Photocatalytic H_2 production from ethanol aqueous solution using TiO_2 with tungsten carbide nanoparticles as co-catalyst

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Abstract

The effect of tungsten carbide as co-catalyst in the photocatalytic H_2 production from ethanol aqueous solutions (25% v/v) is reported. The photocatalytic H_2 production using WC/TiO_2 (1% wt WC), in which tungsten carbide NPs are dispersed onto TiO_2, is compared with that of $TiO_2$800 with morphological and structural characteristics similar to WC/TiO_2 and with the hydrogen produced using commercial TiO_2 P25 as reference. The preparation of WC/TiO_2 was accomplished by using a sol-gel based method which was useful for preparing bulk tungsten carbides. Materials were characterized using N_2 physisorption, XRD, SEM-EDX, TEM, UV-vis RDS, XP and Raman spectroscopy. The presence of 2-3 nm NPs with different tungsten carbide crystalline phases (hexagonal WC and W_2C and cubic WC_{1-x}) onto TiO_2, containing anatase and rutile, was determined.

The presence of tungsten carbide NPs onto TiO_2 improves the photocatalytic behavior of TiO_2 in terms of hydrogen production. The effect of WC_x NPs in the C2-C4 products derived from ethanol is discussed and the reusability of the photocatalyst is also studied.

Keywords: *photocatalytic H_2; WC co-catalyst; WC/TiO_2 photocatalyst; H_2 photoproduction; ethanol photooxidation.*

Introduction

Hydrogen is an ideal carbon-free energy carrier, which production from renewable feedstocks merits to be implemented. Biomass-derived alcohols can be considered an efficient mean to store hydrogen in a form that is easy to handle and transport. Thus, bio-alcohols have been largely investigated as alternative renewable feedstock for H_2 production using catalytic reforming technology [1-3]. Nowadays, ethanol is the biofuel worldwide produced in the greatest amount; most of ethanol is produced from crops, mainly corn and sugarcane. However, new policy and programs in different countries are promoting the construction of new plants, using urban solid residues or lignocellulosic materials for bio-ethanol production, bringing the possibility of a more sustainable approach than the traditional processes [4].

From an environmental point of view, the photocatalytic transformation of bioethanol aqueous solutions could be a suitable method for H_2 production [5-8]. The appropriate photo-irradiation of a semiconductor-based photocatalyst promotes an electron from the valence band to the conduction band of the semiconductor. The photo-generated charges, hole (h^+) and electron (e^-), can move to the surface [9], then, adsorbed organic species could be oxidized by the h^+ or hole-related species [6,10-12], meanwhile H_2 is formed from H^+ reduction in the media [6, 13]. The ethanol oxidation process takes place in different steps and could be adjusted avoiding the CO_2 formation. Thus, besides H_2, other C2-C4 valuable products such as acetaldehyde, 2,3-butanediol or acetone can be rendered [10, 11].

The photocatalytic transformation of ethanol$_{(aq)}$ has been studied mainly using a semiconductor, with a noble metal as co-catalyst, Pt/TiO_2 being one of the most

studied systems. Pt nanoparticles (NPs) favor the electron transport, being sinks of electrons and contributing to the charge separation throughout the interface. Different approaches for the metallic phase or TiO_2 modification in order to improve the photocatalytic behavior have been reported [14-16]. However, the price and scarcity of noble metals have led to proposing alternative catalytic materials in different reactions in which noble metal-based catalysts are usually used. Several transition metal carbides (TMCs) exhibit metallic characteristics and since pioneering work on WC, showing its platinum-like catalytic properties [17], many studies have been carried using TMCs as catalysts in different processes [18-20]. Specifically, WC has electronic properties and density of states close to those of Pt [21, 22] and it has been largely studied in new electrocatalytic systems [23-28]. WC has been also proposed for replacing Pt in different photocatalytic reactions such as water splitting and photocatalytic degradation of organics [29-32]. A limited number of papers deals with the use of WC as co-catalyst for the photocatalytic H_2 generation from H_2O; the role of WC onto CdS and g-C_3N_4 has been studied using h^+ scavengers such as lactic acid, Na_2S/Na_2SO_3 or TEOA [32-35]. However, the use of those sacrificial agents can lead to byproducts, which are not usually studied. An early paper has reported the activity of a commercial TiO_2 (anatase) powder grinded with WC for the photocatalytic hydrogen production using an aqueous methanol solution [36].

In the present study, ethanol is used as h^+ scavenger because as stated above, it is derived from biomass and has a renewable character. Moreover, selective ethanol photo-transformation, can result in forming C2-C4 valuable products such as acetaldehyde, 2,3-butanediol or acetone. Here, the use of tungsten carbide NPs as co-catalyst onto TiO_2 in the photocatalytic H_2 evolution using 25% v/v

aqueous solutions of ethanol is studied. For a better understanding of the overall photocatalytic process, the products coming from the ethanol oxidation were also determined and the O_2 evolution analyzed. For this end, a photocatalyst composed of WC NPs onto TiO_2 was prepared, characterized and tested in the photocatalytic reaction. The photocatalytic behavior of WC/TiO_2 is compared to that of WC-free TiO_2. The amount of H_2 produced using WC/TiO_2, is higher than that yielded using WC-free TiO_2. This accords with the role of WC as co-catalyst in the photocatalytic H_2 generation onto TiO_2. The preparation of WC/TiO_2, was based on a method useful for preparing bulk WC, this method allowed obtaining well dispersed nanoparticles of WC_x on TiO_2.

Materials and Methods

Catalyst preparation and characterization

For the preparation of WC, a sol-gel method based on urea glass route was used [37]. Specifically, a 5% wt/v tungsten (IV) isopropoxide solution (20 mL) and 2.29 g of urea were added to 42 mL of ethanol. After total dissolution, the system was stirred under Ar flow for 4 h and then, the solvent was evaporated in an oven at 343 K for 16 h. After that, the solid was placed in a quartz tube and heated (2 K/min) under Ar flow up to 1073 K for 3 hours. Finally, the solid was cooled down to room temperature under Ar flow and the lustrous black powder material was transferred without passivation and stored.

The 1% wt WC/TiO_2 photocatalyst was obtained following a similar procedure but in the presence of commercial TiO_2 (Tecnan, S_{BET}= 117 m^2g^{-1}, anatase/rutile= 78/22% wt/wt). 1.2 mL of 5% wt/v tungsten (IV) isopropoxide in isopropanol were mixed with 4.5 mL of ethanol and 0.14 g of urea under Ar flow. After dissolution,

a suspension of 2.0 g of TiO_2 in 25 mL of ethanol was added. The mixture was maintained with continuous stirring for 4 h, placed in an oven at 343 K for 16 hours and finally, treated up to 1073 K using the experimental procedure described above for the bulk WC preparation. A dull greyish solid was obtained in this case. For comparative purposes, the commercial TiO_2 used in the preparation of WC/TiO_2 was treated at 1073 K under Ar flow for 4 h, this sample labelled TiO_2800 was characterized and tested. Moreover, the photocatalytic hydrogen production was determined using commercial TiO_2 P25, which is usually used as a standard material in photocatalytic studies [38].

The Brunauer-Emmett-Teller specific surface area (S_{BET}) of the samples was calculated from the nitrogen adsorption-desorption isotherms, the Barret-Joyner-Halender (BJH) method was used for determining the pore size distribution; experiments were carried out using a Micromeritics TriStar II 3020 apparatus. The X-ray diffraction (XRD) patterns were acquired from 20 to 100º with a step of 0.017º using a PAMalytical X'Pert PRO MPD Alpha 1 powder diffractometer; Cu Kα1 radiation (λ = 1.5406 Å) was employed. The crystallite sizes of anatase and rutile were calculated using the Scherrer equation. The weight percentage of rutile in the samples was determined from (110) R and (101) A diffraction peaks [39].

The morphology of the samples was analysed using a field emission scanning electron microscope (FESEM), JEOL J-7100F, operating at 20 kV. The FESEM was coupled with an X-ray analysis system (Oxford Instruments) which allowed acquire energy-dispersive X-ray (EDX) spectra and elemental mapping.

A JEOL JEM-2010 SON transmission electron microscope (TEM) operating at 200 kV was used for obtaining TEM and high resolution TEM (HRTEM) images. For the study, ethanol dispersions of samples on copper grids were used.

The Raman spectra were obtained using a Jobin-Yvon LabRaman HR 800 instrument with a CCD detector and a 532 nm laser at 1.5 mW.

UV-vis diffuse reflectance spectra were acquire using a Perkin Elmer Lambda 950 spectrometer. The Kubelka-Munk formalism was applied, and the band-gap values were calculated through the Tauc plot $(F(R_\infty)\bullet h\upsilon)^n$ versus $h\upsilon$, assuming an indirect allowed transition, n=1/2 [40].

The characterization by X-ray photoelectron spectroscopy (XPS) was performed using a Perkin Elmer PHI-5500 Multitechnique System with a hemispherical electron energy analyser and a 1486.6 eV Al Kα radiation. The adventitious C 1s peak at 284.8 eV was taken as reference of binding energy values. Deconvolution of XPS peaks were done using the CasaXPS software keeping symmetric Gaussian (70%)-Lorentzian (30%) functions.

Photocatalytic tests

The setup used in the photocatalytic tests, including the analysis system has been described elsewhere [10, 11]. In brief, the tests were carried out at atmospheric pressure in a jacketed reactor of 300 mL capacity designed for continuous gas flow operation and equipped with a condenser (kept at 258 K) at the outlet. A UV-visible 175 W Hg lamp (broad-spectrum lamp, maximum power of 25.6 W at λ= 366 nm), placed inside the reactor in a water-cooled jacket was used. Before the photocatalytic reaction, the catalysts were degassed under vacuum at 373 K for 12 h, and then transferred directly to the photoreactor. 500

mg of catalyst and 250 mL of an ethanol$_{(aq)}$ (25% v/v) solution previously purged with Ar, were used. Before irradiation, the suspension was stirred for 30 min under Ar flow, then the system was irradiated and kept at 298 K. The gases evolving from the reactor were analyzed in dark conditions before starting and at the end of the photocatalytic test; H_2 was not produced in any case in dark conditions. After 10 min of light on, the evolved gaseous products were periodically sampled and on-line analyzed. The gaseous products were analyzed on-line using a gas micro-chromatograph Varian CP-4900 equipped with micro-TCD detectors and two columns. The CO_2 and hydrocarbon analysis was carried out using a PPQ (10 m) column and He as carrier gas. For H_2, O_2, N_2 and CO analysis (detection limit for H_2, 50 ppm), a molecular sieve (5Å, 10 m) column and Ar carrier gas were used. The liquid products were separately analyzed by gas chromatography at the end of the photocatalytic test (4 h) in a Bruker 450 GC equipment with FID detector and a CP-Sil 8 CB (30 m x 0.25 mm) capillary column.

The reusability of WC/TiO_2 was studied after separation of the used catalyst by filtration. New photocatalytic tests were carried out with 170 mg of the used and fresh catalysts.

Results and discussion

As stated in the introduction and experimental sections, bulk WC was prepared using a sol-gel based method with urea. This method was also used in the presence of commercial TiO_2 for the preparation of WC/TiO_2, in which the co-catalyst WC is incorporated onto TiO_2. For comparative purposes, a sample of commercial TiO_2 was treated at 1073 K ($TiO_2$800) which is the temperature used

in the preparation of WC/TiO_2. Table 1 shows some characteristics of the materials prepared. BET surface area of WC/TiO_2 (11 m^2g^{-1}) was only slightly lower than that of TiO_2800 (15 m^2g^{-1}). Both, WC/TiO_2 and TiO_2800 were mesoporous materials with mean pore width of 24 and 32 nm, respectively.

Figure 1 shows the XRD patterns of WC, WC/TiO_2 and TiO_2800. For WC, the presence of tungsten carbides with poor crystallinity can be inferred; the presence of hexagonal WC (JCPDS 00-051-0939) and W_2C (JCPDS 00-035-0776) and cubic WC_{1-x} (JCPDS 00-020-1316) can be reasonably proposed. XRD patterns of WC/TiO_2 and TiO_2800 were very similar, only peaks characteristics of anatase (A) (JCPDS 00-021-1272) and rutile (R) TiO_2 (JCPDS 01-076-0317) were present. In both cases, the A/R ratio was 8/92% wt/wt; the crystallite size of A and R in WC/TiO_2 and TiO_2800, was 99, 60 (A) and 60, 59 (R) nm, respectively (Table 1). The absence of peaks characteristics of crystalline carbide phases in the XRD pattern of WC/TiO_2 could be probably due to the low amount of tungsten carbide in the material. Figure 2 shows a SEM image of WC/TiO_2 and the corresponding EDX mapping, which showed, as expected, the presence of Ti, O, W and C in the sample. EDX analysis of different zones pointed to a W content of about 1% wt. In order to confirm the presence of crystalline WC in WC/TiO_2, this sample was analyzed by TEM. TEM images of WC/TiO_2 (Figure 3A and 3B) show particles with a mean size of 2.3 nm (inset in Figure 3C) well dispersed onto TiO_2. HRTEM analysis of different tungsten carbide particles allowed to identify different planes of the W_2C, WC and WC_{1-x} phases (Figure 3C and 3D). Although the presence of crystalline tungsten oxides in WC and WC/TiO_2 could not be determined by XRD nor HRTEM, both samples were analyzed by Raman (Figure 4) to identify surface WO_x species that could be formed when materials were

exposed to air [41]. Raman spectrum of WC show bands characteristics of WO_3: the bands at 805 and 709 cm^{-1} correspond to W-O stretching modes, those at 325 and 265 cm^{-1} to W-O-W bending modes and the bands below 200 cm^{-1} are assigned to lattice vibrations [42, 43]. According with XRD results, Raman spectrum of $TiO_2$800 shows bands related with the presence of anatase (bands at 142, 198, 398, 514 and 636 cm^{-1}) and rutile (bands at 236, 445 and 610 cm^{-1}) [44, 45]. The Raman spectrum of WC/TiO_2 is very similar to that of $TiO_2$800, indicating also the only presence of anatase and rutile; for WC/TiO_2, bands related with the presence of tungsten oxides were not found. A zoom of the 1200-1700 cm^{-1} zone in the spectra of WC and WC/TiO_2 allows to see two low intensity bands with maximum at 1350 and 1600 cm^{-1} (D and G bands), which can be related with the presence of a low amount of carbonaceous residues. The band-gap values determined from UV-vis DRS and using the Kubelka-Munk formalism (Figure S1) for WC/TiO_2 and $TiO_2$800 were 2.85 and 2.87 respectively, slightly lower than that expected for pure rutile (3.00 eV) [46, 47].

WC and WC/TiO_2 were analyzed by XPS; W 4f, W 4d, C1s, N 1s, Ti 2p and O 1s core level spectra were registered. For WC, the analysis of W 4f spectrum pointed out the presence of surface WC (W $4f_{7/2}$ = 32.6 eV) and WO_3 (W $4f_{7/2}$ = 36.6 eV) (Figure S2) [47, 48], according with XRD and Raman results. Although the intensity of W 4d is lower than that of W 4f, for WC/TiO_2, the W 4d (Figure 5) core level spectrum was analyzed because the overlapping of W 4f and Ti 3p levels. The W 4d peaks were deconvoluted into three doublets W $4d_{5/2}$:W $4d_{3/2}$, keeping an intensity ratio W $4d_{5/2}$:W $4d_{3/2}$=3:2 and a spin-orbital splitting of 13 eV [49]. The W $4d_{5/2}$ component at 244.2 eV can be reasonably assigned to the presence of surface tungsten carbide [48] and those at higher BE to different tungsten oxide

species (Figure 5A) [48, 50]. Figure 5A also displays the C 1s core level spectrum of WC/TiO_2, which shows a maximum at 284.8 eV, the component at 283.4 eV is associated to surface tungsten carbide species and those above 284.8 eV to different surface oxygen containing species [51, 52]. Peaks corresponding to N 1s core level were not found (Figure S2), indicating the absence of nitrogen-containing residues coming from the urea used in the preparation. From Ti 2p and O 1s spectra, Ti $2p_{3/2}$ BE of 458.7 eV and O 1s BE of 530.0 eV were found (Figure S2), which corresponded well to those expected for TiO_2.

For proving the influence of tungsten carbide nanoparticles in the photocatalytic transformation of $ethanol_{(aq)}$ (25% v/v) solutions onto TiO_2, commercial TiO_2 P25, $TiO_2$800 and WC/TiO_2 were tested. In all cases, H_2 was the main product obtained; O_2 was not detected in any case. Figure 6 shows that the amount of H_2 produced and the rate of production along 4 hours of catalytic test is higher for WC/TiO_2 than for $TiO_2$800 or commercial TiO_2 P25. A clear improvement in the H_2 production is observed when WC nanoparticles are dispersed onto TiO_2 surface, indicating the role of WC as co-catalyst in this system. Besides H_2, carbon-containing products such CO, CO_2, CH_4, C_2H_4, C_2H_6 and acetaldehyde were also found in the gas phase. However, the amount of CO, CO_2, CH_4, C_2H_4 and C_2H_6 was much lower than that of H_2 (Table 2). As described in the experimental section, the liquid products were analyzed at the end of the catalytic test; acetaldehyde, acetone, 2,3-butanediol and a minor amount of acetal were found (Table 2). As stated above, the use of ethanol aqueous solutions brings the opportunity of producing simultaneously H_2 and valorized compounds coming from ethanol [11]. A first step of the photocatalytic transformation of $ethanol_{(aq)}$ over Pt/TiO_2 has been demonstrated to be acetaldehyde or 2,3-butanediol

formation [10, 11]. The reaction of ethanol with the hole on the surface of TiO_2 and the formation of α-hydroxyethyl radicals ($\bullet CH(OH)CH_3$) (eq. 1) has been proposed to be the first step for the acetaldehyde (eq. 2) and 2,3-butanediol formation (eq. 3):

$CH_3CH_2OH + h^+ \rightarrow \bullet CH(OH)CH_3 + H^+$ (1)

$\bullet CH(OH)CH_3 + h^+ \rightarrow CH_3CHO + H^+$ (2)

$2 \bullet CH(OH)CH_3 \rightarrow CH_3CH(OH)CH(OH)CH_3$ (3)

Then, the photogenerated e^-, could react with H^+ on the surface of Pt and H_2 would be formed. Similar reaction pathways can be reasonably proposed taking place when WC/TiO_2 is used. The small amounts of CO and methane found could be accounted for acetaldehyde decomposition. The addition of ethanol to acetaldehyde could be the responsible of acetal formation. Data in Table 2, indicate that using WC/TiO_2, a higher amount of acetone and a lower amount of 2,3-butanediol is formed than when $TiO_2$800 is used. The photocatalytic transformation of aqueous 2,3-butanediol or acetaldehyde solutions has been demonstrated that produces acetone when Pt/TiO_2 is used [10], these processes could be favored when WC_x nanoparticles are dispersed onto TiO_2 (Table 2). The used catalyst was characterized after the photocatalytic test by XPS (Figure 5B). The presence of W $4d_{5/2}$ component at 244.1 eV and C 1s at 283.3 eV indicates that tungsten carbide species remained on surface after the photocatalytic test. The new component of C 1s XP spectrum of used-catalyst at about 292 eV can be related to carbonate species [49].

In order to study the durability of WC/TiO_2, the used catalyst was separated by filtration and a new photocatalytic test was carried out (Figure 7). The used

catalyst showed a slightly lower H_2 production than the fresh one, 5696 $mmolg^{-1}$ vs. 6121 $mmolg^{-1}$ during 4 h of photocatalytic test.

Conclusions

A WC/TiO_2 photocatalyst containing well-dispersed tungsten carbide (2-3 nm NPs) onto TiO_2 was prepared using a method based on a sol-gel procedure appropriate for the preparation of bulk WC. Different tungsten carbide phases such as hexagonal WC and W_2C and cubic WC_{1-x} were identified in WC/TiO_2. The photocatalytic behavior for H_2 production from $ethanol_{aq}$ of WC/TiO_2 was compared with that of WC-free $TiO_2$800 and commercial TiO_2 P25 as reference. WC_x NPs act as co-catalyst in the process; using WC/TiO_2, the amount of H_2 yielded during the photocatalytic test was more than a 40 % higher than when $TiO_2$800 or TiO_2(P25) were used. Besides H_2, acetaldehyde and 2,3-butanediol were obtained from primary ethanol oxidation; then acetone was produced, its formation likely favored by the presence of tungsten carbide NPs. Tungsten carbide species remained on surface of WC/TiO_2 after the photocatalytic test; the amount of H_2 produced with the reused WC/TiO_2 was kept above 93 % of that provided when the fresh sample was used.

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Legends to the Figures

Figure 1. XRD patterns of bulk WC, $TiO_2$800 and WC/TiO_2.

Figure 2. SEM image and EDX mapping of WC/TiO_2. On the bottom a representative EDX analysis.

Figure 3. TEM (A and B) and HRTEM (C and D) images of WC/TiO_2 sample. Particle size distribution (inset in C).

Figure 4. Raman spectra of WC, $TiO_2$800 and WC/TiO_2. On the right part zoom of the 1225-1625 cm^{-1} zone.

Figure 5. XP spectra of W 4d and C 1s core levels corresponding to WC/TiO_2: A) fresh catalyst; B) after the photocatalytic test.

Figure 6. Amount of H_2 produced and H_2 production rate (inset) along irradiation time for WC/TiO_2, $TiO_2$800 and TiO_2(P25) during the photocatalytic transformation of $ethanol_{aq}$ solution (25% v/v) at 298 K. 500 mg of catalysts were used in all cases.

Figure 7. Reusability of WC/TiO_2 catalyst. Comparison of H_2 produced along irradiation time for fresh and reused WC/TiO_2 during the photocatalytic transformation of $ethanol_{aq}$ solution (25% v/v) at 298 K. 170 mg of catalysts were used in both cases.