Gas-phase ethanol photocatalytic degradation study with TiO$_2$ doped with Fe, Pd and Cu

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Abstract

Ethanol degradation by TiO$_2$ and TiO$_2$ doped with Fe, Pd and Cu has undergone FTIR spectroscopic study. Ethanol interaction with bare-TiO$_2$ and Fe-TiO$_2$ yields the formation of ethoxides on the catalyst surface that can readily be oxidised to acetates by radicals O$_2^{\bullet-}$ and $^{\bullet}$OH. Conversely, ethanol interaction with Pd-TiO$_2$ and Cu-TiO$_2$ generates an intermediate species between ethanol and ethyleneglycol. Acetate-producing oxidation of these latter species is inhibited because electrons that form radicals O$_2^{\bullet-}$ are captured by the respective metallic oxides. In these catalysts a degradation mechanism based on ethanol reaction with photogenerated holes is proposed. Also, different surfacial OH distributions determine ethanol–catalyst interactions. Furthermore, ethanol degradation has been studied in a gaseous continuous flow system. Exhaust gases have been analysed by means of GC and FTIR. These experiments demonstrate that bare-TiO$_2$ and Fe-TiO$_2$ degrade ethanol to provide only acetaldehyde and their catalytic activity progressively decays over time. On the contrary, Pd-TiO$_2$ and Cu-TiO$_2$ have produced ethyleneglycol in addition to acetaldehyde. No deactivation of these catalysts was observed during the experimental time period (6 h).
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1. Introduction

Heterogeneous catalysis in gas phase has been widely studied and applied to industrial processes [1–5]. In this technique adsorption–desorption steps of reagents and products determine process efficiency, especially when using continuous flow reactors. Different metals and compounds have been tested to speed up or inhibit certain reactions [6,7]. Active centres in which reactions are efficient may be very varied or specific. Some authors have indicated that for specific reactions these centres are a minority and/or related to surfacial defects [8,9].

It has also been indicated that some adsorbed species can migrate towards these centres, thus favouring reaction rate reduction. However, the e^-/h^+ couple recombination speed is too fast and no reaction is allowed. Thus much of the research developed in recent years has been focused on reducing reaction rate. In this sense, semiconductor doping with transition metals has often been tested. In fact, metal deposition on TiO$_2$ particles significantly reduces e^-/h^+ couple recombination [10].

Photocatalytic ethanol degradation in batch reactors has been studied by different authors [11,12]. Also the different factors that determine its degradation mechanisms have been well established [13–18]. For instance, in batch conditions in this reaction, the presence of some metals such as TiO$_2$ dopants inhibits acetaldehyde degradation, considered by many authors the first intermediate of ethanol degradation [19]. The fact that these metals occupy important active centres on the TiO$_2$ particle surface explains such inhibition.

In this study we consider doping TiO$_2$ effects with Fe, Pd and Cu on ethanol degradation in a continuous flow gas-phase system. In such a system the reagent contact time is very short so reducing the e^-/h^+ couple recombination

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speed is crucial. FTIR tests of ethanol interaction before and after the catalysts irradiation have also been carried out to ascertain the studied metals' influence on the process.

2. Experimental

2.1. Catalyst preparation

TiO_2 was Degussa P-25 (80% anatase). Doping was performed by impregnation of TiO_2 with aqueous solutions of $Fe(NO_3)_3$, $PdCl_2$, or $CuSO_4$, according to the metal used by an incipient wetness impregnation method [20] at 298 K as follows. The mixture (TiO_2 + metal) was stirred for 48 h. Later, water was evaporated by heating at 373 K over 24 h. Finally, the catalysts were calcined at 773 K for 5 h. Metallic precursor concentration was the one required to obtain 0.5% (w/w) of dopant. Catalysts have been designated using the nomenclature $X-TiO_2$ with X being the doping metal (Fe, Pd, Cu).

Also, a non doped catalyst (bare-TiO_2) was prepared by the same calcination process to compare its catalytic behaviour with that of the doped catalysts.

2.2. Experimental conditions

All the experiments were carried out in a continuous reaction device at 40 °C (Fig. 1). This system consists of a vessel containing a 2:1 (v/v) water–ethanol solution at pH = 5. This vessel is continuously air-bubbled at a flow rate of 150 cm³ min⁻¹. The resulting air containing water and ethanol vapours is introduced in a 15-cm long, 4-mm diameter cylindrical glass reactor containing the catalyst.

Only the outer portion of the catalyst in contact with the inner wall of the reactor is exposed to the light and hence will be reactive. In order to compare their catalytic activities, the reactor was filled up to the same 10 cm height with both catalysts. Thus, similar contact times are obtained. Activity results are given as a function of the employed catalyst mass in grams.

2.3. Equipment

Samples from the reactor were continuously analysed using a gas chromatograph (GC Varian Star 3600) equipped with a gas injection valve and a FID detector. Also, a catalytic chamber Mattson 3000 spectrophotometer (Collector Mattson/Genesis Thermo Spectra-Tech) was used for continuous analysis. FTIR studies in cell with CaF_2 windows, where samples were located, were carried out in a FTIR spectrophotometer model RS/1 from UNICAM. Water reference spectrum was always subtracted from every spectrum.

A 60 W UV-lamp (Philips Cleo HB 071) was employed as UV light source. The incident photon flux was measured by the ferrioxalate actinometry method [21] with a resulting 1.26×10^{-6} einteins l⁻¹ s⁻¹.

3. Results and discussion

3.1. Characterisation

TiO_2 surfacial OH group nature and distribution is in many cases the determining factor of catalyst behaviour [22–24], considerable research has been devoted to characterising these groups present on the surface of many metallic oxides, and especially in TiO_2. From the many FTIR studies published in the literature, these surfacial groups' distribution could be illustrated in the following Scheme 1 [25–29].

Catalysts have been analysed by FTIR in the region between 4000 and 2500 cm⁻¹ to determine the distribution and features of these OH groups. Fig. 2 shows the spec-
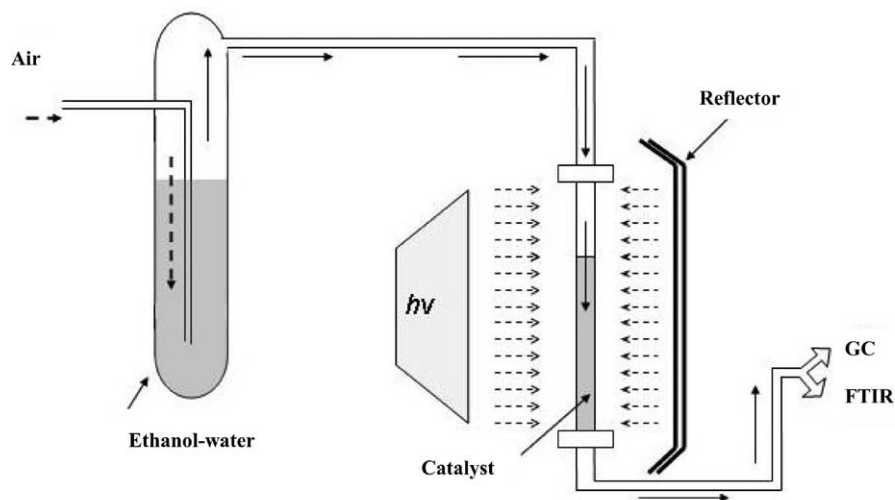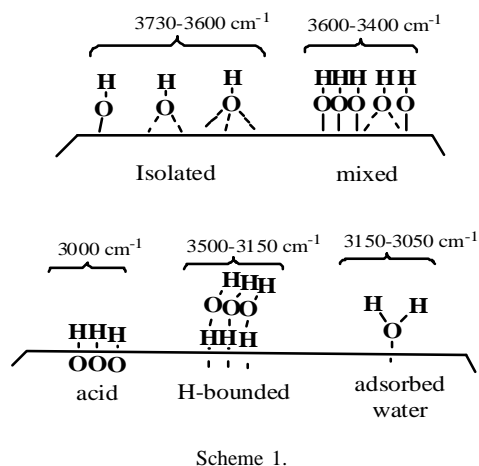

Fig. 1. Reactor system in continuous used in this study.

Scheme 1.

Fig. 2. FTIR spectra in the hydroxyl group region.

tra in this region for the different catalysts. As observed the catalyst bare-TiO$_2$ shows a much higher concentration of H-bounded hydroxyl groups. Contrary to this, Pd-TiO$_2$ and Cu-TiO$_2$ show a lower concentration of these groups. In Fe-TiO$_2$, H-bounded hydroxyl group distribution falls between that of bare-TiO$_2$ and catalysts doped with Pd and Cu.

Also XRD analyses have been obtained from these catalysts. XRD spectra from catalysts doped with Fe and Cu are identical to that from bare-TiO$_2$ (TiO$_2$ calcined at 500 °C) (Fig. 3). This means that both rutile and anatase phases are observed with a higher concentration of the latter, but the presence of iron or copper oxides is not detected. Conversely, in the catalyst doped with Pd, PdO presence is observed in addition to anatase and rutile (Fig. 3). PdO crystalinity is high enough to allow its detection even at the low concentration found in the catalyst.
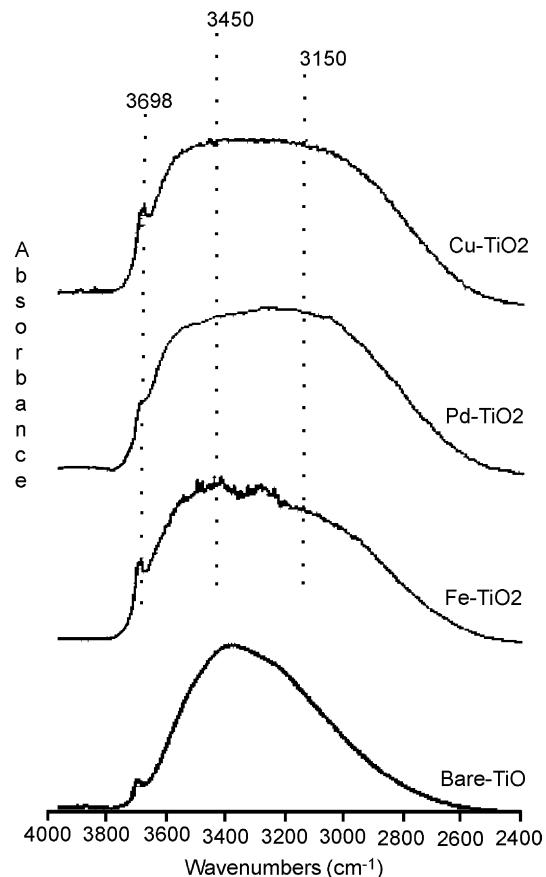
3.2. FTIR study

The spectroscopic characterisation of ethanol interaction with different catalysts has been carried out by 2:1 (v/v) water–ethanol solution impregnation for 2 h by means of
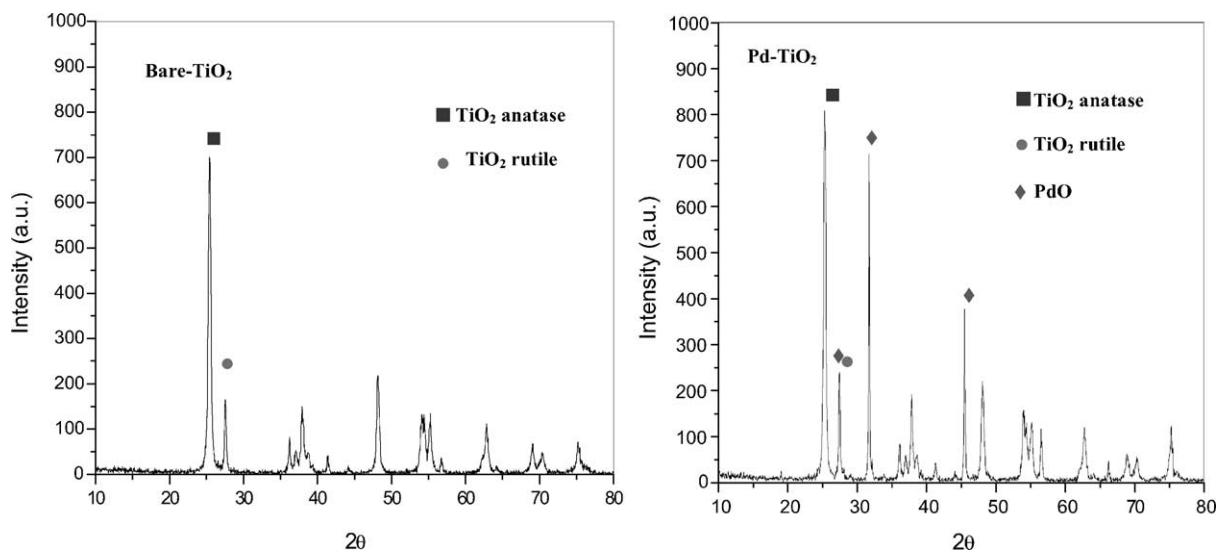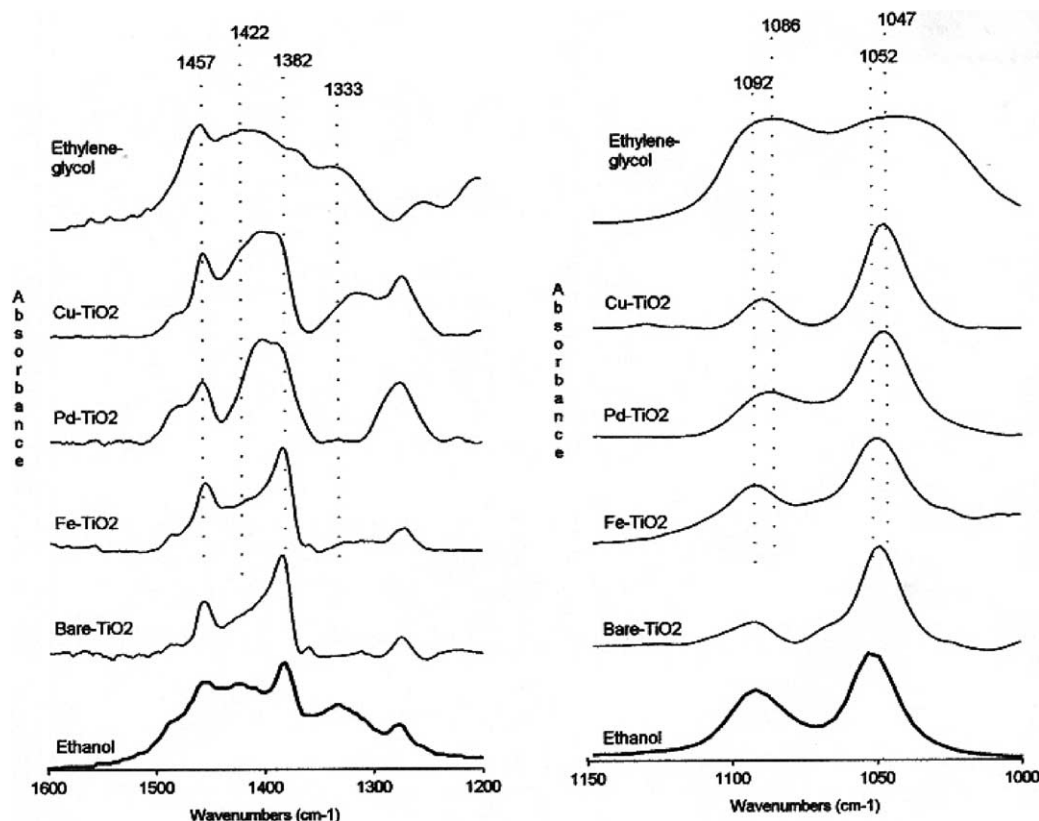

Fig. 3. XRD pattern of bare-TiO$_2$ and Pd-TiO$_2$.

Fig. 4. FTIR spectra from ethanol interaction with different catalysts in the regions between 1600 and 1200 cm^{-1} (A) and 1150 and 1000 cm^{-1} (B).

the system described in Fig. 1. After this, catalysts were carefully taken from the reactor and placed between two CaF$_2$ windows in a proper cell and FTIR-analysed. Once the spectrum was obtained, the cell was irradiated for 5 min and analysed by FTIR again. In this way, the adsorption of the selected molecules onto the catalyst surface and their reaction under irradiation was studied.

Fig. 4(A) and (B) show the spectra from the different catalysts in the regions between 1600 and 1200, and 1150 and 1000 cm^{-1}, respectively, after impregnation.

Spectra obtained in the region between 1600 and 1200 cm^{-1} after the interaction with ethanol show the CH$_2$ and CH$_3$ symmetric and asymmetric deformation vibrations. Table 1 shows the corresponding assignations to those vibrations according to the bibliography [30].

Fig. 4(A) shows that in the spectra from bare-TiO$_2$ and Fe-TiO$_2$ impregnated with ethanol, bands due to δOH and

CH$_2$ wag vibrations have disappeared. However, in Pd-TiO$_2$ and Cu-TiO$_2$, δOH vibration band is shifted towards lower wavenumbers (1402 cm^{-1}).

As mentioned, spectra from the region 1150–1000 cm^{-1} in which νC–C and νC–O vibration bands are found (Fig. 4(B)) have also been studied. In bare-TiO$_2$ and Fe-TiO$_2$, a slight shift towards lower band wavenumbers attributed to νC–O vibration (1052 cm^{-1} in ethanol (Fig. 4B)) is observed. Spectra obtained in this region from Pd-TiO$_2$ and Cu-TiO$_2$ show a significant band shift attributed to νC–C (1092 cm^{-1} in ethanol spectrum) towards lower wavenumbers.

The δOH vibration band disappearance and shift attributed to the νC–C vibration observed in bare-TiO$_2$ and Fe-TiO$_2$ may be caused by the corresponding ethoxide formation:

Ti^{4+}–OCH$_2$–CH$_3$ (monodentate)

or

(Ti^{4+})$_2$–OCH$_2$–CH$_3$ (bridge)
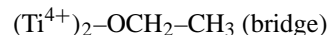
In fact, two forms of ethanol interaction with the catalyst surface have been indicated in the literature [31–34], by means of:

(a) a hydrogen-bonded ethanol species; and
(b) a surface-bound Ti-ethoxide.

In this case ethoxide formation may be favoured.

Table 1
Assignment of ethanol FTIR bands

Vibration	Wavenumber (cm^{-1})
δCH$_{3as}$ + δCH$_2$	1457
δOH	1422
	1264
δCH$_{3s}$	1382
CH$_2$ wag	1333
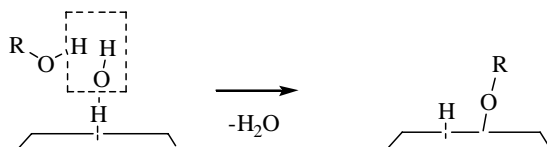
Scheme 2.

In addition to this, spectra obtained from the ethanol interaction with Pd-TiO$_2$ and Cu-TiO$_2$ in both 1600–1200 and 1150–1000 cm^{-1} regions are quite similar to those of ethyleneglycol. Fig. 4(A) and (B) show ethyleneglycol spectrum for comparative purposes.

A different hydroxyl group distribution could be one of the causes of this different interaction. In the literature it has been indicated that the alcoholate formation mechanism is determined by the acidic or basic character of these surfacial OH groups [35].

The H-bounded hydroxyl group high concentration in catalysts bare-TiO$_2$ and Fe-TiO$_2$ could favour the ethoxy group formation by Scheme 2.

Additionally, the presence of H-bounded hydroxyl group low concentration could favour Scheme 3 in catalysts doped with Pd and Cu. The ethoxy group formed this way could generate a stronger electronic destabilisation of the molecule to create, through an inductive effect, a charge defect in the methyl group. This could favour the ethoxy group interaction through its hydrogen atoms with the oxygen atoms of the hydroxylic groups.

Several authors have indicated that in catalysts with low concentration of H-bounded hydroxyl group more localised interactions may occur with methylic groups of the molecule [36].

As mentioned above, after ethanol impregnating the catalysts were irradiated in the same cell. Fig. 5(A) shows the spectra from 1800 to 1000 cm^{-1} region obtained after irradiation. Fig. 5(B) also shows the spectra from 4000 to 2500 cm^{-1} region after irradiation. To highlight the evolution of the surfacial OH groups, these last spectra are showed after subtracting the spectra before irradiation.

In the spectrum obtained after irradiation from bare-TiO$_2$ in the 1800–1000 cm^{-1} region (Fig. 5A) only the presence of bands at 1582 cm^{-1} (with a shoulder at 1550 cm^{-1}), 1438 cm^{-1} (with a shoulder at 1410 cm^{-1}) and 1345 cm^{-1} are visible and attributed to a bridged bidentate acetate (1585–1570, 1420–1410 cm^{-1}) and a quelate bidentate acetate (1550–1540 and 1440–1430 cm^{-1}) [37,38]. However, in Fe-TiO$_2$, Pd-TiO$_2$ and Cu-TiO$_2$ only the quelate bidentate is observed. Furthermore, in the catalysts with Pd and Cu bands from acetates are of low intensity. Also new
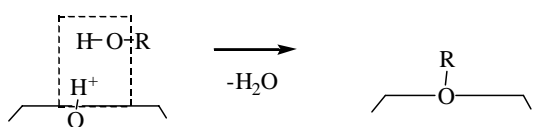
Scheme 3.

bands at 1711, 1264 and 1175–1048 cm^{-1} that correlate quite well with those of physisorbed carboxylic acid and ethyleneglycol, have been observed.

In the OH group region (Fig. 5(B)) bare-TiO$_2$ and Fe-TiO$_2$ show a significant increment of bands centred at 3450 cm^{-1} after irradiation. Contrary to this, in spectra from Pd-TiO$_2$ and Cu-TiO$_2$, almost no increment of these bands is observed. Only bands from terminal OH (3698 cm^{-1}) are enhanced. Additionally, in Cu-TiO$_2$ catalyst the OH group concentration in the 3500–3000 cm^{-1} region are slightly reduced.

3.3. Photocatalytic degradation

Experiments on ethanol degradation with the different catalysts have also been carried out by using the system described in Fig. 1. These studies have lasted 6 h without interruption and the output gases have been analysed initially every half hour and later hourly. Previously, the same experiments were performed under the same conditions but without irradiation to determine the adsorption effect. Only during the first hour of reaction such adsorption processes were observed, being practically of the same order for all the catalysts. After this time the determined intermediate fluxes (mmol g^{-1} cat min) coincide with ethanol concentration reduction. Fig. 6 shows the determined intermediate fluxes during photodegradation.

Ethanol degradation by bare-TiO$_2$ and Fe-TiO$_2$ only gave acetaldehyde as an intermediate. Both catalysts show very similar catalytic behaviour. This means the determined acetaldehyde flow is progressively reduced with reaction time. After 6 h of reaction time, flow was nil suggesting that the catalyst is progressively deactivated. However, when using Cu-TiO$_2$ and Pd-TiO$_2$ determined acetaldehyde flows are higher than those observed in the previous catalysts, especially in Cu-TiO$_2$. In these catalysts, a lower proportion of ethyleneglycol has been obtained in addition to acetaldehyde. Furthermore, no reduction of intermediate fluxes is observed with reaction time, hence no catalyst deactivation seems to occur. These two catalysts showed a darkening colour change after irradiation.

All the catalysts were analysed by FTIR spectroscopy after reactions. In bare-TiO$_2$ and Fe-TiO$_2$, acetate presence was also observed similarly to those determined by FTIR measurements in the cell. Nonetheless, in Pd-TiO$_2$ and Cu-TiO$_2$ no acetates were detected. The progressive formation of acetates on the surface of bare-TiO$_2$ and Fe-TiO$_2$ may be the cause of their deactivation along reaction time.

In the oxidation process with Pd-TiO$_2$ and Cu-TiO$_2$, Cu and Pd oxides can react with the TiO$_2$ photogenerated electrons, explaining the colour change. Thus, the electron reaction with the adsorbed O$_2$ molecules may be decreased and hence the reaction of O$_2^{\bullet-}$ radicals that yield acetates. In fact, some authors have indicated that the deposition of oxidised Pt on TiO$_2$ particles inhibits the formation of O$_2^{\bullet-}$ radicals in comparison with non doped TiO$_2$ [11].
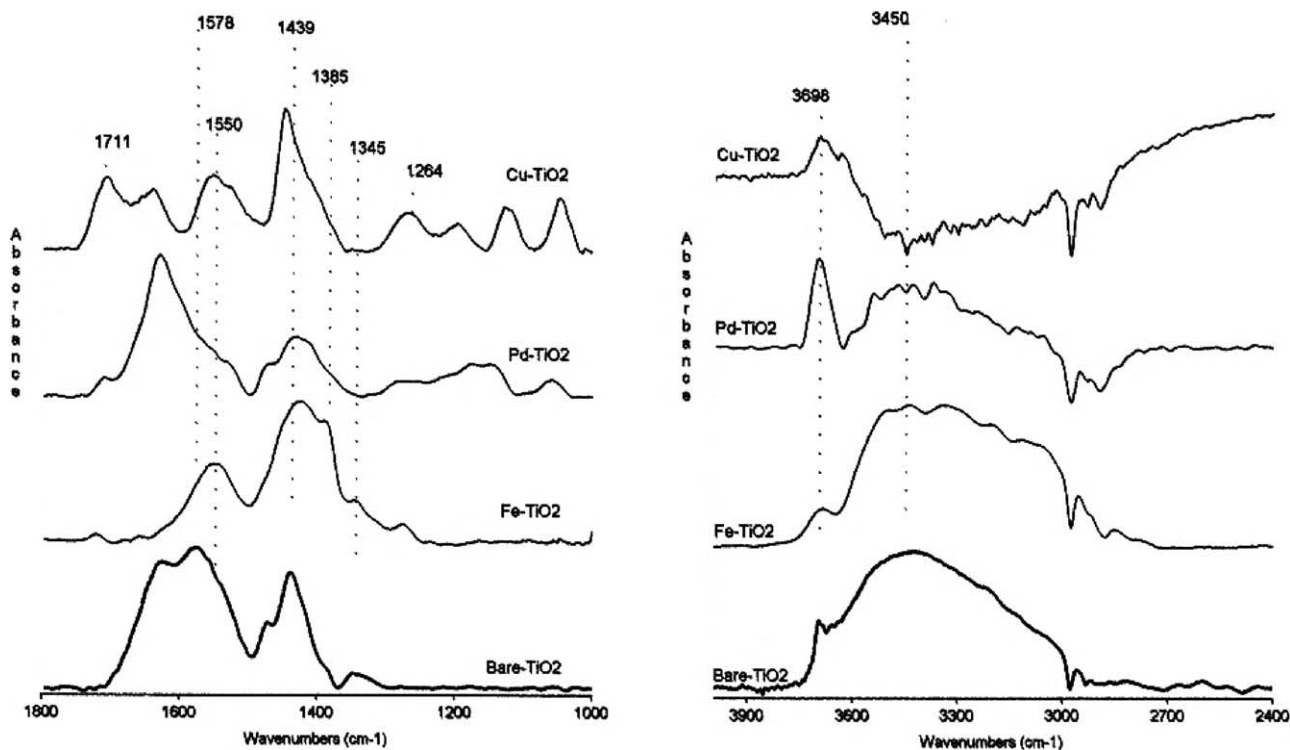
Fig. 5. FTIR spectra from ethanol and ethanol interaction with different catalysts after irradiation for 5 min in the regions between 1800 and 1000 cm^{-1} (A) and 4000 and 2500 cm^{-1} (B). These last spectra are showed after subtract the spectra before irradiate.
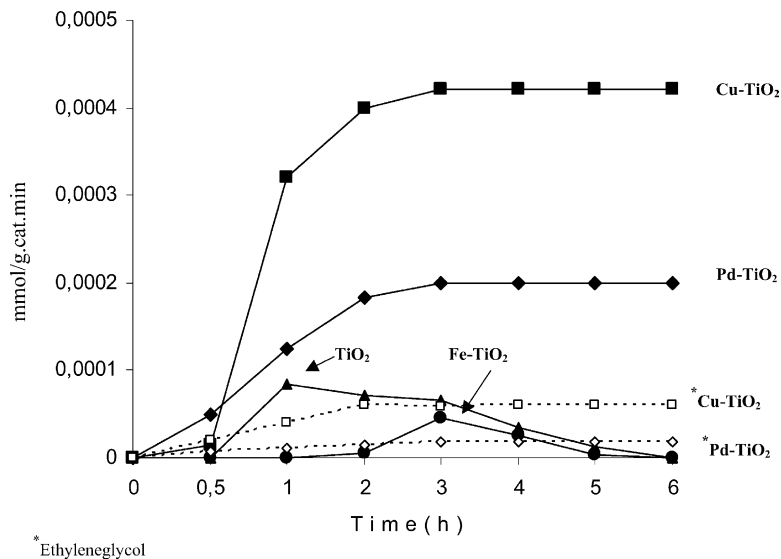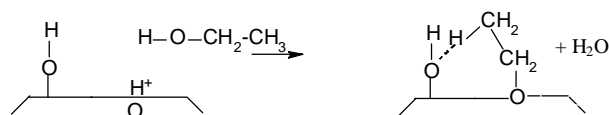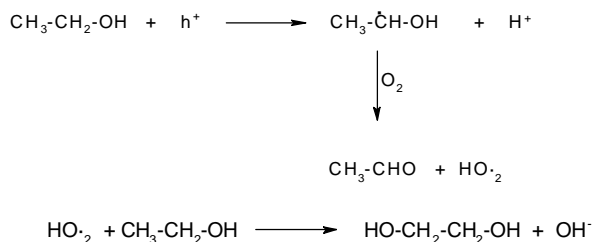

Fig. 6. Acetaldehyde (filled symbol) and ethyleneglycol (empty symbol) flow determined during ethanol photocatalytic degradation with different catalysts.

However, the deposition of Pt in a reduced state has been shown to increase the life time of these radicals. Also, in this way ethanol reaction with the photogenerated holes would be favoured, and its subsequent degradation to acetaldehyde using the mechanism described by some authors [39] (Scheme 4).

The determined species in the surface of these catalysts through FTIR studies (Scheme 5) could also favour this mechanism.

Scheme 4.

$$CH_3\text{-}CH_2\text{-}OH \ + \ h^+ \ \longrightarrow \ CH_3\text{-}\overset{\cdot}{C}H\text{-}OH \ + \ H^+$$

$$\downarrow O_2$$

$$CH_3\text{-}CHO \ + \ HO\cdot_2$$

$$HO\cdot_2 + CH_3\text{-}CH_2\text{-}OH \longrightarrow HO\text{-}CH_2\text{-}CH_2\text{-}OH + OH^-$$

Scheme 5.

In these catalysts it is possible that reduced metals due to electron scavenging may be partially oxidised by holes as observed for other metals [40,41].

4. Conclusions

FTIR and reactivity studies on ethanol interactions with bare-TiO$_2$, Fe-TiO$_2$, Pd-TiO$_2$ and Cu-TiO$_2$ have shown that catalysts bare-TiO$_2$ and Fe-TiO$_2$ show similar behaviour and catalytic abilities.

- A high concentration of H-bounded hydroxyl that favours the formation of ethoxides.
- Ethoxides in these catalysts are readily oxidised to acetates by means of reaction with O$_2{}^{\bullet-}$ and $^\bullet$OH radicals.
- The formation of acetates during the ethanol continuous flow degradation is the cause of the progressive deactivation of bare-TiO$_2$ and Fe-TiO$_2$.

In addition to this, Pd-TiO$_2$ and Cu-TiO$_2$ show very similar catalytic properties but different from those of the above mentioned catalysts.

- The low H-bounded hydroxyl concentration may favour the formation of the intermediate species indicated in Scheme 4, instead of the ethoxyde formation.
- In these catalysts Pd and Cu oxides can be capturing the photogenerated electrons, avoiding the formation of O$_2{}^{\bullet-}$ radicals that generate acetates. This may explain why no deactivation is observed during the in continuous ethanol degradation.

The photocatalytic behaviour of Pd-TiO$_2$ and Cu-TiO$_2$ at the gas-phase ethanol degradation in a continuous flow system have shown very different and promising surfacial properties, for synthesis or photo-synthesis processes, with respect to bare-TiO$_2$ and Fe-TiO$_2$. To improve our understanding about surfacial processes in these catalysts new studies by using extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) are in progress.

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