.27 was registered. The bands at 2069, 1977 and 1538 cm⁻¹ match those observed before and can be ascribed to CO coordinated on different surface sites.

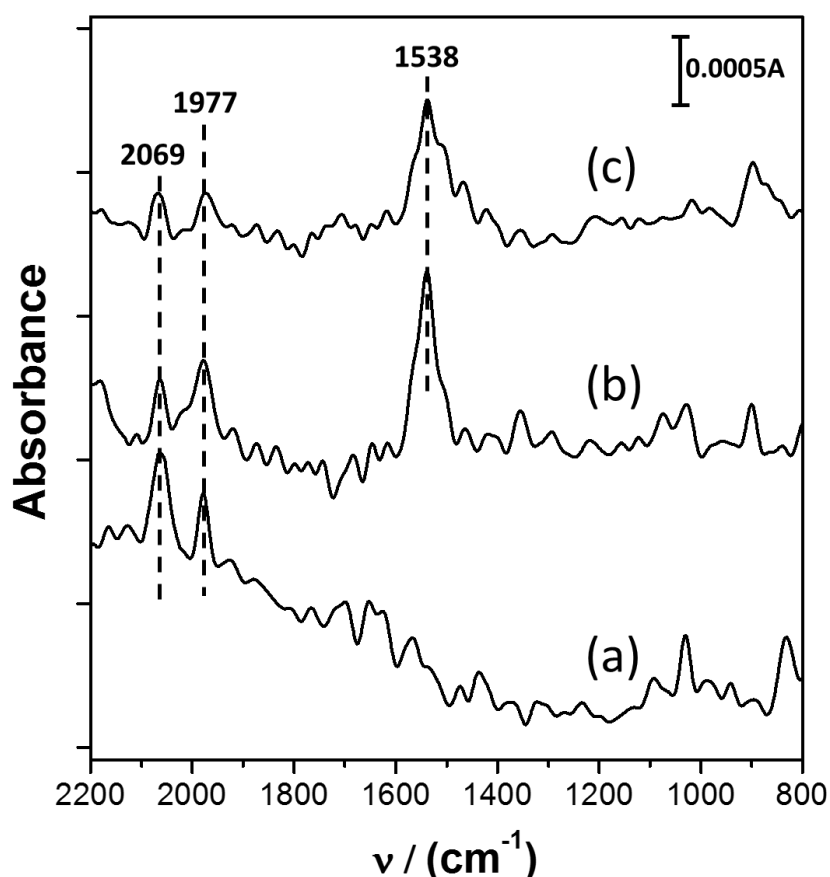


Figure 3.27. Experimental DRIFT spectra after CO₂ adsorption and He flushing over a) VC-1_1623 and b) VC-2, and c) CO adsorption and He flushing over VC-2 (c). T=308 K.

Finally, in a separate experiment, the adsorption of a mixture of $\text{CO}_2/\text{H}_2=1/3$ over the VC-2 sample was studied. Figure 3.26A, spectrum c, shows the registered DRIFT spectrum. As can be seen, similar bands at 2077-2060 cm^{-1} were obtained under CO_2/H_2 and CO_2 flows (spectra c and b). However, a less intense band at 1988 cm^{-1} was observed under CO_2/H_2 flow. As discussed above, the band at 1988 cm^{-1} can be attributed to the C-O stretching of CO over surface oxy-carbide species. The use of the CO_2/H_2 mixture instead of CO_2 flow could favor the continuous conversion of the VOC surface by removing the surface O species by H_2 . Under these conditions, the MS on-line analysis indicates that CO was continuously produced (Figure 3.26B, profile c).

Table 3.6 summarizes the calculated infrared vibrational modes from the simulated model on the most stable (001) surface of stoichiometric NbC and TaC, NbC and TaC with C vacancies (NbC-vac and TaC-vac), and NbOC and TaOC [34].

Table 3.6. Simulated IR vibrational modes (cm^{-1}) in the 2200-700 cm^{-1} range of adsorbed CO_2 or coadsorbed CO+O species on NbC, NbC-vac, NbOC, TaC, TaC-vac and TaOC surfaces [34].

Surface	CO_2	CO+O
NbC	O-C-O symmetric stretching: 1170 O-C-O bending: 763	C-O stretching: 2043 C _{slab} -O stretching: 888
NbC-vac	C-O stretching: 1283 O-C-O bending: 732	C-O stretching: 1097
NbOC		C-O stretching: 1843
TaC	O-C-O symmetric stretching: 1158 O-C-O bending: 761	C-O stretching: 2039 Ta _{slab} -O stretching: 840
TaC-vac	C-O stretching: 1229	C-O stretching: 951
TaOC		C-O stretching: 1888

Figure 3.28A shows the registered CO_2 -DRIFT spectra of NbC-1 and TaC-1 samples. After CO_2 adsorption on NbC-1 sample, bands at 2076-2055 cm^{-1} and 1842 cm^{-1} (Figure 3.28A, spectrum a) can be assigned to coordinated CO on

stoichiometric NbC and NbOC species, respectively. Similarly, for TaC-1 sample, bands at $2077\text{--}2047\text{ cm}^{-1}$ and 1896 cm^{-1} (Figure 3.28A, spectrum b) can be attributed to coordinated CO on stoichiometric TaC and TaOC species, respectively (Table 3.6).

The CO release from CO₂ adsorption on NbC-1 and TaC-1 samples was also detected by on-line MS analysis (Figure 3.28B). In both cases, after the first 200 s of CO₂ adsorption, CO evolution decreased along time.

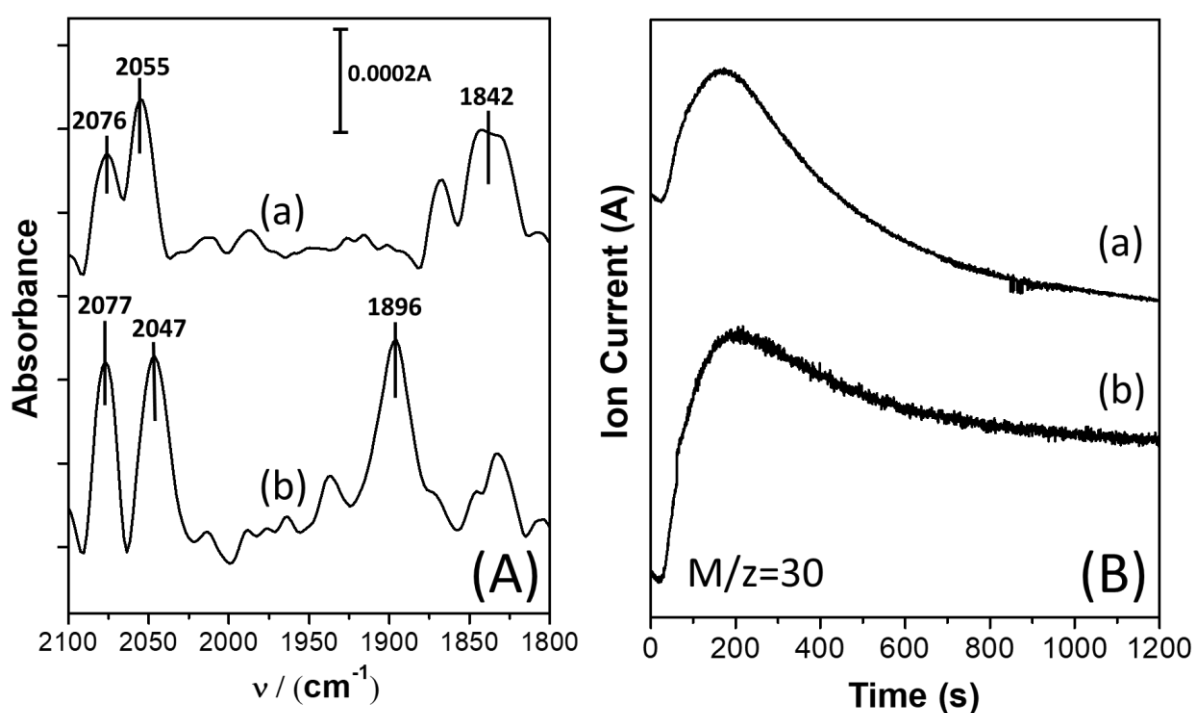


Figure 3.28. DRIFT spectra (A) and CO MS profile (B) of CO₂ adsorption over a) NbC; and b) TaC. T=308 K.

Furthermore, after about 20 min, the CO₂ flow was switched to He in order to remove physisorbed species. Figure 3.29 shows the CO₂-DRIFT spectra in the range of $1300\text{--}700\text{ cm}^{-1}$ of NbC-1 and TaC-1 after He flushing. The bands at 893 and 840 cm^{-1} could be due to the C_{slab}-O and Ta_{slab}-O stretching vibrations of surface species formed after CO₂ adsorption on stoichiometric NbC and TaC (Table 3.6). The presence of C vacancies, NbC-vac and TaC-vac, could be responsible of the observation of small bands in the zone of $1145\text{--}1089\text{ cm}^{-1}$ and

971 cm^{-1} for NbC-1 and TaC-1 samples, respectively. These bands could be assigned to the C-O stretching of coordinated CO on these surfaces according to simulated IR vibrational modes (Table 3.6); thus, the existence of a small number of C vacancies in NbC-1 and TaC-1 cannot be ruled out. Moreover, the bands at 1199 and 1159 cm^{-1} can be assigned to O-C-O stretching of coordinated CO_2 on stoichiometric NbC and TaC, respectively, and the bands at 1283 and 1273 cm^{-1} to coordinated CO_2 on NbC-vac and TaC-vac, respectively (Table 3.6); these bands remained after He flushing.

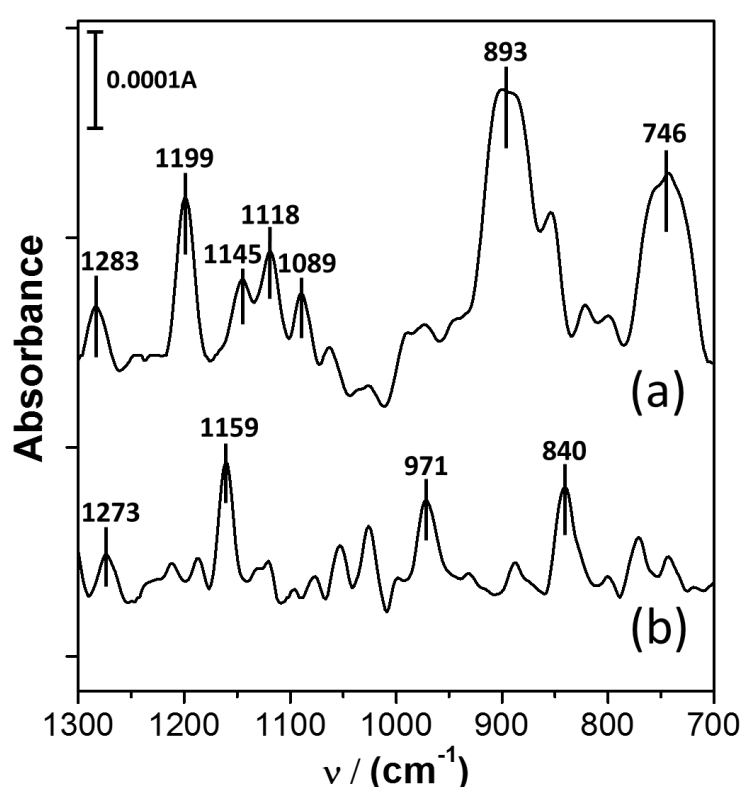


Figure 3.29. Experimental DRIFT spectra after CO_2 adsorption and He flushing over: a) NbC-1 and b) TaC-1. $T=308\text{ K}$.

The presence of adsorbed CO_2 observed in CO_2 -DRIFT spectra of NbC-1 and TaC-1 after flushing with He reveals a stronger adsorption of CO_2 on NbC-1 and TaC-1 than on VC samples. This agrees well with the values of CO_2 adsorption heats obtained in TGA experiments, whereby NbC-1 and TaC-1 showed a higher CO_2 adsorption heats than VC samples. DRIFTS results revealed the coexistence of stoichiometric G5TMC and G5TMC with vacancies

as well as oxy-carbide species, and confirmed the CO₂ dissociation to CO+O on G5TMCs.

3.2.2. Catalytic behavior of bulk G5TMC catalysts in the RWGS reaction

The RWGS reaction was studied over samples at 0.1 MPa, range of temperature of 573-873 K, and using a reactant mixture of CO₂/H₂/N₂=1/3/1 (molar ratio) under a GHSV of 3000 h⁻¹. The catalysts were kept 1.5 h at each temperature.

Figure 3.30 plots the CO₂ conversion values as a function of reaction temperature. VC-based catalysts showed a very low activity below 673 K. However, the CO₂ conversion increased with temperature, reaching values at 873 K of 17%, 33% and 44% for VC-1_1623, VC-1 and VC-2, respectively. NbC-1 and TaC-1 showed a similar profile of CO₂ conversion than that of the blank experiment (SiC), indicating that NbC-1 and TaC-1 were almost not active under the experimental conditions used.

Over VC catalysts, besides CO, only CH₄ was formed. Figure 3.31 shows CO selectivity as a function of reaction temperature. All VC samples were highly CO selective reaching values near to 100% at 773 K. VC-2 showed the highest CO selectivity in the whole range of temperature studied.

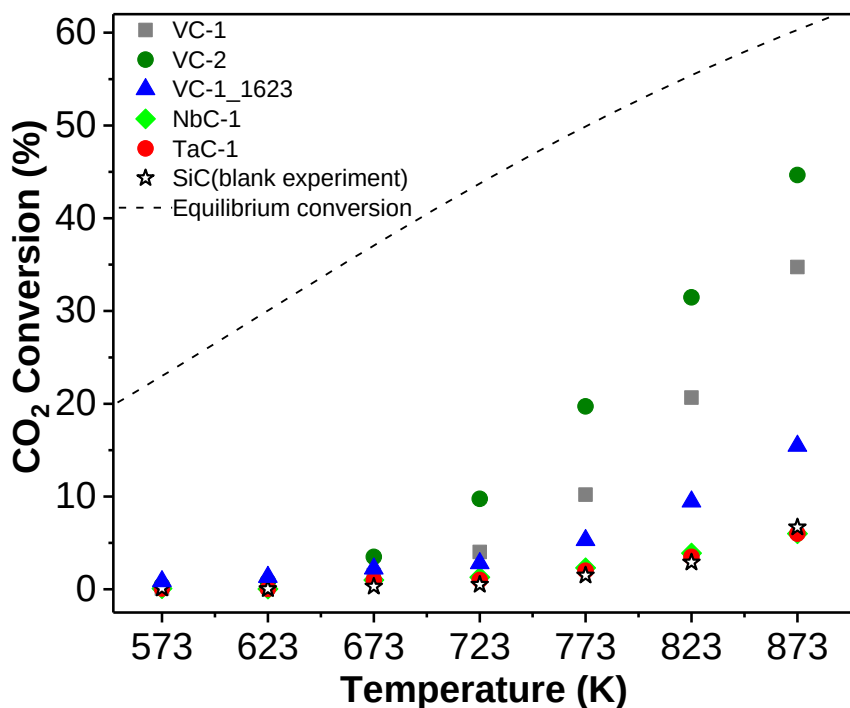


Figure 3.30. CO₂ conversion of G5TMC catalysts in the RWGS reaction as a function of temperature. Reaction conditions: $m_{\text{cat}}=150\text{mg}$, $\text{CO}_2/\text{H}_2/\text{N}_2=1/3/1$, $\text{GHSV}=3000\text{ h}^{-1}$ and $P=0.1\text{ MPa}$.

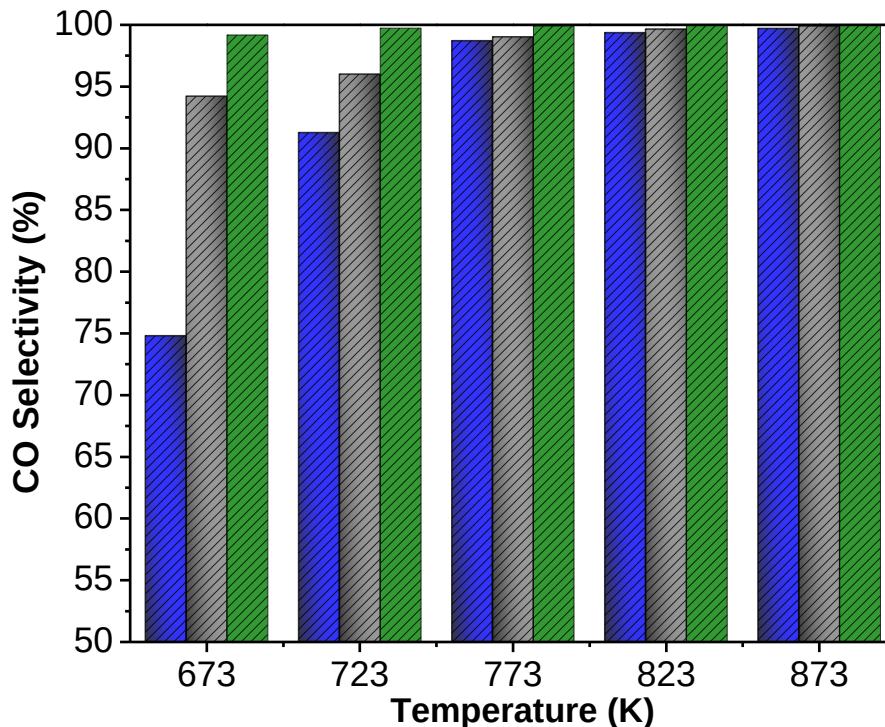


Figure 3.31. CO selectivity of VC catalysts in the RWGS reaction as a function of temperature. Reaction conditions: $m_{\text{cat}}=150\text{mg}$, $\text{CO}_2/\text{H}_2/\text{N}_2=1/3/1$, $\text{GHSV}=3000\text{ h}^{-1}$ and $P=0.1\text{ MPa}$. Blue bars: VC-1_1623. Gray bars: VC-1. Green bars: VC-2.

Figure 3.32 shows the CO yield for VC catalysts. VC-2 displayed the highest CO yield and VC-1_1623 the lowest in the whole range of temperature; as expected, the CO yield increased with temperature in all cases.

The different characteristics of VC catalysts are also reflected in the apparent activation energy (E_a) for CO production (Figure 3.33), showing VC-2 the lowest value of E_a (53.4 kJ mol⁻¹)

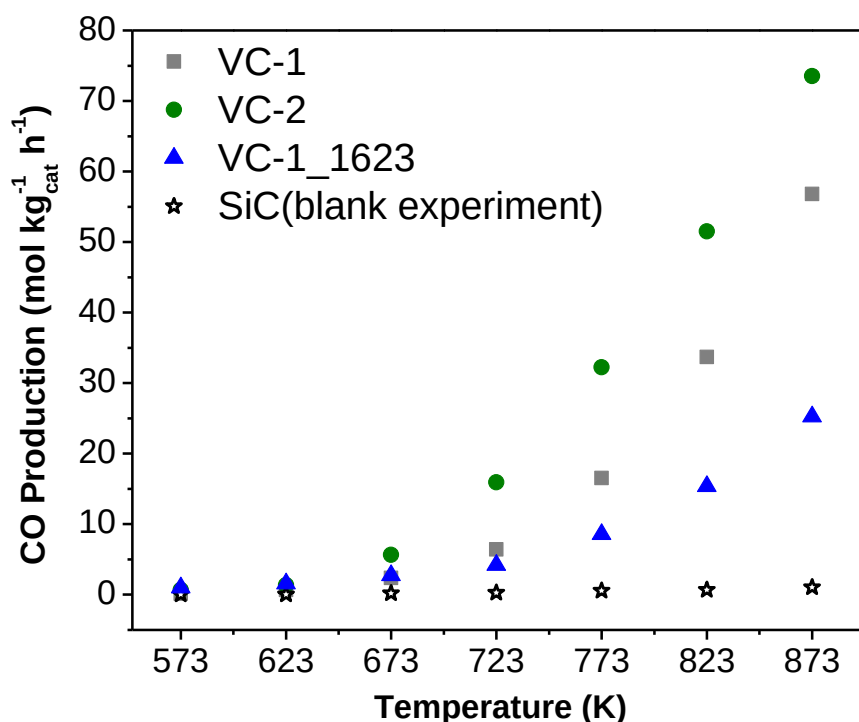


Figure 3.32. CO production as a function of reaction temperature in the RWGS reaction over VC catalysts. Reaction conditions: $m_{\text{cat}}=150$ mg, $\text{CO}_2/\text{H}_2/\text{N}_2=1/3/1$, $\text{GHSV}=3000$ h⁻¹, $P=0.1$ MPa.

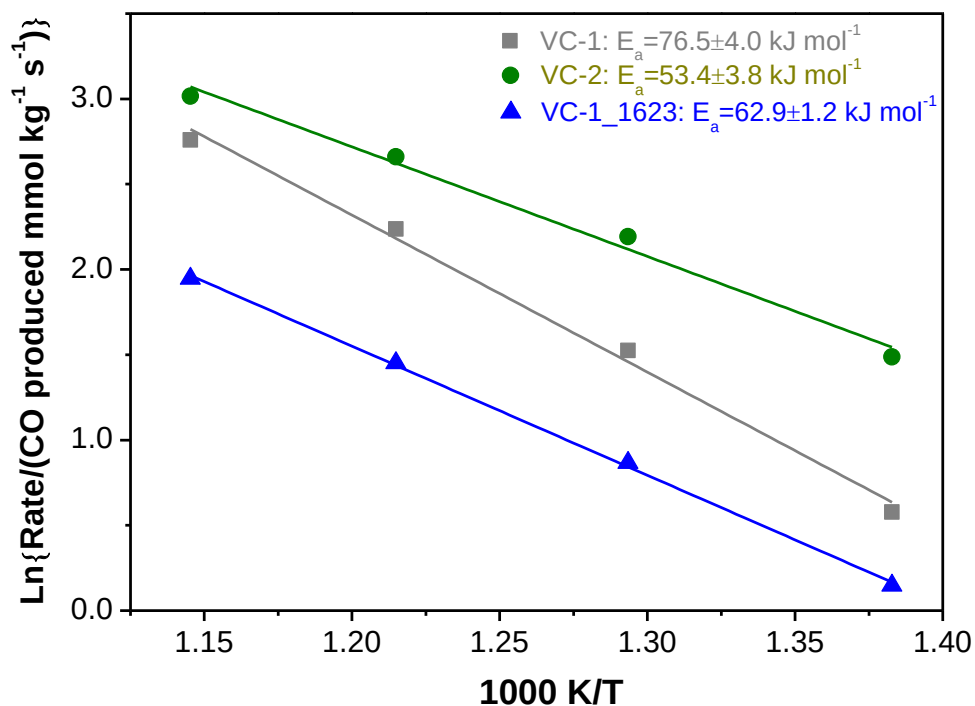


Figure 3.33. Apparent activation energy (E_a) for CO production over VC-1, VC-2 and VC-1_1623. Reaction conditions: $m_{\text{cat}}=150$ mg, $\text{CO}_2/\text{H}_2/\text{N}_2=1/3/1$, $\text{GHSV}=3000$ h⁻¹, $P=0.1$ MPa, $T=723$ - 873 K.

Post-reaction catalysts were characterized by XRD and XPS analysis. Significant structural changes did not occur during reaction according to XRD (Figure 3.34 and 3.35). The crystallite sizes of VC_x, NbC and TaC post-reaction catalysts remained similar to those of the corresponding fresh catalysts. No crystalline metal oxides are observed in any case.

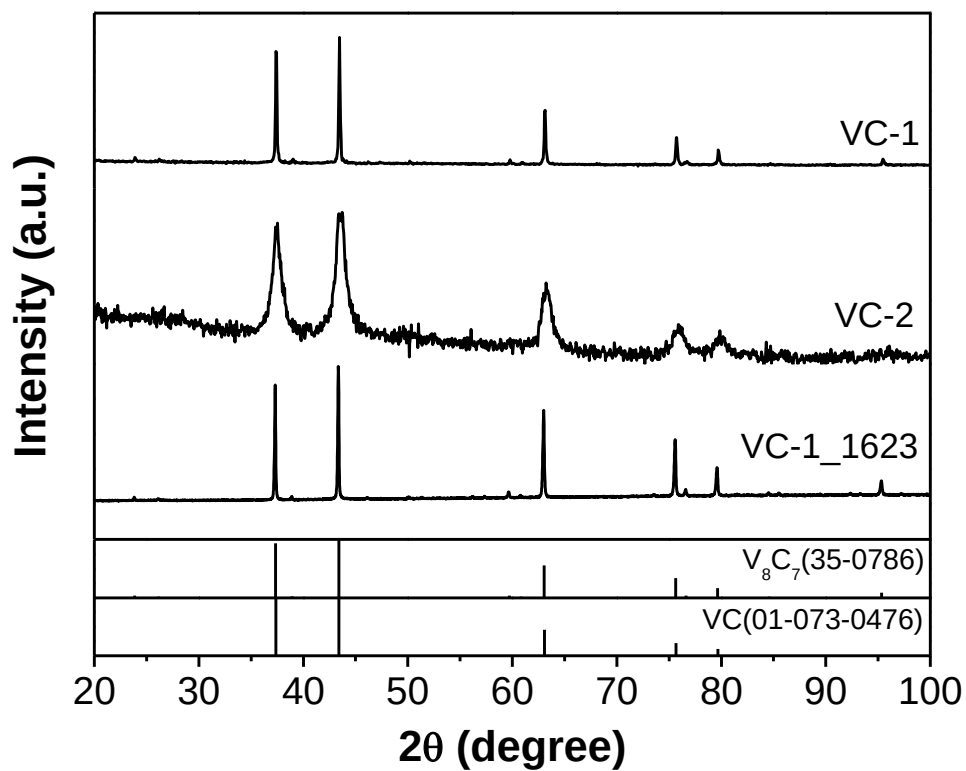


Figure 3.34. XRD patterns of used VC catalysts.

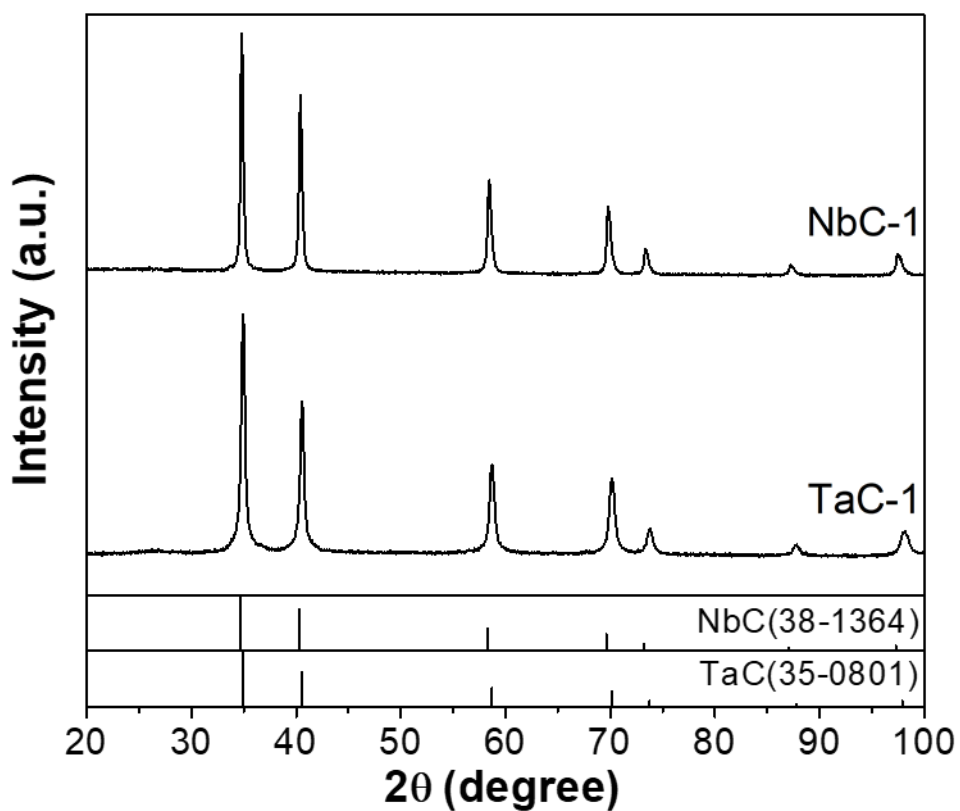


Figure 3.35. XRD patterns of used NbC-1 and TaC-1 catalysts.

Figure 3.36 shows the V $2p$, C $1s$ and O $1s$ core level XP spectra of used VC catalysts. The V $2p$ and C $1s$ XPS spectra indicated the presence of surface V–C species (V $2p_{3/2}$ =513.7-513.8 eV) and (C $1s$ =282.7-282.9 eV). However, an increase in the amount of oxy-vanadium species after reaction is observed when compared with the XPS of fresh catalysts (Figure 3.19). In both cases, components of V $2p_{3/2}$ =514.9-517.5 eV are attributed to different V^{n+} -O species. The O $1s$ spectra (Figure 3.36) is mainly related with the presence of oxy-vanadium and OH and/or oxy-carbide species (O $1s$ =530.2-531.0 eV). The increase of oxy-vanadium species in VC catalysts after reaction suggests that a mild oxidation occurred during reaction.

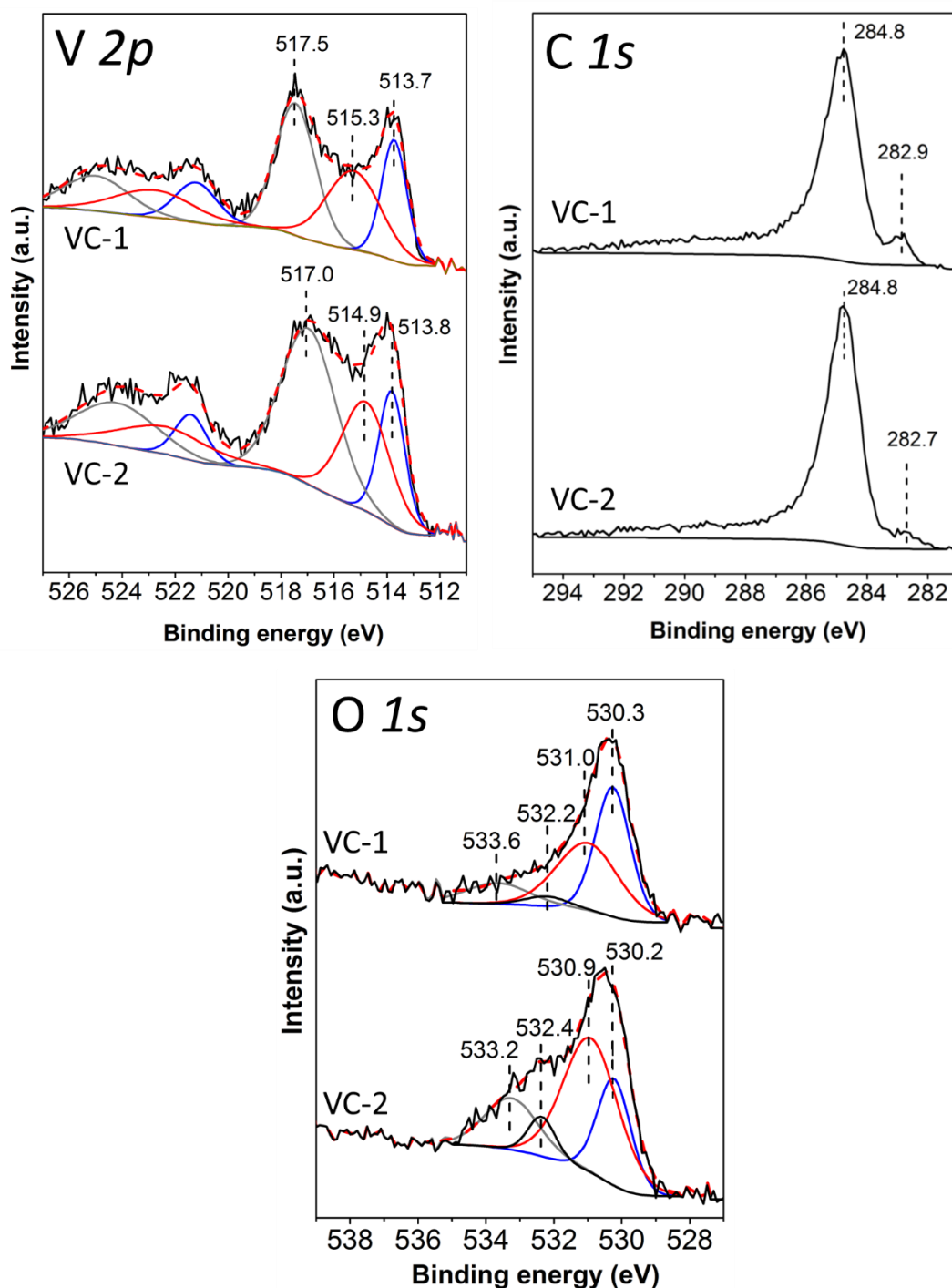


Figure 3.36. XPS profiles of V 2p, C 1s and O 1s levels of used VC-1 and VC-2 catalysts.

A stability test was carried out over the most performant catalyst, VC-2. The long-term catalytic test was performed at 723 K for 4 days (Figure 3.37). Initially, during the first 4 h, CO₂ conversion slightly decreased and the CO selectivity

slightly increased. A slight decrease on CO₂ conversion was observed until 30 h under reaction; then no significant changes in the catalytic behavior of VC-2 were observed during the next 70 h. Meanwhile CO selectivity remained almost constant at 99.9% during the 70 h period.

The catalytic activity was only affected at the initial reaction period, and then was kept similar along reaction time; this could suggest that most of the surface C vacancies remain almost unchanged in the course of the reaction, leading to a good performance.

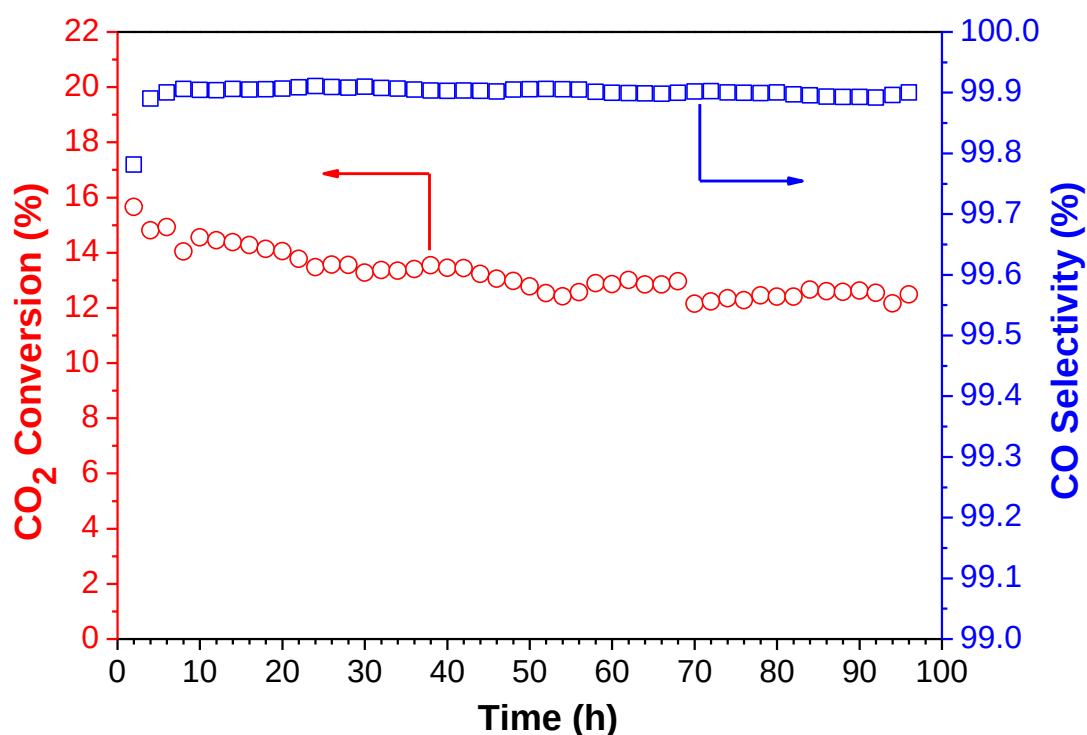


Figure 3.37. Catalytic behavior of VC-2 in RWGS at 723 K as a function of time on stream: CO₂ conversion and CO selectivity. Reaction conditions: $m_{\text{cat}}=300$ mg, CO₂/H₂/N₂=1/3/1, GHSV=3000 h⁻¹, P=0.1 MPa.

The characterization of VC-2 after the long-term catalytic test was performed by means of XRD and XPS analysis.

XRD indicated a good structural stability of the catalyst under reaction conditions at 723 K during 4 days; no crystalline vanadium oxide species were observed (Figure 3.38).

Although, an increase of oxy-vanadium species after the long-term catalytic test was also observed when V 2*p* and O 1*s* levels were analyzed (Figure 3.39), the presence of vanadium carbide species on surface was still determined by XPS analysis (C 1*s*=282.9 eV and V 2*p*_{3/2}=513.9 eV) (Figure 3.39).

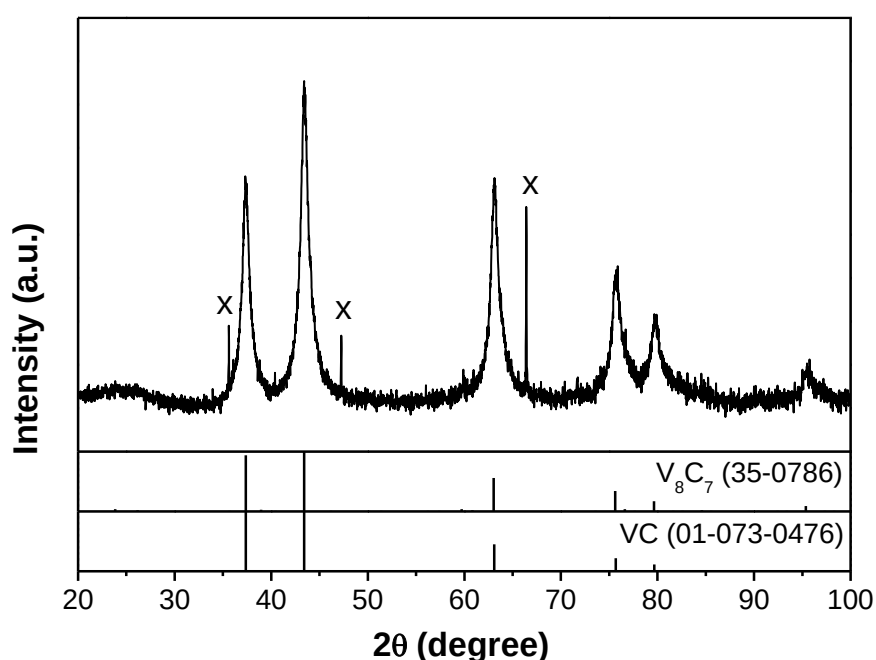


Figure 3.38. XRD pattern of VC-2 after the long-term catalytic test (4 days). Reaction conditions: GHSV=3000 h⁻¹, CO₂/H₂/N₂=1/3/1, P=0.1 MPa and T=723 K. “X” peaks correspond to SiC, which was used as diluent in the catalytic bed.

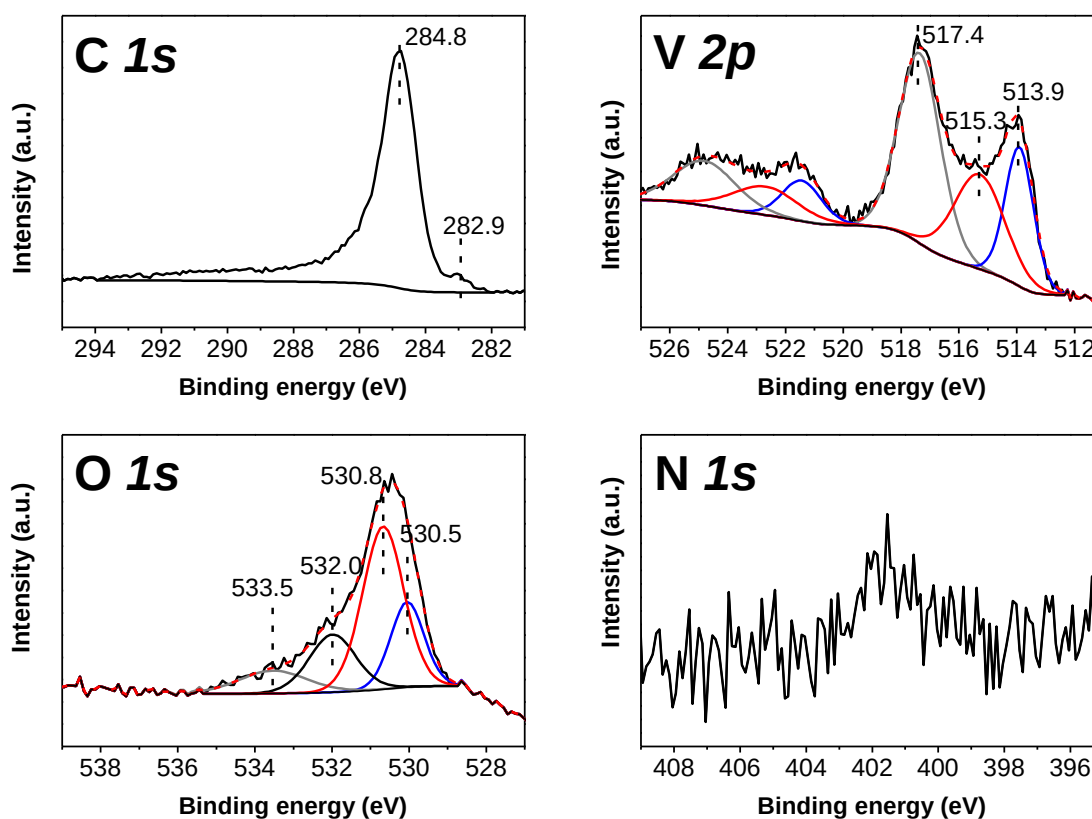


Figure 3.39. XPS profiles of VC-2 catalyst after 4 days of RWGS reaction. Reaction conditions: GHSV=3000 h⁻¹, CO₂/H₂/N₂=1/3/1, P=0.1 MPa and T=723 K.

The catalytic behavior of VC catalysts was analyzed in the basis of theoretical studies concerning the RWGS mechanism on VC models [33].

Figure 3.40 shows the potential energy reaction profiles for the RWGS over the stoichiometric VC (001) and the C-defective VC-vac (001) surface models; the redox mechanism (CO₂ dissociation) and the associative mechanism (COOH formation) are contemplated.

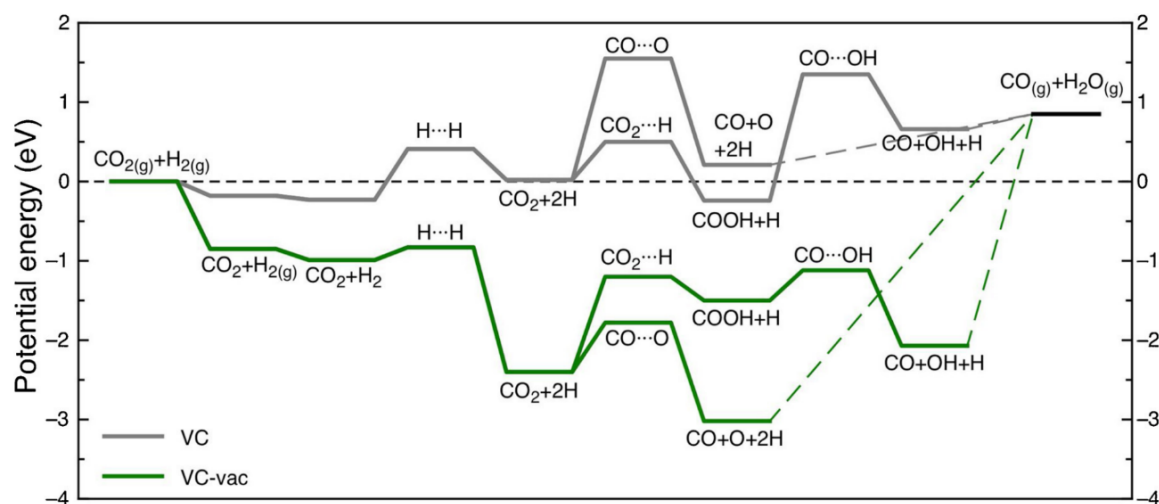


Figure 3.40. Potential energy reaction profiles for the RWGS on the VC(001) surface (grey) and on the VC-vac(001) surface model (green) at $T = 873 \text{ K}$, $p_{\text{CO}_2} = 20.26 \text{ kPa}$, $p_{\text{H}_2} = 60.79 \text{ kPa}$, and $p_{\text{CO}} = p_{\text{H}_2\text{O}} = 0.20 \text{ kPa}$. Taken from Ref 33.

Stoichiometric VC(001) surface model shows low adsorption energies of CO_2 and H_2 , and moderates H_2 dissociation energy barrier of 0.84 eV. Over the stoichiometric VC model, a high energy barrier of 1.53 eV is required for CO_2 dissociation and a low energy barrier of 0.48 eV for the COOH formation. However, the subsequent reaction step of COOH decomposition into $\text{CO} + \text{OH}$, shows a high energy barrier of 1.59 eV, which indicates that the redox mechanism is probably more favored than COOH formation in VC. It is appropriated to consider that both mechanisms would take place on VC, although hardly achievable given their high energy barriers.

The other model studied, VC-vac which was derived from VC(001) with a surface C vacancy, $\text{V}_8\text{C}_7(001)$, changes dramatically with respect to stoichiometric VC. First, the reactants absorb much stronger, with adsorption energies three and five times larger for H_2 and CO_2 than on the stoichiometric VC, respectively. Second, the H_2 dissociation step is considerably enhanced with an energy barrier of 0.16 eV, much lower than that of the VC. Finally, the redox route (CO_2 dissociation) seems to be much favored, with an energy barrier of solely 0.62 eV, much lower compared to that of the associative mechanism (COOH formation) with a high energy barrier of 1.20 eV.

Furthermore, the COOH formation becomes energetically unfavorable in VC-vac compared to the stoichiometric VC surface with energy barriers of 1.20 and 0.48 eV, respectively. Even though, the COOH decomposition into CO + OH is favored in VC-vac with an energy barrier of 0.38 eV, a value much reduced compared to that for the stoichiometric VC surface of 1.59 eV.

The Gibbs free-energy diagram of the RWGS reaction over the VC surfaces models mimics the potential energy ones described above [33]. According to the Gibbs free-energy diagram the preference for the redox mechanism in the VC-vac model is proposed.

The potential and Gibbs free energy profiles of the RWGS reaction suggest that under RWGS conditions the CO₂ dissociation takes place forming CO and O species, the latter subsequently reacting with H₂ forming H₂O. A similar reaction pathway has been proposed from experimental and theoretical studies for the RWGS over α -Mo₂C [24].

Both surfaces (VC and VC-vac models) explain the capabilities of VC with or without C vacancies in the RWGS reaction. Theoretical results are fully consistent with the experimental results exposed above for VC samples, in which VC-2 presents a larger content of C vacancies than VC-1 and showed a better catalytic performance in the RWGS reaction.

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CHAPTER 4

SUPPORTED TRANSITION METAL CARBIDES OF GROUP 5 IN THE RWGS REACTION

This chapter focuses on the preparation, characterization and the study of the catalytic behavior of a series of supported G5TMC catalysts for the CO₂ conversion to CO under RWGS reaction conditions.

The method of preparation of supported G5TMCs are based on those described in Chapter 3 but in the presence of the corresponding support. Characterization of the catalysts before and after reaction by means of XRD, Raman, XPS, BET surface area, H₂-TPR, SEM-EDX and TEM techniques is presented.

The chapter contains two sections corresponding to the study of G5TMC/Al₂O₃ catalysts and supported VC catalysts on different supports.

The first section describes the preparation of catalysts containing G5TMC (VC, NbC and TaC) supported onto Al₂O₃. Three different VC/Al₂O₃ samples were prepared using different vanadium precursor and/or atmosphere (Ar or 5%H₂/Ar) of heating during the carbide preparation. Among G5TMC/Al₂O₃ catalysts, only VC/Al₂O₃ showed catalytic activity in the RWGS under the reaction conditions used. Characteristics of the VC/Al₂O₃ catalysts prepared were reflected in their catalytic behaviors. The most performant Al₂O₃-supported VC catalyst presented a good stability along time.

The second section analyzes the characteristics and catalytic behavior of supported VC catalysts (VC-3/Al₂O₃, VC-3/TiO₂, VC-3/SiO₂, VC-3/CeO₂, VC-3/ZrO₂, VC-3/SBA-15 and VC-3/AC). The characteristics of catalysts depended on the support used. All supported VC samples showed a higher CO production per loaded V than the bulk VC-3 catalyst.

4.1. G5TMC/Al₂O₃ catalysts

4.1.1. Preparation of G5TMC/Al₂O₃ catalysts

G5TMC/ γ -Al₂O₃ (~25% wt G5TMC) catalysts were prepared using a similar method to that employed in the preparation of bulk catalysts (VC-1, VC-2, NbC-1 and TaC-1) but in the presence of a commercial γ -Al₂O₃ (Alfa Aesar, 226 m²g⁻¹).

γ -Al₂O₃ was contacted with the alcoholic solution (ethanol or methanol) containing the corresponding metal precursor and 4,5-dicyanoimidazole. The suspension was kept under continuous stirring and the excess of ethanol or methanol was evaporated at room temperature. All the procedure was performed under inert atmosphere to avoid hydrolyzation of the metal precursor. Then, the solid was placed in a tubular furnace for the thermal treatment.

The following Al₂O₃-supported catalysts were prepared, VC-1/Al₂O₃, VC-2/Al₂O₃, VC-2_H₂/Al₂O₃, NbC-1/Al₂O₃ and TaC-1/Al₂O₃. In all cases the metal precursor/4,5-dicyanoimidazole molar ratio and the treatment temperature used were similar to those used in the preparation of their bulk counterpart VC-1, VC-2, NbC-1 and TaC-1 catalysts. The VC-2_H₂/Al₂O₃ sample was prepared similarly to VC-2/Al₂O₃ but flowing H₂/Ar (5% H₂), instead of Ar during the thermal treatment.

No passivation was performed after thermal treatment.

The details of the preparation of the G5TMC/Al₂O₃ catalysts are shown in ANNEX II.

4.1.2. Characterization of G5MC/Al₂O₃ catalysts

In general, XRD patterns of catalysts mainly showed defined diffraction peaks characteristic of G5TMC: VC (JCPDS 01-073-0476) and/or V₈C₇ (JCPDS 35-0786) for vanadium-containing catalysts, and NbC (JCPDS 38-1364) and TaC (JCPDS 35-0801) for NbC-1/Al₂O₃ and TaC-1/Al₂O₃, respectively (Figure 4.1).

Taking into account that it is not possible to discern from XRD between VC and/or V₈C₇ phases, from now crystalline vanadium carbide in Al₂O₃-supported

VC samples will be referred as VC_x. It could be recalled here that the major presence of VC in VC-1 and that of V₈C₇ in VC-2 was determined by PED-ASTAR, when bulk catalysts were prepared using a similar method but in the absence of γ -Al₂O₃ (Chapter 3) [1].

XRD of VC-2/Al₂O₃ showed wider and less intense characteristic peaks of VC_x phases than the other VC-containing catalysts.

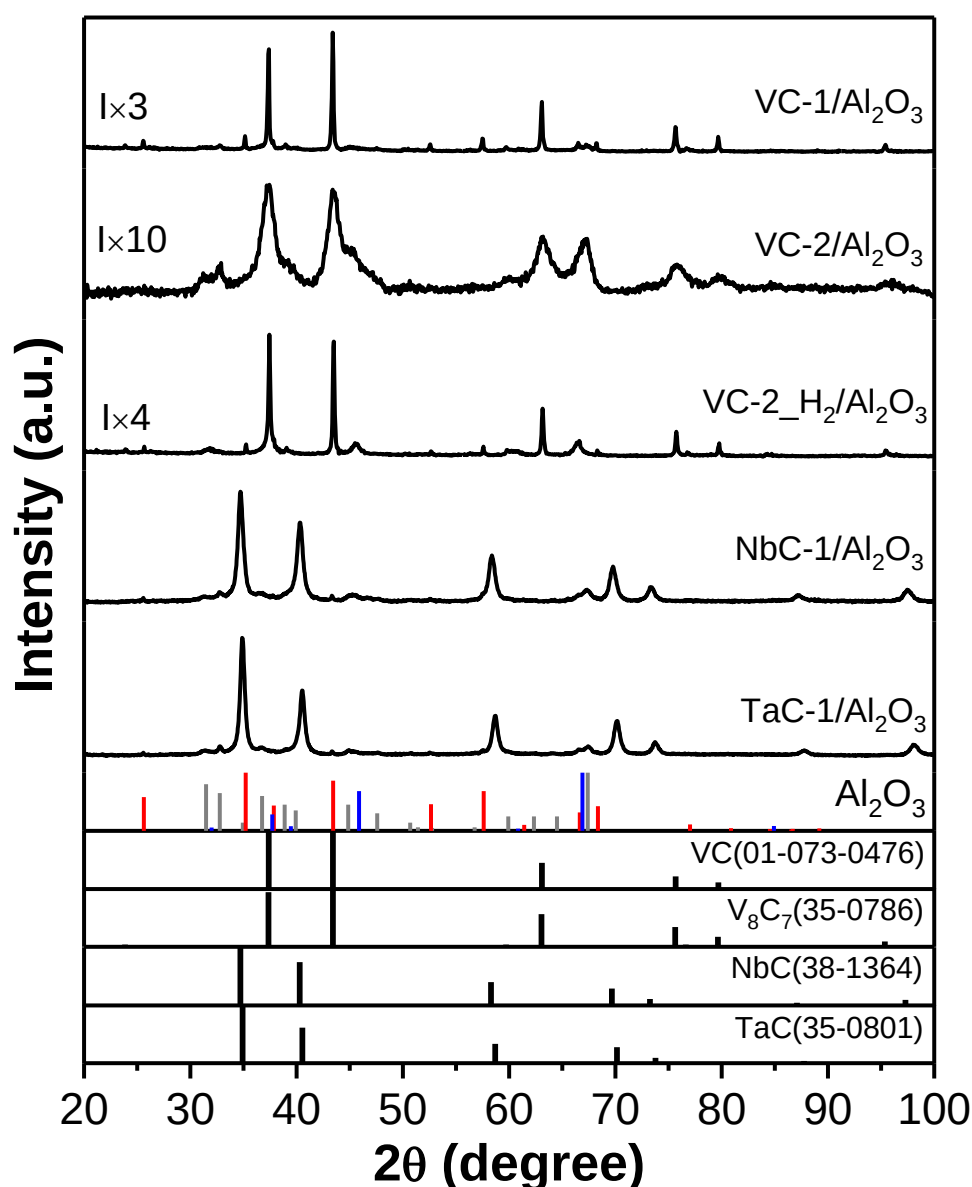


Figure 4.1. XRD patterns of G5MC/Al₂O₃ catalysts. Red lines: rhombohedral Al₂O₃ (10-0173); grey lines: monoclinic Al₂O₃ (35-0121); blue lines: cubic Al₂O₃ (10-0425).

In all cases, except for VC-2/Al₂O₃, small peaks characteristic of both rhombohedral and monoclinic Al₂O₃ are visible in the XRD patterns, indicating the transformation of the initial γ -Al₂O₃ (cubic) during the catalysts preparation. However, the presence of residual γ -Al₂O₃ cannot be ruled out. For VC-2/Al₂O₃, a partial transformation of cubic Al₂O₃ into monoclinic Al₂O₃ can be proposed, no peaks corresponding to rhombohedral Al₂O₃ phase are observed in this case (Figure 4.1).

Table 4.1 shows the crystallite size of G5TMC phases in G5TMC/Al₂O₃ estimated by the Scherrer equation. Crystallite sizes of G5TMC in G5TMC/Al₂O₃ were similar to those of the corresponding bulk G5TMC prepared in absence of γ -Al₂O₃ (Chapter 3, Table 3.2).

Table 4.1. G5TMC crystallite size determined by XRD and BET surface area of G5TMC/Al₂O₃ catalysts before and after RWGS catalytic test.

Catalyst	G5TMC crystallite size/nm.		S _{BET} /m ² g ⁻¹	
	Fresh	Used	Fresh	Used
VC-1/Al ₂ O ₃	57	64	150	144
VC-2/Al ₂ O ₃	7	8	234	210
VC-2_H ₂ /Al ₂ O ₃	54	55	257	248
NbC-1/Al ₂ O ₃	15	16	106	96
TaC-1/Al ₂ O ₃	18	18	50	42
γ -Al ₂ O ₃	-	-	226	-
γ -Al ₂ O ₃ @1373K	-	-	56	-

VC-2/Al₂O₃ had the lowest VC_x crystallite size (7 nm). VC-2_H₂/Al₂O₃ that was prepared similarly to VC-2/Al₂O₃ but with a H₂/Ar (5% H₂) flow instead of Ar during the thermal treatment, showed a much higher crystallite size (54 nm). The thermal treatment with a reductant gas could favor the sintering and/or crystallization of VC_x phase. G5TMC/Al₂O₃ catalysts, except VC-2/Al₂O₃ and VC-

2_H₂/Al₂O₃, showed a lower BET surface-area than the pristine γ -Al₂O₃ (Table 4.1).

For a better comparison, a sample of γ -Al₂O₃ was separately treated at 1373 K for 5 h with Ar flow (γ -Al₂O₃@1373 K); these were the conditions used for the preparation of Al₂O₃-supported VC catalysts.

The BET surface area of VC-1/Al₂O₃, VC-2/Al₂O₃, VC-2_H₂/Al₂O₃ and NbC-1/Al₂O₃ catalysts was higher than that γ -Al₂O₃@1373K. TaC-1/Al₂O₃ showed a slightly lower BET surface area than γ -Al₂O₃@1373K (Table 4.1). However, it is necessary to mention that NbC-1/Al₂O₃ and TaC-1/Al₂O₃ were treated at 1473 K during the preparation (ANNEX II).

As can be observed in Figure 4.2, the crystalline structure of γ -Al₂O₃ changed after heating up to 1373 K; besides the original cubic Al₂O₃, rhombohedral and monoclinic Al₂O₃ can be identified in the XRD pattern of γ -Al₂O₃@1373K [2,3]. This is in agreement with the above discussed XRD patterns obtained for the supported catalysts.

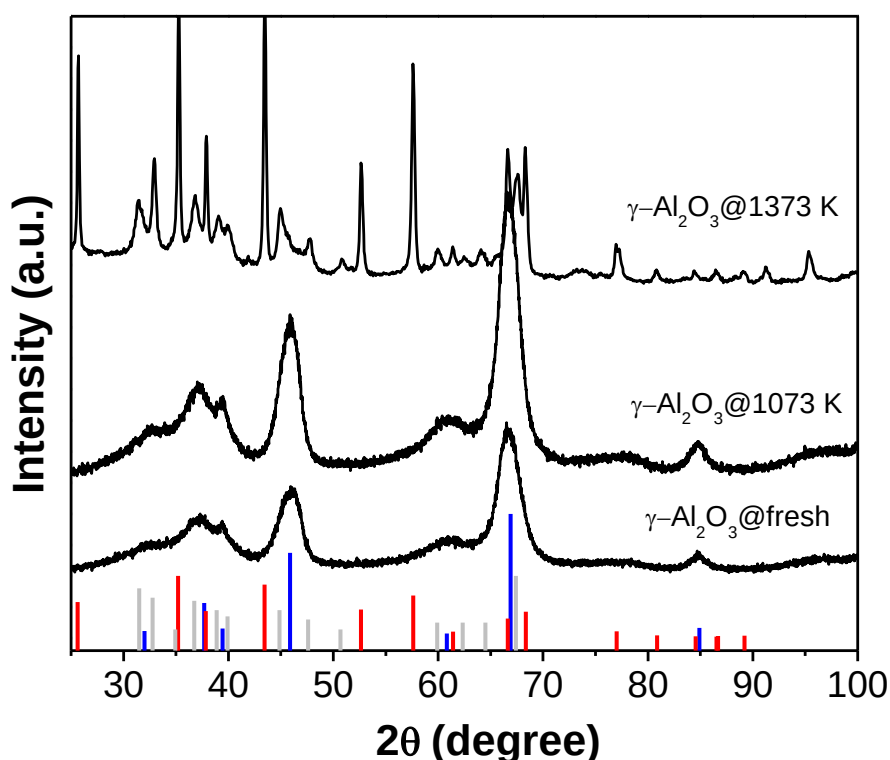


Figure 4.2. XRD patterns of γ -Al₂O₃ treated at 1073 K and 1373 K under Ar. Red lines: rhombohedral Al₂O₃ (10-0173); grey lines: monoclinic Al₂O₃ (35-0121); blue lines: cubic Al₂O₃ (10-0425).

Raman spectra of catalysts (Figure 4.3) showed in all cases the presence of two bands at about 1352 cm^{-1} and 1600 cm^{-1} indicating the presence of residual carbon resulting from the preparation. Very small intensity Raman bands in the $100\text{--}1100\text{ cm}^{-1}$ range, characteristics of oxy-surface species were observed for VC-2/ Al_2O_3 and TaC-1/ Al_2O_3 . No Raman bands corresponding to NbO_x were observed for NbC-1/ Al_2O_3 . The very small peak at 145 cm^{-1} in VC-2/ Al_2O_3 spectrum can be likely related to a small amount of oxy-vanadium species [4,5]. The peak at 991 cm^{-1} associated to crystalline V_2O_5 is not clearly observed in any Al_2O_3 -supported VC sample [6,7]. For VC-1/ Al_2O_3 , the presence of oxy-vanadium species could not be detected by Raman spectroscopy in contrast with the corresponding bulk VC-1 catalyst (Chapter 3). For TaC-1/ Al_2O_3 , the very low intensity bands at 119 and 168 cm^{-1} are assigned to amorphous TaO_x [8,9].

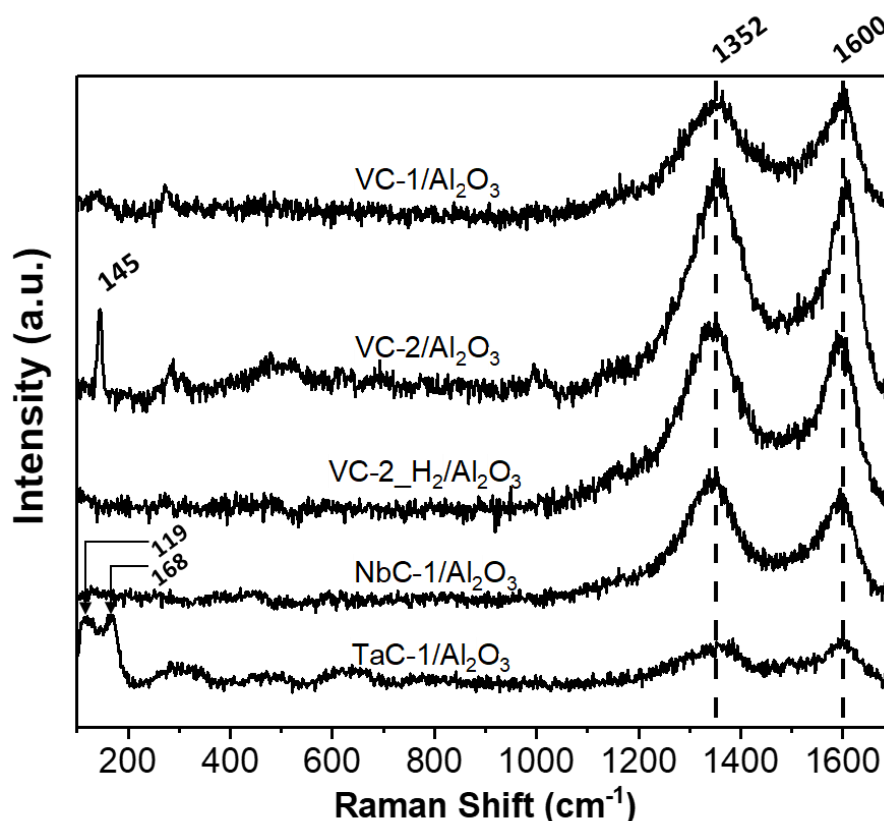


Figure 4.3. Raman spectra of G5MC/ Al_2O_3 catalysts.

Al_2O_3 -supported VC catalysts were more deeply characterized than NbC-1/ Al_2O_3 and TaC-1/ Al_2O_3 because the formers were active in the RWGS under

the reaction conditions used in this work, but NbC-1/Al₂O₃ and TaC-1/Al₂O₃ were not. Moreover, the catalytic behavior of Al₂O₃-supported VC catalysts depended on the preparation method, which in turn determined their characteristics.

Figure 4.4 shows the H₂-TPR profiles of Al₂O₃-supported VC catalysts. VC-2/Al₂O₃ and VC-2_H₂/Al₂O₃, which were prepared using VO(isopropoxide)₃, showed a maximum of hydrogen consumption at low temperatures of 624 K and 576 K, respectively. Meanwhile VC-1/Al₂O₃, which was prepared using VOCl₃, showed a maximum of hydrogen consumption at a higher temperature (727 K). These peaks of hydrogen consumption correlate well with those obtained for the bulk VC-1 and VC-2, according to the vanadium precursor used in the preparation of these catalysts (Chapter 3, Figure 3.18).

The very low amount of H₂ consumed indicated the presence of low amount of oxy-carbide or oxy-vanadium species [1,10-13], this agrees with Raman results. However, the amount of H₂ consumed was higher for VC-2/Al₂O₃ than for VC-1/Al₂O₃ or VC-2_H₂/Al₂O₃, this is probably related with the smaller particle size of VC_x in VC-2/Al₂O₃ when compared with the other two catalysts. It seems reasonable to propose that VC-1/Al₂O₃ and VC-2_H₂/Al₂O₃, with a lower surface of VC_x exposed, would suffer a milder oxidation when exposed to air.

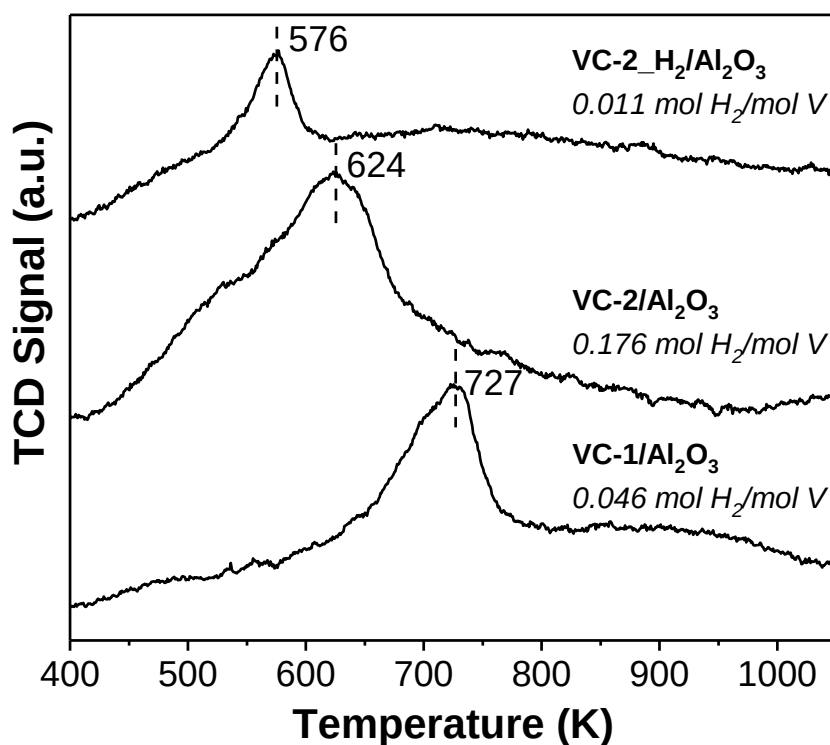


Figure 4.4. H₂-TPR profiles and H₂ consumption of Al₂O₃-supported VC catalysts.

SEM images and EDX mapping of Al₂O₃-supported VC catalysts suggest in all cases a homogenous distribution of VC_x onto the Al₂O₃ support at microscale (Figures 4.5-4.7).

TEM analysis of Al₂O₃-supported VC catalysts (Figures 4.8-4.10) shows that the particle size of vanadium carbide particles depended on the preparation method used. VC-2/Al₂O₃, prepared using an alkoxide as vanadium precursor and Ar treatment, showed VC_x particles with the smallest particle size, 7.5 nm, (Figure 4.9); however, the use of H₂ treatment instead of Ar (VC-2_H₂/Al₂O₃) led to an increase in the particle size, 55 nm, (Figure 4.10). The particle size was also larger when VOCl₃ was used as vanadium precursor, 60 nm, (VC-1/Al₂O₃) (Figure 4.8). These particle size values of the Al₂O₃-supported VC catalysts agree quite well with the crystallite sizes deduced from XRD patterns. For VC-2/Al₂O₃ and VC-2_H₂/Al₂O₃, different planes indexed to VC_x (V₈C₇ or VC) phases were observed by electron diffraction (Figure 4.8, 4.9 and 4.10).

For VC-1/ Al_2O_3 and VC-2_ H_2 / Al_2O_3 , cubic, rhombohedral and monoclinic Al_2O_3 were detected by electron diffraction, verifying the partial transformation of cubic- Al_2O_3 during the preparation.

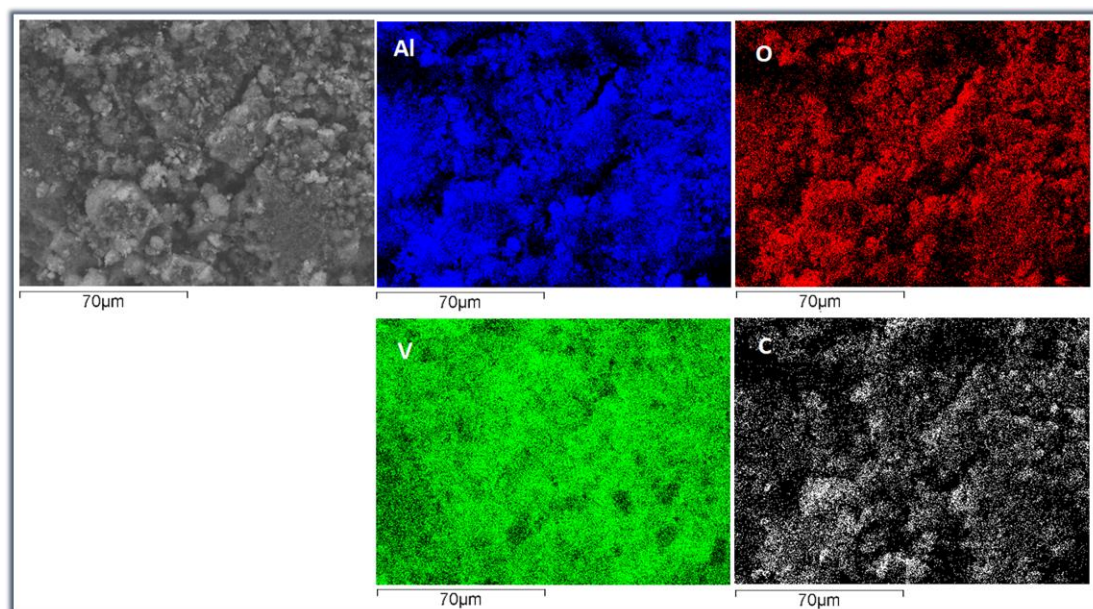


Figure 4.5. SEM image and EDX mapping of VC-1/ Al_2O_3 . Blue: aluminum; red: oxygen; green: vanadium; white: carbon.

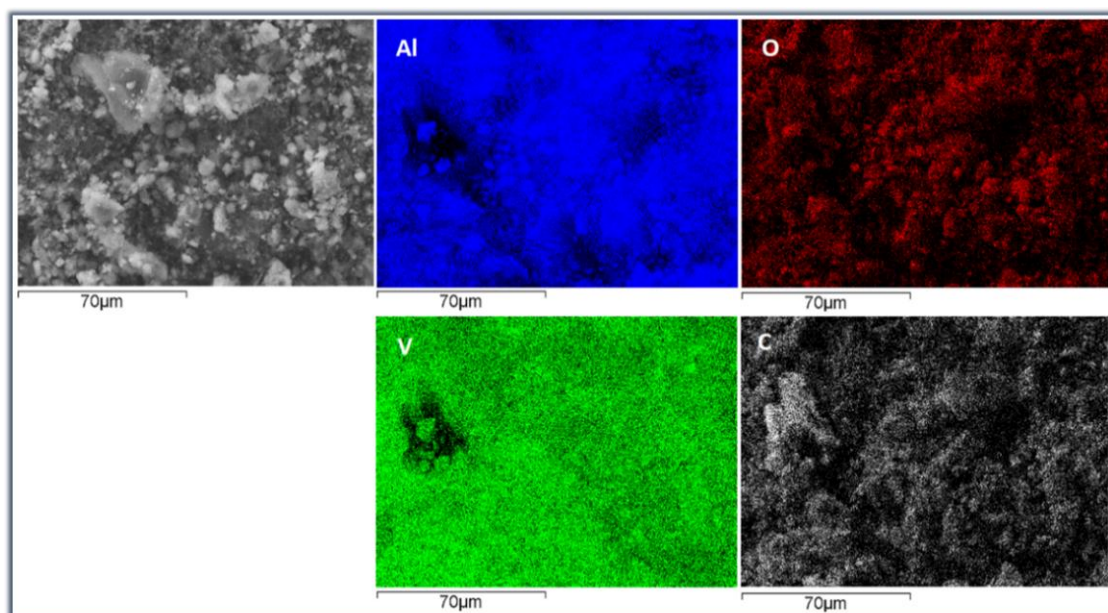


Figure 4.6. SEM image and EDX mapping of VC-2/ Al_2O_3 . Blue: aluminum; red: oxygen; green: vanadium; white: carbon.

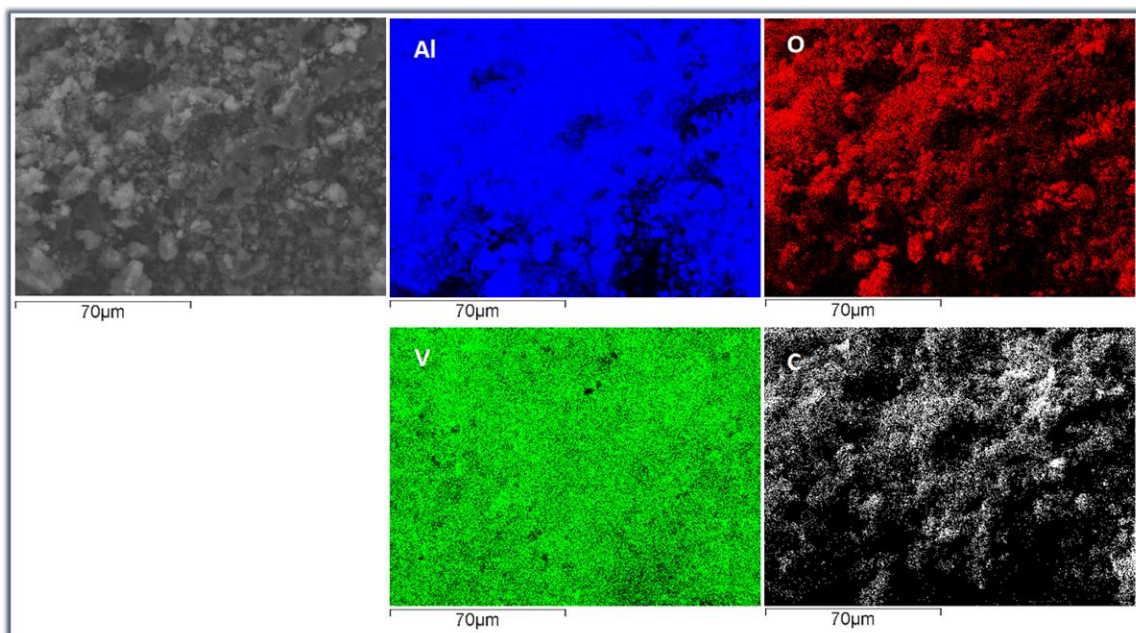


Figure 4.7. SEM image and EDX mapping of VC-2_H₂/Al₂O₃. Blue: aluminum; red: oxygen; green: vanadium; white: carbon.

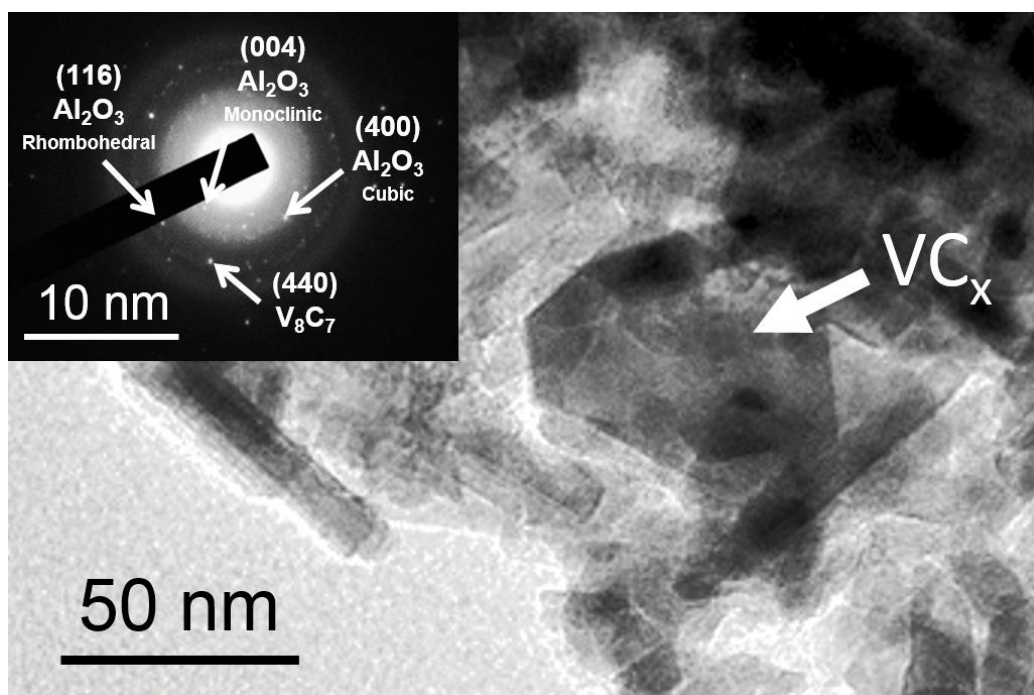


Figure 4.8. TEM image and ED pattern (inset) of VC-1/Al₂O₃ catalysts. VC_x is referred to (440) facet of V₈C₇ phase in ED recognition, corresponding also to (220) facet of VC phase.

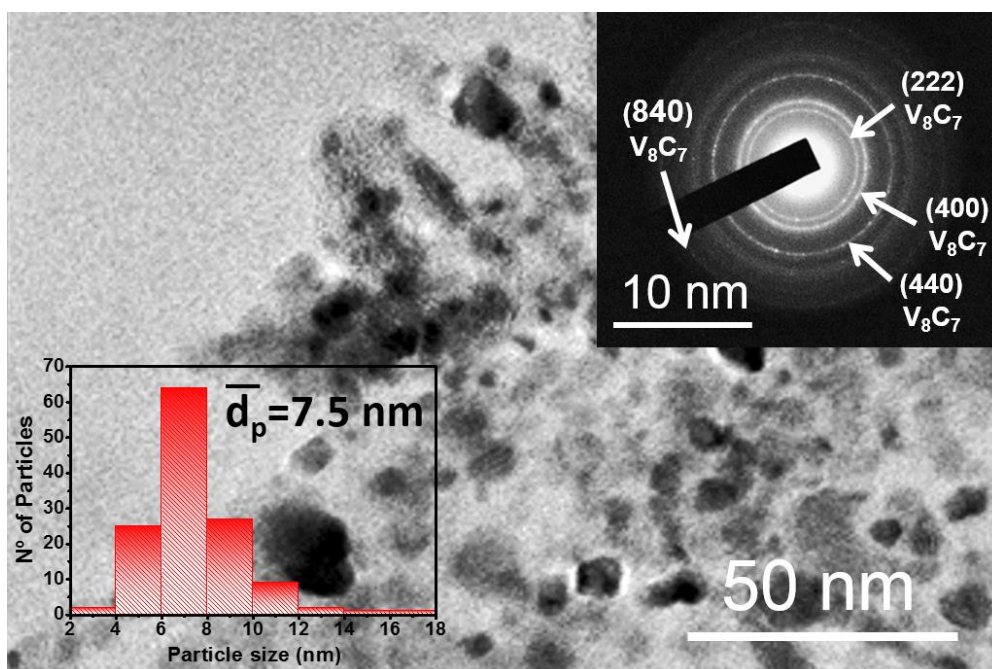


Figure 4.9. TEM image, particle size distribution and ED pattern (inset) of VC-2/ Al_2O_3 catalysts. VC_x is referred to (222), (400), (440) and (840) facets of V_8C_7 phase in ED recognition, corresponding also to (111), (200), (220) and (420) facets of VC phase.

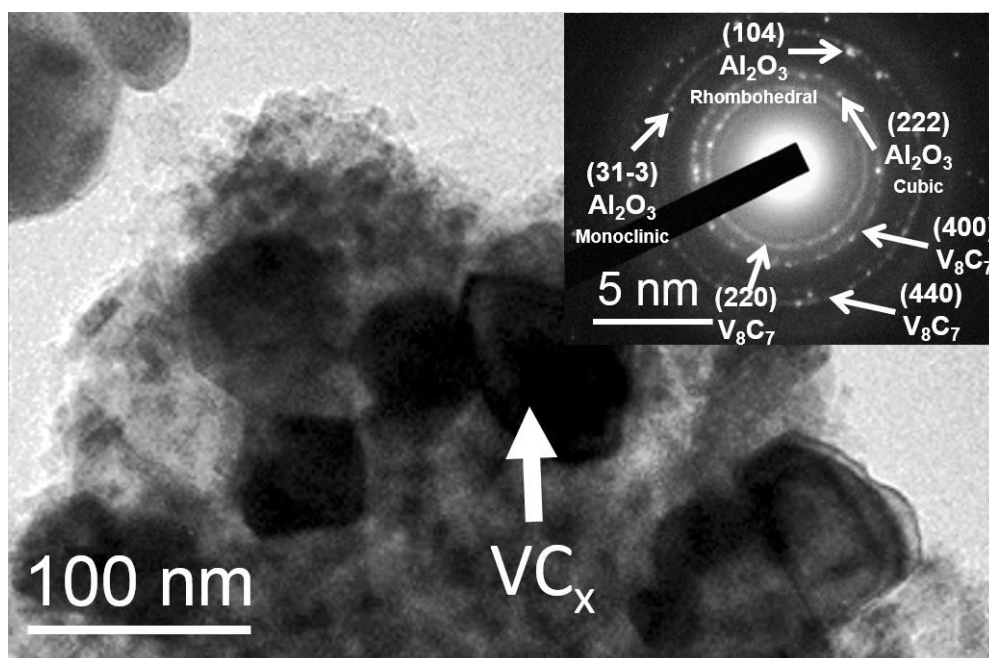


Figure 4.10. TEM image and ED pattern (inset) of VC-2_ H_2 / Al_2O_3 catalysts. VC_x is referred to (220), (400) and (440) facets of V_8C_7 phase in ED recognition, corresponding also to (110), (200), (220) facets of VC phase.

Al₂O₃-supported VC catalysts were characterized by XPS. V 2*p*, C 1*s*, Al 2*p* and O 1*s* core levels were analyzed. Figure 4.11A shows the V 2*p* spectra of the catalysts, in all cases the coexistence of VC_x (V 2*p*_{3/2}= 513.5-513.7 eV) [1,14-18] with other oxy-vanadium species (V 2*p*_{3/2}= 514.3-514.6 eV, 516.3-517.3 eV) can be deduced [1,14-24]. In this context, VC-3/Al₂O₃, which was treated under a reducing atmosphere, showed smaller bands associated to VO_x species compared to the other two samples.

In all cases, C 1*s* spectra (Figure 4.12A) showed a component at 282.8-282.9 eV, related to C-V bonds from VC_x [1,14-17]. The peak with a maximum at 284.8 eV, is associated to C-C bonds formed during preparation and adventitious carbon, and that at 285.6-285.9 eV to C-O bonds; other peaks with small intensity at higher BE are related with C=O and C-O=O bonds [25-27]. As observed, the V 2*p* and C 1*s* spectra profiles are consistent with those of the bulk VC catalysts shown in Chapter 3 (Figure 3.19).

All Al₂O₃-supported VC catalysts showed broad bands corresponding to O 1*s* with maxima at about ~532 eV which were deconvoluted into 4 peaks (Figure 4.13A), Oxy-vanadium and oxy-carbide species contribute to the lower BE part of the O 1*s* peak (about 530-531 eV); VC-2_H₂/Al₂O₃, which was treated under a reducing atmosphere, showed smaller bands associated to VO_x species compared to the other two samples [1,13,14,17]. The peak at about 532 eV is assigned to Al₂O₃ and the presence of O-C and/or O=C are related with components at 533.2-533.6 eV [25-31].

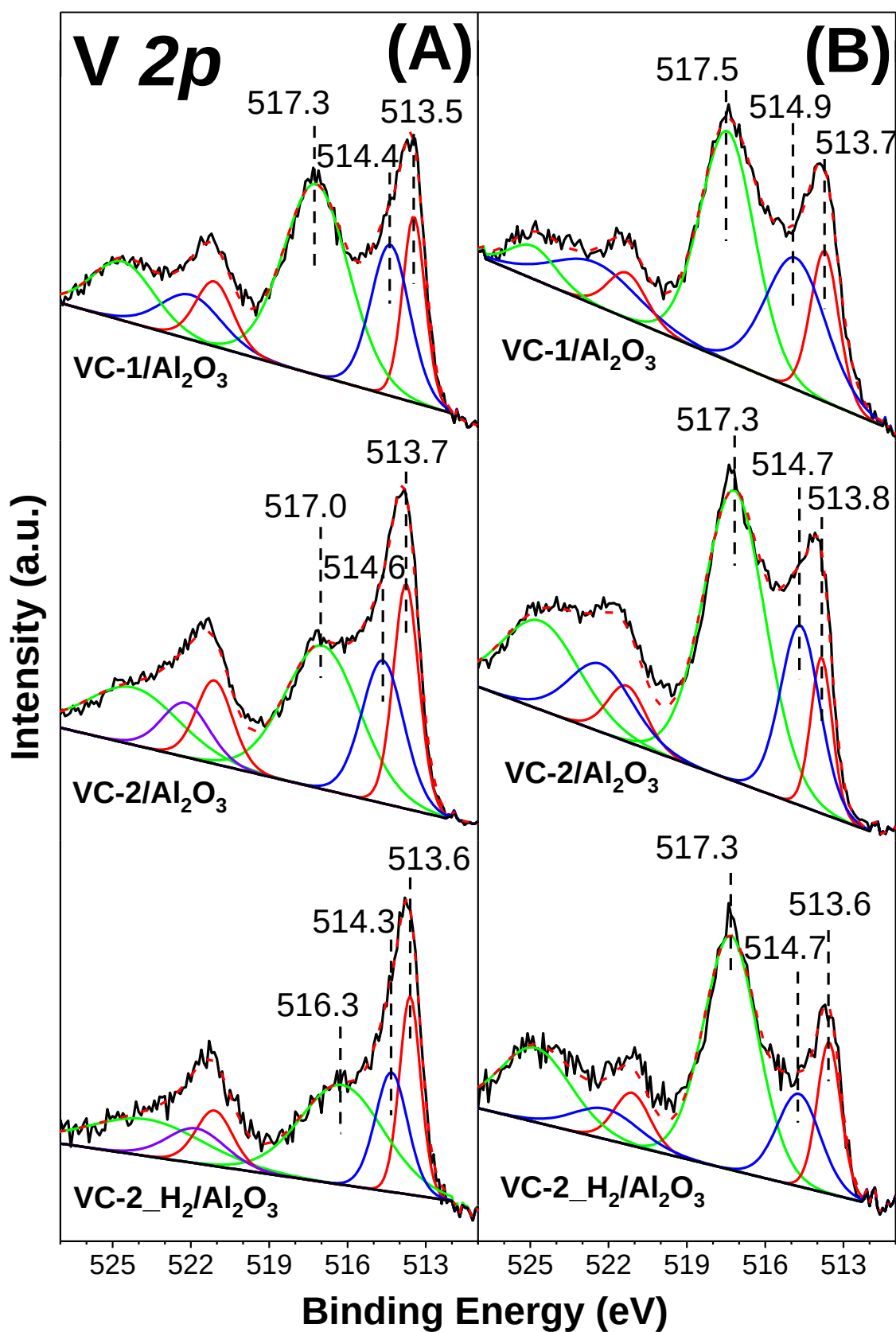


Figure 4.11. V 2p XPS profiles of fresh and used Al_2O_3 -supported VC catalysts. (A) Fresh; (B) Used.

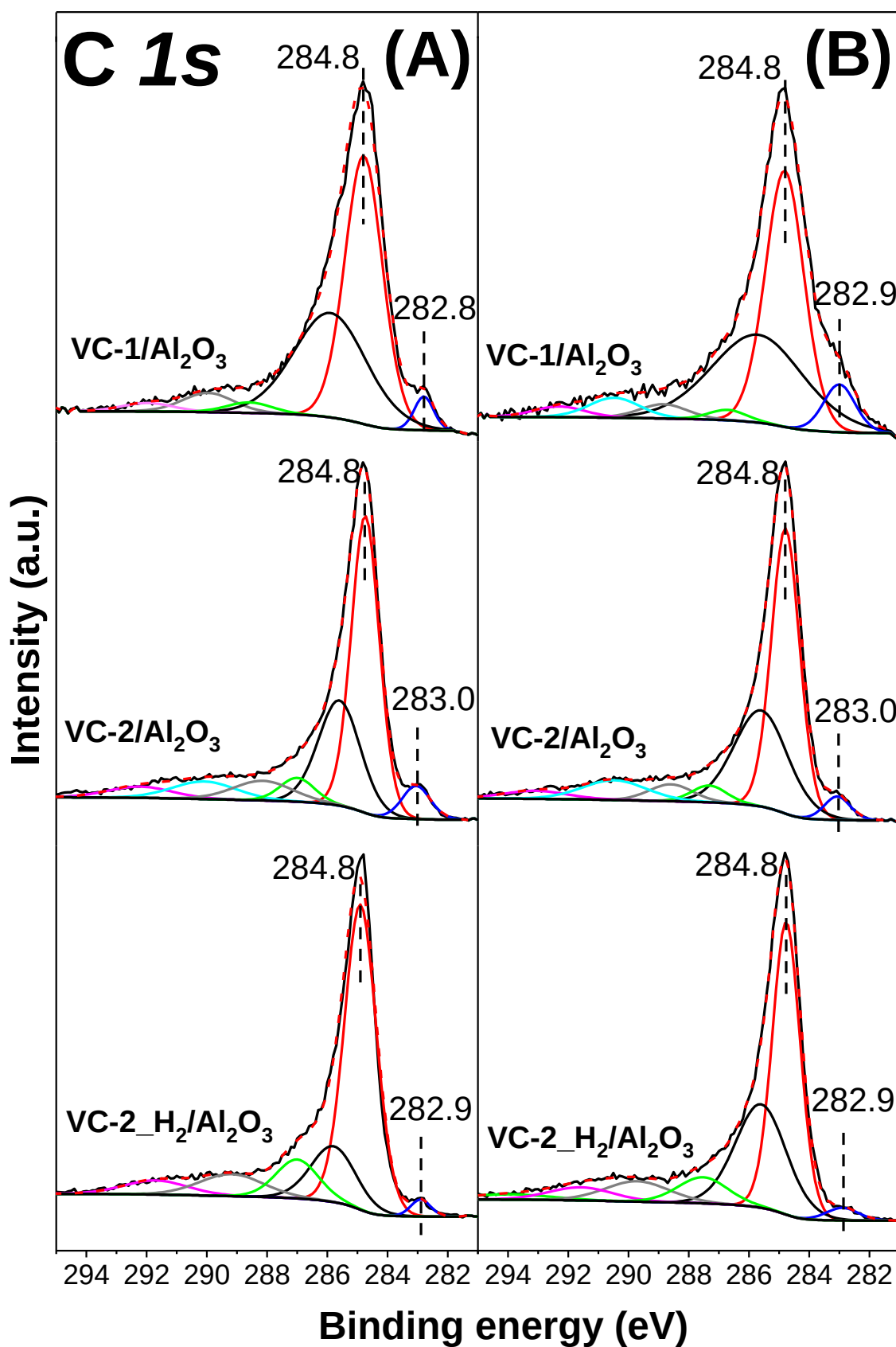


Figure 4.12. C 1s XPS profiles of fresh and used Al_2O_3 -supported VC catalysts. (A) Fresh; (B) Used.

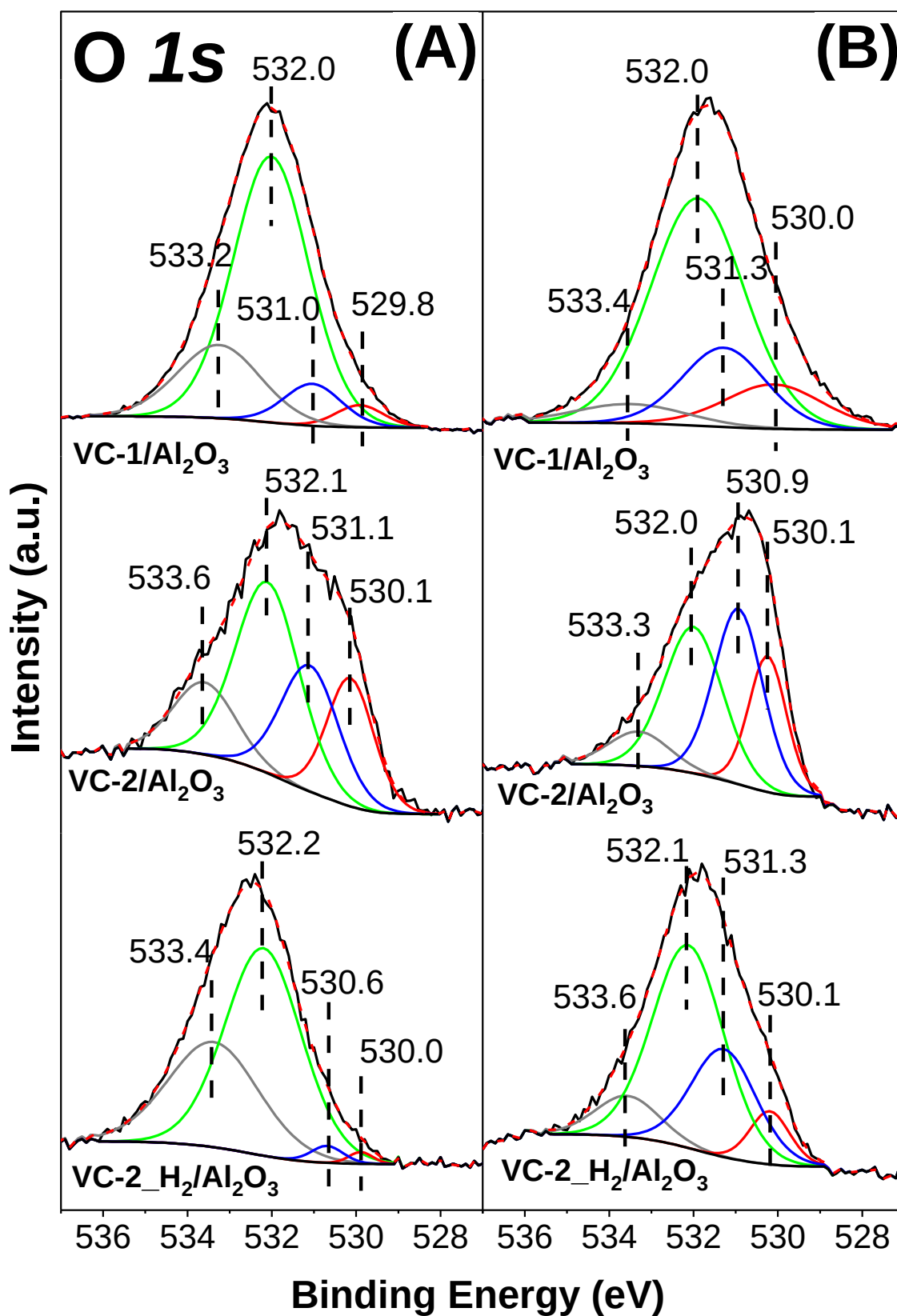


Figure 4.13. O 1s XPS profiles of fresh and used Al_2O_3 -supported VC catalysts: (A) Fresh; (B) Used

Table 4.2 shows the V content of the catalysts and the V/Al molar ratio determined by ICP $((V/Al)_{ICP})$ and that determined by XPS $((V/Al)_{XPS})$. VC-2/Al₂O₃ showed a much higher V/Al surface atomic ratio than the other two catalysts. This can be associated to the much lower crystallite size of VC_x in VC-2/Al₂O₃ (7 nm) than in VC-1/Al₂O₃ (53 nm) and VC-2_H₂/Al₂O₃ (47 nm).

Table 4.2. V content determined by ICP and V/Al (mol/mol) ratio from ICP and XPS of Al₂O₃-supported VC catalysts.

Sample	V content (%wt) V	$(V/Al)_{ICP}$ (mol/mol)	$(V/Al)_{XPS}$ (mol/mol)	
			Fresh	Used
VC-1/Al ₂ O ₃	27.42	0.51	0.182	0.147
VC-2/Al ₂ O ₃	18.84	0.33	3.272	2.616
VC-2_H ₂ /Al ₂ O ₃	22.45	0.44	0.204	0.194

From XPS and chemical analysis, it is possible to describe a dispersion factor, which is considered proportional to the true dispersion (only qualitatively) as set by Leclercq et al., as follows [32]:

$$D = (V/Al)_{XPS}/(V/Al)_{ICP}.$$

The dispersion factor increases in the following order: VC-1/Al₂O₃ (0.36) < VC-2_H₂/Al₂O₃ (0.46) < VC-2/Al₂O₃ (9.1). Despite the different BET surface areas of these catalysts, as stated before, the high value of dispersion factor in VC-2/Al₂O₃ can be related to the small particle size of VC_x compared to the other two samples.

4.1.3. Catalytic behavior of G5TMC/Al₂O₃ catalysts in the RWGS reaction

As stated in the experimental section, the catalytic behavior of G5TMC/Al₂O₃ in the RWGS reaction was determined from 573 K up to 873 K using 300 mg of catalyst with a reactant mixture of CO₂/H₂/N₂=1/3/1 at 0.1 MPa and GHSV of 3000 h⁻¹. The catalysts were kept 1.5 h at each temperature. Moreover, at 873 K, the RWGS reaction was followed for 4 h in order to check the stability of catalysts.

Figure 4.14A displays the CO₂ conversion values for all catalysts, which, as expected, increased with temperature. Only Al₂O₃-supported VC catalysts were active. The behavior of Al₂O₃-supported NbC and TaC was similar to that of bulk NbC-1 and TaC-1 (Chapter 3), they were not active under the reaction conditions used. For Al₂O₃-supported VC catalysts, the CO₂ conversion at 873 K was in the following order: VC-2/Al₂O₃ (40.8%) > VC-2_H₂/Al₂O₃ (29.9%) > VC-1/Al₂O₃ (22.4%).

Figure 4.14B shows the CO₂ conversion of Al₂O₃-supported VC catalysts during the last part of the catalytic test, when the temperature was kept at 873 K for 4 h. Although for VC-2/Al₂O₃ and VC-2_H₂/Al₂O₃, an initial decrease in the CO₂ conversion was observed, after 2 h at 873 K, the decrease of the CO₂ conversion was significantly lower.

Besides CO, which was the main product, only small amounts of CH₄ were produced. At 773 K or higher temperatures, the CO selectivity was in all cases higher than 99.5%; constant selectivity values were found in all cases during the 4 h at 873 K. At temperature lower than 773 K, a higher selective behavior of VC-2/Al₂O₃ was observed (Figure 4.15).

For a better comparison, the CO production plots per mol of vanadium in the samples are displayed in Figure 4.16. VC-2/Al₂O₃ showed the highest CO production in all the range of temperature tested at 873 K. CO production values of 3.38, 8.86 and 5.44 mol_{CO} mol_V⁻¹ h⁻¹ were obtained for VC-1/Al₂O₃, VC-2/Al₂O₃ and VC-2_H₂/Al₂O₃, respectively (Figure 4.16).

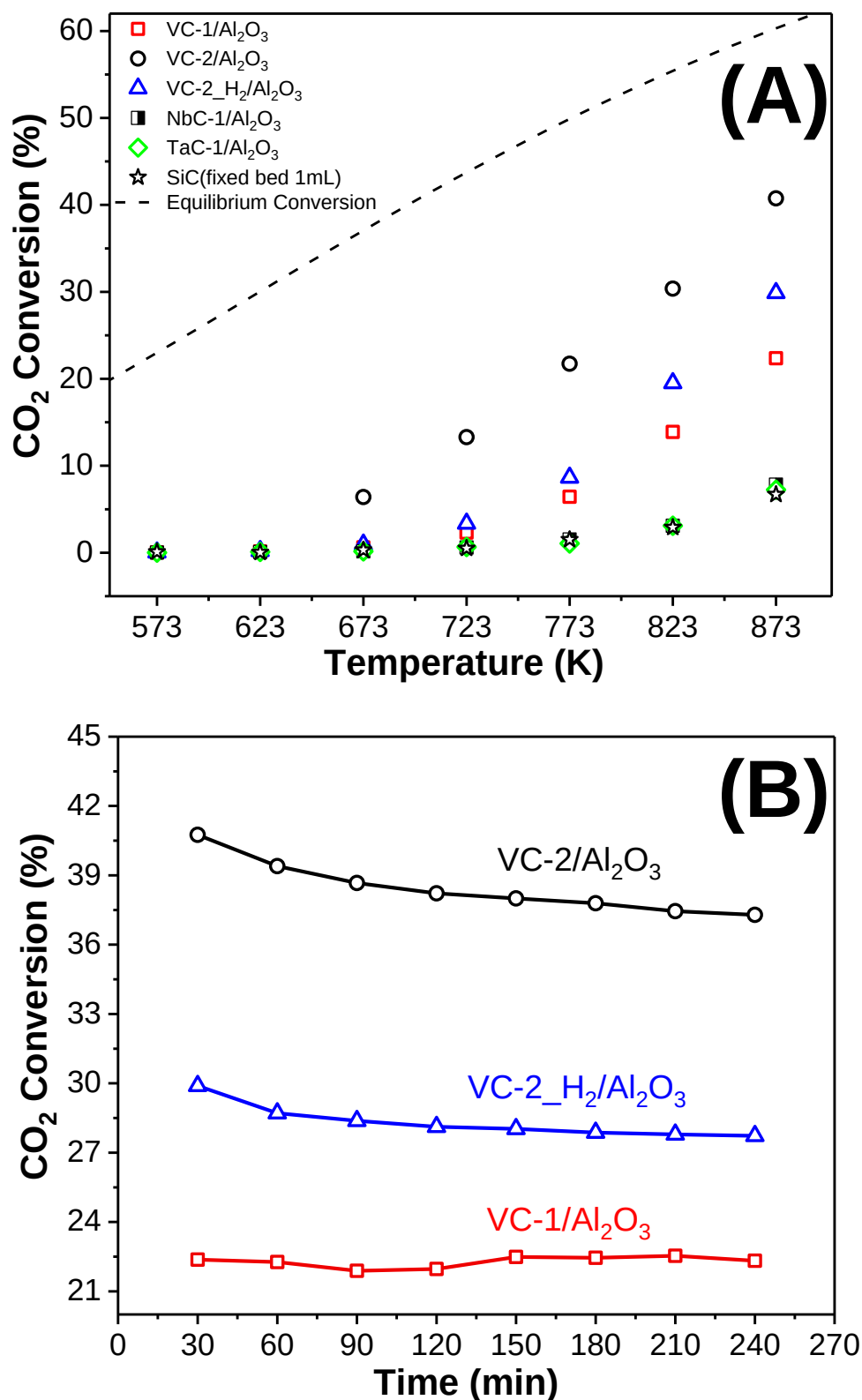


Figure 4.14. Catalytic behavior of Al₂O₃-supported VC catalysts in the RWGS reaction: A) CO₂ conversion as a function of reaction temperature; B) CO₂ conversion at 873 K as a function of reaction time. Reaction conditions: CO₂/H₂/N₂=1/3/1; GHSV=3000 h⁻¹; P=0.1 MPa; m=300 mg.

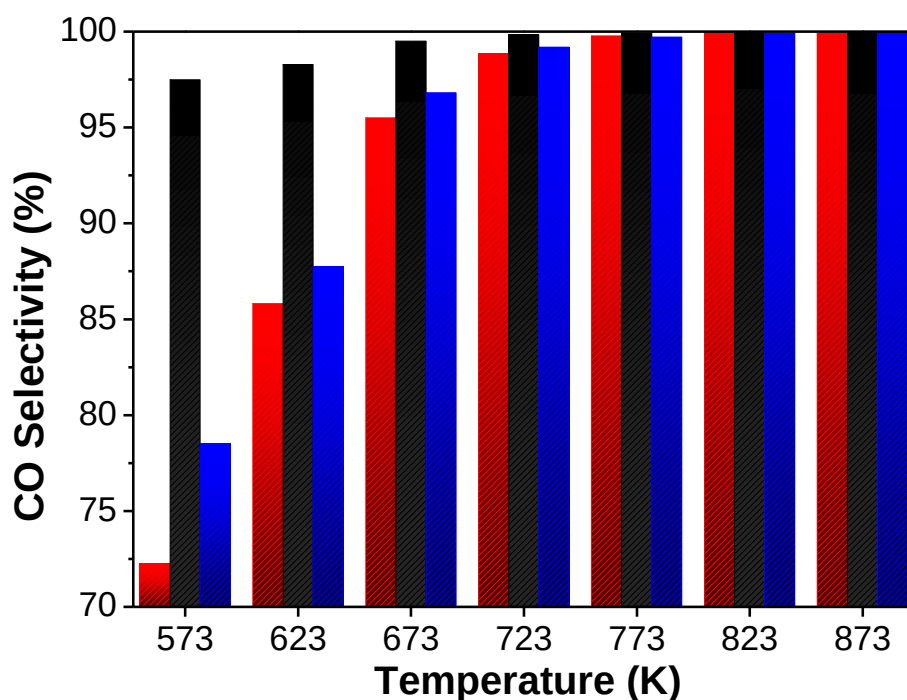


Figure 4.15. CO Selectivity of Al₂O₃-supported VC catalysts in the RGWS reaction. Red bars: VC-1/Al₂O₃; black bars: VC-2/Al₂O₃; blue bars: VC-2_H₂/Al₂O₃. Reaction conditions: CO₂/H₂/N₂=1/3/1; GHSV=3000 h⁻¹; T=573-873 K; P=0.1 MPa; m=300 mg.

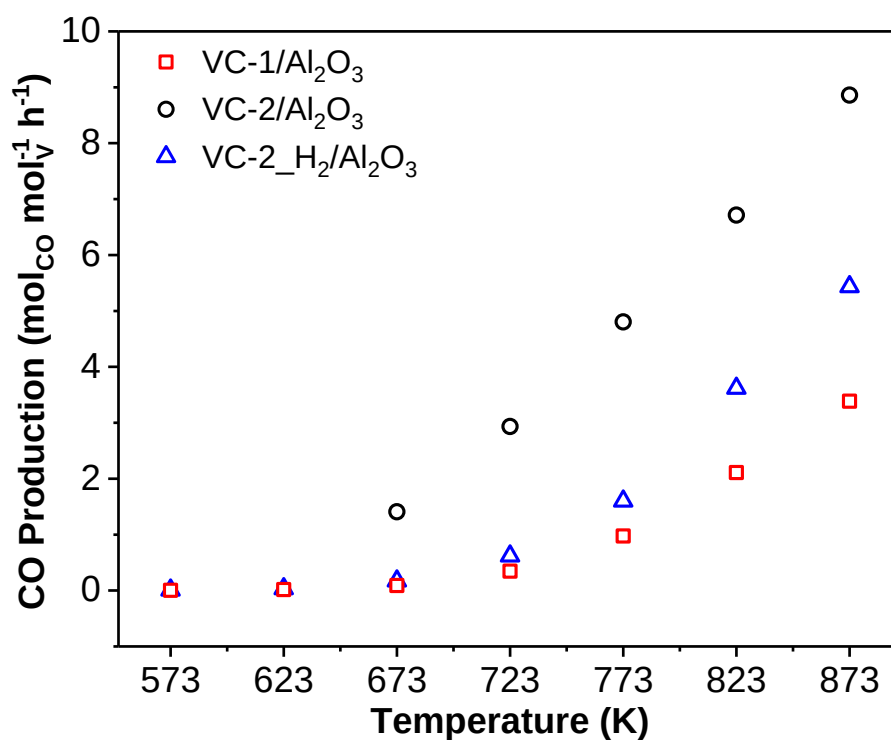


Figure 4.16. CO production per mol of V as a function of reaction temperature. Reaction conditions: CO₂/H₂/N₂=1/3/1; GHSV=3000 h⁻¹; P=0.1 MPa; m=300 mg.

Using the Arrhenius plot, the apparent activation energies for CO production in the 723-823 K range were calculated (Figure 4.17). For comparison, Figure 4.17 also displays the Arrhenius plot for bulk VC-1 and VC-2 in the 723-823 K range. Catalysts with VC_x crystallite size in the 54-61 nm range (VC-1/Al₂O₃, VC-2_H₂/Al₂O₃ and VC-1) showed apparent activation energy values of 82-89 kJ mol⁻¹. Meanwhile, catalysts with lower VC_x crystallite size, VC-2/Al₂O₃ (7nm) and VC-2 (8 nm) showed much lower apparent activation energy values; VC-2/Al₂O₃ ($E_a=41.2\pm2.9$ kJ mol⁻¹) and VC-2 ($E_a=58.1\pm4.1$ kJ mol⁻¹).

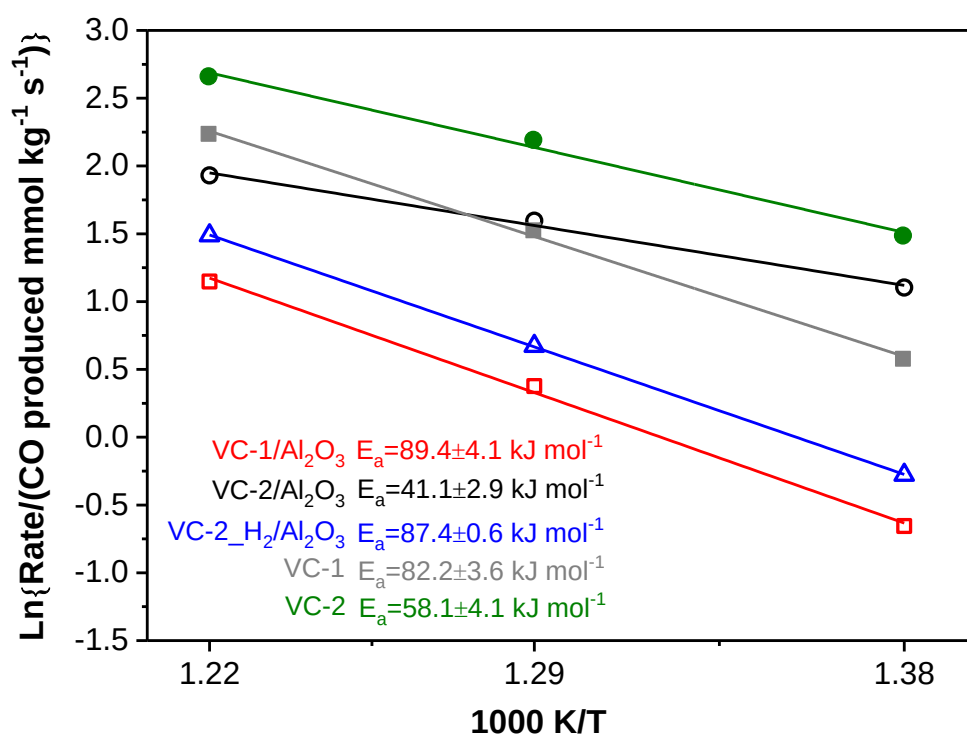


Figure 4.17. Arrhenius plot for CO production from RWGS over Al₂O₃-supported VC catalysts. Temperature: 723-823 K. Reaction conditions: CO₂/H₂/N₂=1/3/1; GHSV=3000 h⁻¹; P=0.1 MPa; m=300 mg. Apparent activation energy data of VC-1 and VC-2 samples taken from Chapter 3.

As a summary, for VC/Al₂O₃ catalysts, CO productivity and the E_a depended on the crystallite size of VC_x, which in turn depended on the vanadium precursor and preparation method as was previously stated for the bulk VC catalysts. We relate the catalytic performance of VC-2/Al₂O₃ with the presence of small VC_x

crystallites containing C defective VC phase (V_8C_7) as it was discussed in Chapter 3 for VC-2 bulk catalyst.

Post-reaction Al_2O_3 -supported VC catalysts were characterized by N_2 adsorption/desorption isotherms, XRD and XPS. The BET surface area of post-reaction catalysts was only slightly lower than that of fresh catalysts (Table 4.1). XRD patterns of post-reaction catalysts (Figure 4.18) were also similar to those of fresh catalysts. Only slight changes in the crystallite size of VC_x were determined after the RWGS catalytic test (Table 4.1).

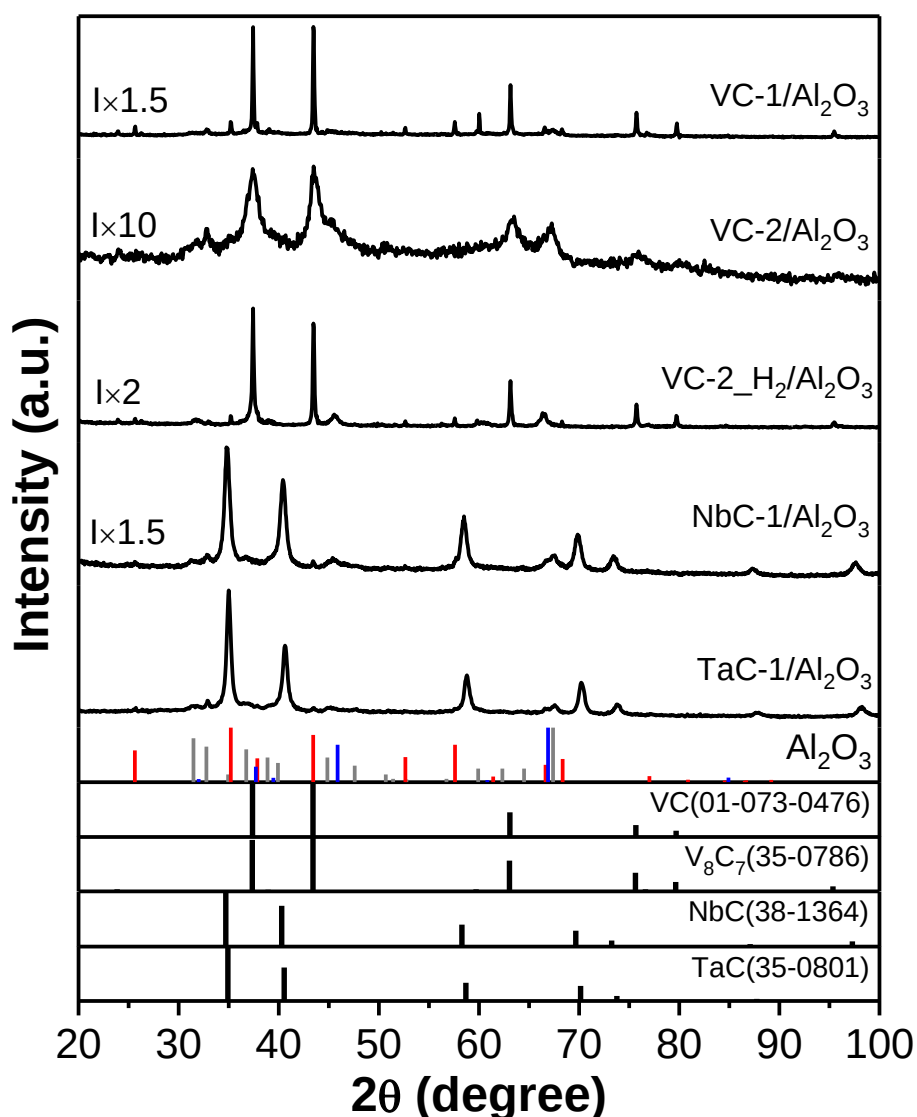


Figure 4.18. XRD patterns of catalysts after RWGS reaction. Blue Lines: cubic Al_2O_3 (10-0425). Red Lines: Rhombohedral Al_2O_3 (10-0173). Gray Lines: Monoclinic Al_2O_3 (35-0121).

Figures 4.11 and 4.12 compare the V $2p$ and C $1s$ level spectra of post-reaction catalysts with those of fresh catalysts discussed before. The bands corresponding to V-C bonds (V $2p_{3/2}$ =513.6-513.8 eV and C $1s$ =282.9-283.0 eV) are still visible after the catalytic test. An increase of the intensity of the bands located at V $2p_{3/2}$ =517.3-517.5 eV was observed, this might be related with a surface oxidation during the reaction. This accords with the increase after the catalytic test of the intensity of O $1s$ components assigned to oxy-vanadium species (O $1s$ =530.0-531.3 eV) (Figure 4.13B).

V/Al surface atomic ratios of post reaction Al_2O_3 -supported VC catalysts are given in Table 4.2. A small decrease in the V/Al ratio is observed in all cases compared to the fresh catalysts.

Although, NbC-1/ Al_2O_3 and TaC-1/ Al_2O_3 did not show catalytic activity in the RWGS reaction, they were also characterized after reaction by XRD (Figure 4.18) and N_2 adsorption/desorption isotherms (Table 4.1). The results obtained were similar to those of fresh catalysts.

The RWGS reaction was followed over the most performant catalyst, VC-2/ Al_2O_3 , at 723 K during 4 days (Figure 4.19). An initial deactivation was observed, but after 30 h, the catalytic behavior remained almost constant, reaching about 11% of CO_2 conversion ($5.25 \text{ mol}_{\text{CO}} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$) and 99.85 % of CO selectivity after about 90 h.

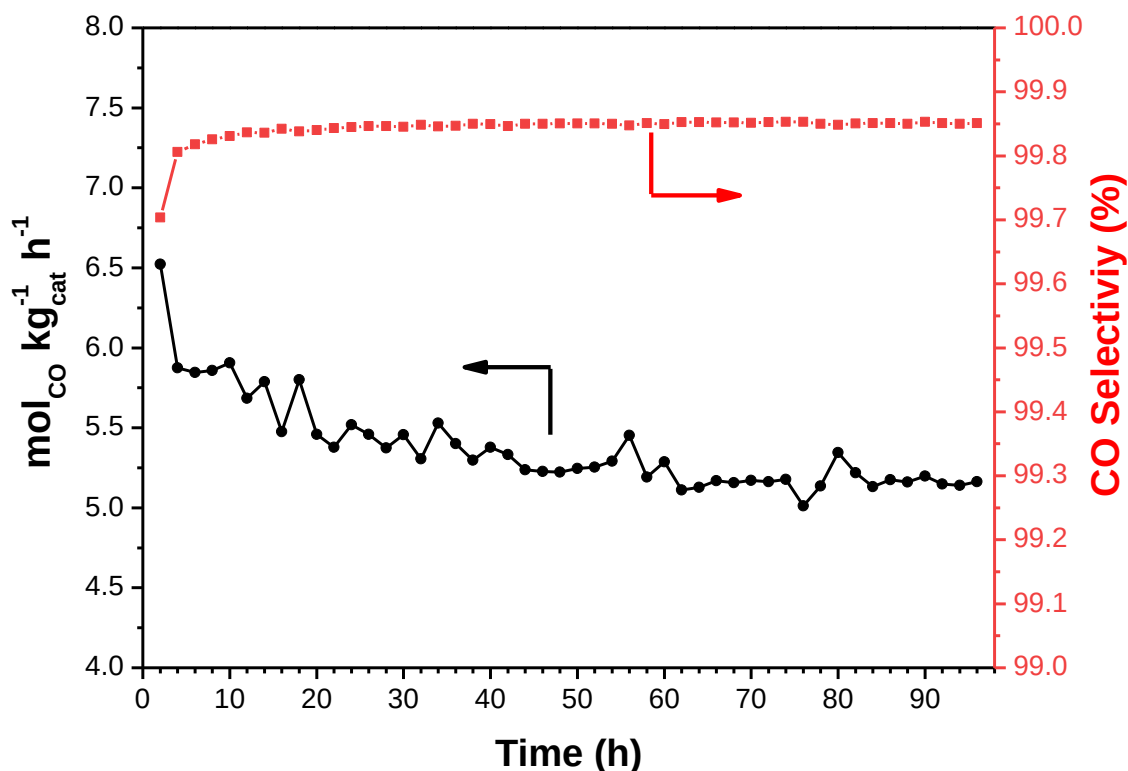


Figure 4.19. Catalytic behavior of VC-2/Al₂O₃ in RWGS at 723 K as a function of time on stream. CO production and CO selectivity. Reaction conditions: CO₂/H₂/N₂=1/3/1; GHSV=3000 h⁻¹; P=0.1 MPa; m=500 mg.

VC-2/Al₂O₃ was characterized after the long-term catalytic test by N₂ adsorption/desorption isotherms and XRD (Figure 4.20). After 4 days of reaction at 723 K, VC-2/Al₂O₃ showed a lower BET surface area (133 m² g⁻¹) than fresh catalyst (234 m² g⁻¹). However, VC_x crystallite size calculated from XRD patterns (8 nm) is similar to that of fresh catalyst (7 nm). XPS characterization of long-term post-reaction VC-2/Al₂O₃ catalyst (Figure 4.21) shows that the bands corresponding to V-C bonds (V 2p_{3/2}=513.8 eV and C 1s=282.9 eV) are still visible. The intensity of the components corresponding to V-O (V 2p_{3/2}=514.8-517.2 eV and O 1s=530.2-530.9 eV) increased with respect to the fresh catalyst, showing a surface oxidation of VC_x particles.

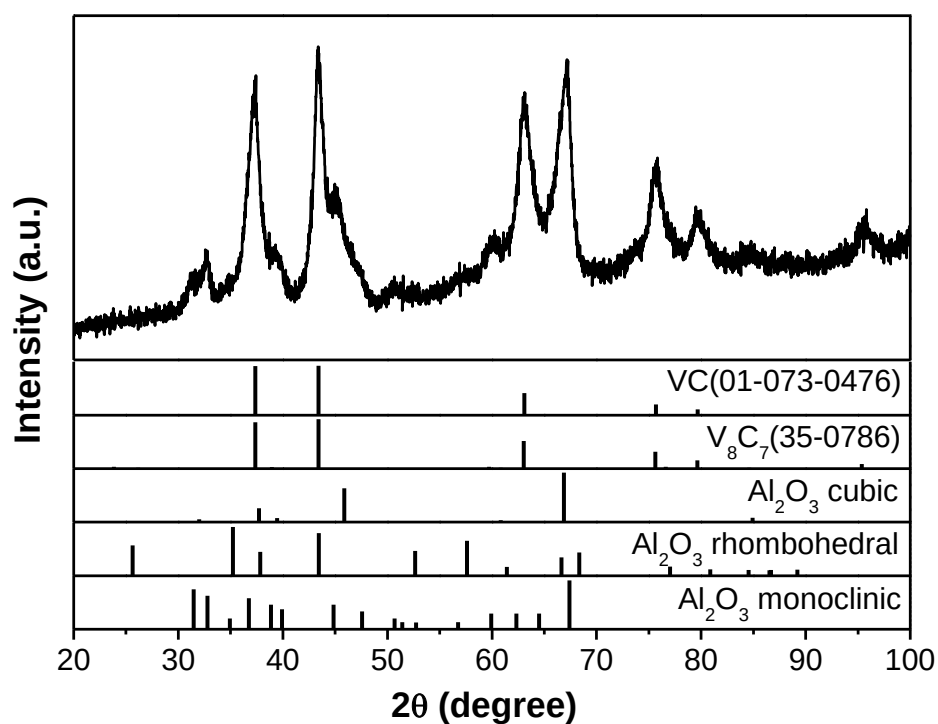


Figure 4.20. XRD pattern of VC-2/ Al_2O_3 after RWGS catalytic test at 723 K for 4 days of reaction. Cubic Al_2O_3 (10-0425). Rhombohedral Al_2O_3 (10-0173). Monoclinic Al_2O_3 (35-0121).

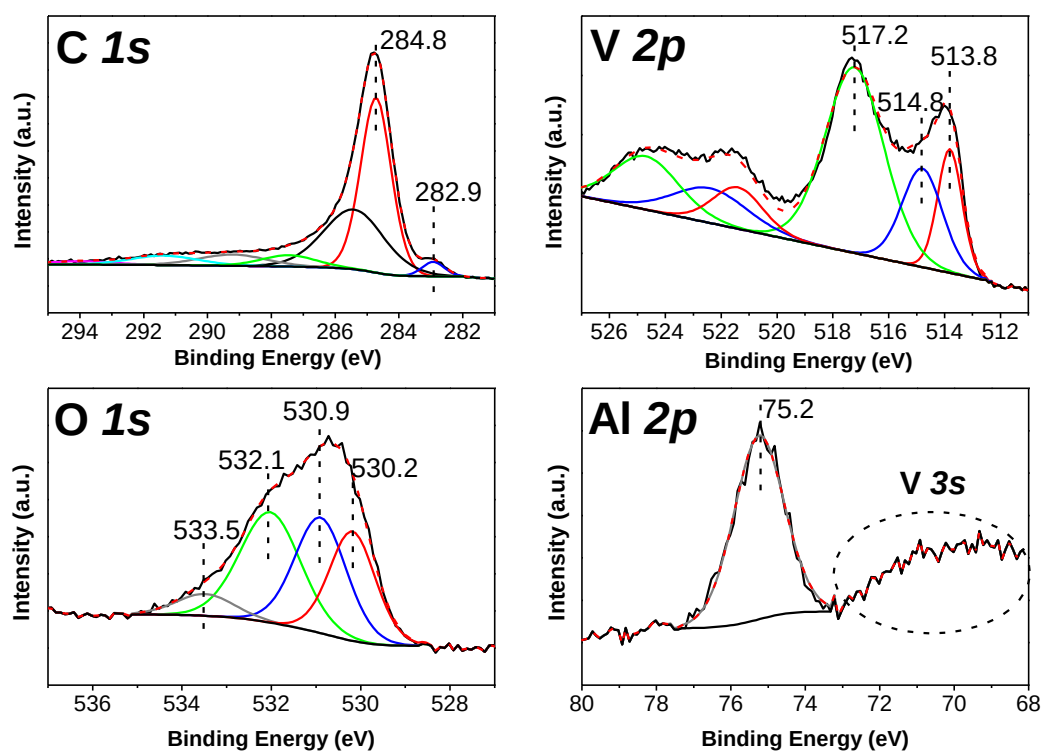


Figure 4.21. XPS profiles of VC-2/ Al_2O_3 after RWGS catalytic test at 723 K for 4 days.

4.2. Supported VC catalysts

4.2.1. Preparation of supported VC catalysts

Several supported VC catalysts (~25%wt V) on different supports were prepared to study the influence of the support in their characteristics and catalytic behavior.

The preparation method employed was similar to that used for the preparation of VC-2/Al₂O₃ discussed in the Section 4.1 but using VO(isopropoxide)₂/4,5-dicyanoimidazole molar ratio R=1 instead of R=1.35 in order to minimize the carbonaceous residues in the final catalysts. The treatment temperature was 1373 K in all cases and no passivation was performed after thermal treatment. The details of the preparation of the catalysts are described in ANNEX II.

For the preparation of supported VC catalysts, γ -Al₂O₃ (*Alfa Aesar*, 226 m²g⁻¹), activated carbon (AC) (*Sigma Aldrich*, 650 m²g⁻¹), TiO₂ (*Tecnan*, 117 m²g⁻¹ anatase/rutile=78/22% wt/wt), SiO₂ (*Degussa*, 200 m²g⁻¹), SBA-15 (*Glantreo*, 450 m²g⁻¹), CeO₂ (*Tecnan*, 90 m² g⁻¹) and ZrO₂ (*Tecnan*, 50 m²g⁻¹) were used as supports.

The catalysts were named VC-3/Al₂O₃, VC-3/AC, VC-3/TiO₂, VC-3/SiO₂, VC-3/SBA-15, VC-3/CeO₂ and VC-3/ZrO₂ according to the support used in the preparation. For comparison, bulk VC-3 was prepared following the procedure described above in the absence of support.

4.2.2. Characterization of supported VC catalysts

Table 4.3 shows the content of V in the samples measured by ICP-AES, which is near to the set value in the preparation of the catalysts.

Table 4.3. Several characteristics of supported VC catalysts before and after RWGS reaction

Catalyst	V content (%wt)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)		Pore size (nm)		Crystallite size of VC_x (XRD)
		Fresh	Used	Fresh	Used	
VC-3/AC	21.3	448	188	4	4	11
VC-3/SBA-15	23.4	72	15	13	26	20
VC-3/ CeO_2	22.5	86	45	6	6	36
VC-3/ ZrO_2	21.6	119	59	6	6	25
VC-3/ SiO_2	21.3	216	92	7	9	9
VC-3/ Al_2O_3	22.1	210	101	9	11	9
VC-3/ TiO_2	23.0	158	82	17	18	20
VC-3	-	271	219	7	10	11

The corresponding adsorption-desorption isotherms and the pore size distributions are shown in Figure 4.22. The S_{BET} values obtained for all catalysts were in the range of 72-448 $\text{m}^2 \text{g}^{-1}$ (Table 4.3). The S_{BET} of VC-3/AC, VC-3/SBA-15, VC-3/ Al_2O_3 and VC-3/ CeO_2 decreased respect to that of their corresponding fresh supports (see Section 4.2.1). However, for VC-3/ ZrO_2 , VC-3/ TiO_2 and VC-3/ SiO_2 an increase of the S_{BET} was observed. All catalysts are mesoporous materials with average pore widths of 4-17 nm (Table 4.3).

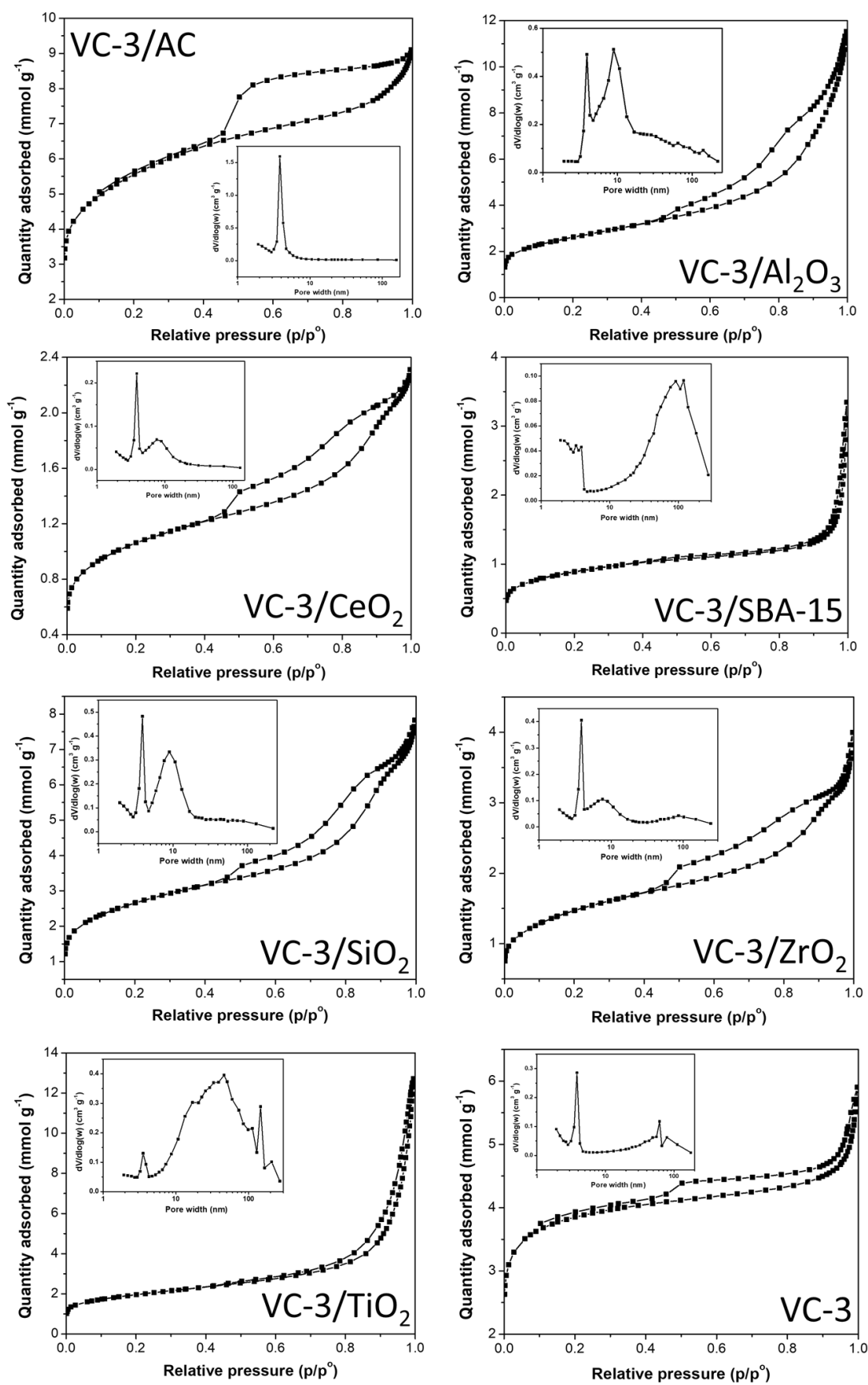


Figure 4.22. Adsorption-Desorption isotherms and pore size distribution (inset) of VC-based catalysts.

Figures 4.23-4.26 show the XRD patterns of the fresh catalysts. In all cases, the presence of cubic VC_x (VC and/or V₈C₇) can be deduced. XRD peaks characteristics of crystalline VO_x species were not found.

Note that some supports change their structure during the preparation of catalysts. γ -Al₂O₃ (cubic phase) (JCPDS 10-0425) was partially converted to monoclinic (JCPDS 35-0121) and rhombohedral (JCPDS 10-0173) phases in VC-3/Al₂O₃ sample (Figure 4.23) [2,3].

The presence of tetragonal (JCPDS 50-1089) and monoclinic (JCPDS 37-1484) ZrO₂ were determined in VC-3/ZrO₂ (Figure 4.24). A slight increase of the intensity of peaks assigned to the monoclinic phase is observed in VC-3/ZrO₂ compared to the pristine ZrO₂ support. Metastable tetragonal ZrO₂ is transformed to monoclinic with thermal treatment [33].

For VC-3/TiO₂, the formation of a solid solution (Ti_{0.9}V_{0.1})₂O₃ (rhombohedral phase) (JCPDS 01-071-0275) could be proposed (Figure 4.25). The existence of other species as oxy-carbides cannot be ruled out [34-37].

CeO₂ (cubic) (JCPDS 34-0394) and graphite (JCPDS 26-1076) were identified in VC-3/CeO₂ and VC-3/AC, respectively (Figures 4.24 and 4.26).

The crystallite sizes of VC_x determined from XRD for all catalysts are listed in Table 4.3. VC-3/Al₂O₃, VC-3/SiO₂ and VC-3/AC showed similar crystallite size (9-11 nm) to bulk VC-3 (11 nm). A higher crystallite size was obtained for VC-3/SBA-15 (20 nm), VC-3/CeO₂ (36 nm), VC-3/TiO₂ (20 nm) and VC-3/ZrO₂ (25 nm) catalysts.

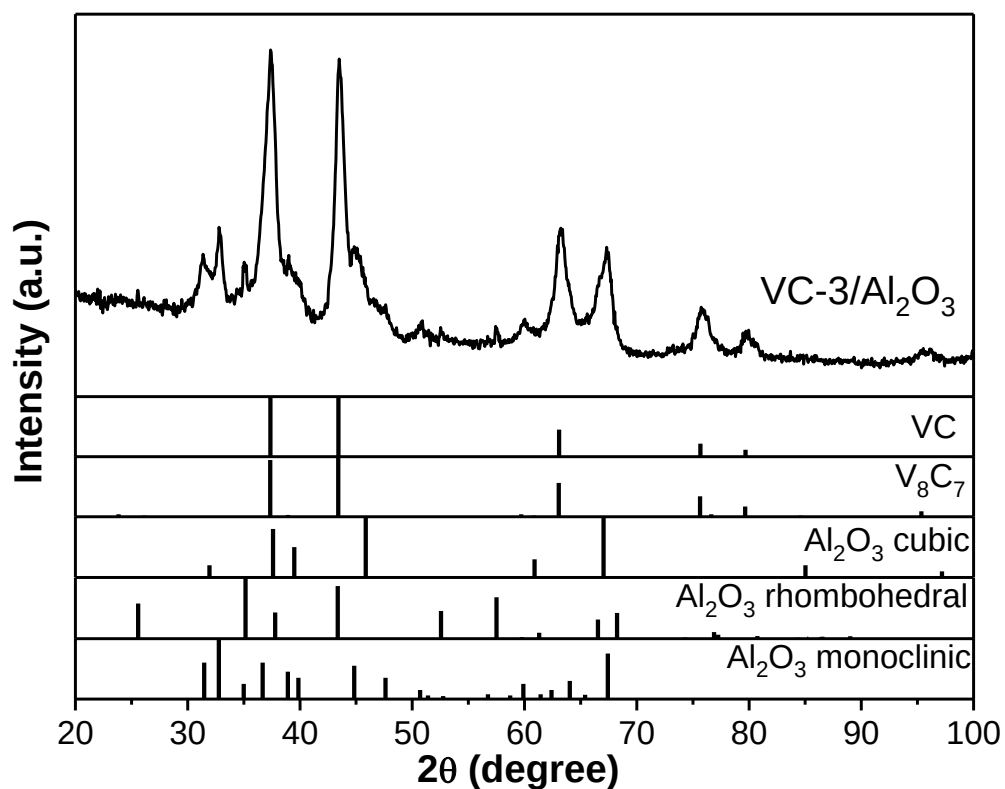


Figure 4.23. XRD pattern of VC-3/Al₂O₃.

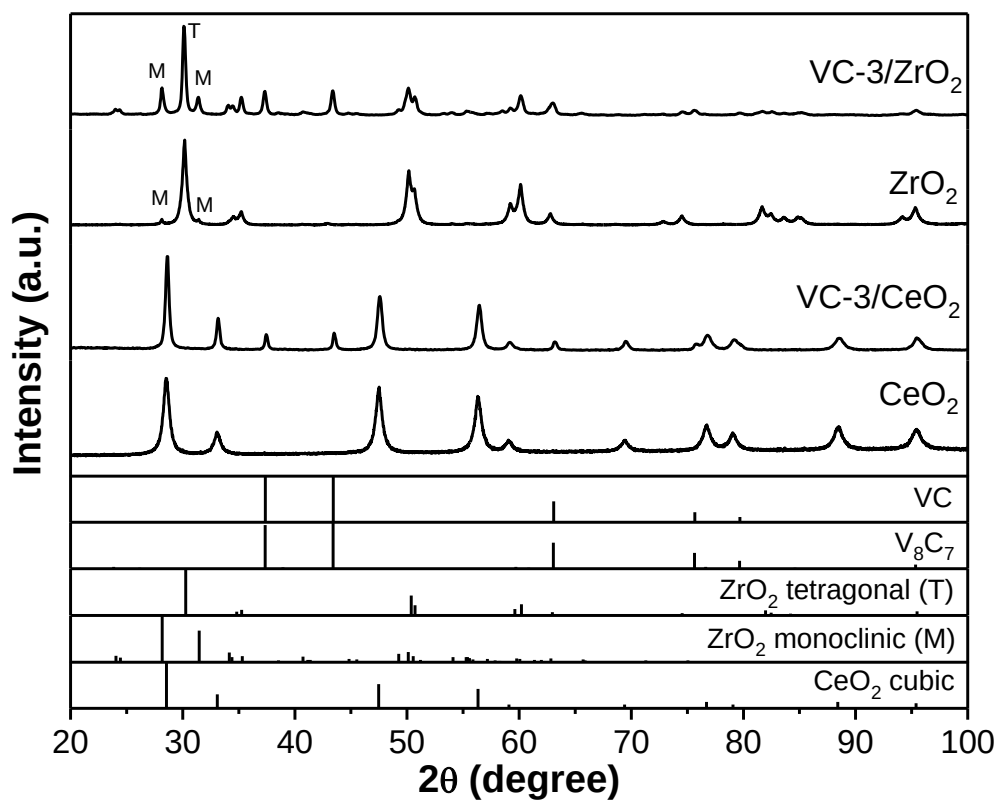


Figure 4.24. XRD patterns of VC-3/ZrO₂, VC-3/CeO₂, and pristine ZrO₂ and CeO₂.

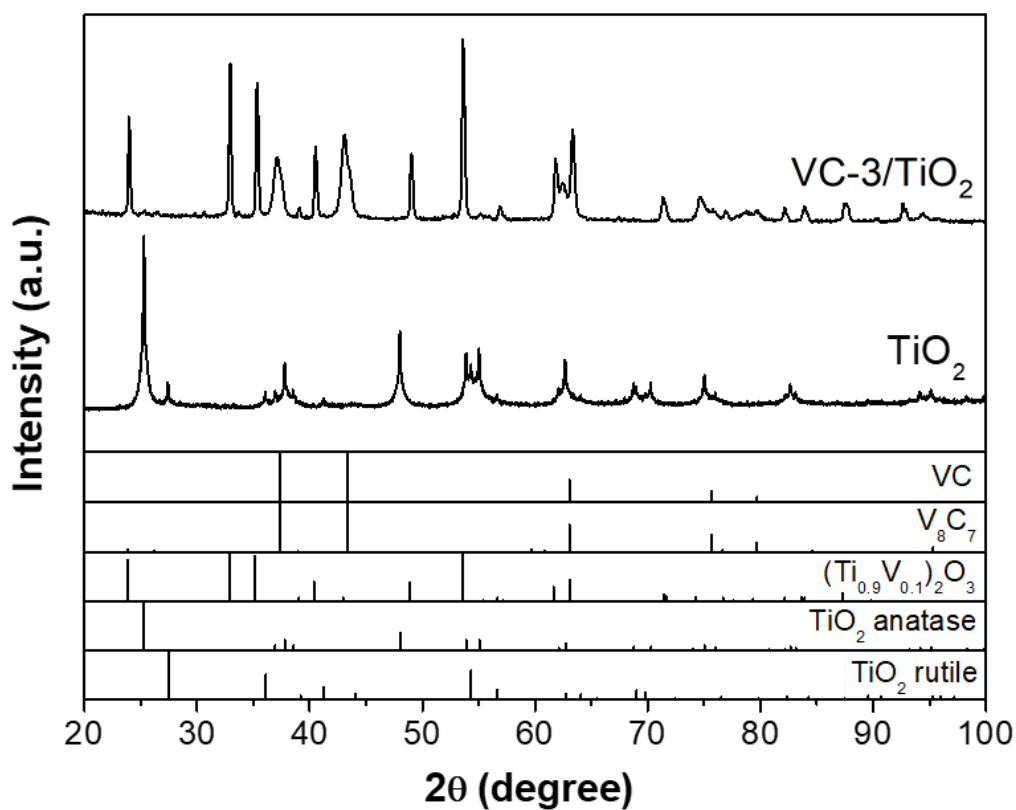


Figure 4.25. XRD pattern of VC-3/TiO₂ and pristine TiO₂.

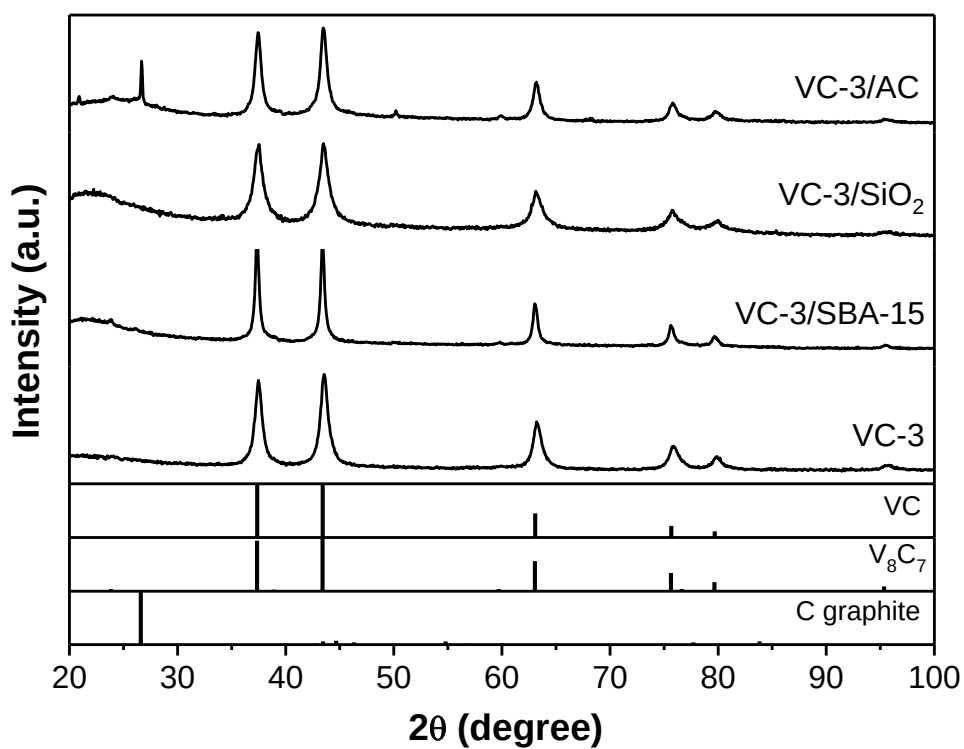


Figure 4.26. XRD patterns of VC-3/AC, VC-3/SiO₂, VC-3/SBA-15 and bulk VC-3.

Figure 4.27 shows the Raman spectra of the samples. The bands at 1350 and 1598 cm^{-1} are assigned to residual carbon formed during the preparation. The Raman bands at 97, 143, 192, 285, 694 and 995 cm^{-1} observed in VC-3/ Al_2O_3 , VC-3/ ZrO_2 and VC-3 could be related to the presence of oxy-vanadium species [4-7]. No bands corresponding to ZrO_2 phases were detected for VC-3/ ZrO_2 .

The Raman spectrum of VC-3/ CeO_2 shows a band at 461 cm^{-1} attributed to CeO_2 , and bands at 122, 264, 375, 785 and 854 cm^{-1} related with the presence of CeVO_4 [38-40], which could have been formed during preparation of VC-3/ CeO_2 and was not observed from the XRD analysis. For VC-3/ TiO_2 , poorly defined Raman bands of TiO_2 rutile were observed at 269, 413 and 603 cm^{-1} [41,42].

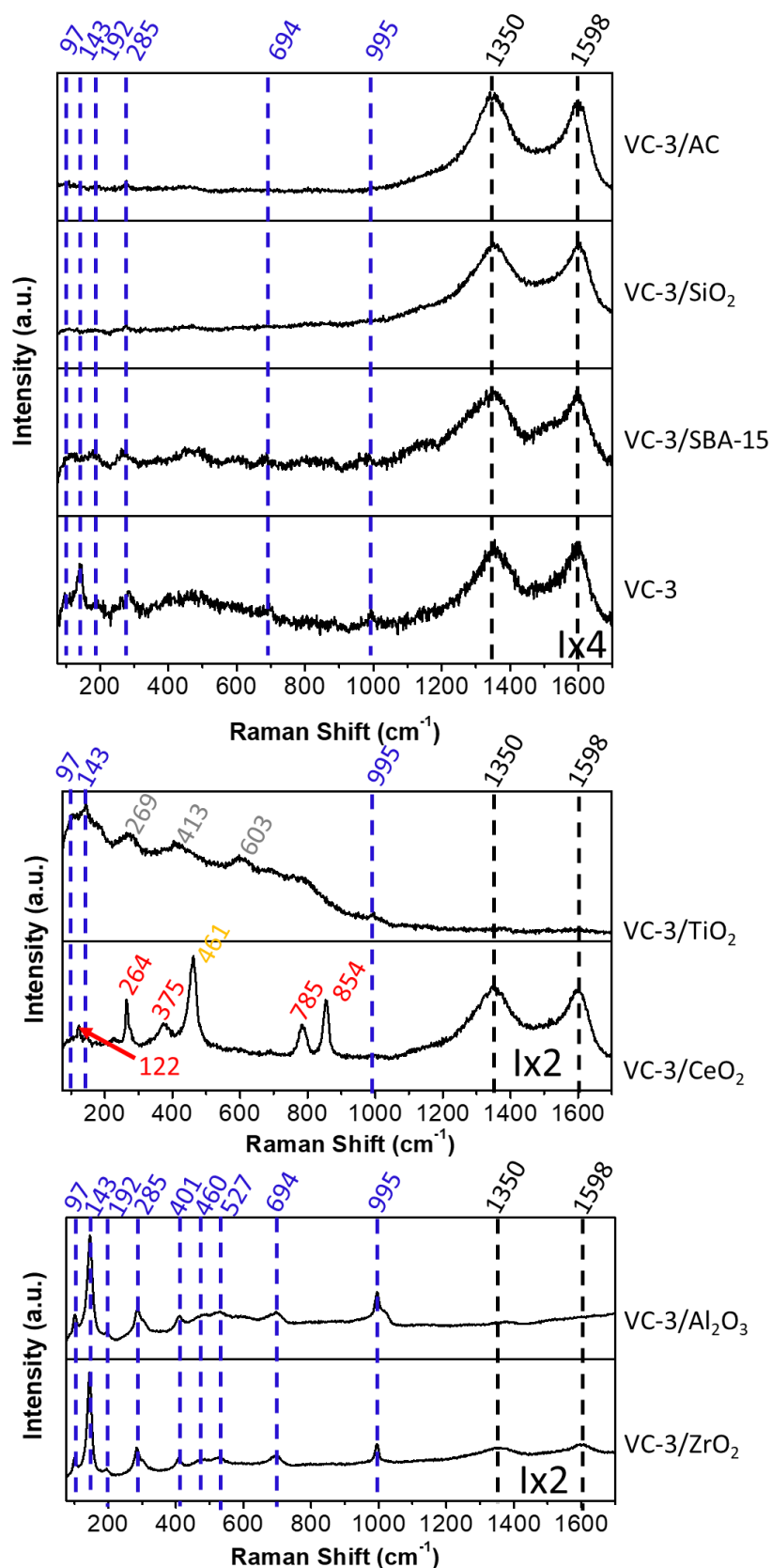


Figure 4.27. Raman spectra of supported and bulk VC catalysts. Blue dashed lines corresponds to oxy-vanadium species.

Figure 4.28 presents the H₂-TPR profiles of the different samples. For VC-3/Al₂O₃, VC-3/ZrO₂, VC-3/SBA-15 and VC-3/CeO₂ samples, the H₂-consumption peak at 685-750 K is attributed to the reduction of mono-or polymeric oxy-vanadium (V) species on the surface; the reduction of amorphous V₂O₅ would take place at ~852 K and that of crystalline V₂O₅ at higher temperatures [1,10-13]. VC-3/CeO₂ shows an additional peak at a higher temperature (1010 K) which can be related with the reduction of VCeO₄ or CeO₂ [43]. The H₂ consumption at lower temperatures (498-623 K) in VC-3/AC, VC-3/SiO₂ and bulk VC-3 can be associated to the reduction of vanadium oxy-carbide species as proposed for VC systems reported in Chapter 3 [1]. VC-3/TiO₂ showed a wide poorly defined peak from 400 K to 700 K, which could be associated to the presence of different species including oxy-carbide.

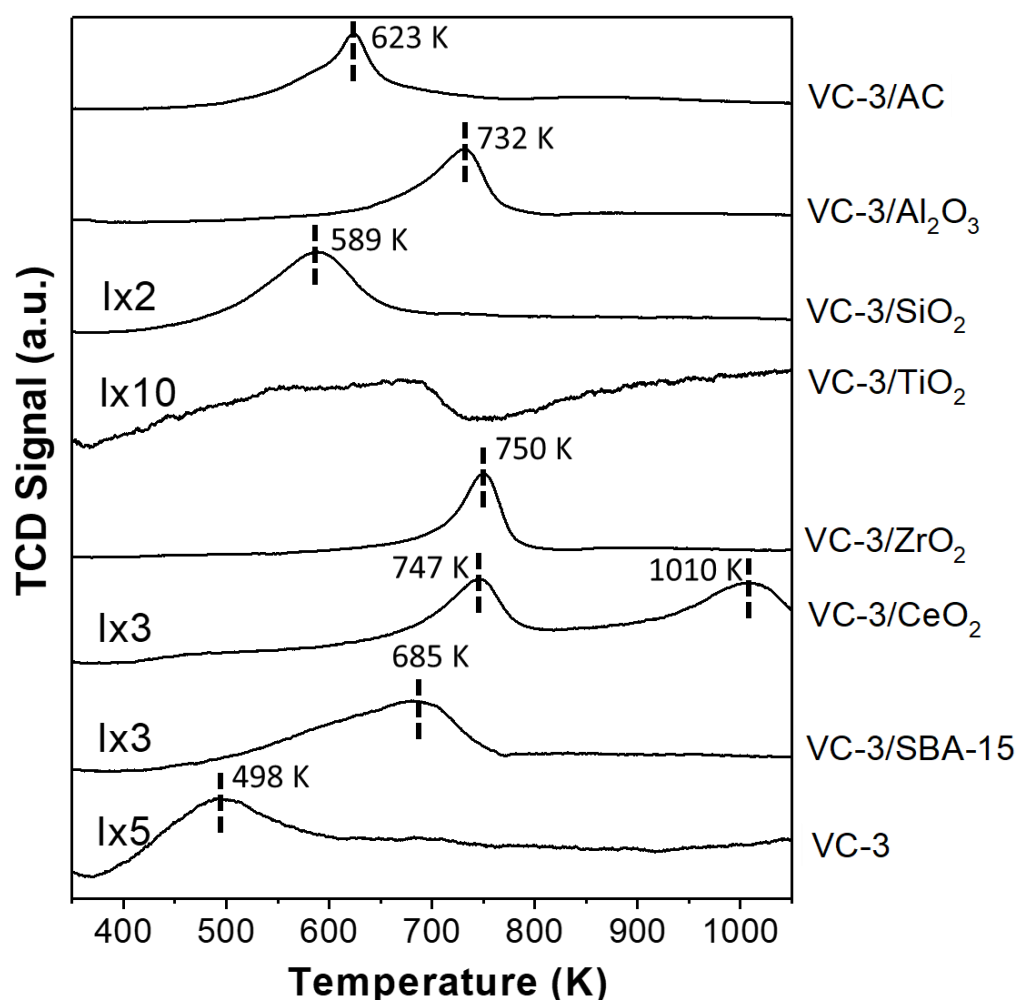


Figure 4.28. H₂-TPR of supported VC catalysts.

All catalysts showed small H₂ consumption amounts (Table 4.4). However, all the supported catalysts showed a higher H₂ consumption than the bulk VC-3 catalyst. This could be associated to the dispersion of the particles on the surface of the supports.

Table 4.4. H₂ consumption of catalysts determined by TPR, V/M (mol/mol) ratio from chemical analysis and XPS, and dispersion factor determined by XPS (D).

Catalyst	H ₂ consumption (mol H ₂ /mol V)	(V/M) _{ICP} (M=Si,Ce,Zr,Al,Ti) (mol/mol)	(V/M) _{XPS} (M=Si,Ce,Zr,Al,Ti) (mol/mol)		D ^c	
			Fresh	Used	Fresh	Used
VC-3/AC	0.275	-	0.038 ^a	0.046 ^a	-	-
VC-3/SBA-15	0.102	0.478	0.105	0.147	0.222	0.308
VC-3/CeO ₂	0.050	2.714	2.654	3.139	0.978	1.156
VC-3/ZrO ₂	0.160	0.862	1.242	1.801	1.441	2.089
VC-3/SiO ₂	0.181	0.447	1.664	1.739	3.723	3.890
VC-3/Al ₂ O ₃	0.198	0.388	0.735	0.648	1.894	1.670
VC-3/TiO ₂	0.046	0.529	0.674	0.959	1.274	1.813
VC-3	0.015 ^b	-	-	-	-	-

^aBased on C 1s; ^bAssuming 100% of VC on the sample; ^cD=Dispersion factor:

$$D=(V/M)_{XPS}/(V/M)_{ICP}$$

The samples were characterized by XPS analysis. V 2p, C 1s, O 1s, Al 2p, Si 2p, Ce 3d, Ti 2p and Zr 3d core levels were analyzed.

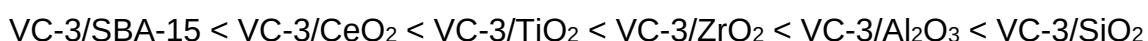
Figures 4.29-4.35 show the C 1s and V 2p XPS profiles of all supported catalysts. In general, C 1s and V 2p spectra are similar to those of VC-based samples discussed in previous sections. For all samples, the C 1s core level spectra display components at 282.8-283.1 eV assigned to the carbidic phase, C-V bonds, in VC_x [1,14-17]. The major band at 284.8 eV is attributed to C-C bonds of graphitic carbon formed during preparation and adventitious carbon [45]. The shoulders at BE higher than 284.8 eV are associated to surface species with C-O, C=O and O=C-O bonds [25-27].

The V 2p spectra were deconvoluted into 3 or 4 doublets (V 2p_{3/2} – V 2p_{1/2}) depending on the sample. V 2p_{3/2} peaks at low BE (513.5-514 eV) were attributed to V-C bonds involved in VC_x [1,14-18]. Bands at higher BE are assigned to oxy-vanadium species [1,14-24].

The O 1s spectra of supported VC catalysts are shown in ANNEX III. For all the oxide-supported catalysts, the most intense peak in the O 1s spectra is assigned to the support. The band centered at 531.8 eV is associated to Al₂O₃ for VC-3/Al₂O₃ (Figure AIII.1), the bands with maxima at 533.4 and 533.5 eV are attributed to SiO₂ for VC-3/SBA-15 and VC-3/SiO₂, respectively (Figures AIII.2 and AIII.3) [28-31,45]. The bands at BE of 530.0 eV are assigned to CeO₂ and TiO₂ for VC-3/CeO₂ and VC-3/TiO₂, respectively (Figures AIII.5 and AIII.6); the band at 530.3 eV to ZrO₂ (Figure AIII.7) [46-48]. As stated above, O 1s BE associated with the presence of oxy-vanadium and oxy-carbide species would contribute to signals at about 530-531.2 eV [25-27].

The XP spectra corresponding to core levels Al 2p, Si 2p, Ce 3d, Ti 2p and Zr 3d of the different supported catalysts appear in ANNEX III (Figures AIII.1-AIII.7).

The dispersion factor determined from XPS and chemical analysis (Table 4.4) increases in the following order.



VC-3/SiO₂ and VC-3/Al₂O₃ showed the highest dispersion factor among the catalysts (VC-3/AC not included). This could be associated to the high S_{BET} and small crystallite size of VC_x of these two samples.

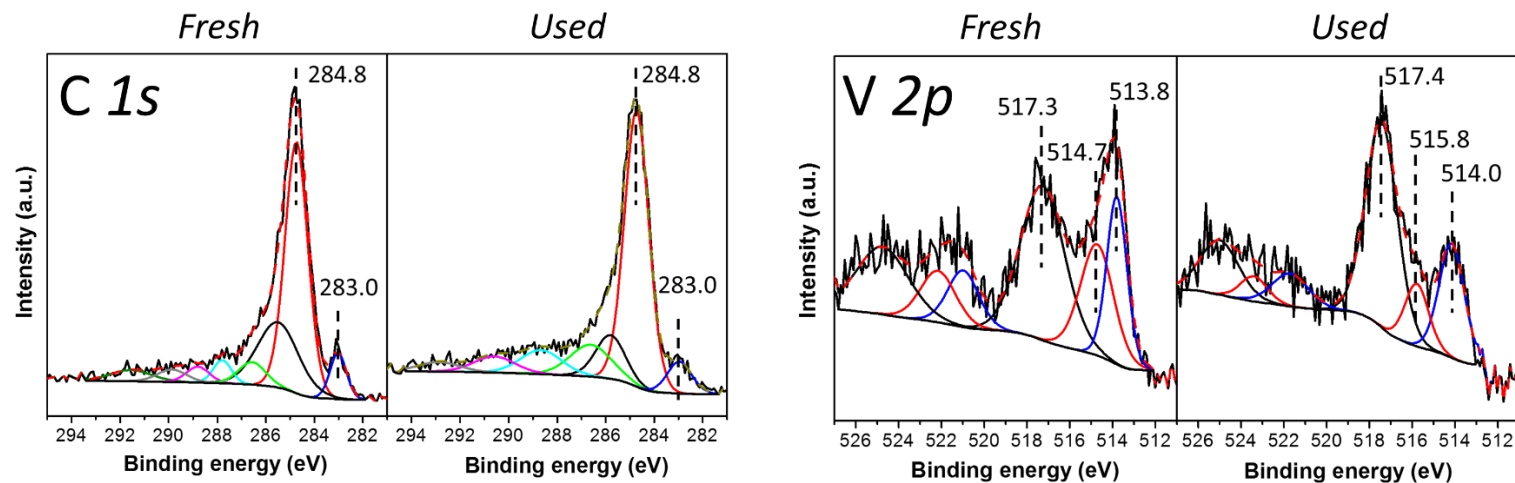


Figure 4.29. C 1s and V 2p XPS profiles of fresh and used VC-3/Al₂O₃ catalyst.

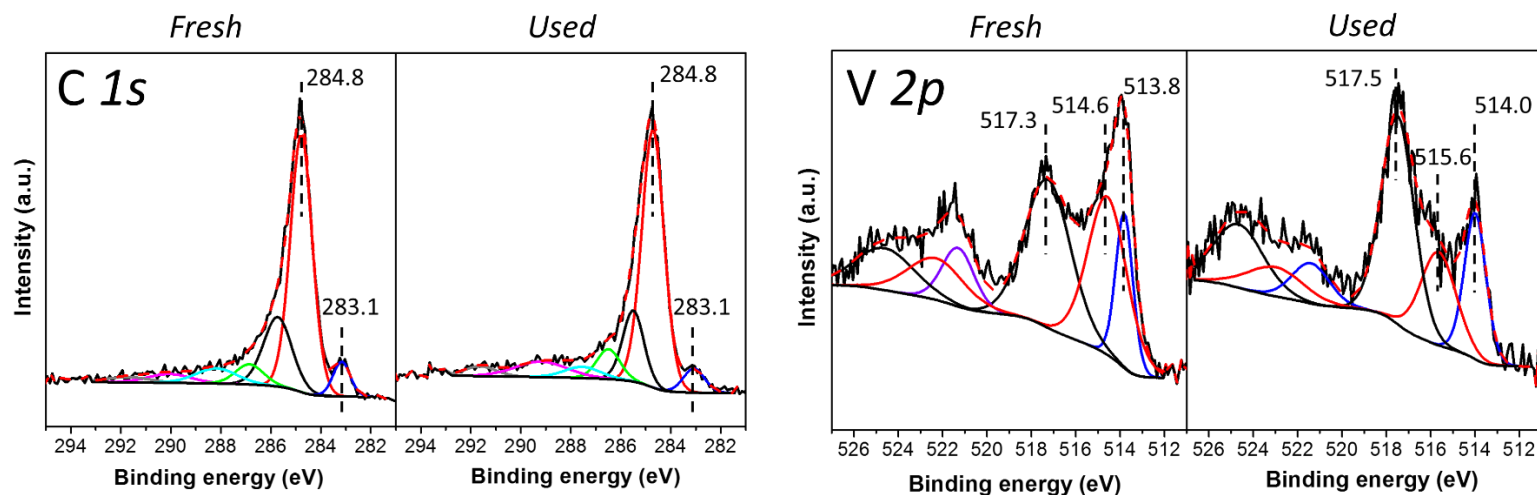


Figure 4.30. C 1s and V 2p XPS profiles of fresh and used VC-3/SiO₂ catalyst.

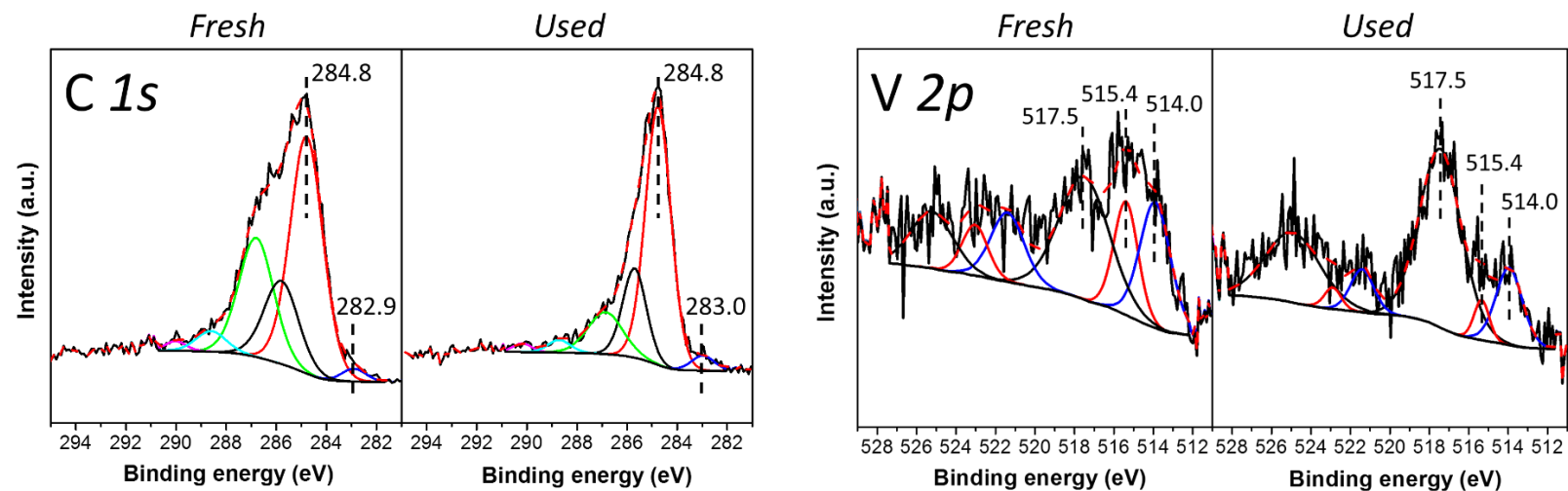


Figure 4.31. C 1s and V 2p XPS profiles of fresh and used VC-3/SBA-15 catalyst.

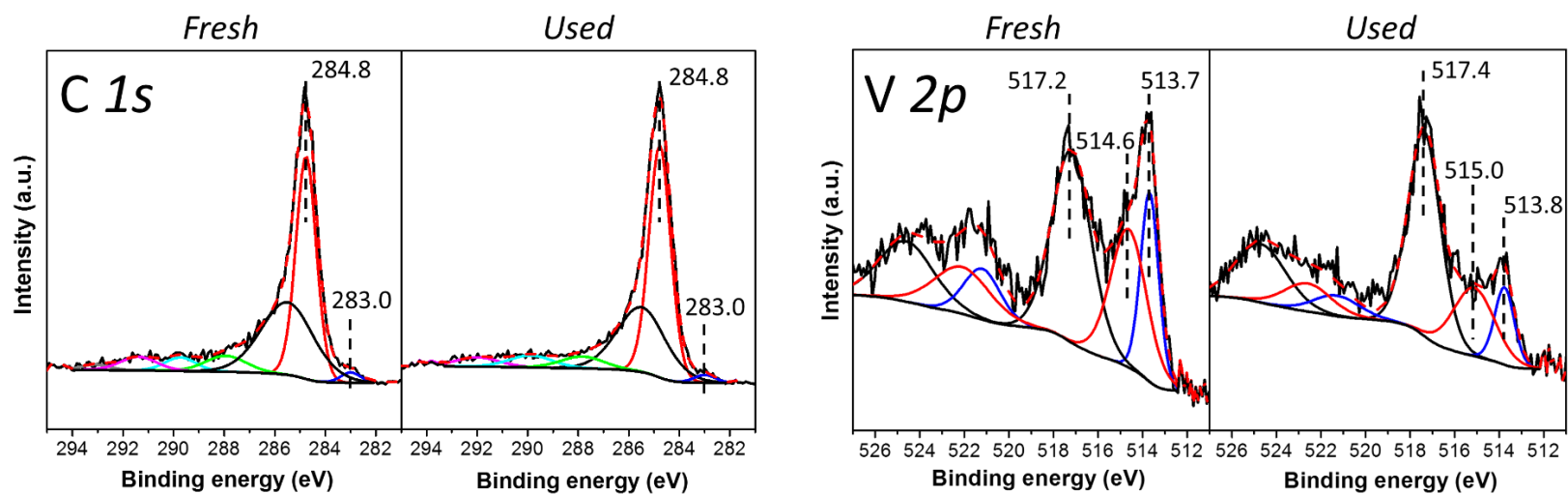


Figure 4.32. C 1s and V 2p XPS profiles of fresh and used VC-3/AC catalyst.

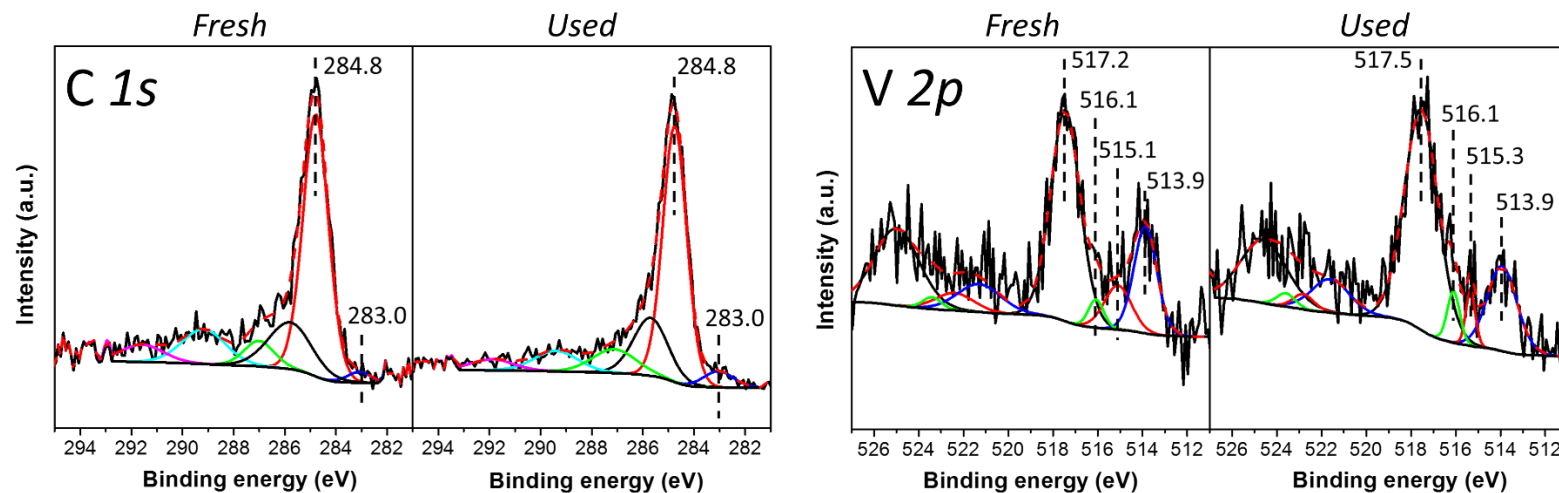


Figure 4.33. C 1s and V 2p XPS profiles of fresh and used VC-3/CeO₂ catalyst.

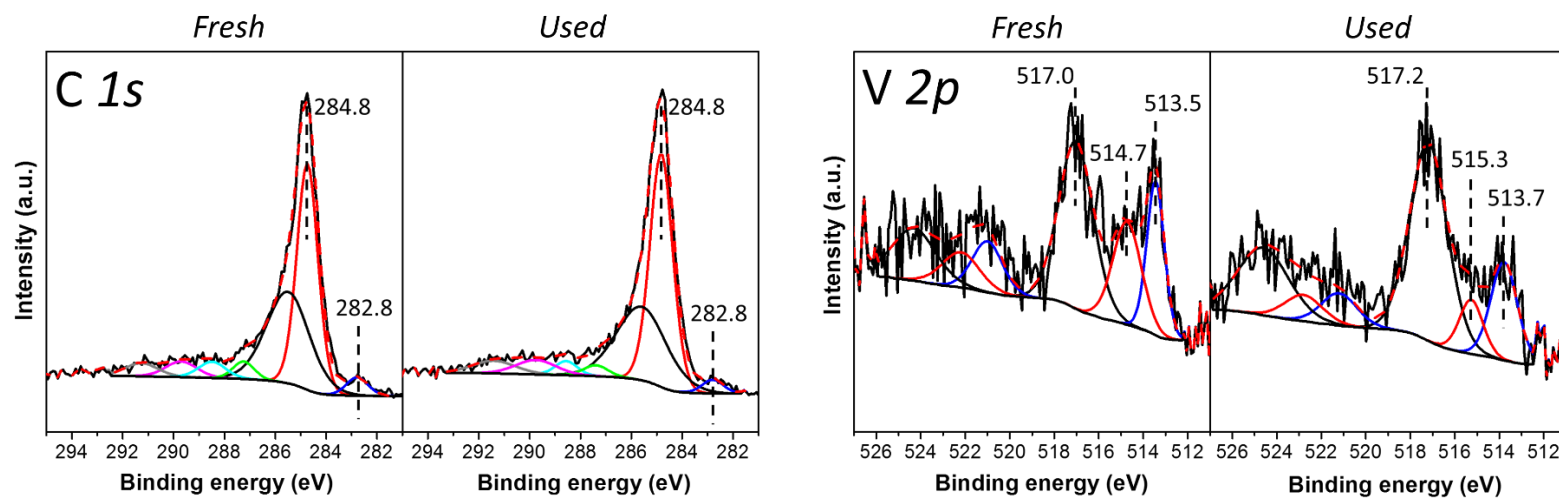


Figure 4.34. C 1s and V 2p XPS profiles of fresh and used VC-3/TiO₂ catalyst.

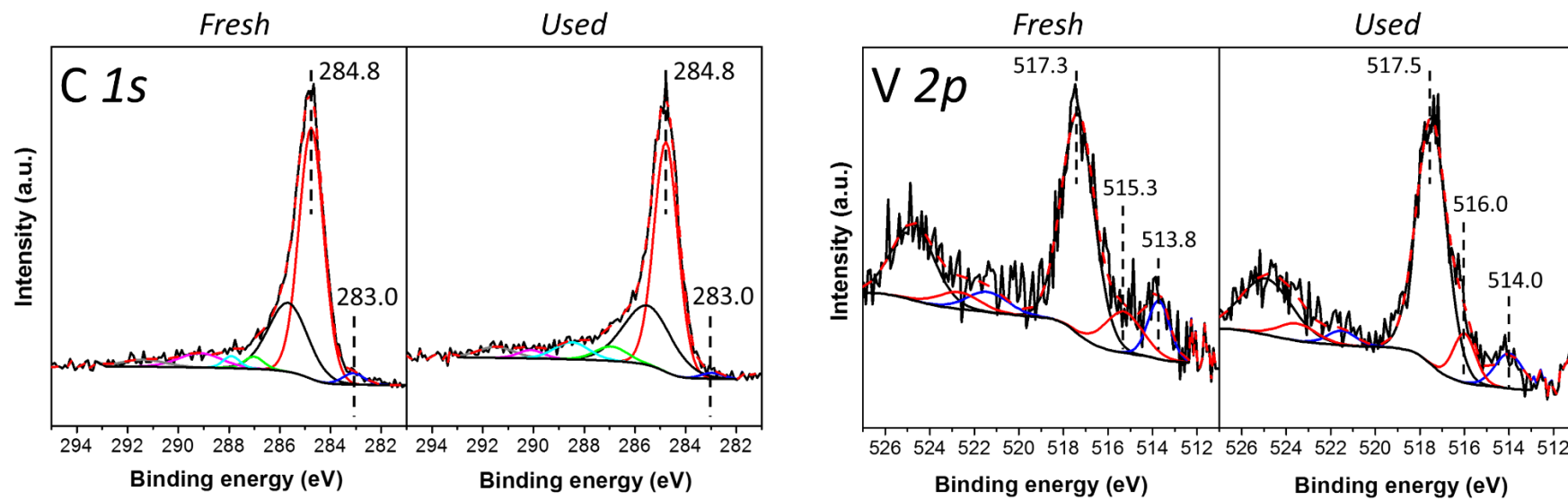


Figure 4.35. C 1s and V 2p XPS profiles of fresh and used VC-3/ZrO₂ catalyst.

4.2.3. Catalytic behavior of supported VC catalysts in the RWGS reaction

The catalytic behavior of catalysts in the RWGS reaction was determined in the range of 523-873 K, at 0.1 MPa, GHSV of 3000 h⁻¹ and using a reactant mixture of CO₂/H₂/N₂=1/3/1. In all cases, 300 mg of catalyst and a catalytic bed of 1 mL were used. SiC was employed as diluting agent. In these experiments, the catalysts were kept 2.5 h at each temperature. Bulk VC-3 was tested for comparison.

The Figure 4.36 shows the CO₂ conversion and CO selectivity achieved by the supported VC catalysts. As expected, the CO₂ conversion increased with the temperature. The catalysts showed a high CO₂ conversion, 27-52% at 873 K (equilibrium conversion=60% at 873K) depending on support used. All catalysts showed an increase of the CO selectivity in the range of 573-873 K reaching up to 100 % at 873 K. CH₄ was the main byproduct in all cases.

For a proper comparison, the CO production was normalized according to the amount of active phase (VC_x) present in the supported catalysts (Figure 4.37); supported catalysts showed a higher amount of CO produced per mol of V (mol_{CO} mol_V⁻¹ h⁻¹) than that of bulk VC-3 catalyst. The values of mol_{CO} mol_V⁻¹ h⁻¹ produced at 873 K were the following: VC-3/Al₂O₃ (12.3) > VC-3/AC (11.9) > VC-3/SiO₂ (11.7) > VC-3/ZrO₂ (11.2) > VC-3/CeO₂ (10.0) > VC-3/TiO₂ (6.8) > VC-3/SBA-15 (6.3) > VC-3 (2.8).

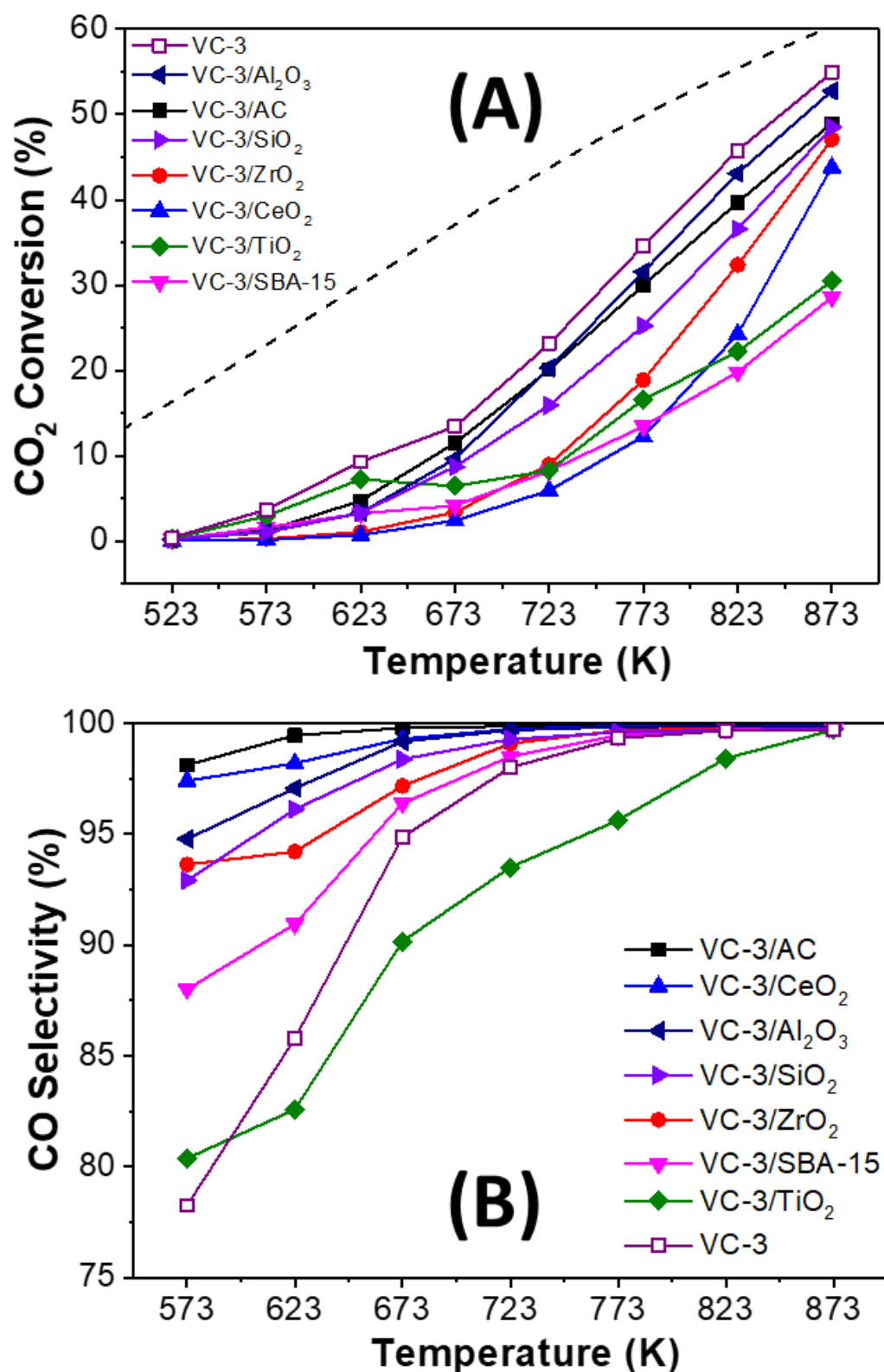


Figure 4.36. Catalytic behavior in the RWGS reaction for the supported VC catalysts and bulk VC as a function of reaction temperature. (A) CO₂ conversion. Dashed line: equilibrium conversion values (B) CO selectivity. Reaction conditions: CO₂/H₂/N₂=1/3/1; GHSV=3000 h⁻¹; P=0.1 MPa; m=300 mg.

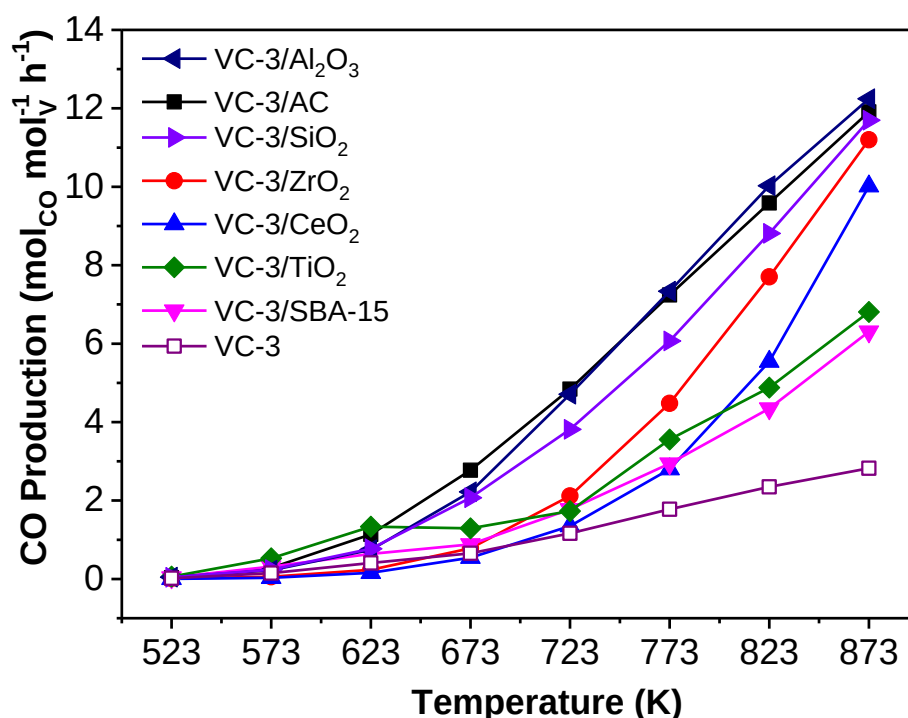


Figure 4.37. CO production per mol of V in the RWGS reaction in the 523-873 K range. Reaction conditions: $\text{CO}_2/\text{H}_2/\text{N}_2=1/3/1$; GHSV=3000 h^{-1} ; $P=0.1$ MPa; $m=300$ mg.

Among the supported VC catalysts, VC-3/ Al_2O_3 , VC-3/ SiO_2 and VC-3/AC having a VC_x crystallite size in the 9-11 nm range, similar to that of the VC-3 bulk catalyst (11 nm) showed the highest CO production above 673 K referred to V mol. The corresponding E_a in the 673-773 K were, within the experimental error, near to that obtained for VC-3 bulk catalyst (See Figure 4.38 and Table 4.5).

On the other hand, VC-3/ CeO_2 and VC-3/ ZrO_2 with VC_x crystallite sizes of 36 and 25 nm, respectively showed the highest E_a (Table 4.5). Note that the E_a corresponding to VC-3/ TiO_2 could not be determined due to its anomalous catalytic behavior along temperature, which could be related with a structural transformation of the catalyst, as it will be discussed latter.

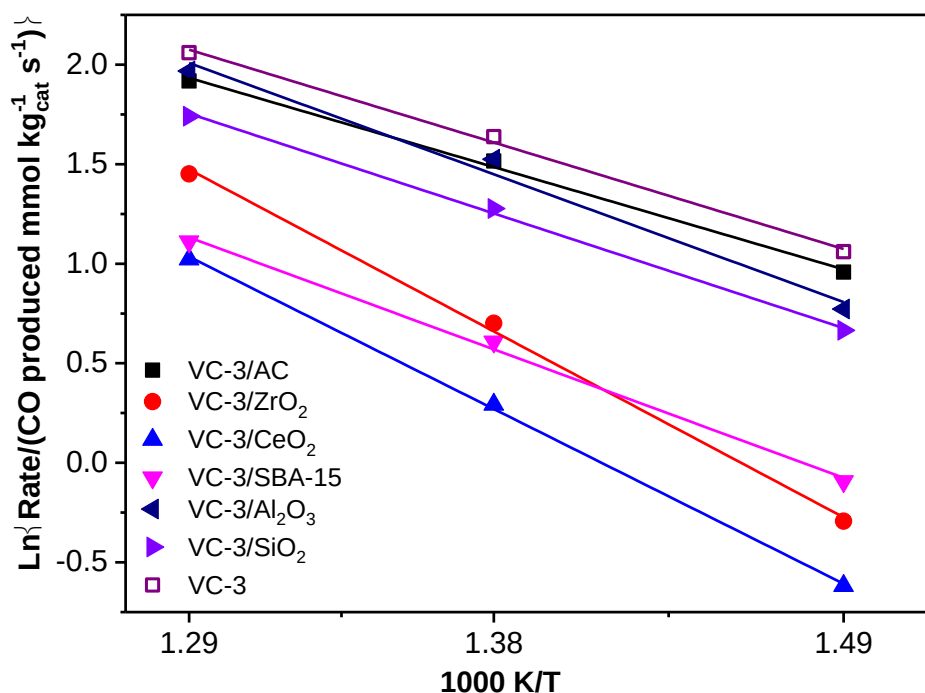


Figure 4.38. Arrhenius plot for CO production in the RWGS reaction of VC-based catalysts. Temperature 673-773 K. Reaction conditions: $\text{CO}_2/\text{H}_2/\text{N}_2=1/3/1$; GHSV=3000 h^{-1} ; $P=0.1$ MPa; $m=300$ mg.

Table 4.5. Apparent activation energy values of VC-based catalysts in the RWGS reaction. Temperature 673-773 K. Reaction conditions: $\text{CO}_2/\text{H}_2/\text{N}_2=1/3/1$; GHSV=3000 h^{-1} ; $P=0.1$ MPa; $m=300$ mg

Catalyst	E_a (kJ mol^{-1})
VC-3/AC	41.6 ± 2.2
VC-3/SBA-15	52.2 ± 2.9
VC-3/ CeO_2	71.0 ± 1.7
VC-3/ ZrO_2	75.7 ± 3.1
VC-3/ SiO_2	46.6 ± 1.8
VC-3/ Al_2O_3	51.5 ± 5.7
VC-3	43.2 ± 2.2

Under the RWGS conditions studied here, the catalytic behavior of the different supported vanadium carbide catalysts seems to be mainly related to the VC_x characteristics. A small crystallite size of VC_x could be related with a major presence of C defective VC (V_8C_7) phase. The interaction of the sol-gel precursor with the different supports could determine the final VC_x crystallite size. At this respect, a recent report [49] conclude for supported Mo_2C catalysts, prepared by impregnation and carburization, the importance of the support in the characteristics of Mo_2C obtained and its catalytic performance in the RWGS.

TEM analysis of the most performance catalyst, VC-3/ Al_2O_3 , is shown in Figure 4.39. TEM and HRTEM images of fresh VC-3/ Al_2O_3 showed small VC_x particles with an average size of 9 nm in well agreement with the crystallite size calculated by XRD. A d-spacing of 0.241 nm was measured for the small particles of V_8C_7 phase ((111) facet) or stoichiometric VC phase ((222) facet). A homogeneous dispersion of V on the support was determined from STEM and EDX mapping (Figure 4.39).

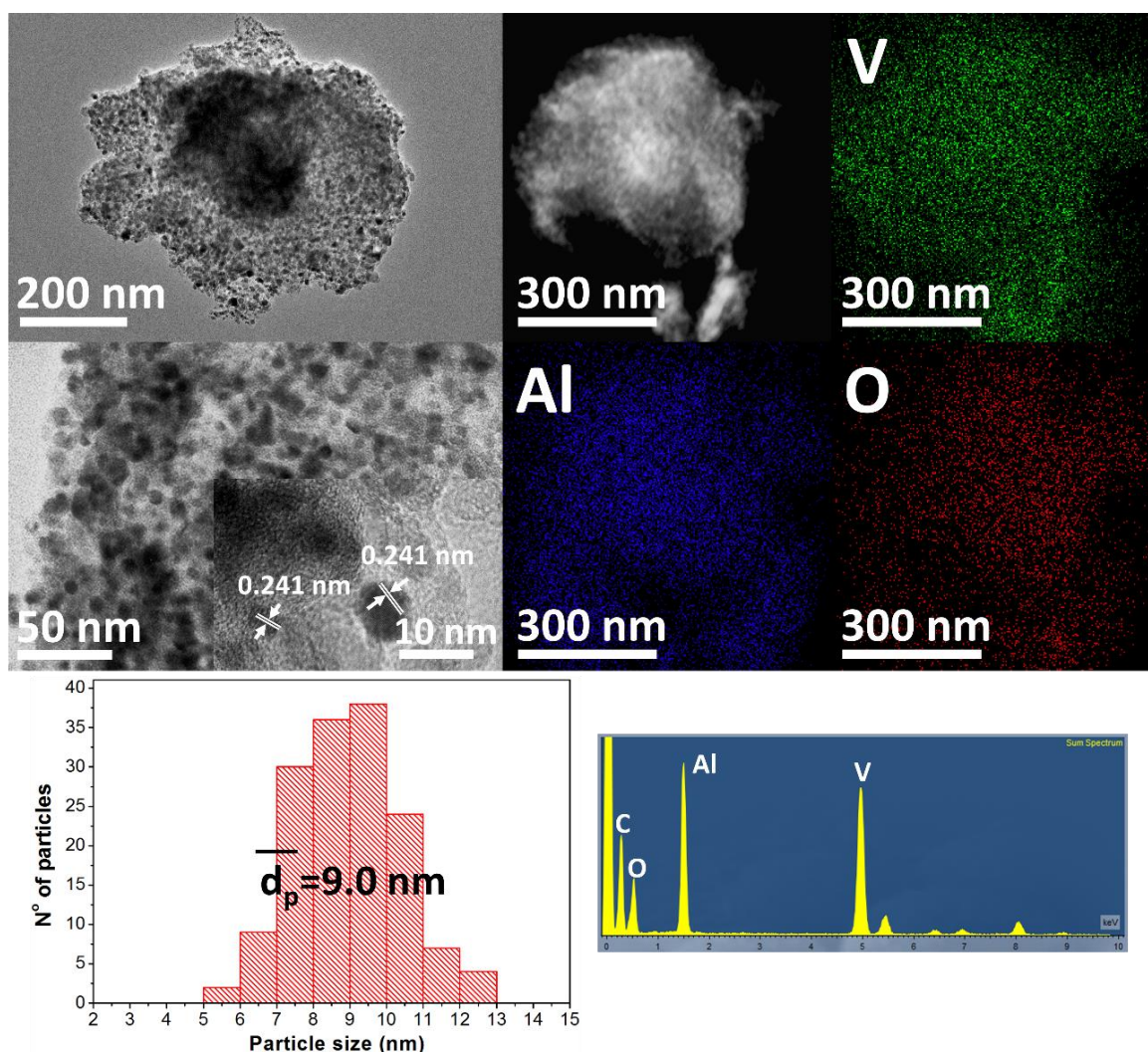


Figure 4.39. Characterization of VC-3/Al₂O₃: TEM, HRTEM, STEM and EDX mapping, particle size distribution and EDX spectrum.

Post-reaction catalysts were characterized by XRD, N₂ adsorption/desorption isotherms, and XPS.

XRD patterns of post-reaction catalysts are shown in Figure 4.40-4.43. No modifications were observed for VC-3, VC-3/AC, VC-3/Al₂O₃, VC-3/SiO₂, VC-3/SBA-15 and VC-3/CeO₂ (Figures 4.40-4.42). For VC-3/ZrO₂, an increase of the amount of monoclinic ZrO₂ phase was detected compared to the fresh catalyst (Figure 4.42). For VC-3/TiO₂, besides the presence of vanadium carbide and oxy-carbide species, XRD indicated an increase of the presence of anatase and rutile phases after reaction; the peaks characteristics of the solid solution (Ti_{0.9}V_{0.1})₂O₃

were no longer observed (Figure 4.43). The crystallite sizes of VC_x phase of spent catalysts calculated by XRD were quite similar to those of fresh catalysts.

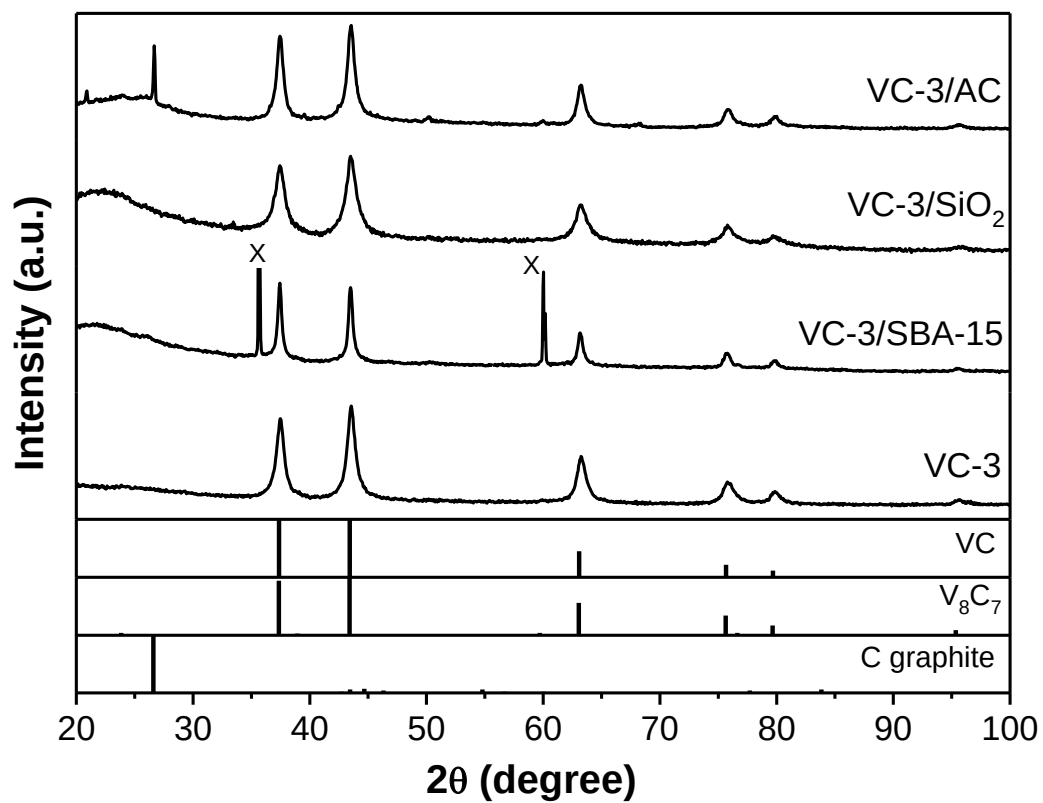


Figure 4.40. XRD patterns of used VC-3/AC, VC-3/SiO₂, VC-3/SBA-15 and bulk VC-3 samples. X:SiC.

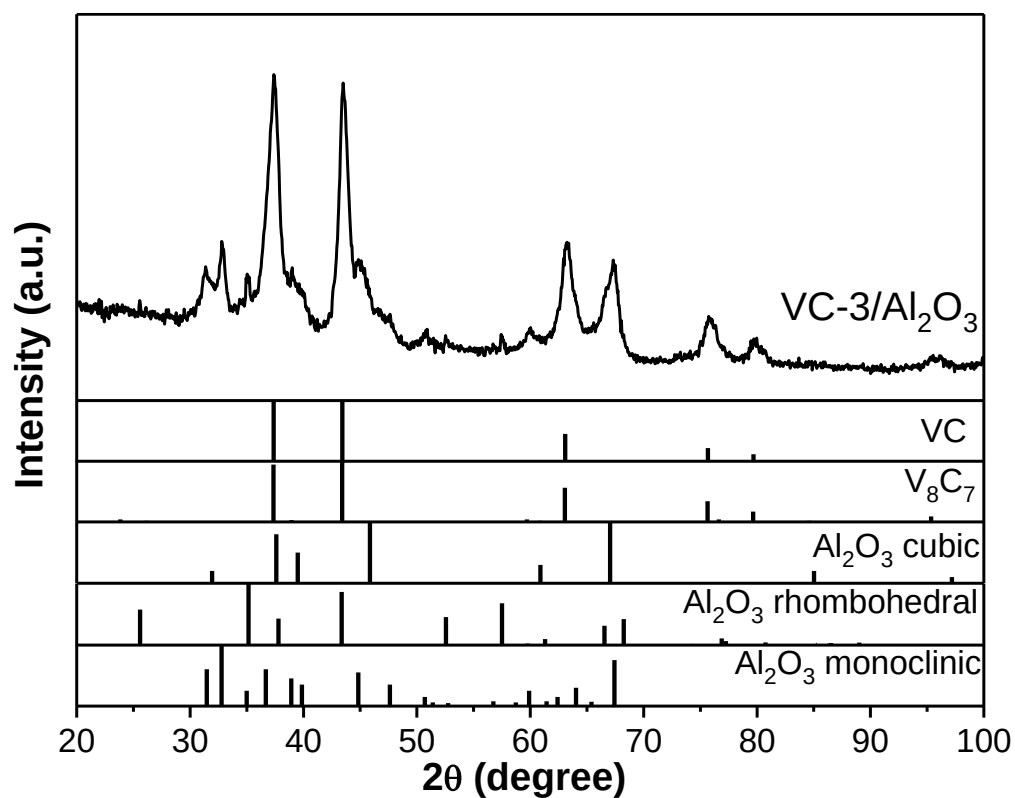


Figure 4.41. XRD pattern of used VC-3/ Al_2O_3 sample.

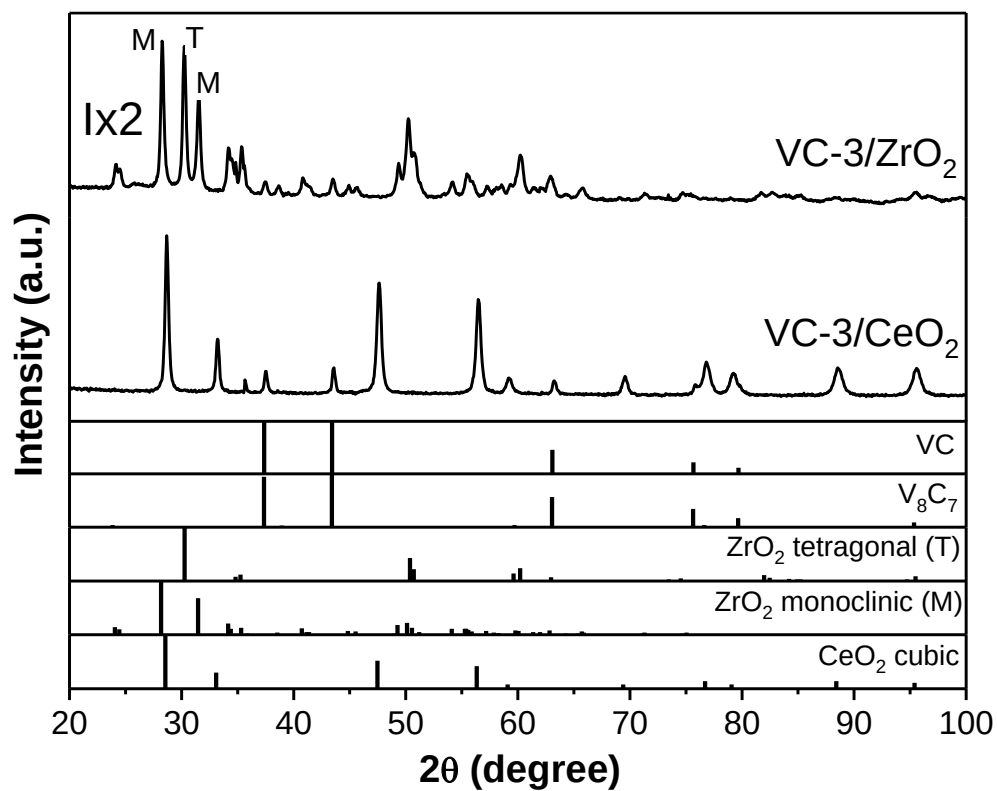


Figure 4.42. XRD patterns of used VC-3/ ZrO_2 and VC-3/ CeO_2 samples. X: SiC.

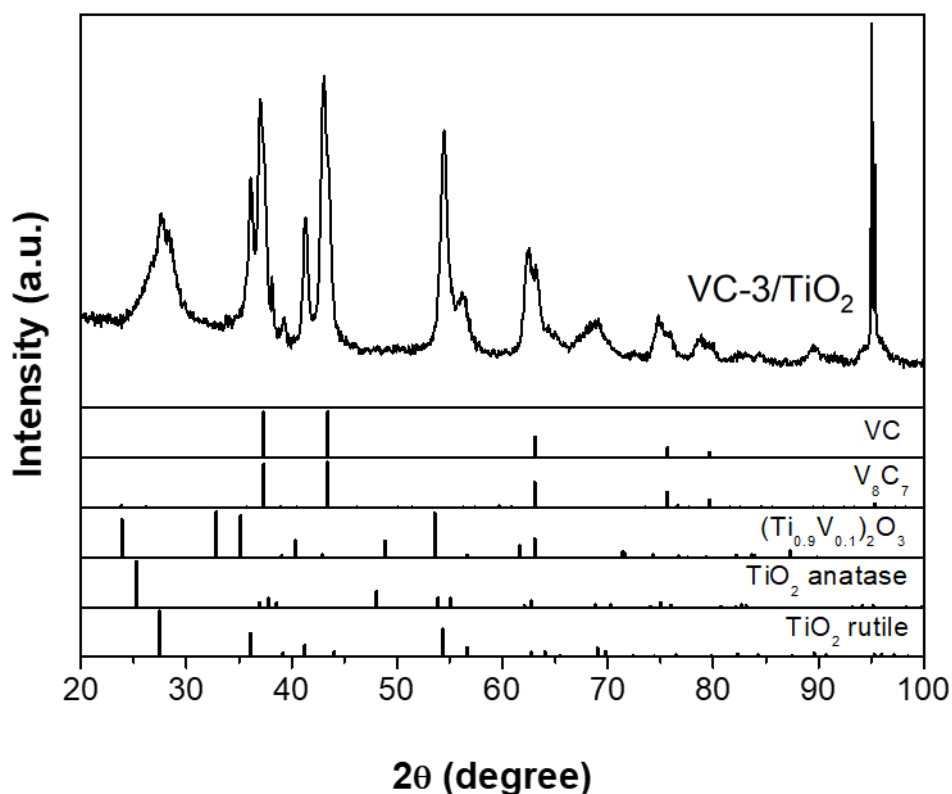


Figure 4.43. XRD pattern of used VC-3/TiO₂ sample.

In all cases, the S_{BET} area of spent catalysts was lower than that of fresh ones. However, no significant variation in the pore width was observed except for VC-3/SBA-15 (from 13 to 26 nm) (Table 4.3).

In all cases, the XPS analysis of the used catalysts showed the presence of carbidic species, VC_x , (Figures 4.29-4.35). BE of C $1s=282.8\text{--}283.1$ eV and V $2p_{3/2}=513.7\text{--}514.0$ eV are assigned to VC_x . Moreover, the intensity of the bands at V $2p_{3/2}=517.0\text{--}517.5$ eV in the V $2p$ level spectra attributed to oxy-vanadium species increased with respect to fresh catalyst in all cases. This is also observed in the O $1s$ level spectra (see ANNEX III); the intensity of the bands assigned to oxy-vanadium species increased compared to the fresh catalysts. This means a slight surface oxidation might have occurred during reaction.

No significant changes are observed in the Al $2p$, Si $2p$, Ce $3d$, Ti $2p$ and Zr $3d$ levels corresponding to the supports of the different catalysts (See ANNEX III).

The dispersion factor of the spent catalysts showed generally higher values than the fresh catalysts, this could be related to the decrease on S_{BET} area after reaction (Table 4.4).

4.3. References

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CHAPTER 5

TRANSITION METAL CARBIDES OF GROUP 5 IN THE MSR REACTION

In this chapter, the preparation and characterization of bulk G5TMCs with similar crystallite size are presented. The catalysts were studied in the MSR reaction in the range of temperature of 573-723 K at atmospheric pressure.

Moreover, supported VC catalysts presented in Chapter 4 (VC-3/Al₂O₃, VC-3/AC, VC-3/SiO₂, VC-3/ZrO₂, VC-3/CeO₂ and VC-3/TiO₂) are studied in the MSR reaction under similar experimental conditions.

Different products such as H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆ and HCHO were identified in all tests. Among bulk G5TMC catalysts, a high production of CH₄ was observed on VC; however, a high concentration of HCHO was detected for NbC and TaC.

Supported VC catalysts produced, as it was in the case of bulk VC, CH₄ as main product. However, some variations of the product composition were observed according to the support used.

All catalysts suffered high deactivation under the MSR reaction conditions used.

Catalysts were characterized before and after reaction using different techniques such as, N₂ adsorption-desorption isotherms, XRD, Raman spectroscopy, H₂-TPR, XPS and TEM.

5.1. Preparation of catalysts

Based on the study of G5TMC preparation discussed in Chapter 3, two new catalysts, NbC-2 and TaC-2, were prepared with the aim of obtaining bulk carbides with crystallite sizes similar to that of VC-3 studied in the Chapter 4. NbC-2 was prepared using a 4,5-dicyanoimidazole/ NbCl_5 molar ratio of 2 and a treatment temperature of 1373 K. TaC-2 was prepared using a 4,5-dicyanoimidazole/ TaCl_5 molar ratio of 3 and a treatment temperature of 1423 K. The details of preparation of these bulk G5TMCs are shown in ANNEX II.

The preparation of supported VC catalysts (VC-3/ Al_2O_3 , VC-3/AC, VC-3/ SiO_2 , VC-3/ ZrO_2 , VC-3/ CeO_2 and VC-3/ TiO_2) has been already given in Chapter 4 and ANNEX II.

5.2. Characterization and catalytic behavior in the MSR reaction

5.2.1. Bulk G5TMC catalysts

Although some characteristics of VC-3 have already been discussed in Chapter 4, the characterization of the newly synthesized VC-3 used in the MSR is also included in this chapter. This is with the aim of testing the reproducibility of the preparation method, and to compare the characteristics of all the G5TMC prepared.

As it is shown in Figure 5.1, the presence of cubic VC_x ($\text{VC}/\text{V}_8\text{C}_7$), NbC and TaC phases in VC-3, NbC-2 and TaC-2 samples respectively, was confirmed by XRD. No XRD peaks corresponding to crystalline oxides were found in any case.

Small crystallite sizes (9-11 nm) were obtained from XRD analysis for all samples (Table 5.1).

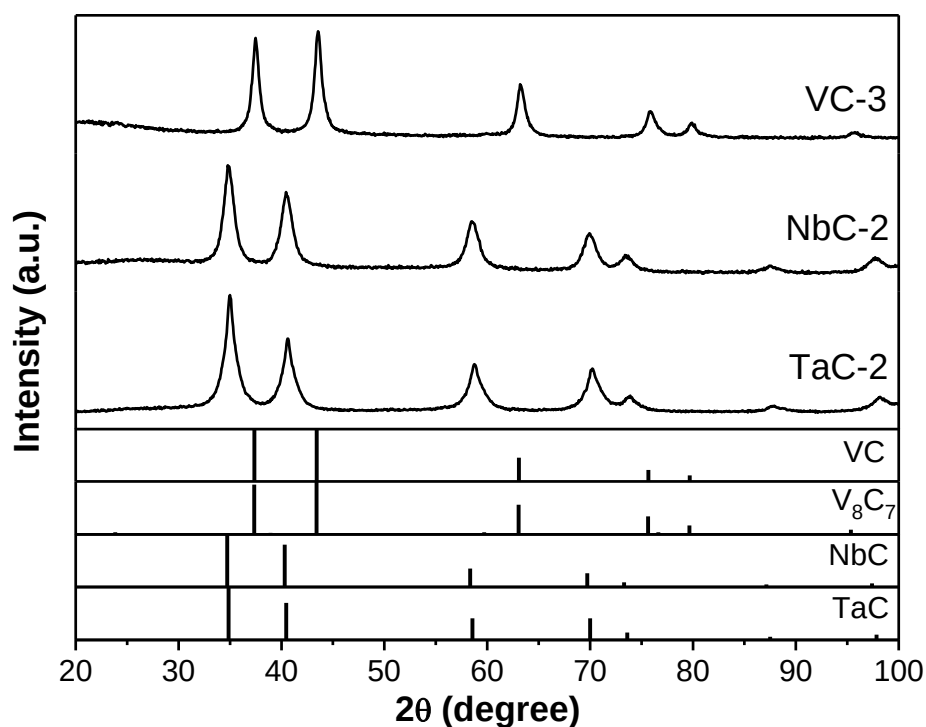


Figure 5.1. XRD patterns of bulk G5TMC samples.

Table 5.1. Crystallite size, S_{BET} area and pore diameter of bulk G5TMC catalysts and after their use in MSR.

Catalyst	Crystallite size of TMC (nm)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)		Pore size (nm)	
		Fresh	Used	Fresh	Used
VC-3	11	271	<10	7	35
NbC-2	9	290	110	2	3
TaC-2	9	220	<10	2	40

All bulk catalysts prepared are mesoporous materials (pore size in the 2-7 nm range) and showed high S_{BET} (Table 5.1).

HRTEM allowed the identification of cubic VC and/or V_8C_7 , NbC and TaC (Figures 5.2-5.4) according to XRD results.

The average of particle size determined by TEM was 11.6, 10.0 and 9.5 nm for VC-3 (Figure 5.2), NbC-2 (Figure 5.3) and TaC-2 (Figure 5.4), respectively,

these values agree with the crystallite sizes calculated from XRD (Table 5.1). However, for NbC-2 and TaC-2, a small number of particles have around 35-50 and 18-26 nm sizes, respectively (see histograms in Figures 5.3 and 5.4)

The NbC-2 and TaC-2 samples showed a smaller particle size and higher S_{BET} compared to those described in Chapter 3. This can be related to the higher 4,5-dicyanoimidazole/metal precursor molar ratio used now, which could also favor a higher presence of residual carbon.

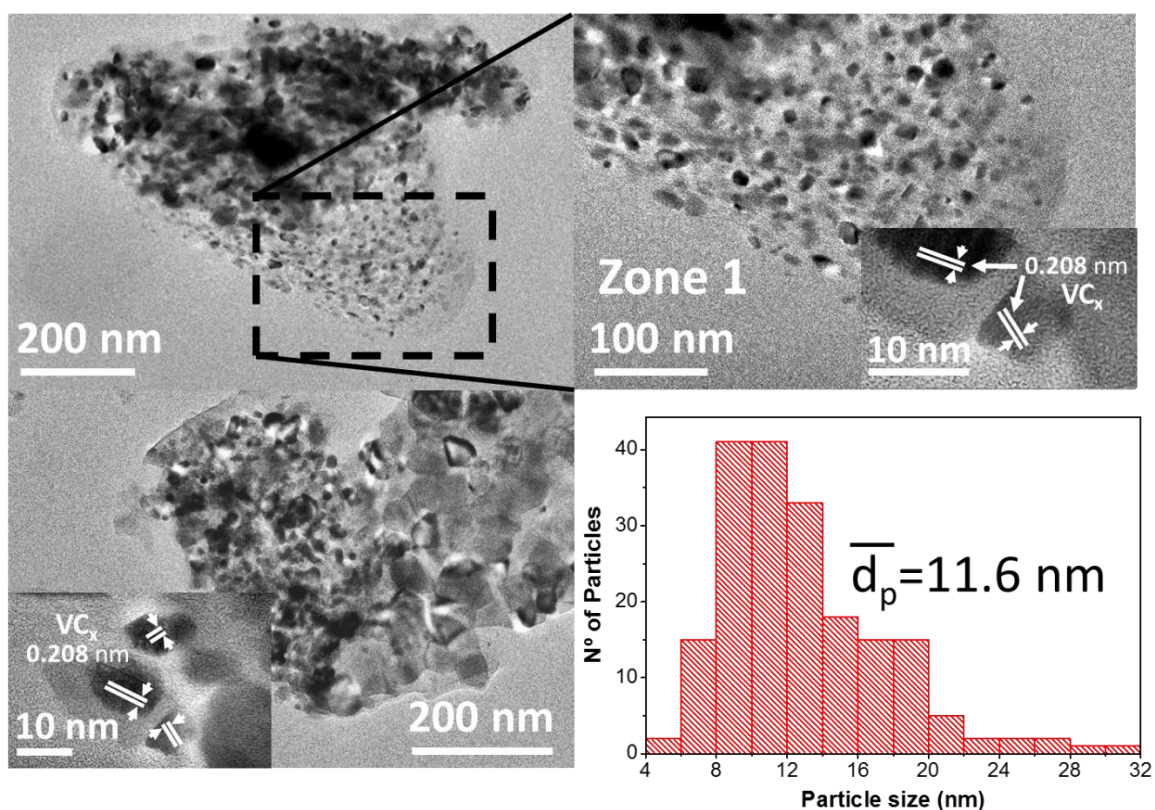


Figure 5.2. TEM, HRTEM (inset) images and particle size distribution of VC-3.

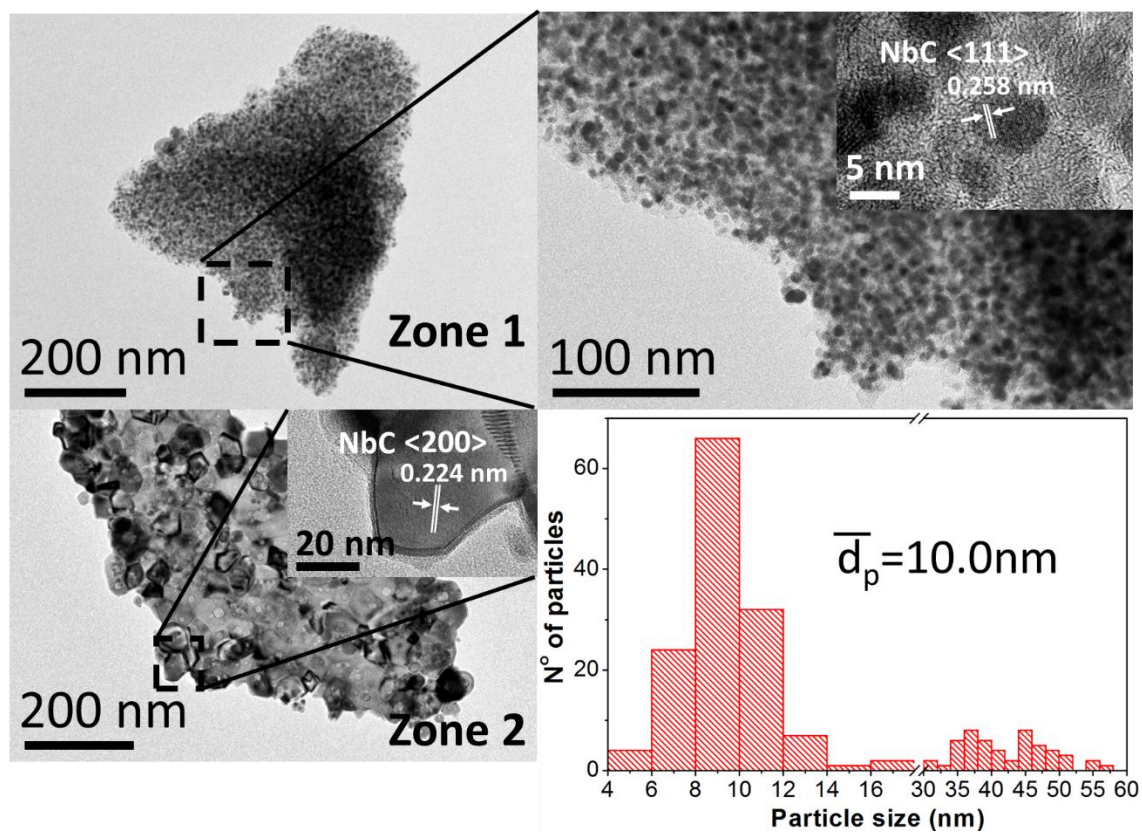


Figure 5.3. TEM, HRTEM (inset) images and particle size distribution of NbC-2.

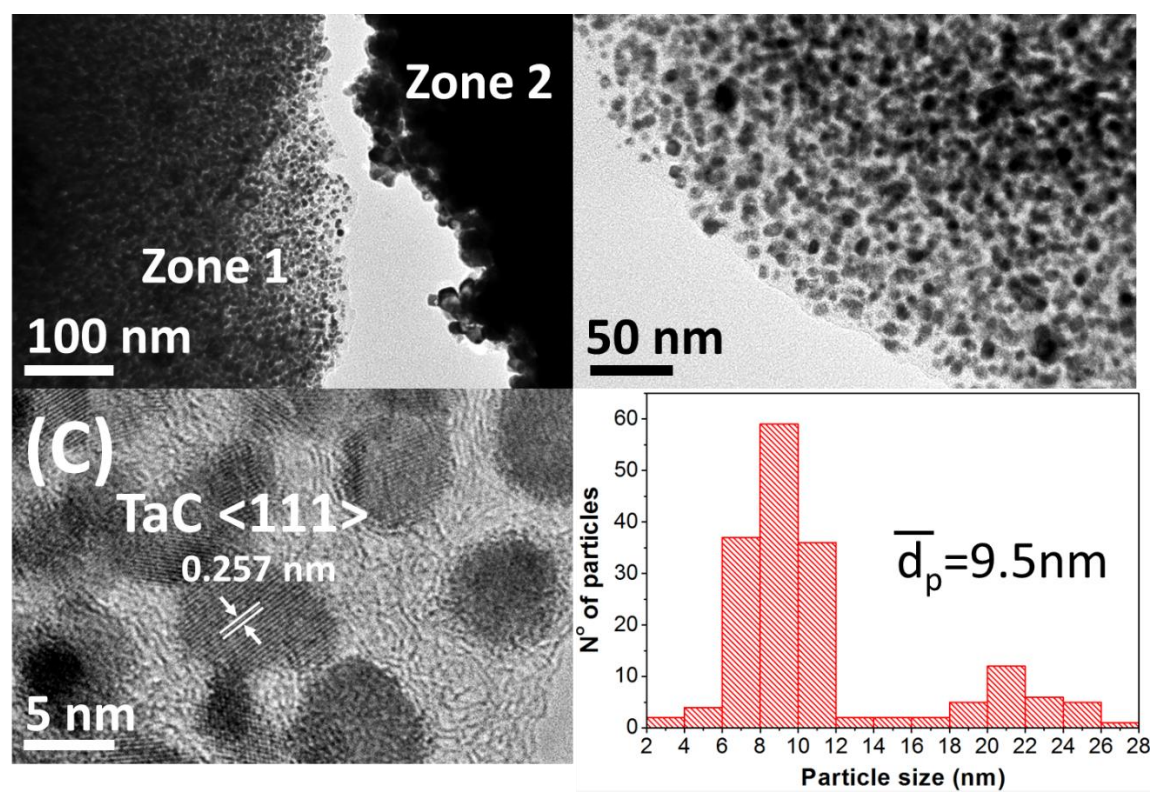


Figure 5.4. TEM, HRTEM images and particle size distribution of TaC-2.

Figure 5.5 shows the Raman spectra of samples. No bands in the range 100-1000 cm^{-1} attributed to metal oxides (VO_x , NbO_x and TaO_x) are observed. The bands at 1353 and 1598 cm^{-1} are assigned to the G and D bands from residual carbon in the samples.

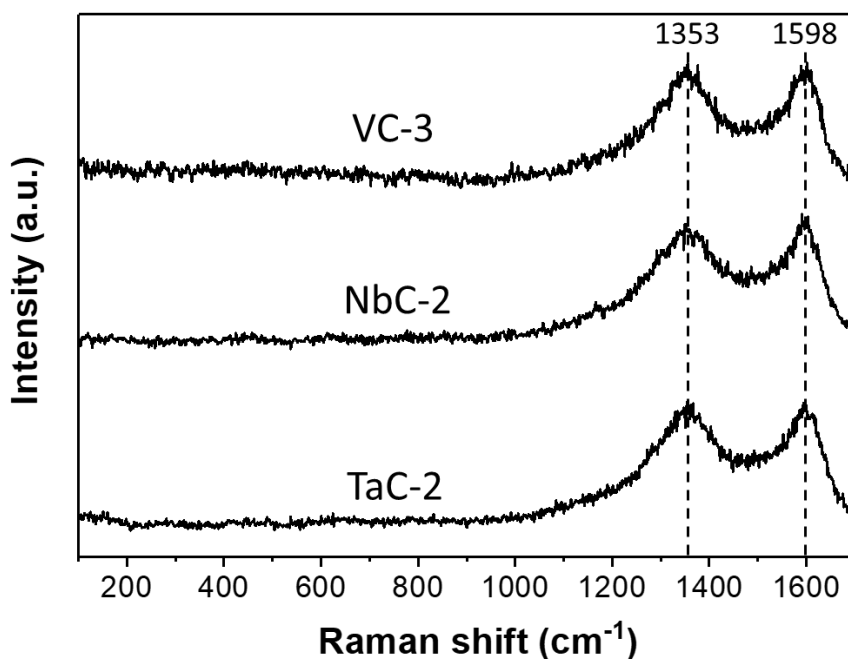


Figure 5.5. Raman spectra of bulk G5TMC catalyst.

Figure 5.6 shows the H_2 -TPR profiles of samples. For NbC-2 and TaC-2 samples, the very small H_2 -consumption at about 630 K could be associated to niobium and tantalum oxy-carbide reduction or to impurities remained from the preparation. Nb_2O_5 and Ta_2O_5 reductions cannot be observed in this range of temperature because they take place at higher temperatures (> 1173 K) [1-3].

The H_2 -TPR profile of VC-3 has already been discussed in Chapter 4, the H_2 -consumption at about 498 K could be related to the reduction of oxy-carbide species.

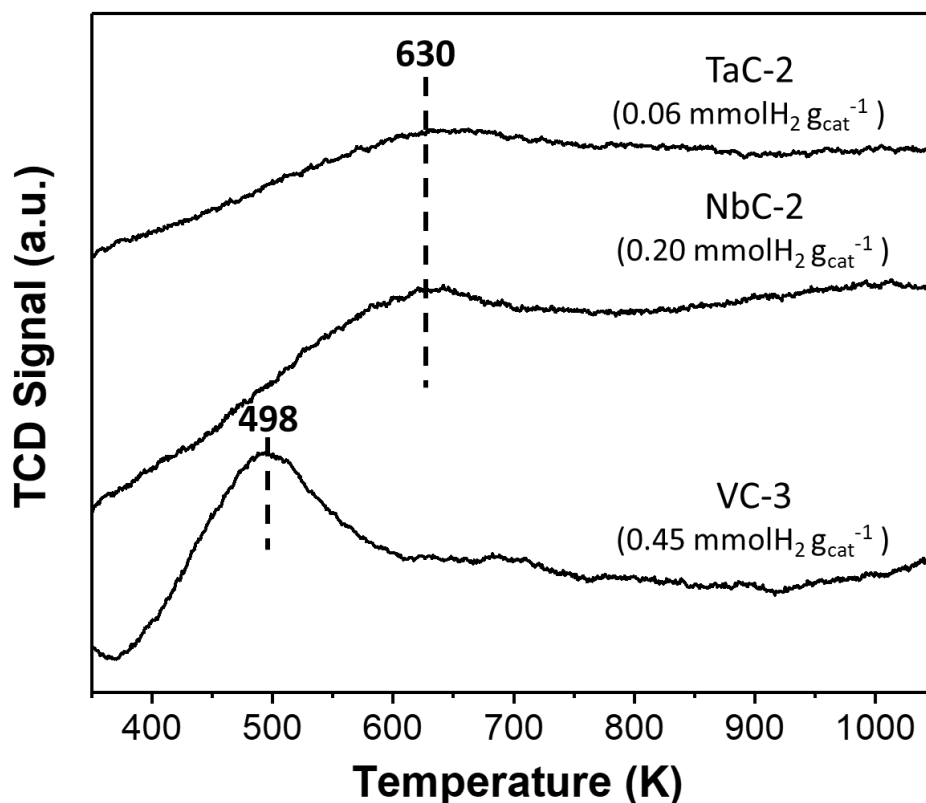


Figure 5.6. H₂-TPR profiles of bulk G5TM catalysts.

The bulk G5TMC catalysts were analyzed by XPS. Figure 5.7 shows the C 1s core level spectra of the samples. In all cases, a C 1s component centered at 283.0-283.2 eV assigned to carbidic phase (VC_x, NbC and TaC) is found [4-14]. The component at 248.8 eV is referred to C-C bond corresponding to residual and adventitious carbon and those at higher BE are assigned to species with C-H, C-O, C=O and/or C-O=O bonds [15-18].

The V 2p, Nb 3d and Ta 4f core levels corresponding to VC-3, NbC-2 and TaC-2 samples, respectively, were also analyzed (Figure 5.8).

V 2p core level XP spectrum shows a band at V 2p_{3/2}=513.6 eV attributed to VC_x [4-8]. Additionally, the bands at higher BE (V 2p_{3/2}=514.5 and 517.0 eV) are assigned to different vanadium oxide species [4-6,8,19-21]. Similar V 2p XP spectra were found in VC catalysts displayed in Chapter 3 (Figure 3.19) and Chapter 4 (Figures 4.11 and 4.29-4.35).

Nb 3d core level XP spectrum has been deconvoluted into 5 doublets ($3d_{5/2}$ and $3d_{3/2}$), keeping an intensity ratio Nb $3d_{5/2}$ /Nb $3d_{3/2}$ =3/2 and a spin-orbital splitting of 2.8 eV. The Nb $3d_{5/2}$ component at 204.1 eV is attributed to NbC [9-11]. The other components at higher BE (Nb $3d_{5/2}$ =204.6, 205.3, 206.2 and 207.5 eV) are assigned to niobium oxide species. [10,11,22].

Ta 4f core level XP spectrum has been deconvoluted into 3 doublets ($4f_{7/2}$ and $4f_{5/2}$), keeping an intensity ratio Ta $4f_{7/2}$ /Ta $4f_{5/2}$ =4/3 and a spin-orbital splitting of 1.9 eV. The Ta $4f_{7/2}$ component at 23.8 eV is assigned to TaC [12-14]. The other components at higher BE (Ta $4f_{7/2}$ =24.3 and 26.4 eV) are assigned to tantalum oxide species [12,13,23].

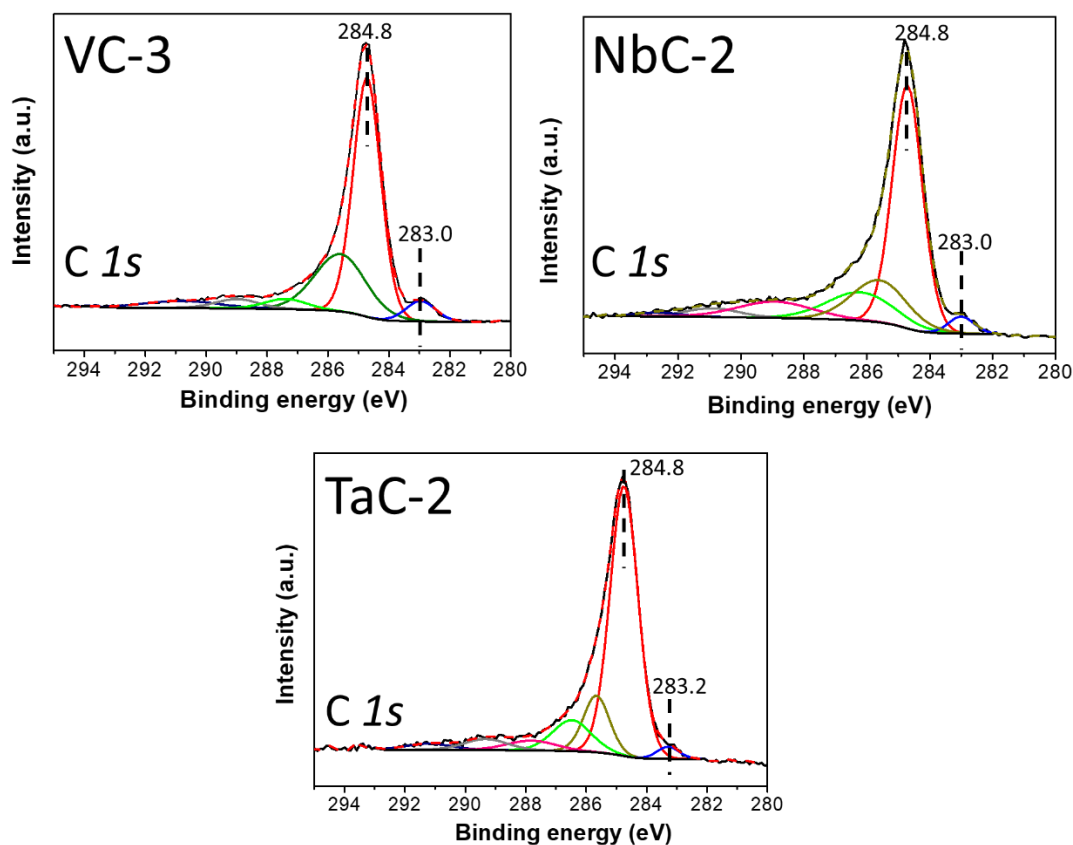


Figure 5.7. XPS profiles of C 1s level of VC-3, NbC-2 and TaC-2 samples.

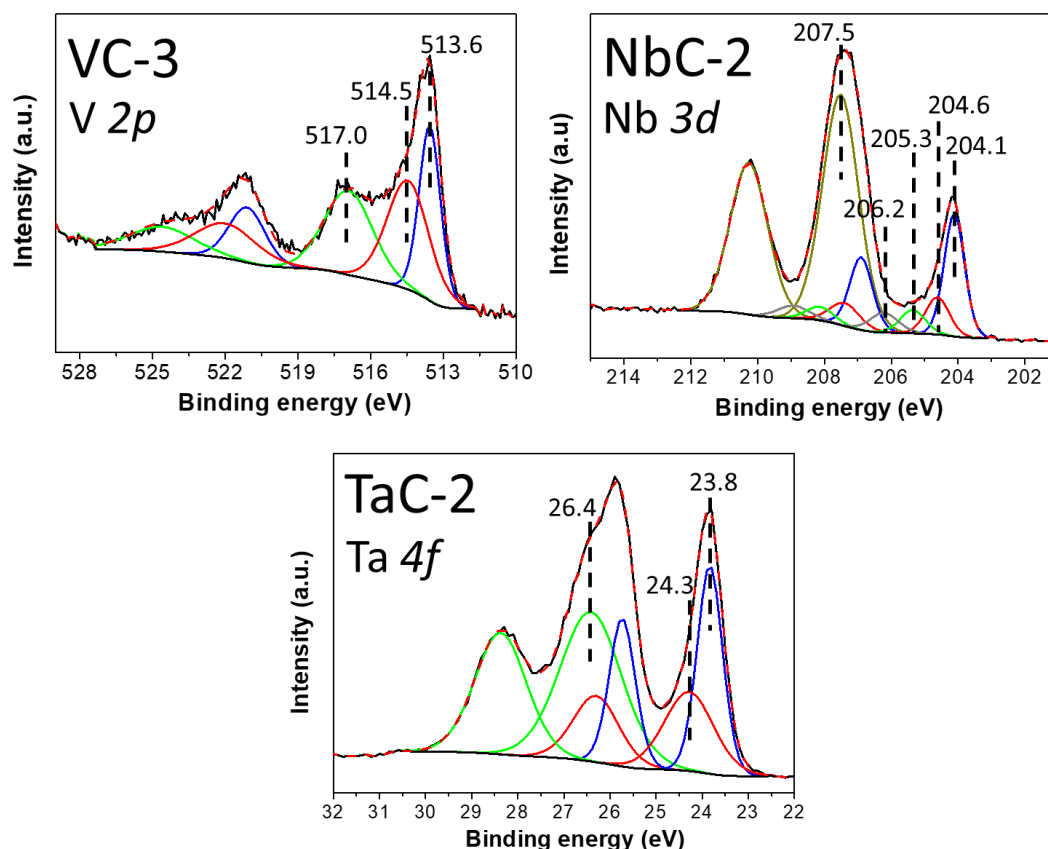


Figure 5.8. XPS spectra of V $2p$, Nb $3d$ and Ta $4f$ levels of VC-3, NbC-2 and TaC-2 samples, respectively.

The catalytic behavior of bulk G5TMC in the MSR reaction was studied in the range 573–723 K, at 0.1 MPa, GHSV of 2500 h^{-1} and using a reactant mixture of $\text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{N}_2=1/1/1.2$ (molar ratio). In all cases, 300 mg of catalyst and a catalytic bed of 1 mL were used. SiC was employed as diluting agent. The catalysts were kept for 1.5 h at each temperature.

Figure 5.9 displays the methanol conversion values as a function of temperature. All samples showed low MeOH conversion ($\sim 3\%$) at 573 K but it increased with the temperature increase up to 723 K.

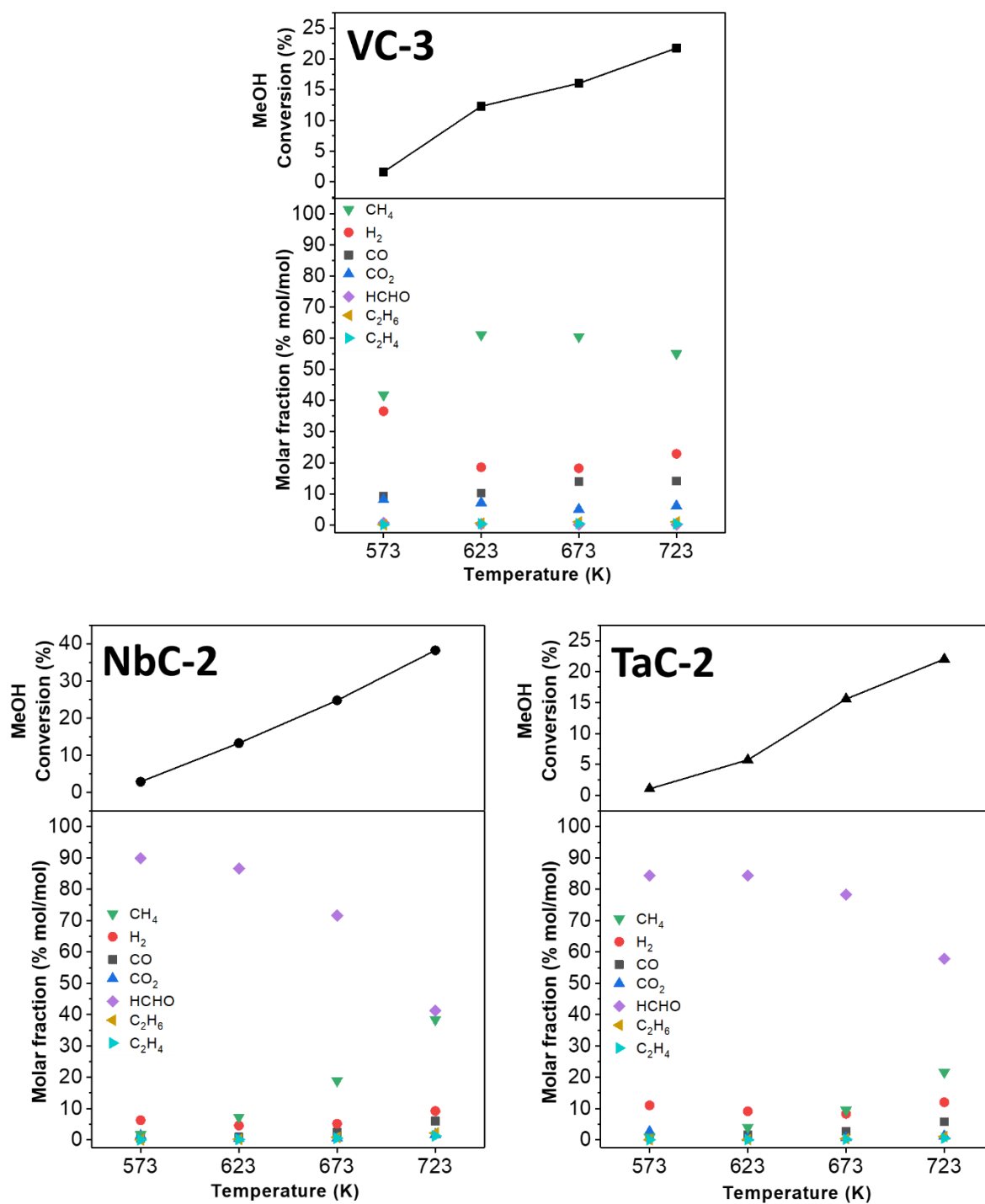


Figure 5.9. Methanol conversion and product distribution in the MSR reaction over bulk G5TMC as a function of reaction temperature. Reaction conditions: 300 mg of catalyst, CH₃OH/H₂O/N₂=1/1/1.2, P=1 bar and GHSV=2500 h⁻¹.

Figure 5.9 also shows the product distribution for all bulk G5TMCs. H_2 , CH_4 , CO , CO_2 , HCHO , C_2H_4 and C_2H_6 were detected as products.

In the overall temperature range, CH_4 was the major product found when VC-3 was used as catalyst. At 723 K, H_2 , CO and CO_2 concentrations were about 23%, 14% and 6%, respectively. Small amounts of HCHO , C_2H_4 and C_2H_6 were also detected (<1%).

On the other hand, for NbC-2 and TaC-2 samples, the major product formed was HCHO , which concentration decreased with the increase of temperature, meanwhile the methanol conversion increased (Figure 5.9). The second main product was CH_4 which production increased with temperature in both cases by reaching concentrations up to 38% and 22% for NbC-2 and TaC-2, respectively at 723 K. H_2 , CO and CO_2 kept a similar concentration in all the range of temperature studied. Small amounts of C_2H_4 and C_2H_6 were formed (<3%).

All catalysts were kept at 723 K for 20 h at the final part of the catalytic test. Figure 5.10 shows the behavior of the catalysts during this period. In all cases, a high deactivation is observed.

For the VC-3 catalyst, the methanol conversion decreased from about 22% to 3%. The CH_4 concentration decreased gradually from 55% to 45%, meanwhile, H_2 concentration increased from 23% to 32%, and CO and CO_2 kept a similar concentration. HCHO , C_2H_6 and C_2H_4 were always very minor products.

After 20 h of reaction at 723 K, the methanol conversion decreased from about 38% to 1% for NbC-2 and from about 22% to 1% for TaC-2. A decrease of HCHO concentration is observed for NbC-2, meanwhile the HCHO concentration remained constant for TaC-2. The H_2 concentration increased in both cases, meanwhile CH_4 concentration slightly decreased.

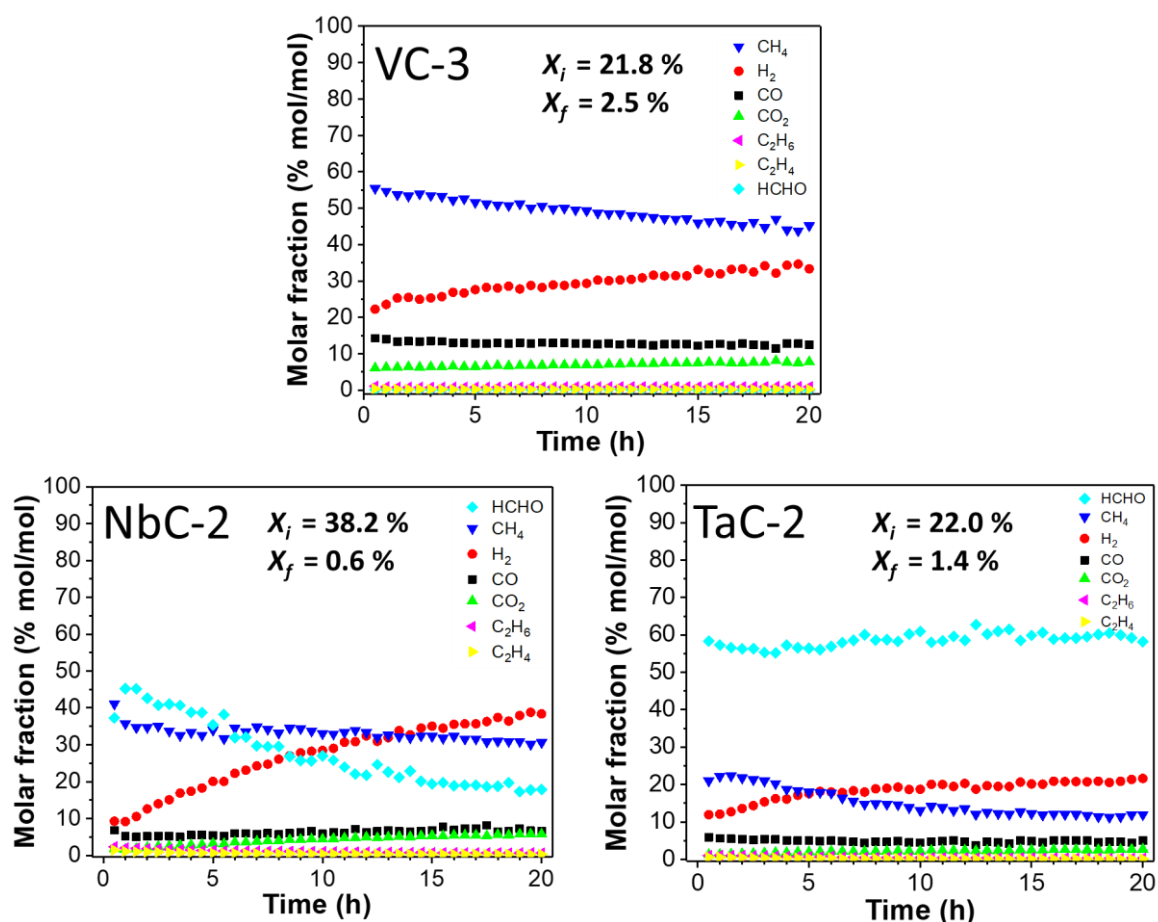
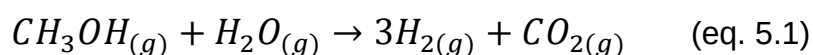
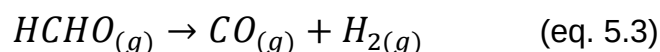
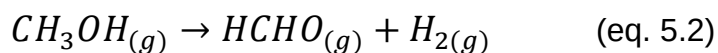


Figure 5.10. Product distribution for the MSR reaction over bulk G5TMC at 723 K along the time. Reaction conditions: 300 mg of catalyst, CH₃OH/H₂O/N₂=1/1/1.2, P=1 bar and GHSV=2500 h⁻¹. X_i : Methanol conversion after 1 h. X_f : Methanol conversion after 20 h.

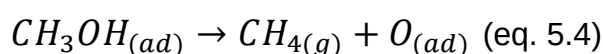
As stated in the introduction section. The production of H₂ and CO₂ is expected from the MSR reaction (eq. 5.1).



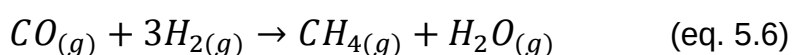
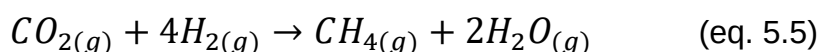
However, other products such as formaldehyde and CO can also be expected through methanol dehydrogenation and HCHO decomposition reactions (eq. 5.2 and eq. 5.3).



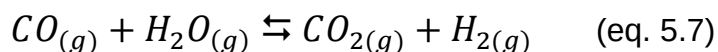
The high CH₄ formation, which is observed in all cases but is predominant over VC-3, could be associated to the methanol decomposition, which results in CH₄ and an O adsorbed on the surface (eq. 5.4) [24-30], the latter could form surface oxy-carbide species. The oxy-carbide species subsequently could react with H₂ to recover the corresponding metal carbide producing H₂O.



Studies of methanol decomposition over VC single crystals have shown that VC could break C-O instead of C-H bonds leading to CH₄ production at ~500 K; this is possibly associated to the presence of defect sites (C vacancies) [31,32]. The presence of C vacancies has also been proposed as active centers for methanol activation on Mo₂C systems [33]. A similar process could take place under MSR conditions used in this work. However, methanation reactions cannot be ruled out for CH₄ formation (eq. 5.5 and 5.6).



Moreover, it is necessary to take into account the WGS equilibrium (eq. 5.7).



The CH₄ decomposition can lead to coke formation on surface as observed on Mo₂C in the MSR [24,34]. The coke formation is probably related with the decrease in the catalytic activity of catalysts after 20 h of reaction at 723 K. After methanol adsorption, the complete decomposition of methanol with final carbon formation was also observed on VC(100) single crystals by Chen et al [31].

On the other hand, over NbC-2 and TaC-2, the dehydrogenation of methanol to formaldehyde seems to be the main reaction pathway (eq. 5.2). The scission of C-H in CH₃O species would take place before C-O bond cleavage on both samples. CH₃O groups have been observed on NbC single crystals after methanol adsorption at 293 K [35]. Although, the use of TaC in methanol decomposition and MSR have not been yet reported, a similar catalytic behavior might be proposed.

The high HCHO/H₂ molar ratio, found when NbC-2 and TaC-2 were used, could be associated with the reaction of part of H₂ formed with surface oxy-carbide species formed under reaction conditions to recover the corresponding metal carbide.

Post-reaction bulk G5TMC catalysts were characterized by N₂ adsorption/desorption isotherms and XRD. In all cases a high decrease of the S_{BET} area and an increase of pore size were observed (Table 5.1). XRD patterns of the used bulk G5TMC catalysts showed the presence of a wide peak at $\theta=25.0^\circ$ in all cases, this could be associated to the presence of carbon deposits formed during reaction (Figure 5.11). Crystallite sizes of VC_x, NbC and TaC of post-reaction catalysts remained similar to those of the corresponding fresh catalysts. No crystalline metal oxides were observed in any case.

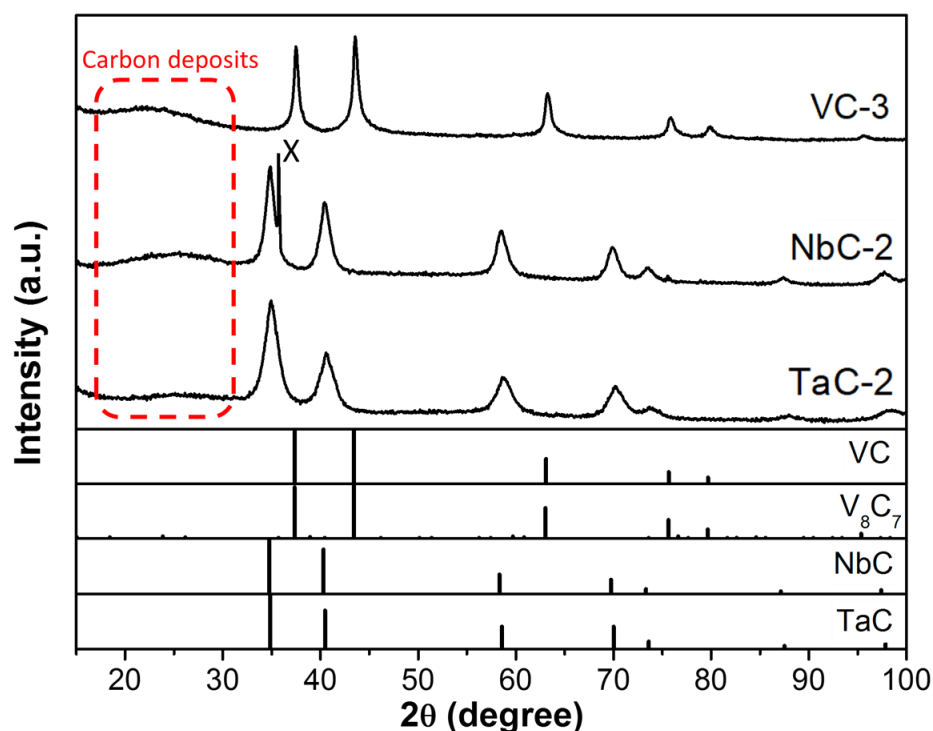


Figure 5.11. XRD of used bulk G5TMC catalysts. X:SiC used as diluent agent in catalytic bed.

The effect of the contact time (GHSV) was studied at 598 K and 623 K for VC-3 and NbC-2 catalysts to analyze variations in the product distribution. The increase of GHSV was performed increasing N_2 flow to reach a reactant mixture molar ratio of $CH_3OH/H_2O/N_2=1/1/5.5$ and $CH_3OH/H_2O/N_2=1/1/8$ for a GHSV of 6000 and 8000 h^{-1} , respectively.

Table 5.2 shows the effect of GHSV on methanol conversion and product distribution; the selectivity to carbon compounds is shown in Table 5.3. As expected, VC-3 and NbC-2 showed a decrease of methanol conversion when the GHSV was increased from 6000 to 8000 h^{-1} ; CH_4 and $HCHO$ were the major products for VC-3 and NbC-2 catalysts, respectively. In general, a decrease of H_2 and CO_2 concentrations was observed in both cases at higher GHSV.

Table 5.2. MeOH conversion and product distribution in the MSR reaction at different contact time (GHSV) conditions for VC-3 and NbC-2 catalysts. Reaction conditions: 500 mg of catalyst and $P=0.1$ MPa.

Catalysts		VC-3				NbC-2			
GHSV (h^{-1})		6000 ⁽¹⁾		8000 ⁽²⁾		6000 ⁽¹⁾		8000 ⁽²⁾	
Temperature (K)		598	623	598	623	598	623	598	623
MeOH Conversion (%)		10.3	21.4	3.6	14.9	5.4	13.6	3.7	10.3
Product Distribution (%)	H ₂	25.3	19.8	22.9	18.7	8.1	5.9	5.9	6.2
	CH ₄	55.6	59.0	61.7	62.4	5.6	8.1	8.2	10.0
	CO ₂	7.3	6.4	4.0	5.1	1.0	0.6	0.4	0.5
	CO	10.7	13.5	9.7	12.5	0.4	1.6	1.5	1.3
	HCHO	0.4	0.2	0.8	0.2	84.7	83.3	83.6	81.4
	C ₂ H ₆	0.4	0.7	0.6	0.7	0.1	0.3	0.2	0.3
	C ₂ H ₄	0.3	0.4	0.3	0.4	0.1	0.2	0.2	0.3

⁽¹⁾CH₃OH/H₂O/N₂=1/1/5.5 ⁽²⁾CH₃OH/H₂O/N₂=1/1/8.

Table 5.3. MeOH conversion and selectivity to carbon compounds in the MSR reaction at different contact time (GHSV) conditions for VC-3 and NbC-2 catalysts. Reaction conditions: 500 mg of catalyst and $P=0.1$ MPa.

Catalysts		VC-3				NbC-2			
GHSV (h^{-1})		6000 ⁽¹⁾		8000 ⁽²⁾		6000 ⁽¹⁾		8000 ⁽²⁾	
Temperature (K)		598	623	598	623	598	623	598	623
MeOH Conversion (%)		10.3	21.4	3.6	14.9	5.4	13.6	3.7	10.3
Selectivity (%)	CH ₄	74.3	73.4	79.7	76.3	6.1	8.5	8.6	10.5
	CO ₂	9.6	7.8	4.9	6.0	1.0	0.6	0.4	0.5
	CO	14.1	16.5	12.3	15.0	0.5	1.6	1.5	1.3
	HCHO	0.3	0.1	0.8	0.1	92.0	88.4	88.7	86.5
	C ₂ H ₆	0.9	1.3	1.5	1.7	0.2	0.5	0.4	0.6
	C ₂ H ₄	0.8	0.9	0.8	0.9	0.2	0.4	0.4	0.6

⁽¹⁾CH₃OH/H₂O/N₂=1/1/5.5 ⁽²⁾CH₃OH/H₂O/N₂=1/1/8.

Despite the different MeOH conversion values, CH₄ was produced with a selectivity above 70% in all cases for VC-3 catalyst. An increase of CH₄ selectivity is observed with the decrease of contact time for VC-3 catalyst, pointing out CH₄ as primary product. The main reaction pathway seems to be the direct CH₄ formation from C-O scission of CH₃OH (eq. 5.4).

For NbC-2, HCHO selectivity was above 85% in the conditions analyzed; over this catalyst, the dehydrogenation of methanol could be proposed as the main reaction pathway (eq. 5.2). However, for NbC-2, increasing the temperature and GHSV, a slight diminution on HCHO and a slight increase of CH₄ selectivity was observed. This indicates that CH₄ formation through methanol decomposition (eq. 5.4) could also proceed in some extension.

Moreover, the $n_{CH_4}/(n_{CO} + n_{CO_2})$ ratio decreased when the methanol conversion increased (varying GHSV) at the same temperature for VC-3 and NbC-2. This point to a low contribution, if it exists, of the methanation reactions (eq. 5.5 and 5.6).

5.2.2. Supported VC catalysts

Supported VC catalysts reported in Chapter 4 (Section 4.2) were studied in the MSR using the same reaction conditions discussed above for bulk G5TMC catalysts. Table 5.4 shows a summary of the characteristics already discussed (Chapter 4) of the supported VC catalysts.

Table 5.4. Several characteristics of fresh supported VC catalysts and after their use in MSR.

Catalyst	V (% wt)	Crystallite size of VC_x (nm)	S_{BET} (m² g⁻¹)		Pore size (nm)	
			Fresh	Used	Fresh	Used
VC-3/AC	21.3	11	448	20	4	6
VC-3/CeO ₂	22.5	36	86	9	6	6
VC-3/ZrO ₂	21.6	25	119	8	6	21
VC-3/SiO ₂	21.3	9	216	37	7	10
VC-3/Al ₂ O ₃	22.1	9	210	24	9	9
VC-3/TiO ₂	23.0	20	158	48	17	16

Figures 5.12 and 5.13 show the variation of MeOH conversion with respect to reaction temperature of supported VC catalysts. In general, supported VC catalysts showed higher MeOH conversion than that of bulk VC-3 catalyst under the reaction conditions studied.

As it was shown for bulk VC-3, all supported VC catalysts showed low catalytic activity at 573 K and MeOH conversion increased with temperature. VC-3/ZrO₂ and VC-3/Al₂O₃ were the most active reaching values of MeOH conversion at 673 K of 100% and 93%, respectively. VC-3/AC, VC-3/SiO₂, VC-3/TiO₂ and VC-3/CeO₂ samples reached values of MeOH conversion at 723 K of 86%, 50%, 79% and 83%, respectively (Figures 5.12 and 5.13).

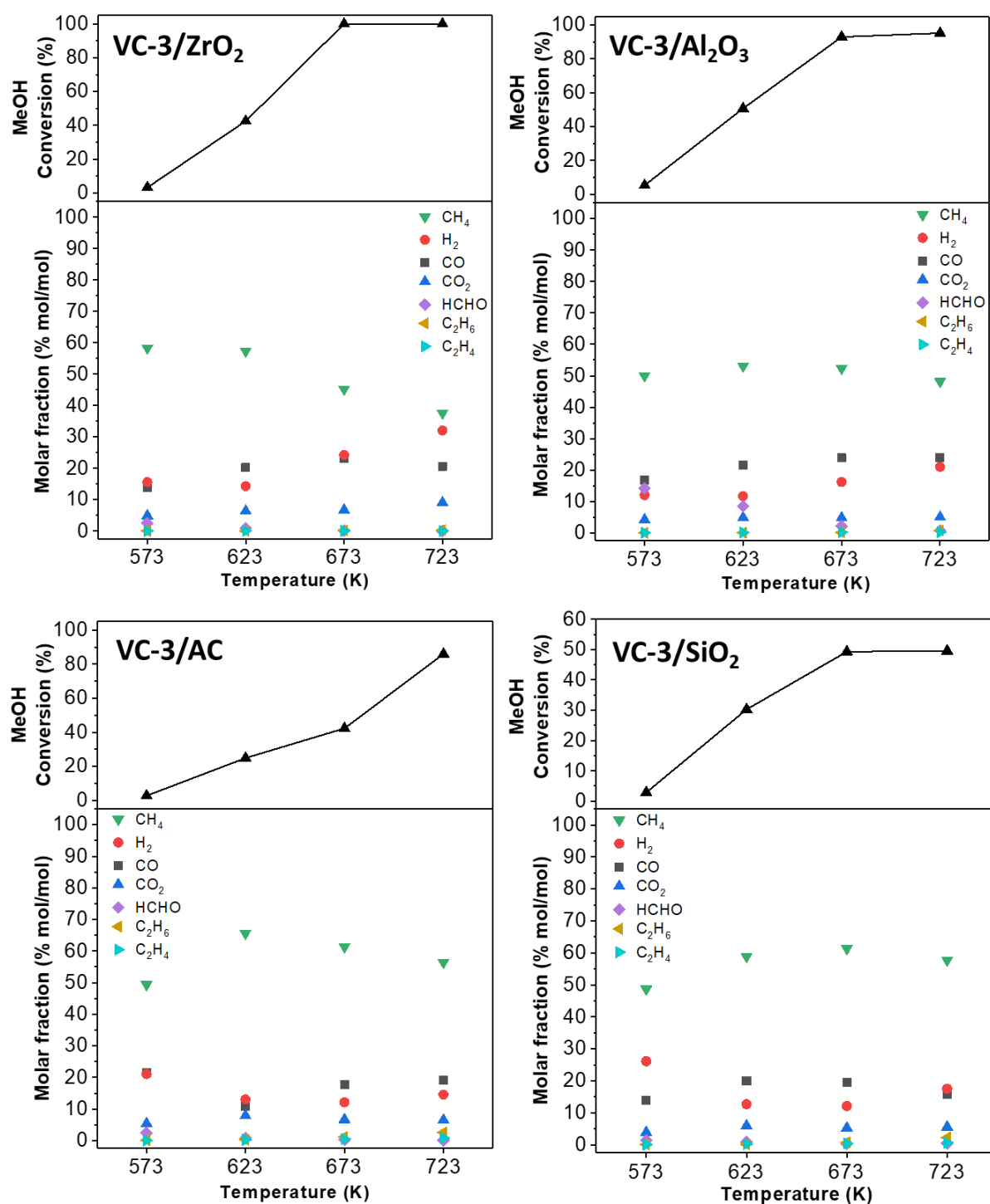


Figure 5.12. Methanol conversion and product distribution for the MSR reaction over VC-3/ZrO₂, VC-3/Al₂O₃, VC-3/AC and VC-3/SiO₂ as a function of reaction temperature. Reaction Conditions: 300 mg of catalyst, CH₃OH/H₂O/N₂=1/1/1.2, P=1 bar and GHSV=2500 h⁻¹.

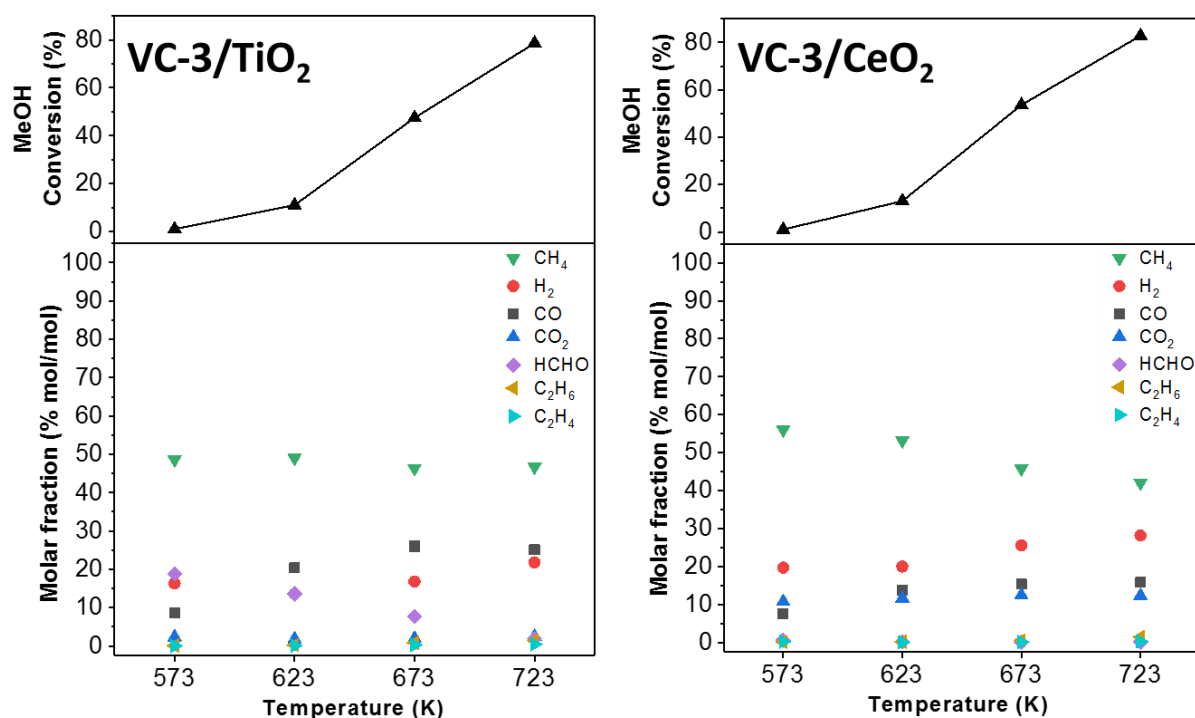


Figure 5.13. Methanol conversion and product distribution for the MSR reaction over VC-3/TiO₂ and VC-3/CeO₂ as a function of reaction temperature. Reaction Conditions: 300 mg of catalyst, CH₃OH/H₂O/N₂=1/1/1.2, P=1 bar and GHSV=2500 h⁻¹.

Figures 5.12 and 5.13 also show the product distribution obtained under the reaction conditions used. In all cases, CH₄ was the major product formed in the whole range of temperature tested, as observed for bulk VC-3 sample (Figure 5.9). The H₂ concentration increased in all cases from 623 K to 723 K, being VC-3/ZrO₂ and VC-3/CeO₂ catalysts the most performant to H₂ formation, reaching values of ~30% at 723 K. For a Mo₂C/ZrO₂ catalyst used in the MSR [33], the preferential H₂ formation in relation to CH₄ has been associated to the ability of zirconia to retain methoxy groups on its surface. This could be also the case for VC-3/ZrO₂.

For VC-3/Al₂O₃ and VC-3/TiO₂ at 573K, HCHO concentrations of 14% and 19% were found, respectively. Then, an increase of temperature produced a decrease of HCHO concentration and an increase of CO and H₂ concentrations. The HCHO production at low temperature (573 K) can be related with the

methanol dehydrogenation reaction (eq. 5.2) but increasing the temperature the formaldehyde decomposition (eq. 5.3) would take place leading to an increase of CO and H₂ concentrations.

For VC-3/ZrO₂, VC-3/AC, VC-3/SiO₂ and VC-3/CeO₂, the amount of HCHO obtained was very low (<1%) and the CO and CO₂ concentrations remained almost constant along the temperature range tested.

Additionally, small amounts of C₂H₄ and C₂H₆ (<2%) were detected in all cases.

To analyze the stability of the samples, the reaction was extended for 20 h at 723 K (Figure 5.14). All catalysts displayed deactivation. VC-3/ZrO₂ showed the highest methanol conversion after 20 h under reaction going from 100% (1h) to 46% (20 h).

For VC-3/ZrO₂ and VC-3/TiO₂, the product distribution was stable along time. For all the other catalysts, a decrease of CH₄ concentration and an increase of H₂ concentration along time was observed. This is probably related with the methane decomposition and formation of carbon deposits. CO, CO₂, C₂H₄ and C₂H₆ concentrations remained almost constant along reaction. For VC-3/Al₂O₃, an increase of HCHO concentration along time is detected, going from <1% at the first hour to 16% after 20 h of reaction, this might also be associated with the catalyst deactivation.

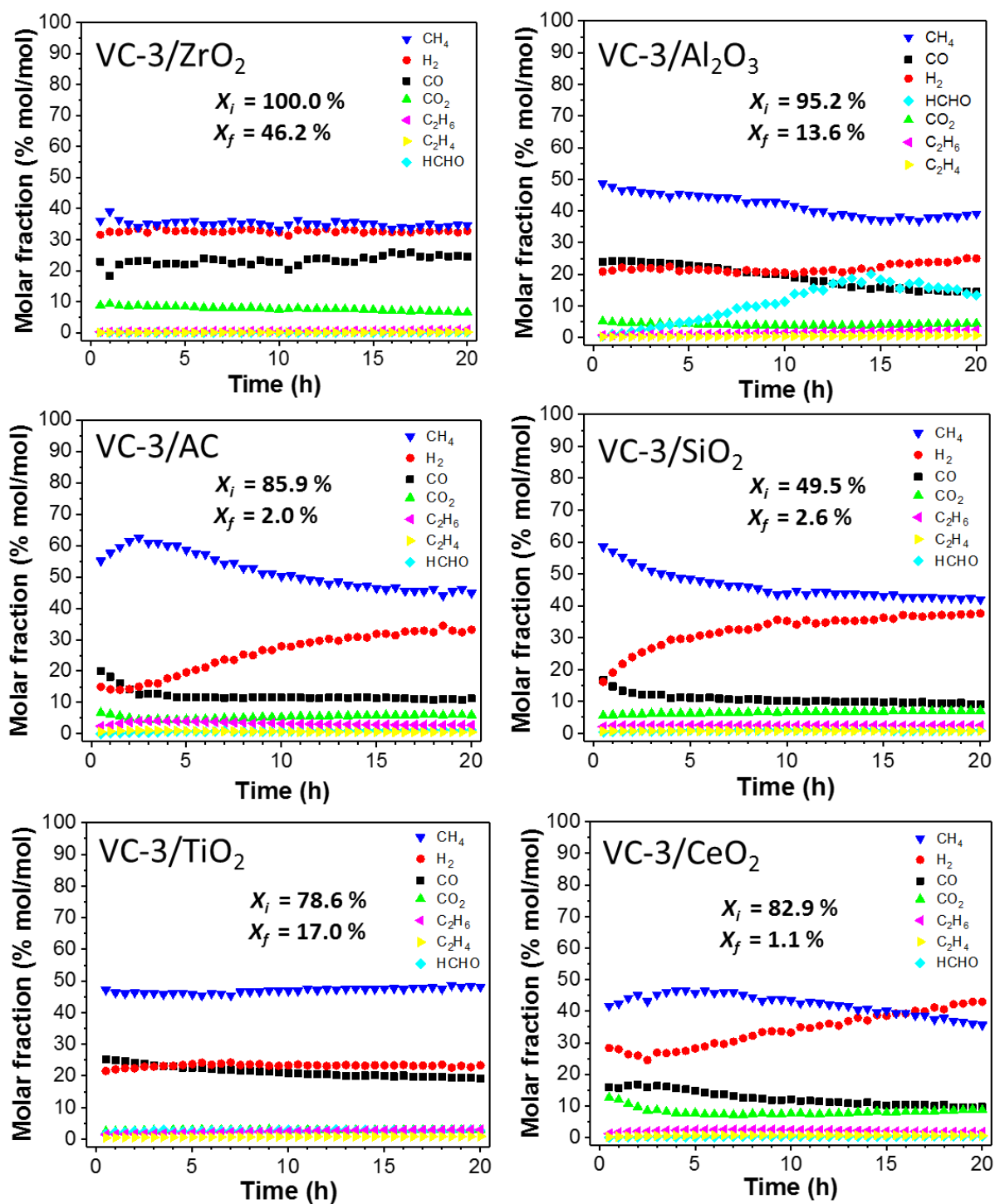


Figure 5.14. Product distribution for the MSR reaction over supported VC catalysts at 723 K along the time. Reaction Conditions: 300 mg of catalyst, $\text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{N}_2 = 1/1/1.2$, $P = 1$ bar and $\text{GHSV} = 2500 \text{ h}^{-1}$. X_i : Methanol conversion after 1 h. X_f : Methanol conversion after 20 h.

Characterization of supported VC catalysts after MSR reaction was performed by means of XRD, BET surface area and XPS techniques.

Figures 5.15-5.20 show the XRD patterns of spent catalysts. In some cases, the presence of carbonaceous deposits can be deduced, this is in agreement with the results obtained with bulk G5TMC catalysts. VC_x crystallite sizes of used catalysts remain similar to that of the corresponding fresh catalysts. No XRD peaks corresponding to crystalline VO_x species were detected in any case.

Some structural changes of the support oxide are deduced from the XRD patterns of VC-3/ZrO₂ and VC-3/TiO₂ after reaction. More intense peaks of monoclinic ZrO₂ phase were observed in the used VC-3/ZrO₂ (Figure 5.16). For VC-3/TiO₂, small peaks corresponding to rutile and anatase TiO₂ phase were detected, which could result from a partial transformation of the initial solid solution, (Ti_{0.9}V_{0.1})₂O₃, present in the fresh catalyst (Figure 5.17). Moreover, a high reduction of the S_{BET} areas of spent catalysts compared to fresh catalysts is observed (Table 5.4). A high deactivation along time has also been reported for Mo₂C based catalysts during the MSR reaction [36,37].

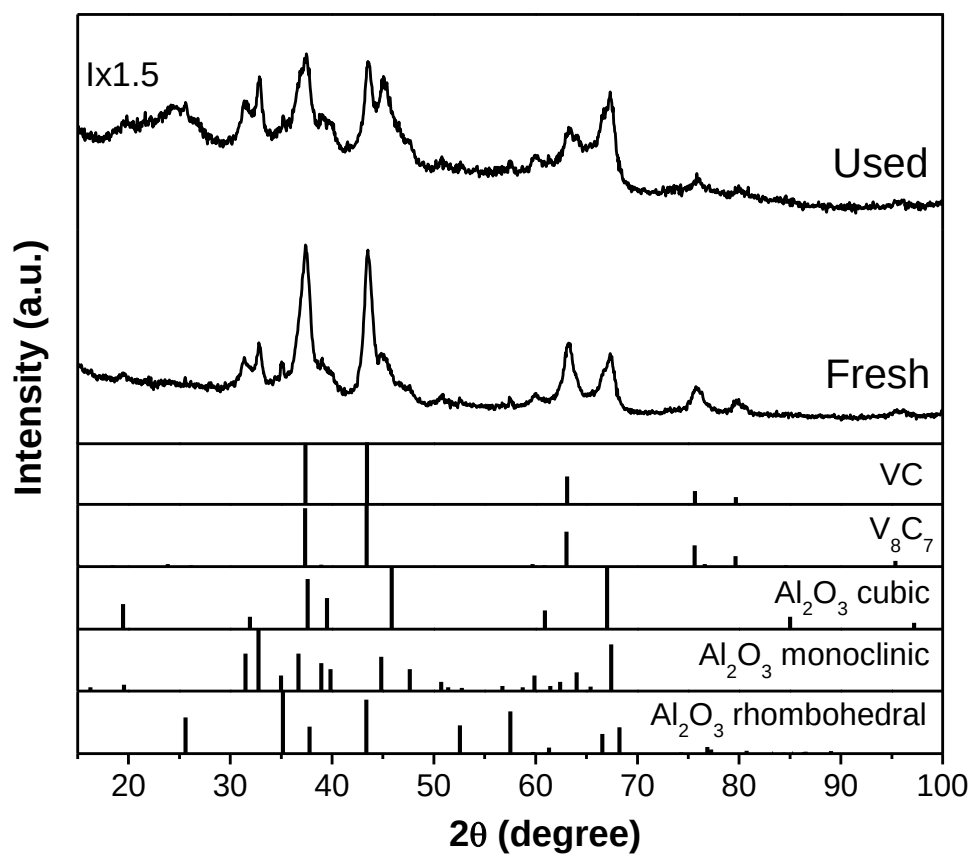


Figure 5.15. XRD pattern of used and fresh VC-3/Al₂O₃ catalyst.

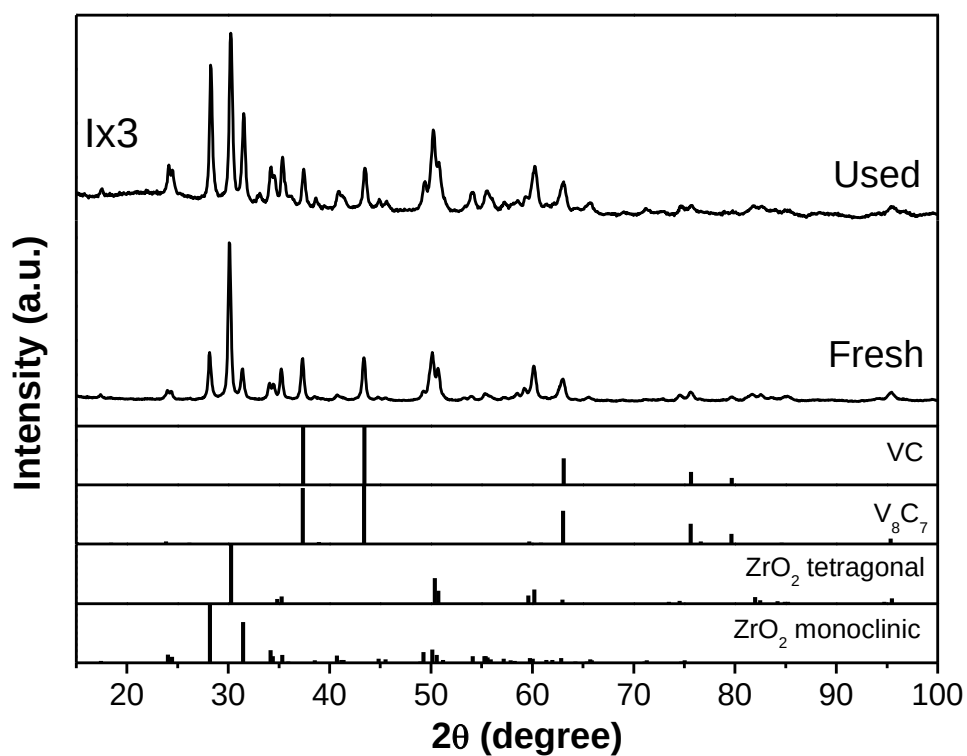


Figure 5.16. XRD patterns of used and fresh VC-3/ZrO₂ catalysts.

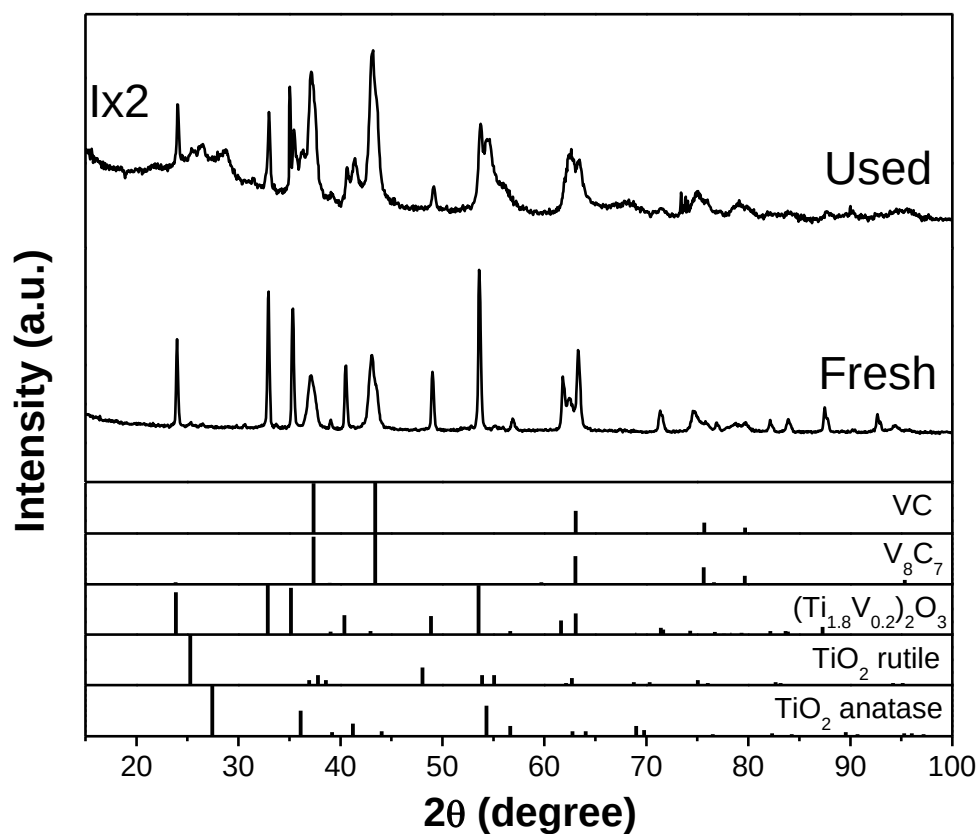


Figure 5.17. XRD pattern of used VC-3/TiO₂ catalyst.

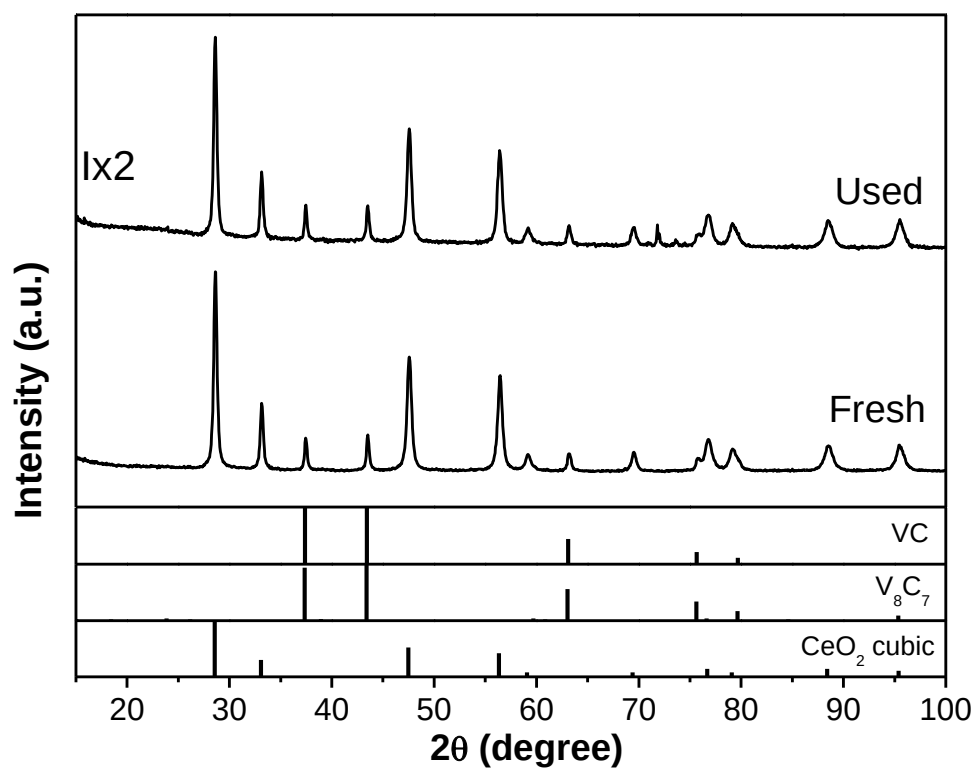


Figure 5.18. XRD patterns of used and fresh VC-3/CeO₂ catalysts.

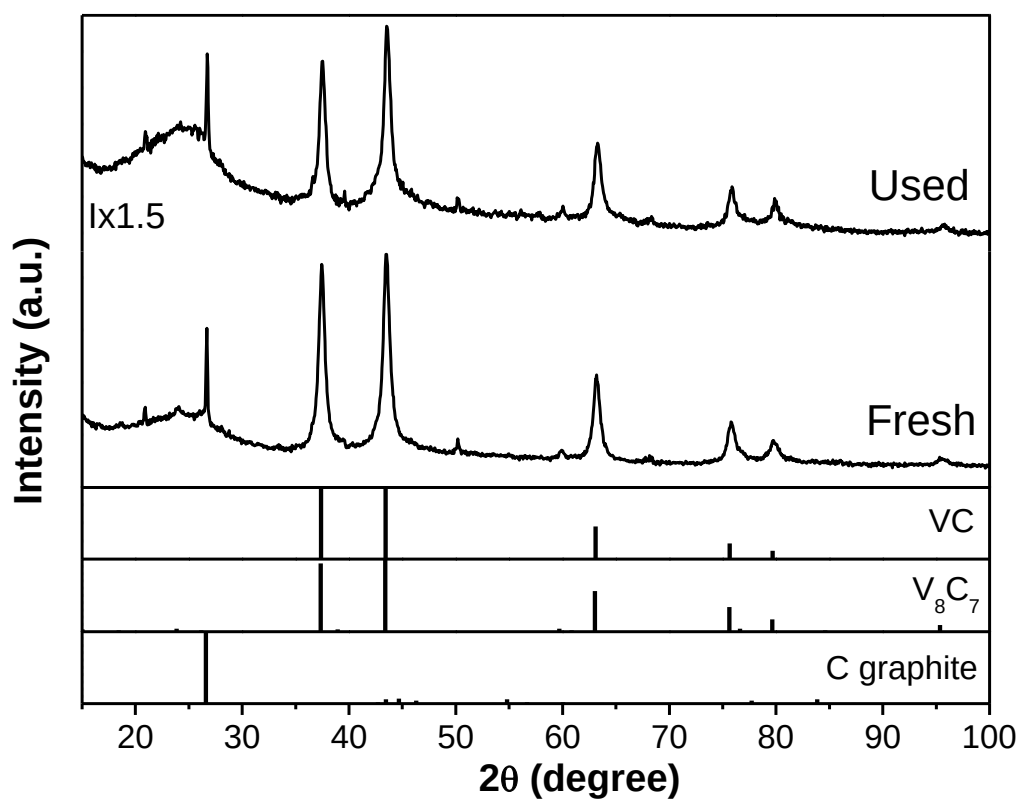


Figure 5.19. XRD patterns of used and fresh VC-3/AC catalysts.

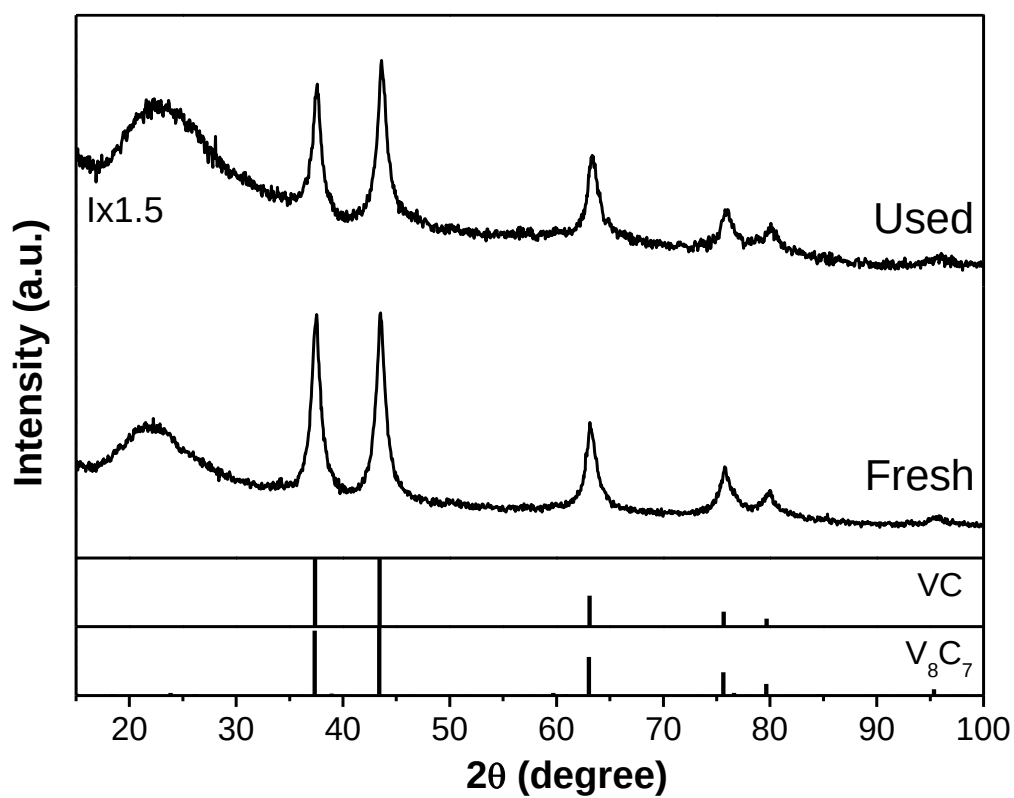


Figure 5.20. XRD patterns of used and fresh VC-3/SiO₂ catalysts.

Figures 5.21 and 5.22 show the XPS profiles of the V $2p$ and O $1s$ core levels corresponding to spent supported and bulk VC catalysts. XP spectra of the fresh catalysts are displayed for comparison.

A new wide band, in O $1s$ core level side, at higher BE is observed in all samples. The new bands clearly visible at 537-542 eV are attributed to adsorbed CH_3OH and H_2O species [38].

Moreover, the intensity of the V $2p_{3/2}$ band at 513.5-513.8 eV assigned to the presence of VC_x species decreased compared to the fresh catalysts, meanwhile the components at V $2p_{3/2}$ =517.1-517.5 eV, attributed to oxy-vanadium species, increased. No surface vanadium species were detected on VC-3/ CeO_2 after reaction.

Figures 5.23 and 5.24 show the C $1s$ core level XP spectra of the spent catalysts. In all cases, the carbidic carbon corresponding to VC_x (C $1s$ at ~ 283.0 eV) is difficult to be observed, probably due to the overlapping with the high intensity peak associated to C-C bond (284.8 eV), which considerably increased compared to the fresh samples. This could be attributed to the carbon deposits formed during reaction.

We could speculate that the carbon deposition observed by XRD and XPS analysis of used catalysts and the high reduction of their S_{BET} could be associated with the high deactivation of the samples.

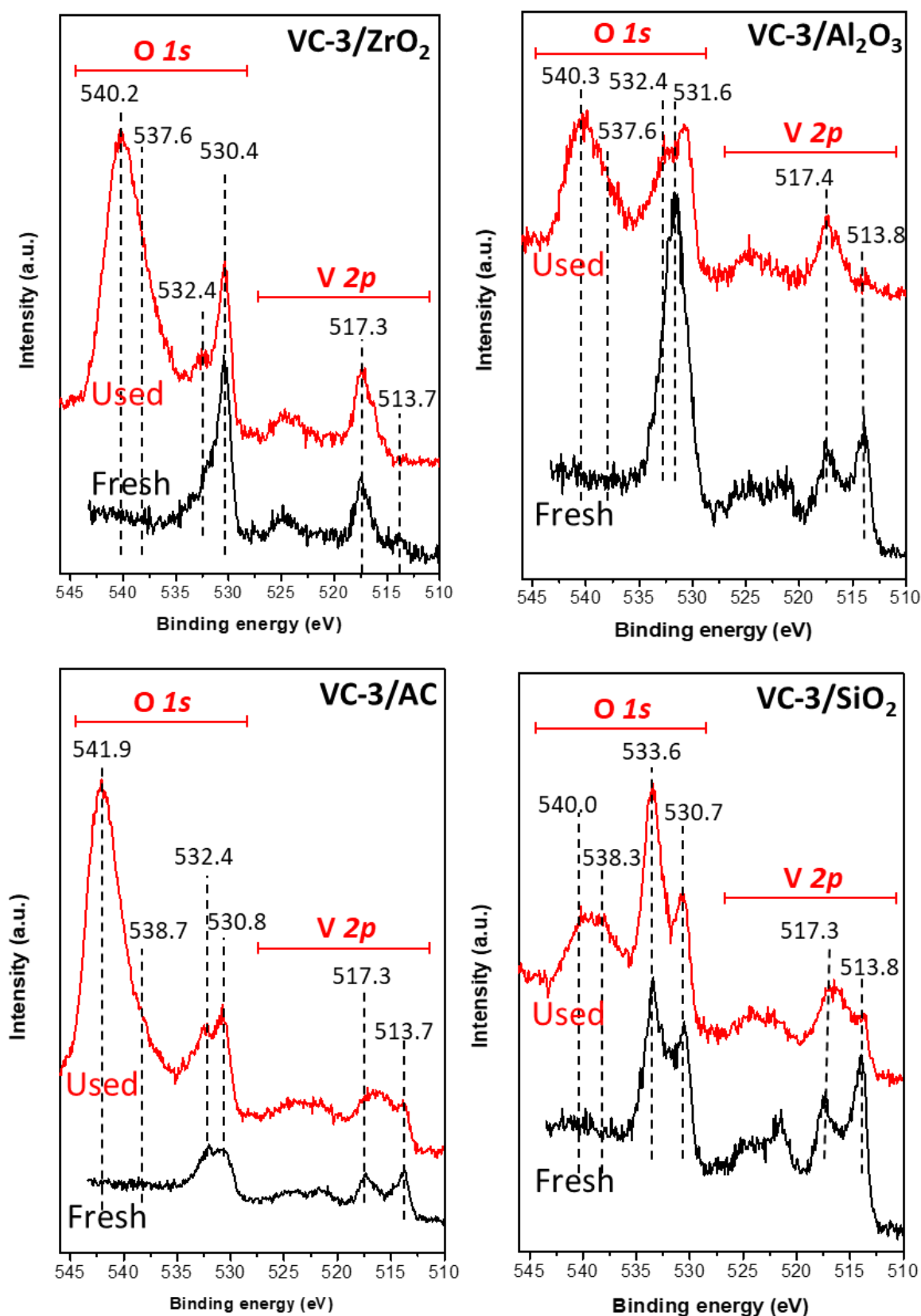


Figure 5.21. XP spectra of V 2p and O 1s core levels (combined) before and after MSR reaction of VC-3/ZrO₂, VC-3/Al₂O₃, VC-3/AC and VC-3/SiO₂.

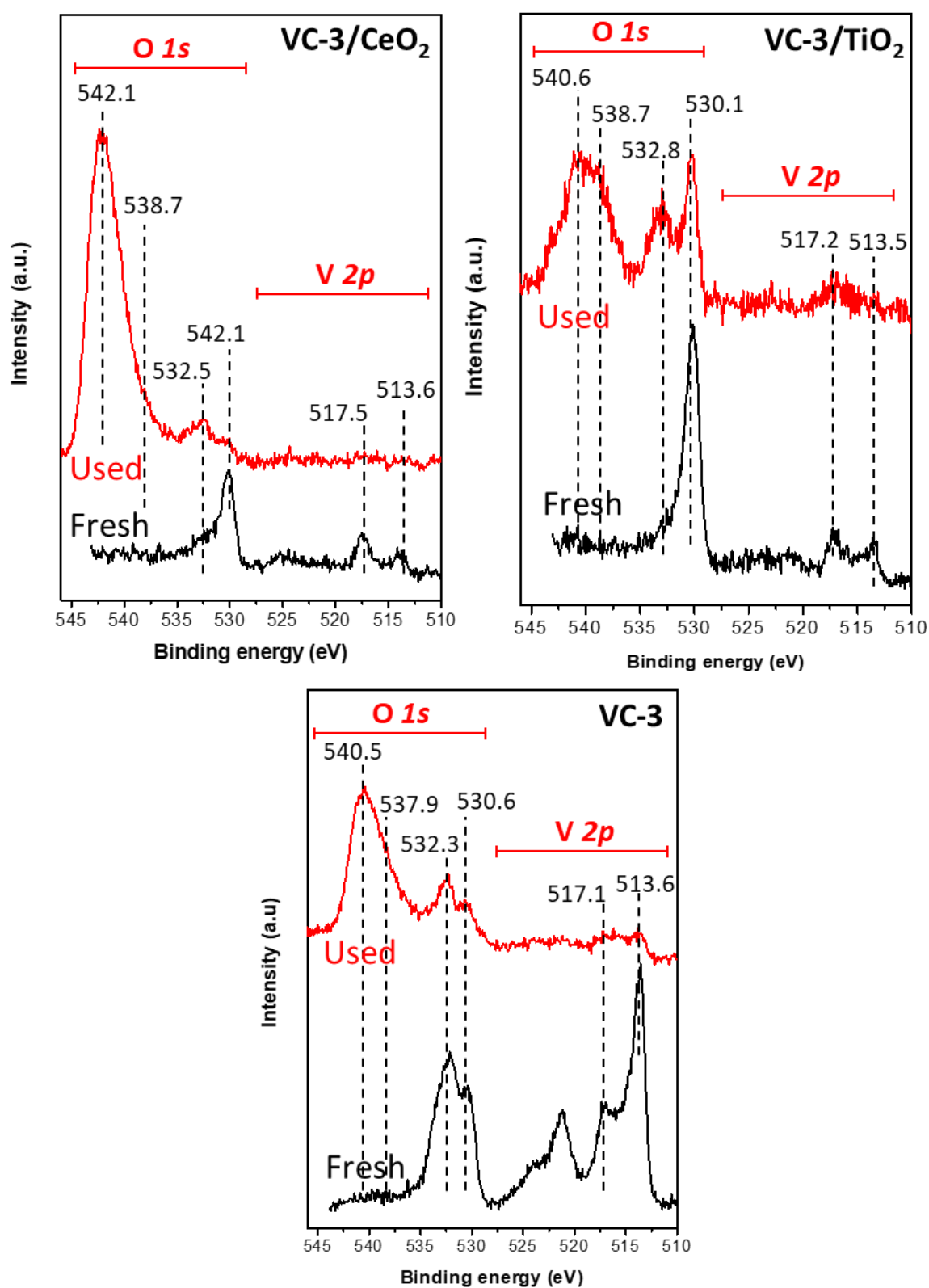


Figure 5.22. XPS profiles of V 2p and O 1s core levels (combined) before and after MSR reaction of VC-3/CeO₂, VC-3/TiO₂ and VC-3.

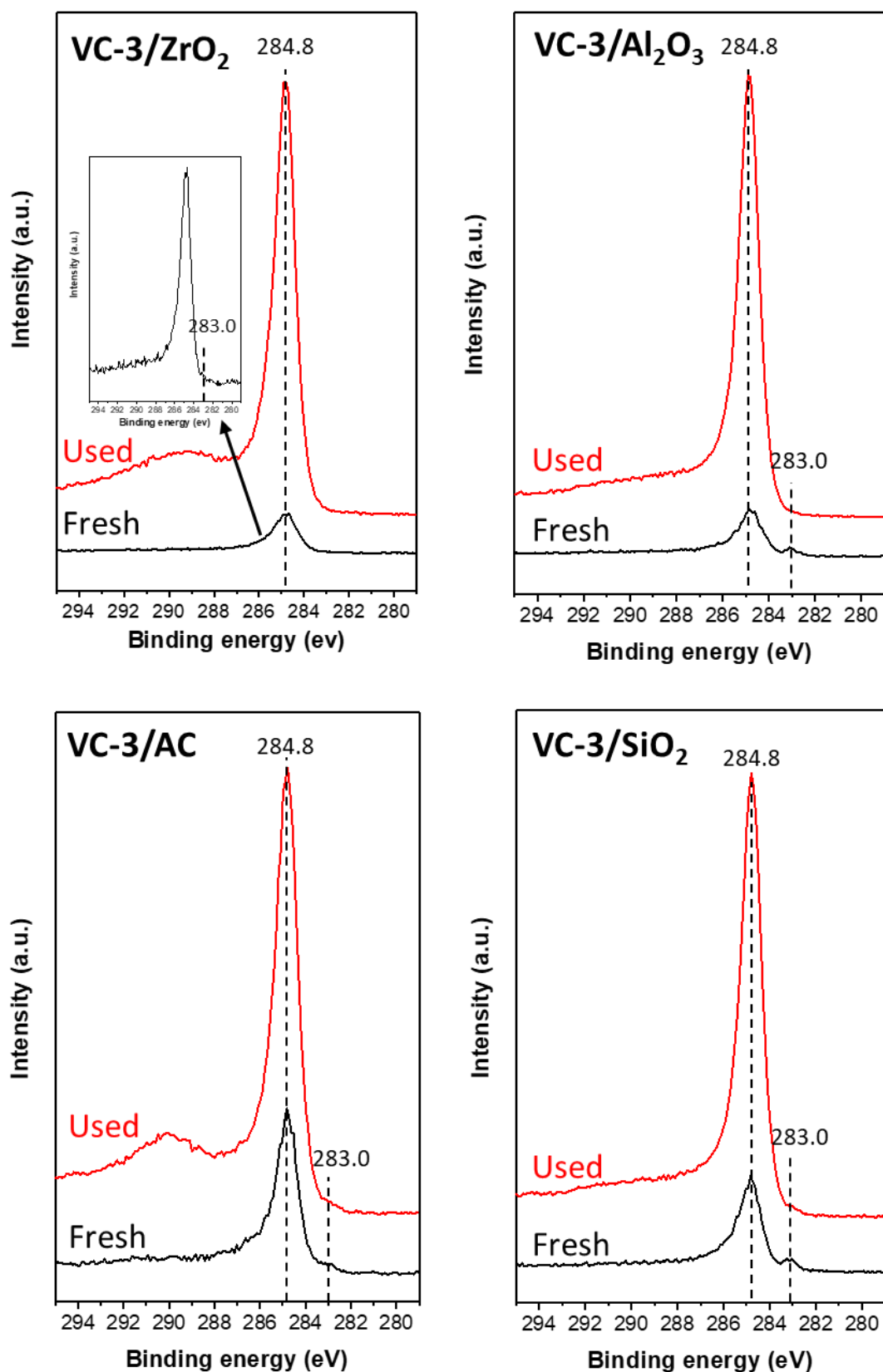


Figure 5.23. XPS profiles of C 1s core level before and after MSR reaction of VC-3/ZrO₂, VC-3/Al₂O₃, VC-3/AC and VC-3/SiO₂.

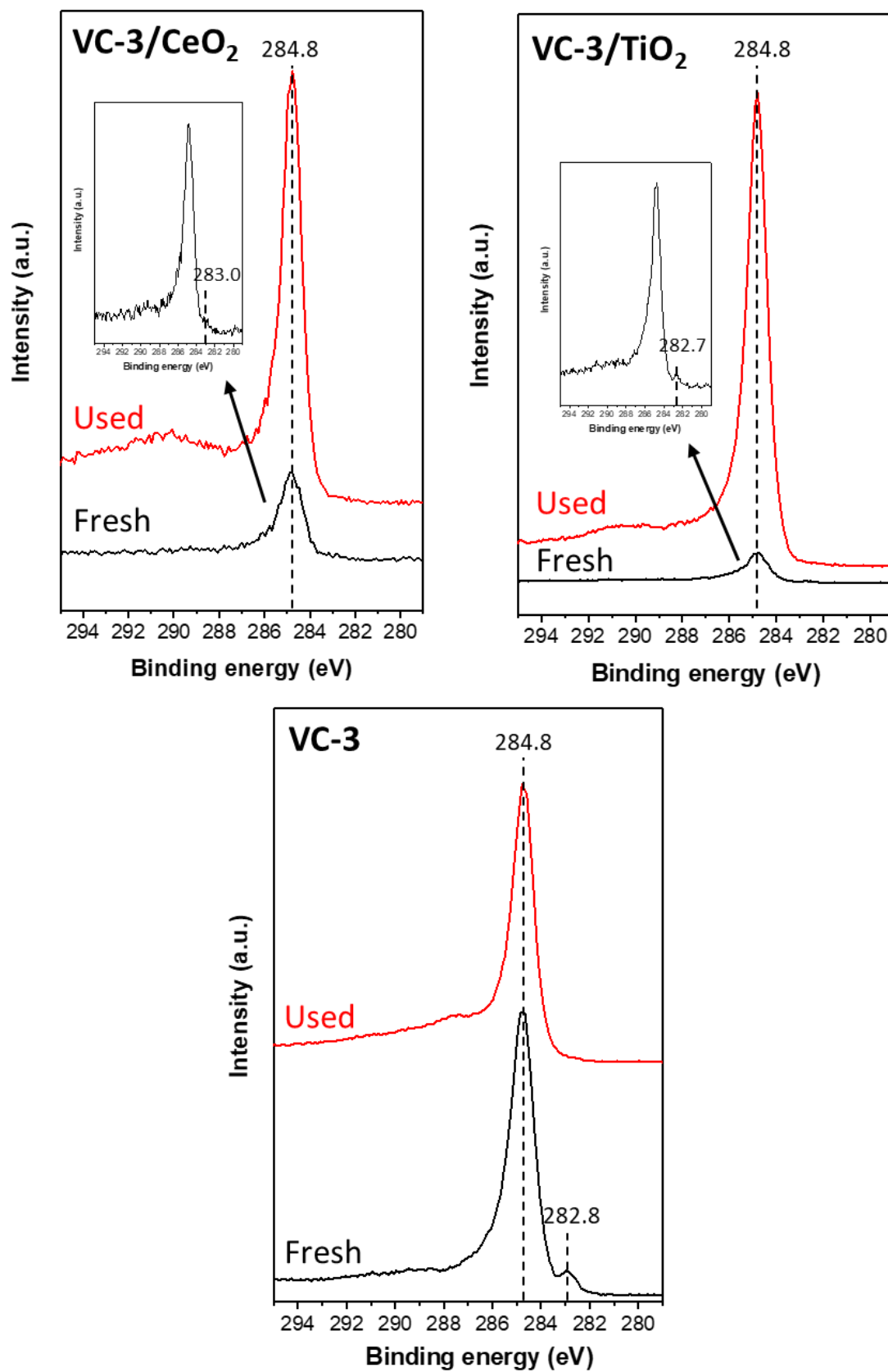


Figure 5.24. XPS profiles of C 1s core level before and after MSR reaction of VC-3/CeO₂, VC-3/TiO₂ and VC-3.

5.3. References

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CHAPTER 6

CONCLUSIONS

Transition metal carbides of group 5, VC, NbC and TaC (G5TMCs), were successfully prepared through a novel sol-gel method using 4,5-dicyanoimidazole as carbon source and different metal precursors. The use of metal alkoxide as metal precursor resulted in the preparation of bulk G5TMCs with a smaller crystallite size compared to those obtained when metal chloride was used. Moreover, for metal alkoxide precursors, a decrease of the crystallite size of G5TMCs was observed when the 4,5-dicyanoimidazole/metal precursor molar ratio (R) was increased. An increase of temperature of treatment led to a higher crystallite size of the G5TMCs.

Using the sol-gel method developed in this work, in the presence of the corresponding support, G5TMCs supported over γ -Al₂O₃, TiO₂, SBA-15, SiO₂, CeO₂, ZrO₂ and activated carbon (AC) were effectively prepared. Supported VC_x catalysts with different crystallite size were obtained as a function of the support and/or the method of preparation used. For Al₂O₃-, SiO₂- and AC-supported catalysts, the VC_x crystallite sizes were similar to that of the corresponding bulk catalyst.

Vanadium carbide catalysts were active in the RWGS reaction under the conditions used in this work (CO₂/H₂=1/3, T=573-873K), meanwhile niobium and tantalum carbides were not.

The CO₂ adsorption on the G5TMC proceeds via dissociation into CO+O; this process occurs in much lesser extension over niobium and tantalum carbides.

The characteristics of vanadium carbide catalysts were related with their catalytic behavior in the light of theoretical studies performed under a collaborative work. The presence of a carbon deficient phase (V₈C₇) is related with a higher CO₂ adsorption heat and a better catalytic behavior in the RWGS, which are shown by catalysts with a smaller VC_x crystallite size.

VC-2, prepared using VO(isopropoxide)₃ and R=1.35, showed a crystallite size of 8 nm and a major presence of V₈C₇. For VC-1, which was prepared using VOCl₃ and R=1, a crystallite size of 64 nm and a major presence of stoichiometric VC was determined. CO₂ adsorption heats on VC-2 and VC-1 were -52.5 and -24.4 kJ mol⁻¹, respectively. The presence of a higher amount of C vacancies in

VC-2 is also related with its lower apparent activation energy (E_a) for CO production; E_a values in the 723-873 K range were 53.4 ± 3.8 and 76.5 ± 4.0 kJ mol⁻¹ for VC-2 and VC-1, respectively. The CO selectivity over VC-2 was near 100 % above 673 K (CO₂ conversion values of 4% at 673 K and 44% at 873 K).

All supported vanadium carbide catalysts showed a higher CO production per loaded V than the corresponding bulk catalyst. The catalytic behavior of the different supported catalysts seems to be mainly related to the VC_x characteristics. Among the supported vanadium carbide catalysts, those supported on Al₂O₃, SiO₂ and AC, having a VC_x crystallite size in the 9-11 nm range, showed the highest CO production values above 673 K referred to V mol.

Post-reaction bulk and supported vanadium carbide catalysts showed a similar crystallite size of VC_x compared to the fresh catalysts. After reaction, the presence of surface vanadium carbide species was still evidenced. Long-term catalytic tests (4 days) carried out over VC-2 and VC-2/Al₂O₃ indicated a high stability of these systems.

Under MSR reaction conditions (CH₃OH/H₂O=1/1, T=573-723K), vanadium carbide-based catalysts mainly produced CH₄, which is related with methanol decomposition. For niobium and tantalum carbide catalysts, the methanol dehydrogenation to HCHO is proposed to be the main reaction pathway. All catalysts presented high deactivation under the MSR conditions used. The crystallite size of the post reaction G5TMCs remained similar to that of the corresponding fresh catalyst and crystalline metal oxides were not detected. However, a significant increase of the amount of surface oxy-vanadium species, a high S_{BET} area reduction and the presence of abundant carbon deposits were determined after MSR catalytic tests.

ANNEXES

Annex I: Preparation and characterization of Mo_xC and WC_{1-x} catalysts

Molybdenum Carbide

For the preparation of Mo_xC (1 g), the corresponding amounts of MoCl_5 and 4,5-dicyanoimidazole were added under stirring to 15 mL of ethanol under a flow of Ar to avoid hydrolyzation of the metal precursor. Then, ethanol was evaporated forming a gel, which was placed into a tubular furnace and treated under Ar flow for 5 h at the set temperature (2.5 K min^{-1}).

The preparation of different phases of molybdenum carbide has been carried out using different 4,5-dicyanoimidazole/ MoCl_5 molar ratio (R) and varying the treatment temperature ($T=973, 1073, 1173 \text{ K}$ and 1373 K).

When the preparation was performed using a $R=0.5$, the XRD patterns of the resulting samples (Figure AI.1) indicate the presence of different Mo_xC phases with different crystallinity degree as a function of the temperature of treatment. Peaks corresponding to hexagonal Mo_2C (JCPDS 35-0787) and cubic MoC (JCPDS 03-065-0280) were observed with crystallite sizes of 10 and 4 nm, respectively when $T=973 \text{ K}$. Only diffraction peaks corresponding to hexagonal Mo_2C phase with high crystallinity were observed when the treatment temperature was carried out up to 1073 K and 1173 K , the crystallite sizes were 23 and 31 nm, respectively.

On the other hand, a sample prepared using $R=1$ and a $T=1373 \text{ K}$ only showed peaks characteristics of the cubic MoC phase with a crystallite size of 4 nm (Figure AI.1).

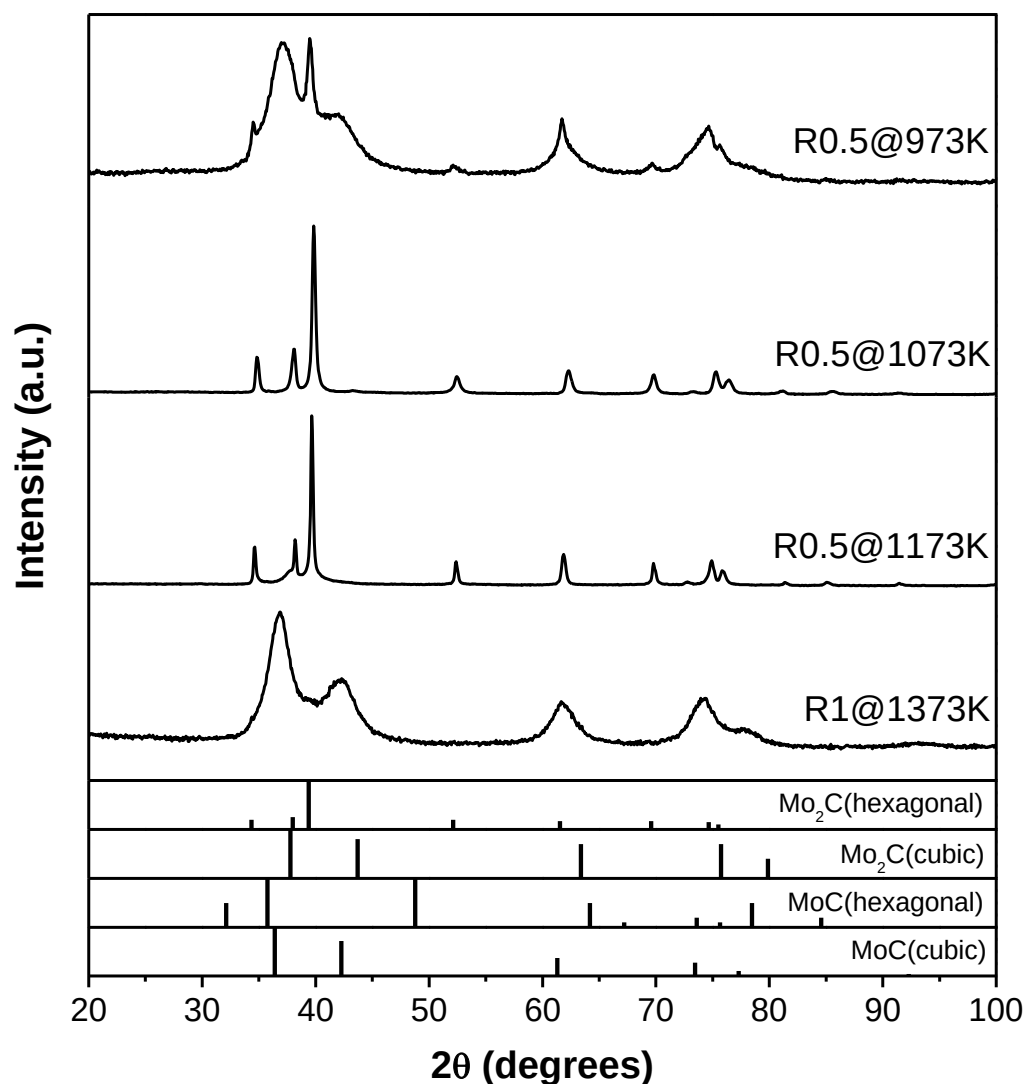


Figure A1.1. XRD patterns of Mo_xC samples prepared using MoCl_5 , different 4,5 dicyanoimidazole/ MoCl_5 molar ratios (R) and treatment temperatures. (They are indicated in the name of samples).

Tungsten Carbide

For the preparation of cubic WC_{1-x} (1 g), the corresponding amounts of WCl_6 and 4,5-dicyanoimidazole were added under stirring to 15 mL of ethanol using a 4,5-dicyanoimidazole/ WCl_6 molar ratio of $R=1$. The procedure was performed under a flow of Ar to avoid hydrolyzation of the metal precursor. Then, ethanol was evaporated forming a gel, which was placed into a tubular furnace and treated under Ar flow up to 1073 K (2.5 K min^{-1}) for 5 h.

The XRD pattern (Figure Al.2) shows the presence of cubic WC_{1-x} phase (JCPDS 20-1316) with a crystallite size of 2.4 nm.

Additionally, WC_{1-x} was deposited onto commercial TiO_2 containing anatase (A) and rutile (R) (A/R=78/22% wt/wt) by sonication. TiO_2 was prior separately treated at 1073 K under Ar flow for 4 h. For the preparation of WC_{1-x}/TiO_2 (~1%wt W), cubic WC_{1-x} (0.03 g) was sonicated in hexane (150 mL) in the presence of TiO_2 (2.97 g) at room temperature for 1h under N_2 , using a high-intensity ultrasonic device (20 kHz, 50% amplitude, Sonics VCX-750). Then, the suspension was dried under N_2 at 323 K overnight.

XRD pattern of WC_{1-x}/TiO_2 (Figure Al.2) shows only peaks characteristics of anatase (JCPDS 21-1272) and rutile TiO_2 (JCPDS 01-076-0317). The A/R ratio was 8/92% wt/wt; the crystallite size of A and R in WC_{1-x}/TiO_2 was 60 and 59 nm, respectively. The absence of peaks corresponding to tungsten carbide phases in the XRD pattern of WC_{1-x}/TiO_2 could be reasonably due to the low amount of tungsten carbide in the material.

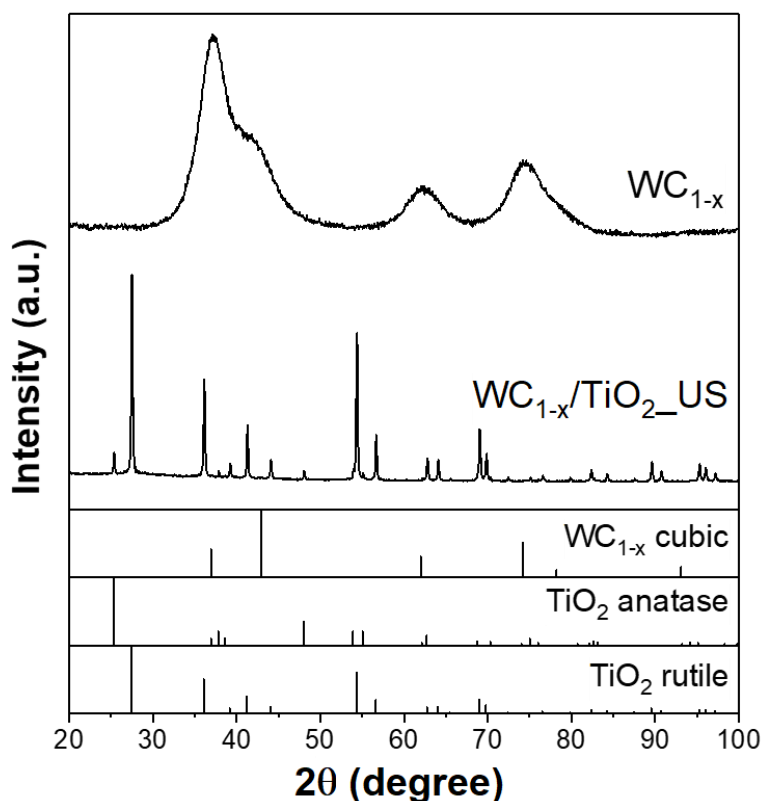


Figure Al.2. XRD patterns of bulk WC_{1-x} and WC_{1-x}/TiO_2 .

Figure Al.3 shows SEM images and the EDX mapping of WC_{1-x}/TiO_2 . A homogeneous distribution of W is observed with a W loading of 0.4% wt/wt determined by EDX. TEM and HRTEM analysis displayed the presence of small particles (2-5 nm) of cubic WC_{1-x} in WC_{1-x}/TiO_2 (Figure Al.4). A d-spacing of 0.242 nm was measured for the particles which corresponds to the (111) facet of cubic WC_{1-x} phase (Figure Al.4).

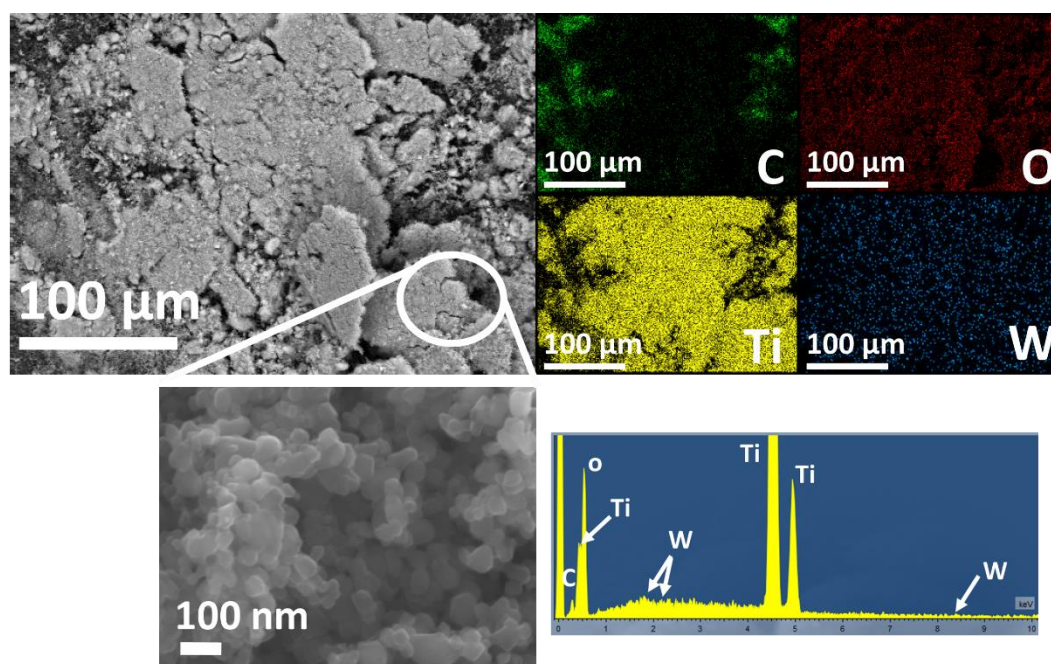


Figure Al.3. SEM images and EDX mapping of WC_{1-x}/TiO_2 .

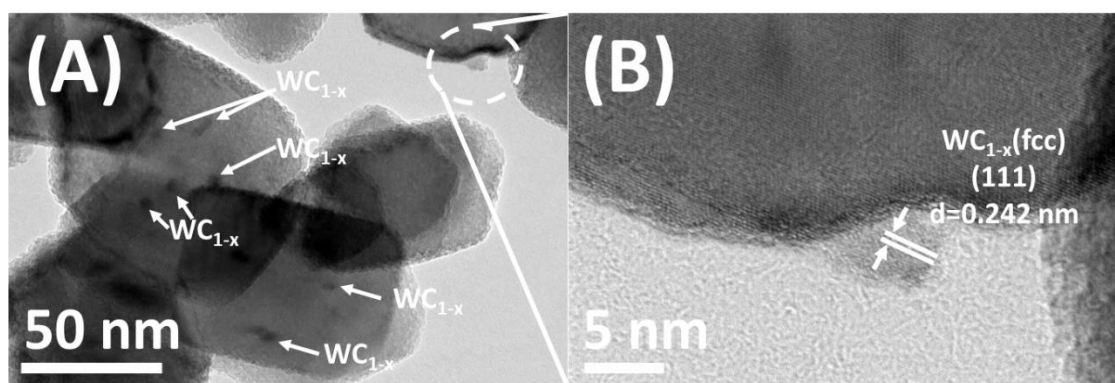


Figure Al.4. TEM (A) and HRTEM (B) images of WC_{1-x}/TiO_2 .

Annex II: Preparation details of G5TMC used as catalysts in the RWGS and MSR reaction

Preparation of bulk G5TMC catalysts

For the preparation of 1 g of bulk G5TMC (VC, NbC and TaC), an appropriate amount of 4,5-dicyanoimidazole was added, under Ar flow and stirring, to 15 mL of alcoholic solution (methanol or ethanol) containing the corresponding amount of metal precursor. Then alcohol was evaporated forming a gel, which was placed into a tubular furnace for thermal treatment to the set temperature (for 5h at 2.5 K min⁻¹). The details for the preparation of the catalysts are described in Table AII.1.

Table AII.1. *Synthesis conditions of G5TMC used as catalysts in the RWGS and MSR.*

Catalyst	Metal Precursor	Solvent	R ⁽¹⁾	Temperature (K)
VC-1	VOCl ₃	Ethanol	1	1373
VC-2	VO(isopropoxide) ₃	Ethanol	1.35	1373
VC-1_1623	VC-1 treated up to 1623 K			
VC-3	VO(isopropoxide) ₃	Ethanol	1	1373
NbC-1	Nb(OC ₂ H ₅) ₅	Ethanol	1	1473
NbC-2	NbCl ₅	Ethanol	2	1373
TaC-1	TaCl ₅	Methanol	1.75	1473
TaC-2	TaCl ₅	Methanol	3	1423

⁽¹⁾R:4,5-dicyanoimidazole/metal precursor molar ratio.

Preparation of supported G5TMC catalysts

For the preparation of about 3 g of supported G5TMC catalysts with ~25%wt of G5TMC loading, 2.25 g of the corresponding support, was immersed into 50 mL of alcohol solution by forming a suspension. Then the solution containing the appropriate amounts of metal precursor and 4,5-dicyanoimidazole was added to the suspension. The 4,5-dicyanoimidazole/metal precursor molar ratio was the same used for bulk G5TMC preparation listed in Table AII.1. The mixture was kept under continuous stirring and the excess of ethanol or methanol was evaporated at room temperature until obtaining a solid. All the procedure was performed under inert atmosphere to avoid hydrolyzation of metal precursor. The thermal treatment was the same used for bulk G5TMC preparation (Table AII.1).

Annex III: XPS profiles of supported VC used as catalysts in the RWGS reaction

The XPS profiles corresponding to O *1s*, Al *2p*, Si *2p*, Ce *3d*, Ti *2p* and Zr *3d* levels of the supported VC catalysts (VC-3/Al₂O₃ (Figure AIII.1), VC-3/SiO₂ (Figure AIII.2), VC-3/SBA-15 (Figure AIII.3), VC-3/AC (Figure AIII.4), VC-3/CeO₂ (Figure AIII.5), VC-3/TiO₂ (Figure AIII.6) and VC-3/ZrO₂ (Figure AIII.7)) described in Chapter 4-Section 4.2 are shown below.

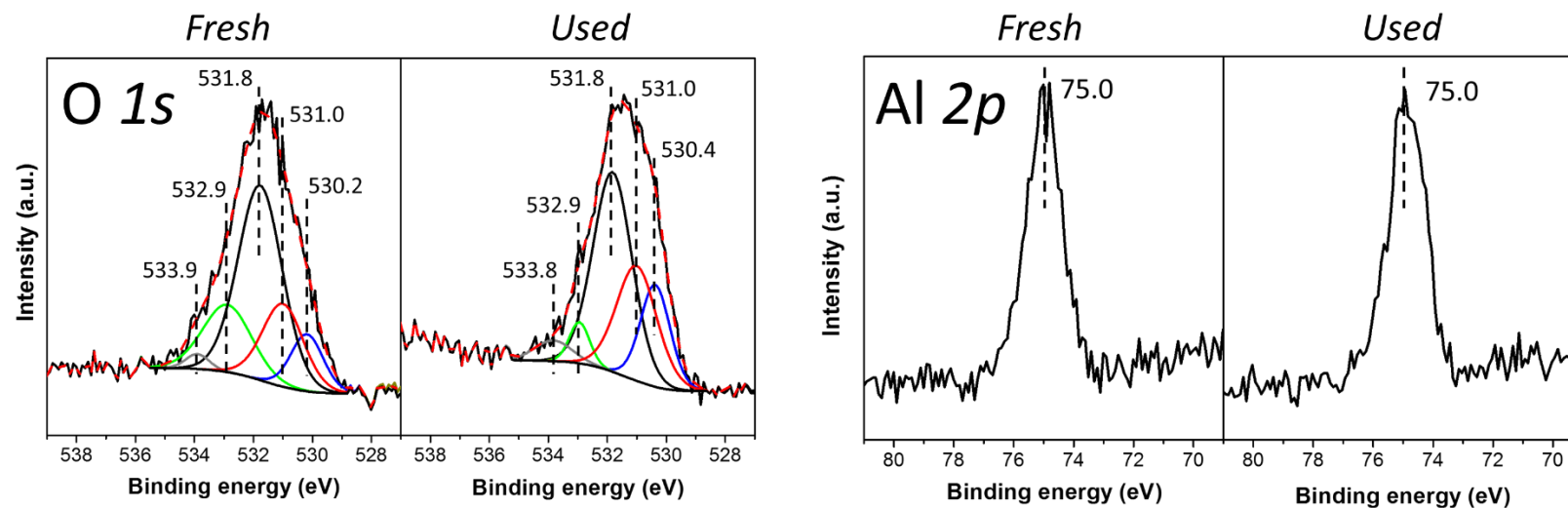


Figure AIII.1. O 1s and Al 2p XPS profiles of fresh and used VC-3/Al₂O₃ catalyst.

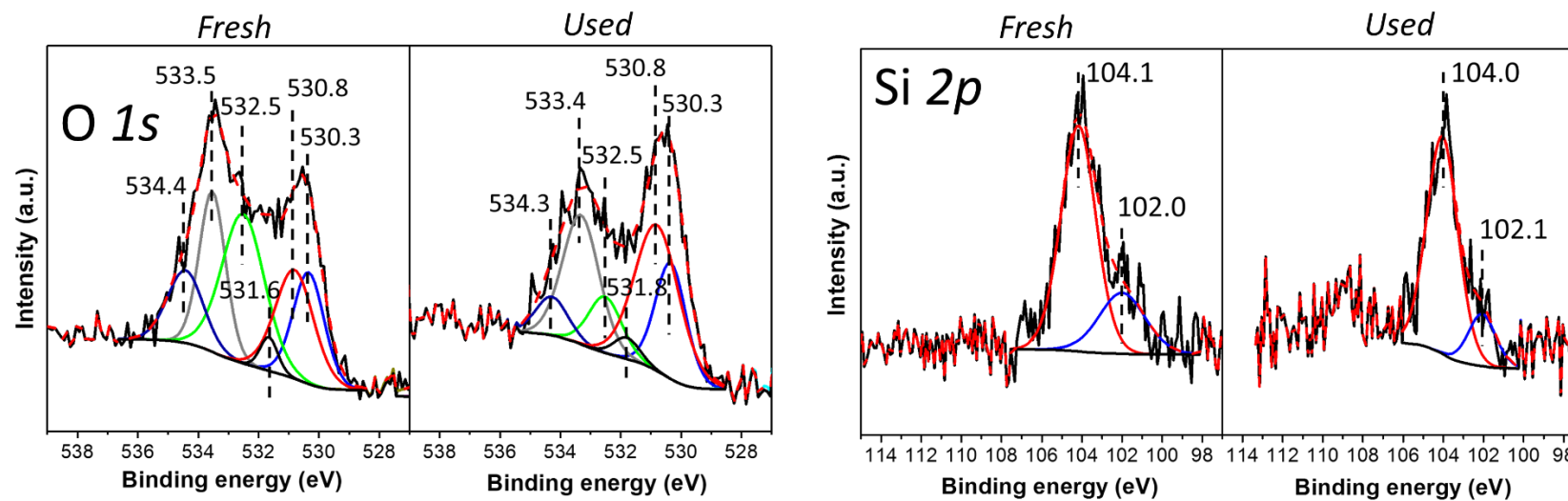


Figure AIII.2. O 1s and Si 2p XPS profiles of fresh and used VC-3/SiO₂ catalyst.

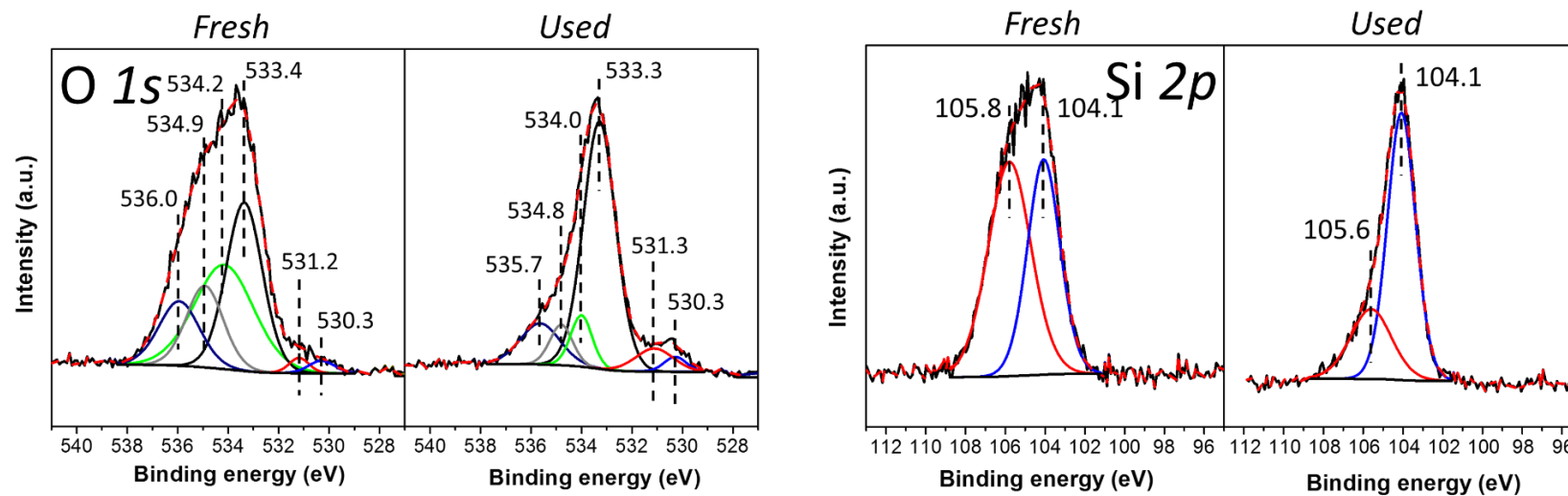


Figure AIII.3. O 1s and Si 2p XPS profiles of fresh and used VC-3/SBA-15 catalyst.

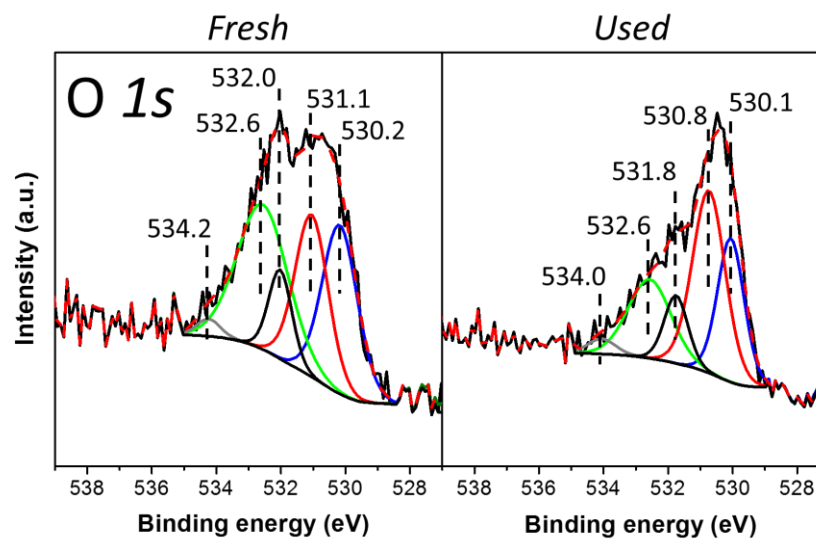


Figure AIII.4. O 1s XPS profile of fresh and used VC-3/AC catalyst.

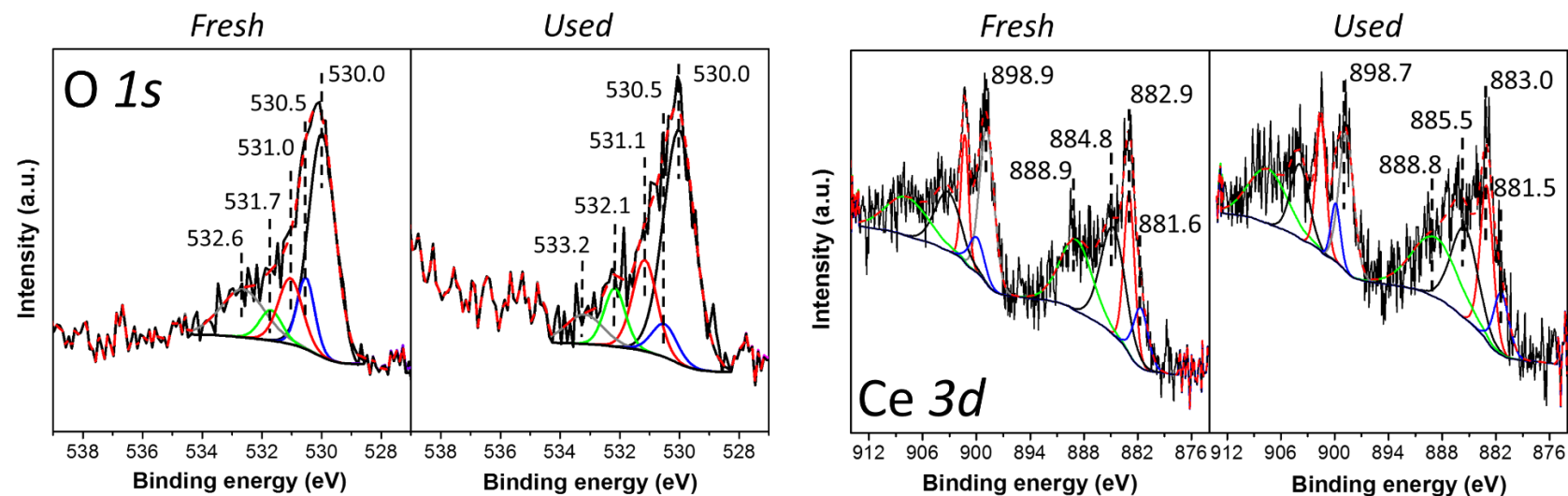


Figure AIII.5. O 1s and Ce 3d XPS profiles of fresh and used VC-3/CeO₂ catalyst.

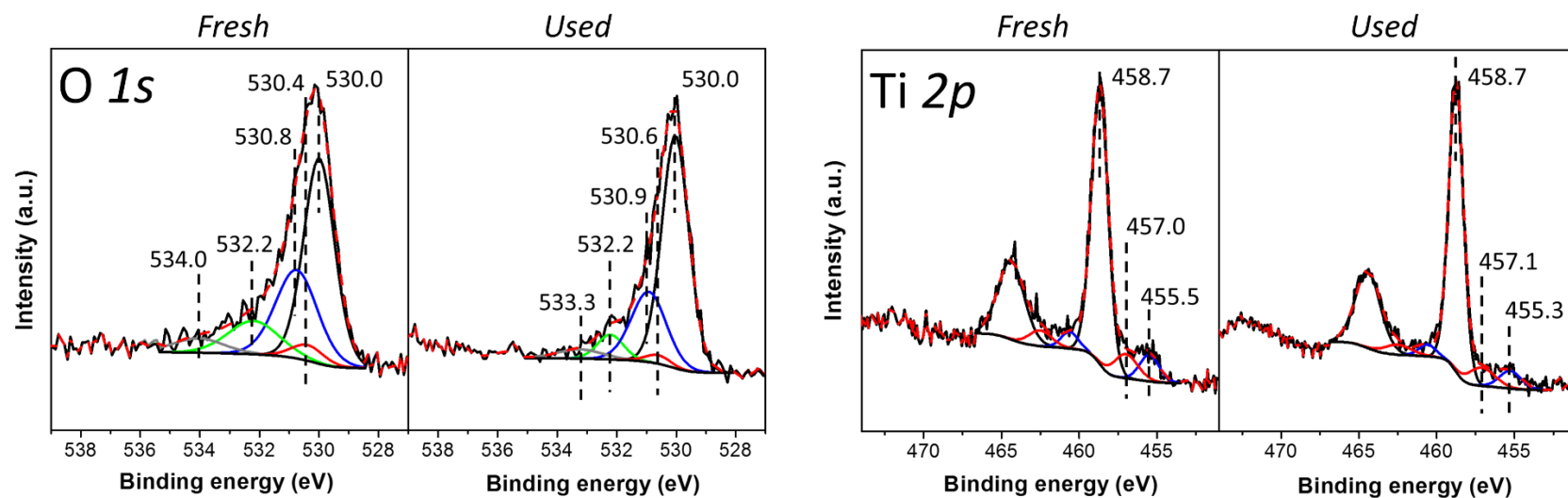


Figure AIII.6. O 1s and Ti 2p XPS profiles of fresh and used VC-3/TiO₂ catalyst.

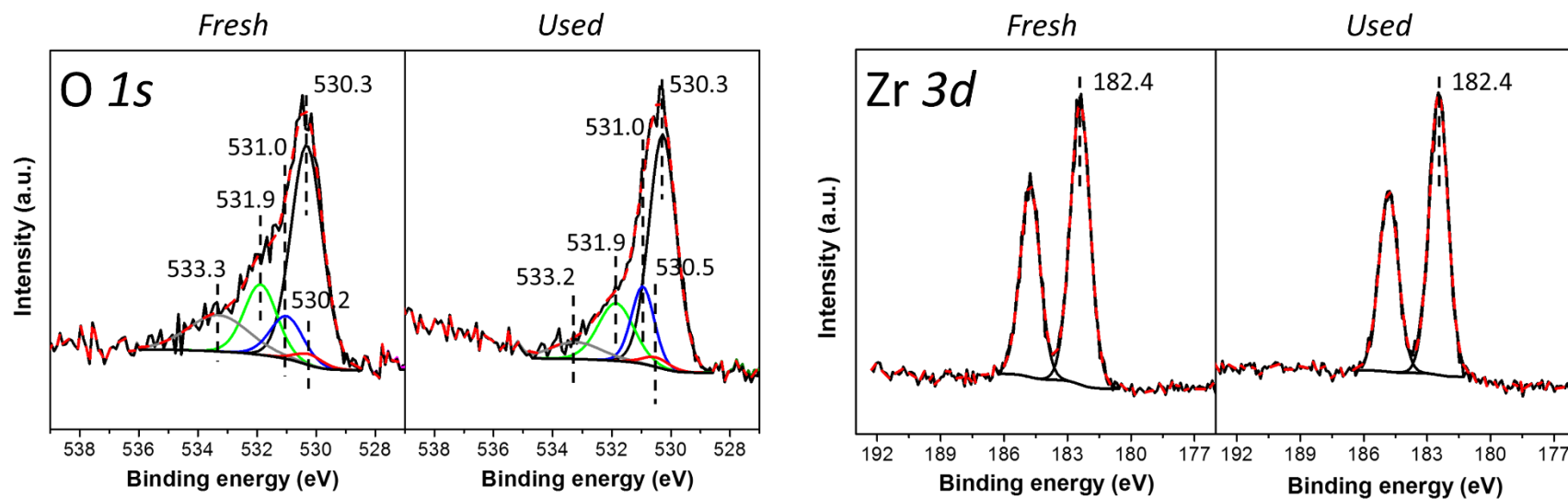


Figure AIII.7. O 1s and Zr 3d XPS profiles of fresh and used VC-3/ZrO₂ catalyst.

For VC-3/ Al_2O_3 , the band at 75 eV in the Al 2*p* spectrum (Figure AIII.1) corresponds to Al_2O_3 [1,2].

In Figures AIII.2 and AIII.3, the presence of the band at 104.1 eV in the Si 2*p* level spectra of VC-3/ SiO_2 and VC-3/SBA-15 is associated to Si-OH bond [3-5]. Additionally, the component at 102.0 eV in Si 2*p* level spectrum in VC-3/ SiO_2 indicates that some vanadium cations bind to the SiO_2 forming Si-O-V [3]. The component at 105.8 eV in VC-3/SBA-15 is associated to Si-O-Si bonds [4,5] (Figure AIII.3).

The Ce 3*d* spectrum is rather complex due to the coexistence of different final states and unclear peaks are observed at different binding energies. The nomenclature of peaks was followed according to literature [6,7] whereby considering the coexistence of Ce^{3+} and Ce^{4+} species, two doublets ($3d_{5/2}=\nu^0, \nu'$ and $3d_{3/2}=w^0, w'$) can be associated to Ce_2O_3 and three doublets ($3d_{5/2}=\nu, \nu'', \nu'''$ and $3d_{3/2}=w, w'', w'''$) to CeO_2 . The corresponding Ce 3*d* XP spectrum of VC-3/ CeO_2 is shown in Figure AIII.5. The presence of Ce^{3+} and Ce^{4+} can be determined from the components at $\nu^0=881.6$ eV and $\nu=882.9$ eV, respectively [6,7].

Figure AIII.6 shows the Ti 2*p* XP spectrum of VC-3/ TiO_2 , in which the most intense Ti 2*p*_{3/2} peak at 458.7 eV is associated to TiO_2 , and the observation of low intensity components at lower BE (457.0 and 455.5 eV) points out the presence of $\text{Ti}^{n<4+}$ species [8,9].

For VC-3/ ZrO_2 , the Zr 3*d*_{5/2} band at 182.4 eV in the Zr 3*d* level spectrum is assigned to ZrO_2 (Figure AIII.7) [10].

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