INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–7

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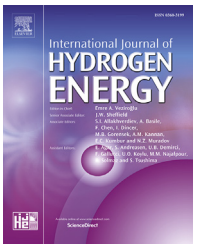

An *in-situ* DRIFTS-MS study of the photocatalytic H_2 production from ethanol$_{(aq)}$ vapour over Pt/TiO_2 and Pt–Ga/TiO_2 catalysts

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ARTICLE INFO

Article history:
Received 15 September 2017
Received in revised form
6 February 2018
Accepted 15 February 2018
Available online xxx

Keywords:
H_2 photoproduction
Renewable H_2
Pt–Ga/TiO_2 photocatalyst
In-situ DRIFTS
Photocatalytic H_2
Ethanol photoconversion

ABSTRACT

In this paper, Pt/TiO_2 and Pt–Ga/TiO_2 catalysts with similar Pt dispersion and similar structural and morphological characteristics were compared in the H_2 production from the phototransformation of aqueous solutions of ethanol. Catalysts were characterized by means of N_2 adsorption-desorption, XRD, Raman, H_2-TPR, UV–Vis diffuse reflectance spectroscopy, XPS and CO chemisorption. The photocatalytic reaction was carried out in liquid and vapour phase. The photocatalytic transformation of ethanol$_{(aq)}$ vapour over Pt/TiO_2 and Pt–Ga/TiO_2 catalysts was studied by in situ DRIFTS-MS. Differences in the photocatalytic transformation of ethanol$_{(aq)}$ over Pt/TiO_2 and Pt–Ga/TiO_2 were determined. The effect of Ga is analysed in the light of the evolution of surface species under photocatalytic reaction conditions.

Introduction

Since pioneer work of Sakata and Kawai [1], numerous studies have dealt with the photocatalytic hydrogen production using a metal-modified TiO_2 photocatalyst and ethanol-water solutions [2–7]. In particular, the photocatalytic production of H_2 from aqueous ethanol solutions over Pt/TiO_2 has been widely studied [8–12]. Ethanol, which is the sacrificial agent, is oxidized by photogenerated holes in TiO_2 and H_2 is produced by H^+ reduction at the surface of Pt nanoparticles [13,14]. The final product of ethanol oxidation would be CO_2 if the process is totally completed. However, ethanol oxidation takes place in several consecutive steps; intermediate products such as acetaldehyde and acetic acid are usually found in the solution when the reaction takes place in liquid phase [14–16]. If the photocatalytic process is carried out in a semi-batch reactor, in which the liquid products are not removed, the intermediate products formed could compete with ethanol for the adsorption sites and this could affect the rate of H_2 production over the reaction time. In this context, we have recently shown that using a Pt/anatase photocatalyst the irradiation of ethanol$_{(aq)}$ resulted in higher rates of hydrogen production than those obtained from acetaldehyde or acetic acid solutions [12].

There are many works in which the effect of dopants in the photocatalytic behaviour of TiO_2 has been studied [11,17,18].

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https://doi.org/10.1016/j.ijhydene.2018.02.098
0360-3199/

However, when dopants are introduced in Pt/TiO_2-based catalysts, they can also influence the characteristics of Pt nanoparticles producing a change in the photocatalytic behaviour of the initial Pt/TiO_2.

We have recently reported the promoter effect of Ga related with the modification of surface Pt species. $Pt–Ga/TiO_2$ catalysts containing about 0.5% wt Pt and small amounts of Ga (0.2–0.6% wt) showed higher Pt dispersion values and lower relative amount of surface oxidized Pt species than related Pt/TiO_2 (0.5% wt Pt). In this initial work, the photocatalytic conversion of ethanol$_{(aq)}$ was studied in liquid phase and the behaviour of $Pt–Ga/TiO_2$ catalysts was compared to that of a Pt/TiO_2 catalyst having similar Pt content but much lower Pt dispersion [19].

For a better insight of the effect of Ga on the photocatalytic behaviour of Pt/TiO_2 catalysts, here we report an *in-situ* DRIFTS-MS study of the photocatalytic transformation of ethanol/H_2O vapour mixtures over a $Pt–Ga/TiO_2$ catalyst. The surface species formed and their evolution during irradiation are compared with those formed when a Pt/TiO_2 catalyst with a similar Pt dispersion is used.

Experimental

Preparation and characterization of catalysts and catalytic tests in liquid phase

Pt/TiO_2 catalysts were prepared by incipient wetness impregnation using $H_2PtCl_6 \cdot 6H_2O$ aqueous solutions and anatase TiO_2 from Sigma Aldrich. After the impregnation, the catalysts were dried at 70 °C for 1 h and calcined at 400 °C for 4 h. A similar method was used for the preparation of $Pt–Ga/TiO_2$. In this case, Ga was previously impregnated using $Ga(NO_3)_3 \cdot xH_2O$ as precursor and then, after drying and calcination, the resulting solid was used for Pt incorporation as described elsewhere [19].

Pt and Ga contents were determined by inductively-coupled plasma (ICP) atomic emission spectrometry using a Perkin Elmer Optima 3200RL.

The surface area (S_{BET}), pore volume (V_{pore}) and pore diameter (D_{pore}) of the photocatalysts were determined by N_2 adsorption-desorption isotherms at −196 °C using a Micromeritics TriStar II 3020 system.

H_2-TPR analysis and CO chemisorption experiments were performed using a Micromeritics Autochem II 2920 system. For the H_2-TPR experiments, a 10% (v/v) H_2/Ar flow and a heating rate of 10 °C min^{-1} were used. CO chemisorption was carried out at 35 °C. Before the CO chemisorption, the samples were reduced at 125 °C under a 10% (v/v) H_2/Ar stream for 45 min and then purged with He (30 min at 125 °C).

XRD analysis was done using an Xpert PRO-diffractometer equipped with a CuKα radiation source ($\lambda = 1.5406$ Å) and a graphite monochromator. The XRD patterns were collected between $2\theta = 10°$ and $2\theta = 100°$, with a step width of 0.05°, counting 3 s at each step. The Scherrer equation was used for the estimation of the mean TiO_2 crystallite size.

UV–Vis diffuse reflectance spectroscopy was used for the determination of the band-gap values. The spectra were registered using a Perkin Elmer Lambda 950 UV/Vis Spectrometer with a 3 nm slit width and a speed of 654.92 nm min^{-1}; $BaSO_4$ was used as the reference. The reflectance was converted into the equivalent absorption coefficient, F (R_∞), using the Kubelka-Munk formalism. The band-gap values were calculated using the Tauc plot, $(F(R_\infty) \cdot h\upsilon)^n$ versus $h\upsilon$, where $n = 1/2$ indicates an indirect allowed transition [20].

A Perkin Elmer PHI-5500 spectrometer equipped with an Al Kα source (1486.6 eV) and a hemispherical analyser was used to perform the X-ray photoemission spectra. The pressure in the analysis chamber was maintained below 10^{-8} torr during data acquisition. The adventitious C 1 s peak at 284.8 eV was used as reference for the determination of binding energy (BE) values.

The experimental setup used for carried out the catalytic tests in liquid phase has been described elsewhere [12,19]. In short, photocatalytic experiments were carried out at 25 °C using a semi-batch reactor equipped with inlet and outlet opening for gases and a 175 W Hg lamp (broad spectrum lamp, maximum power at $\lambda = 366$ nm: 25.6 W); the lamp was placed in a water-cooled quartz jacket inside the reactor. For the photocatalytic test, 0.5 g of catalysts and 250 mL of an ethanol/water solution 25% (v/v) were used; the suspension was magnetically stirred and flushed with inert gas during the tests. The gaseous products were periodically sampled and analysed by gas chromatography. The liquid was analysed at the end of the test by gas chromatography and IR-ATR spectroscopy.

In situ *DRIFTS-MS study*

In situ DRIFTS experiments were carried out using a FTIR spectrophotometer Bruker Vertex 70 in DRIFT mode, coupled to a mass spectrometer ThermoStar GSD320T1. The samples were deposited into a reaction chamber and irradiated with a Hamamatsu Lightning Cure lamp ($\lambda = 365$ nm, 20 mW cm^{-2}). The samples were pre-treated at 150 °C under He flow for 30 min, and the background spectrum was registered at 25 °C. Then, a He flow saturated with ethanol/water vapour = 1/9.6 (mol/mol) was entered into the chamber at room temperature. After the adsorption, the ethanol/water flowing mixture was stopped and the catalysts were treated under He flow at room temperature until negligible evolution of reactants was detected by MS (about 15 min). Then, the initial DRIFT spectrum was recorded, and the catalyst was irradiated under He flow at 25 °C. During irradiation under He flow, DRIFT and mass spectra were recorded as a function of time (total time 50 min). DRIFT spectra were recorded at a resolution of 4 cm^{-1} and corrected with the adsorbed water spectrum. The *m*/z fragments corresponding to CH_3CH_2OH, CH_3CHO, CH_3COOH, CH_4, CO_2, CO and H_2 were analysed by MS.

Results and discussion

Characteristics of the catalysts and photocatalytic behaviour in liquid phase

Table 1 shows several characteristics of the photocatalysts studied in this work. Although all catalysts had similar values

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Table 1 – Several characteristics of catalysts.

Catalysts	S_{BET} ($m^2\ g^{-1}$)	V_{pore} ($cm^3\ g^{-1}$)	D_{pore} (nm)	Band gap (eV)	Pt (%wt)	Ga (%wt)	Pt dispersion (%)	d_{Pt} (nm)	$molH_2$/molPt[a]
0.3Pt/TiO_2	56	0.27	29.1	3.18	0.27	–	70	1.6	2.9
0.4Pt/TiO_2	56	0.27	29.1	3.18	0.38	–	68	1.7	2.5
Pt–Ga/TiO_2[b]	46	0.24	23.0	3.14	0.51	0.19	75	1.5	1.7

[a] H_2 consumption from H_2-TPR experiments.
[b] Results from [19].

of surface-area, pore volume and pore width, the values corresponding to 0.4Pt/TiO_2 and 0.3Pt/TiO_2 were slightly higher than those of Pt–Ga/TiO_2. XRD patterns (not shown) indicated in all cases the presence of anatase as the solely crystalline phase with an estimated size of 22 nm. According with XRD results, Raman spectra only revealed bands at ca. 639 cm^{-1} (E_g), 515 cm^{-1} ($A_{1g} + B_{1g}$), 399 cm^{-1} (B_{1g}), 197 cm^{-1} (E_g) and 144 cm^{-1} (E_g), characteristic of anatase [21]. The band-gap values were slightly lower than that of the TiO_2 used in the preparation of catalysts (TiO_2 band gap: 3.23 eV). Catalysts containing only Pt showed somewhat higher band-gap than Pt–Ga/TiO_2 according with previous results [19].

In all cases, the analysis of calcined catalysts by XPS showed Pt $4f_{7/2}$ peaks centred at 72.2–72.6 eV, which were attributed to PtO_x surface species (Fig. 1). Ti $2p_{3/2}$ peaks centred at 458.7 eV and O 1 s peaks with maximum at 529.9 eV were found and related to Ti^{4+} and surface oxide species, respectively [22].

H_2-TPR profiles (Fig. 2) pointed out differences in the reduction characteristics of the catalysts. For 0.4Pt/TiO_2 and 0.3Pt/TiO_2 the reduction peaks were clearly asymmetric and the corresponding H_2 consumption (Table 1) was higher than the theoretical if the reduction of PtO_2 is assumed (H_2/Pt = 2 mol/mol). This excessive H_2 consumption is associated with the partial reduction of TiO_2, which can be favoured by the H_2 adsorption onto Pt and the ulterior spill over effect on TiO_2. For Pt–Ga/TiO_2, the partial decomposition of PtO_2 during the calcination forming PtO and/or Pt could justify the H_2/Pt < 2 (mol/mol) obtained [23].

In order to evaluate the Pt dispersion of the catalysts, CO chemisorption experiments were performed at 35 °C over the catalysts previously reduced at 125 °C. Using a stoichiometry of adsorption 1:1 (adsorbed CO molecule: surface Pt atom) and considering the presence of cubic Pt particles, both the dispersion and the Pt particle size were determined. Values of Pt dispersion in the range 68–75% and Pt particle size of 1.7–1.5 nm were obtained (Table 1). Table 2 shows Pt/(Ti + Ga) atomic ratios determined from XPS for the calcined catalysts. Taking into account the Pt content of the catalysts, Pt dispersion values are in good agreement with their relative $(Pt/(Ti + Ga))_{XPS}$. We have recently shown that for a given Pt content (about 0.5% wt) the preparation method used in this work led to Pt/TiO_2 catalysts with a lower Pt dispersion than the corresponding Pt–Ga/TiO_2 catalyst [19]. In this work we prepared Pt/TiO_2 catalysts with a slightly lower Pt content than that of Pt–Ga/TiO_2 turning out catalysts with similar values of Pt dispersion.

Catalysts were tested at 25 °C in the photocatalytic production of H_2 in liquid phase using 25% v/v ethanol aqueous solutions. Table 2 also shows the rate of H_2 production during the photocatalytic tests. The initial rate of H_2 production was slightly higher for 0.4Pt/TiO_2 and 0.3Pt/TiO_2 than for Pt–Ga/TiO_2. However, after 4 h, 0.4Pt/TiO_2 and 0.3Pt/TiO_2 showed a rate of H_2 production slightly lower than Pt–Ga/TiO_2. Although

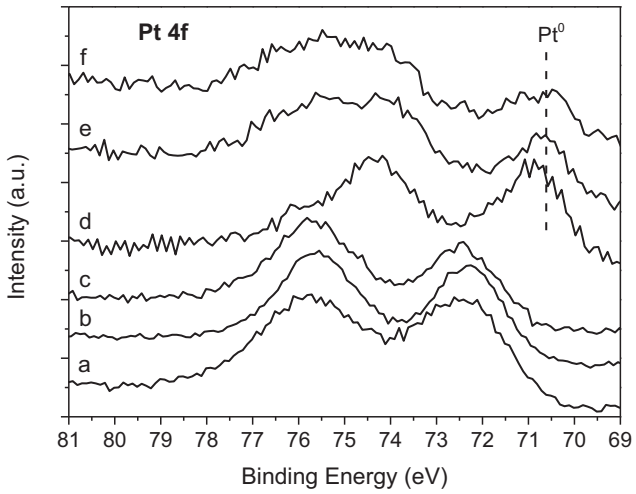

Fig. 1 – XPS spectra corresponding to the Pt 4f core level of catalysts: a) fresh Pt–Ga/TiO_2; b) fresh 0.4Pt/TiO_2; c) fresh 0.3Pt/TiO_2; d) post-reaction Pt–Ga/TiO_2; e) post-reaction 0.4Pt/TiO_2; f) post-reaction 0.3Pt/TiO_2.

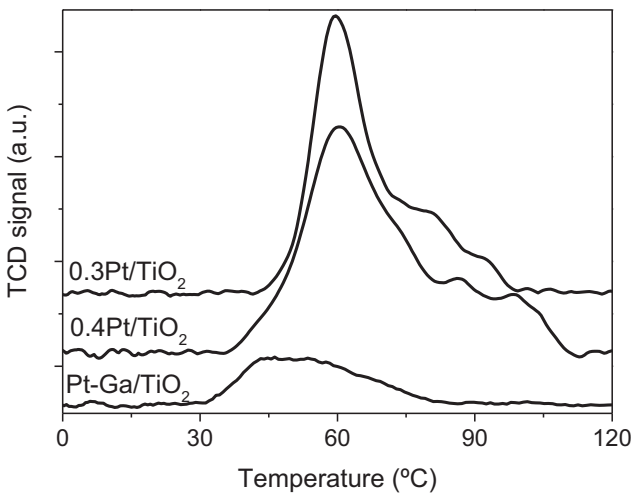

Fig. 2 – Temperature programmed H_2-reduction profiles of catalysts.

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Table 2 – Pt/(Ti + Ga) atomic ratio determined by XPS before and after the photocatalytic test and rate of H_2 production during the photocatalytic transformation of 25% (v/v) ethanol$_{(aq)}$ solutions.

Catalyst	Initial $(Pt/(Ti + Ga))_{XPS}$	Final $(Pt/(Ti + Ga))_{XPS}$	Initial mmolH_2/min	Final (4 h) mmolH_2/min
0.3Pt/TiO_2	0.0111	0.0030[a]	0.617	0.211
0.4Pt/TiO_2	0.0080	0.0050[a]	0.598	0.214
Pt–Ga/TiO_2	0.0183	0.0152[b]	0.535	0.224

[a] Post-reaction (4 h).
[b] Post-reaction (24 h) [19].

for all photocatalysts the $(Pt/(Ti + Ga))_{XPS}$ decreased during the test, the diminution was lower for Pt–Ga/TiO_2 than for non-containing Ga catalysts (Table 2).

Table 3 compiles the gaseous products determined after 4 h under irradiation. As can be seen, although the main gas-phase product was H_2, lower amounts of CO_x, CH_4, and C2 hydrocarbons were also formed. Using 0.4Pt/TiO_2 and 0.3Pt/TiO_2 the total amount of H_2 produced was slightly higher than that produced over Pt–Ga/TiO_2 (Table 3). In the liquid phase, besides acetaldehyde, which was the main product, minor amounts of 2,3-butanediol, acetic acid and acetone were found.

According with previous results, under the experimental conditions used, the main reaction is the oxidative dehydrogenation of ethanol to acetaldehyde; the photocatalytic reactions related with the formation of all the other products have been previously discussed [12].

In-situ *DRIFTS-MS studies*

In-situ DRIFTS-MS studies of the photocatalytic H_2 production from ethanol$_{(aq)}$ in vapour phase were carried out with Pt–Ga/TiO_2 and 0.3Pt/TiO_2 at 25 °C. Fig. 3 shows the initial spectra in the 1900-1000 cm^{-1} region after the ethanol/H_2O adsorption and the evolution of the spectra with the irradiation time. For Pt–Ga/TiO_2, the initial spectrum showed clear bands related with the presence of adsorbed bridged ethoxide species at 1088 cm^{-1} (υ(C–C)) and 1049 cm^{-1} (υ(C–O)); bands centred at 1458 cm^{-1} and 1396 cm^{-1} can be reasonably ascribed to the corresponding $\upsilon_{as}(CH_3)$ and $\upsilon_s(CH_3)$ absorptions [24–27]. The intense and broad band centred at 1654 cm^{-1} can be related with the υ(C=O) vibration of adsorbed aldehydes such as formaldehyde, acetaldehyde and/or unsaturated aldehydes; weak bands in the region 2725-2830 cm^{-1} (not shown) could be related with the corresponding υ(C–H) bands [24,28–33]. Moreover, we cannot discard the presence of physisorbed acetic acid which would show a characteristic υ(C=O) band at 1750 cm^{-1} [33]. The initial spectrum of Pt–Ga/TiO_2 also showed low intensity bands in the 1600-1300 cm^{-1} region characteristic of $\upsilon_{as}(COO)$ and $\upsilon_s(COO)$ of different surface carboxylate species. Absorptions at 1583 cm^{-1} and 1423 cm^{-1} can be related with $\upsilon_{as}(COO)$ and $\upsilon_s(COO)$ bands of bridged bidentate acetate; the small intensity absorptions at 1547 cm^{-1} and 1311 cm^{-1} can be assigned to $\upsilon_{as}(COO)$ and $\upsilon_s(COO)$ bands of adsorbed formate species [34]. During the irradiation, the progressive diminution of the intensity of the

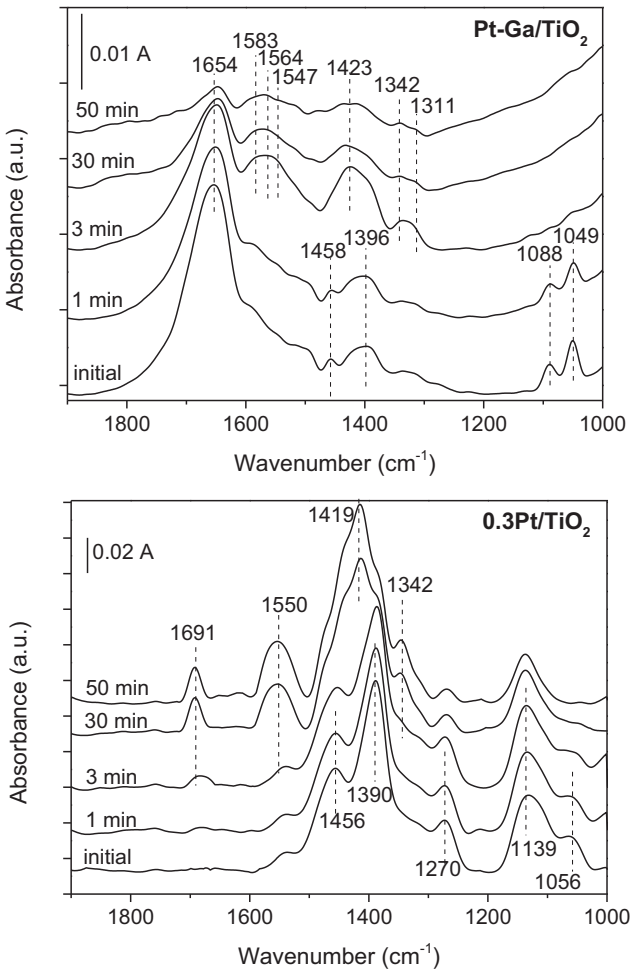

Fig. 3 – DRIFT spectra in 1900–1000 cm^{-1} region of Pt–Ga/TiO_2 and 0.3Pt/TiO_2 catalysts after ethanol$_{(aq)}$ vapour adsorption and evolution with the irradiation time.

Table 3 – Gaseous products obtained during the photocatalytic transformation of 25% (v/v) ethanol$_{(aq)}$ solutions (t = 4 h).

Catalyst	Total amount (mmol)					
	H_2	CO_2	CH_4	CO	C_2H_6	C_2H_4
0.3Pt/TiO_2	85.8	2.2	2.5	1.4	0.5	0.0
0.4Pt/TiO_2	91.3	2.5	2.9	1.4	0.4	0.0
Pt–Ga/TiO_2	72.6	1.6	2.1	1.1	0.5	0.1

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bands characteristic of ethoxide and aldehyde species took place. The intensity of the bands corresponding to carboxylate (acetate and formate) initially increased under irradiation but then progressively decreased (Fig. 3).

Moreover, during the irradiation ν(CO) bands related with CO on Pt centres were found. After 3 min of irradiation clear bands at 2086 cm^{-1} and 2022 cm^{-1} related with linearly coordinated CO onto different Pt species appeared (Fig. 4). The intensity of the band at 2086 cm^{-1} decreased and that of the band at a lower wavenumber increased with the irradiation time; after 50 min of irradiation only one band centred at 2040 cm^{-1} and assigned to CO over Pt^0 remained [35–37]. During the irradiation, MS analysis of the products evolved showed the formation of H_2 and other fragments associated to CH_3CHO, CH_3COOH, CH_4, CO_2 and CO.

A similar DRIFTS-MS study carried out with the 0.3Pt/TiO_2 indicated several differences in the photocatalytic behaviour of 0.3Pt/TiO_2 and Pt–Ga/TiO_2 (Fig. 3). After adsorption of ethanol$_{(aq)}$ vapour onto 0.3Pt/TiO_2, wide bands centred at 1139 cm^{-1} and 1056 cm^{-1} were generated, the breadth of these bands could indicate the presence of different surface ethoxide species bridged and monodentate [26,34]; besides ν(C–C), ν(C–O) of monodentate ethoxide species could contribute to the band centred at 1139 cm^{-1}. The corresponding $\upsilon_{as}(CH_3)$ and $\upsilon_s(CH_3)$ bands characteristic of adsorbed ethoxide can be seen at 1456 cm^{-1} and 1390 cm^{-1} respectively (Fig. 3). The band at 1270 cm^{-1} could be related with the corresponding δ(OH) of molecularly adsorbed ethanol whose ν(C–C) is expected at 1100 cm^{-1} and could contribute to the band centred at 1139 cm^{-1} (initial spectrum of 0.3Pt/TiO_2 in Fig. 3). The intensity of all these bands related with the presence of adsorbed ethanol and ethoxide species decreased with the irradiation time. Meanwhile, under irradiation bands at 1691 cm^{-1}, 1550 cm^{-1}, and a broad band in the 1500-1300 cm^{-1} region with maxima at 1419 cm^{-1} and 1342 cm^{-1} were progressively formed. The band at 1691 cm^{-1} could be indicative of the presence of acyl species [26,38], and the broad band in the 1500-1300 cm^{-1} region is related with different carboxylate species as discussed above. Moreover, small bands at 2740 cm^{-1} and 2710 cm^{-1} (zone not shown) could be related with the presence of adsorbed aldehydic species. After 50 min of irradiation, the intensity of the band at 1691 cm^{-1} (ν(C=O) of acyl species) and that of bands in the region 1600-1300 cm^{-1} (ν(COO), $\delta(CH_3)$, δ(CH) of acetate/formate species) increased. MS analysis of gases evolved indicated the formation of H_2 and small amounts of CH_4.

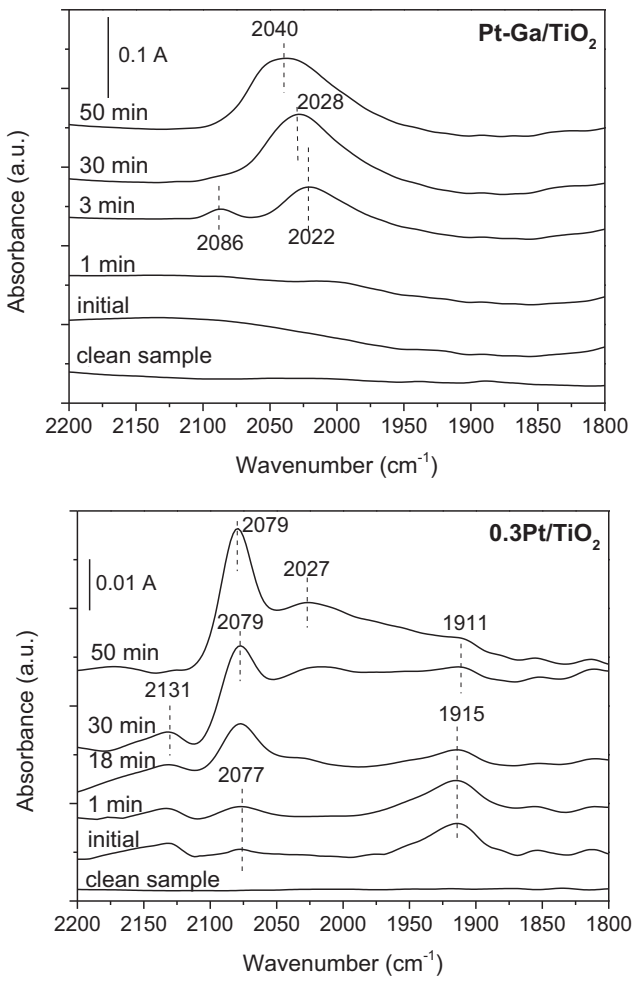

Fig. 4 – DRIFT spectra in 2200–1800 cm^{-1} region of Pt–Ga/TiO_2 and 0.3Pt/TiO_2 catalysts after ethanol$_{(aq)}$ vapour adsorption and evolution with the irradiation time.

For the 0.3Pt/TiO_2 catalyst, bands in the ν(CO) zone at 2131 cm^{-1}, 2077 cm^{-1} and 1915 cm^{-1} appeared from the initial stage (Fig. 4). The ν(CO) band with maximum at 2131 cm^{-1} is related with CO linearly coordinated onto oxidized Pt. After 50 min of irradiation this band disappeared and a main band at 2079 cm^{-1} related with terminal CO coordinated to Pt^0 was clearly visible. This is probably due to the reduction of surface Pt under the photocatalytic process. Clear absorptions below 2000 cm^{-1} are related with the presence of bridged CO. The formation of bridged CO species over 0.3Pt/TiO_2 during the irradiation process contrasts with the behaviour of Pt–Ga/TiO_2 discussed above (Fig. 4). These results pointed to different characteristics of Pt centres on Pt–Ga/TiO_2 and 0.3Pt/TiO_2; an effect of Ga in the characteristics of surface Pt centres is shown.

For a better insight in the different transformation of surface species over Pt–Ga/TiO_2 and 0.3Pt/TiO_2 during irradiation, Fig. 5 illustrates the evolution along the irradiation time of the bands related to the surface ethoxide (ν(C–O)) and carboxylate ($(\upsilon_{as}(COO)$ and $\upsilon_s(COO))$ species corresponding to Pt–Ga/TiO_2 and 0.3Pt/TiO_2.

Fig. 5 clearly shows that in both cases the amount of initial ethoxide species decreased with the irradiation time. However, for Pt–Ga/TiO_2 the initial high decrease in the amount of ethoxide species is accompanied by a high increase of the surface carboxylate species; after the initial increase, the amount of carboxylate species decreased along time. The degradation of carboxylate species and the diminution of the band at 1654 cm^{-1} characteristic of aldehydic species, is related with the evolution of CH_3CHO, CH_3COOH, CH_4, CO_2 and CO determined by MS. For 0.3Pt/TiO_2, the amount of surface carboxylate species increased along irradiation time; as stated above, in this case only H_2 and a small amount of CH_4 were detected by MS.

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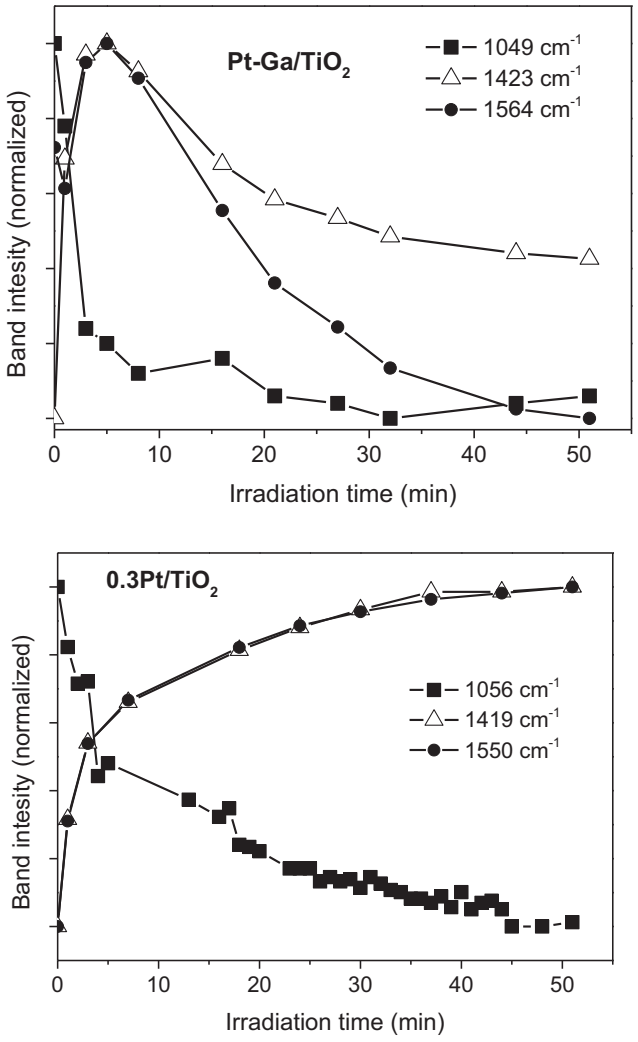

Fig. 5 – Evolution of IR bands corresponding to ethoxide (υ(C-O)) and carboxylate (υ_{as}(COO) and υ_{s}(COO)) species along the irradiation time for Pt–Ga/TiO_2 and 0.3Pt/TiO_2 after ethanol$_{(aq)}$ vapour adsorption.

Conclusions

Anatase-supported Pt (0.3–0.4% wt) and Pt–Ga (0.5% wt Pt) catalysts with similar Pt dispersion and morphological characteristics were studied in the photocatalytic production of H_2 using ethanol as sacrificial agent. In the photocatalytic test in liquid phase (4 h), H_2 and acetaldehyde were the main products found. The total amount of H_2 produced and the initial rate of H_2 production were slightly higher for Pt/TiO_2 than for Pt–Ga/TiO_2. However, Pt/TiO_2 showed slightly lower final rate of H_2 production than Pt–Ga/TiO_2; for Pt–Ga/TiO_2, the $(Pt/(Ti + Ga))_{XPS}$ diminution during the test was lower than for Pt/TiO_2 catalysts.

In situ DRIFTS-MS studies carried out with Pt–Ga/TiO_2 and 0.3Pt/TiO_2 evidenced the formation of aldehydic and carboxylate surface species after vapour adsorption of ethanol$_{(aq)}$. The photocatalytic transformation of these surface species was more effective over Pt–Ga/TiO_2 than over 0.3Pt/TiO_2. For Pt/TiO_2, the amount of surface carboxylate species increased along the irradiation time and only H_2 and a small amount of CH_4 were evolved. For Pt–Ga/TiO_2, a clear degradation of carboxylate species during the irradiation was found, and besides H_2 and CH_4, CH_3CHO, CH_3COOH, CO_2 and CO were detected in the gas phase. The υ(CO) bands risen during the DRIFTS-MS experiments pointed to an effect of Ga, likely a dilution effect on surface Pt species, for the Pt–Ga/TiO_2 catalyst.

Acknowledgements

The authors are grateful to the projects MAT2014-52416-P and MAT2017-87500-P for financial support. A. C. Sola also thanks the IREC for his PhD grant 06/10.

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