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Role of Pd and Cu in gas-phase alcohols photocatalytic degradation with doped TiO_2

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Abstract

Propan-1-ol and butan-1-ol photo-degradation with TiO_2 (bare-TiO_2) and TiO_2 doped with Pd or Cu has been studied in a gaseous continuous flow system. Exhaust gases have been analysed by means of GC and FTIR. During propan-1-ol and butan-1-ol degradations, catalysts were not deactivated. Nevertheless, important differences in concentrations and distributions of intermediates were obtained, depending on the catalyst studied.

These alcohols interactions with TiO_2 surface give alcoholates. However, their interactions with Pd–TiO_2 and Cu–TiO_2 do not yield alcoholates. Doped catalysts have progressively grown dark during the experiments, especially when N_2 atmospheres were used. This colour change may be given by the reduction of metal oxides deposited on the catalyst surface. These different photocatalytic behaviours may be explained by means of the alcoholate interaction with the catalysts surfaces, their ability to scavenge photogenerated electrons and react with radicals formed from propan-1-ol and butan-1-ol.

Keywords: Photocatalysis; Propan-1-ol; Butan-1-ol; Gas-phase; TiO_2 doped

1. Introduction

In recent years many different studies have focused on improving TiO_2 photocatalytic activity. For instance, increased catalyst specific area and dispersion have been tried by depositing or synthesing TiO_2 on silica, alumina or activated carbon [1–12]. In this way, a synergistic or combined effect between adsorption and reaction has been attempted, but rarely achieved.

Also, oxidising agents such as H_2O_2, $S_2O_8{}^{=}$ or O_3 [13–19] have been used to improve catalytic response. In these cases, the reaction of these species with the photogenerated holes or electrons to give new radicals and improve the procees was expected:

$$TiO_2 \xrightarrow{h\nu} TiO_2(h^+, e^-), \qquad h^+ + OH^- \rightarrow \cdot OH \tag{1}$$

$$H_2O_2 + e^- \rightarrow {}^\bullet OH + OH^- \tag{2}$$

$$S_2O_8{}^{=} + e^- \rightarrow SO_4{}^{\bullet -} + SO_4{}^{=} \tag{3}$$

$$SO_4{}^{\bullet -} + OH^- \rightarrow SO_4{}^{=} + {}^\bullet OH \tag{4}$$

$$O_3 + e^- \rightarrow O_3{}^{\bullet -} \tag{5}$$

$$H^+ + O_3{}^{\bullet -} \rightarrow HO_3{}^\bullet \rightarrow O_2 + HO^\bullet \tag{6}$$

Photosensitizers have also been employed to improve TiO_2 catalytic efficiency [20,21]. When these compounds are adsorbed on the catalyst surface and irradiated with visible light is promoted an excited state. Then, an electron may be injected in the catalyst conduction band to form a new radical.

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TiO_2 doping with metals such as Cu, Fe, Mo or Pt, has been another important line of research. Its main goal is that the metallic oxides formed on the catalyst surface scavenge the photogenerated electrons, thus reducing the h^+/e^- couple recombination [22–26]. This is thermodynamically possible if the metal (M^{n+}) reduction potential is more positive than the conduction band edge [27].

$$M^{n+} + e^- \rightarrow M^{(n-1)+}$$

$$M^{n+} + h^+ \rightarrow M^{(n+1)+}$$

Nonetheless, it has been indicated that the correlation between the M^{n+} reduction potential and the photocatalytic activity of the photocatalyst M/TiO_2, has not been achieved until now [28]. Many factors may intervene in these processes to inhibit a direct, successful correlation. For instance, if metallic atoms are not located close to the centres where the photogenerated e^- is formed, their scavenging is very hard [29]. It is also evident that if these metallic deposits reduce the incoming photon flux to the catalyst photoactive centres or drastically reduce its active surface, lower photocatalytic efficiencies will be obtained.

Most photocatalytic studies with TiO_2 doped with metals have been carried out in aqueous media. Consequently, metals may be extracted from the catalyst surface by photo-corrosion or interactions between reagents or reaction intermediates [30–33]. However, few papers regarding the effect of the dopant on photocatalytic reactions in gas phase have been published. Our research group has recently investigated ethanol degradation in gas phase by TiO_2 doped with Fe, Cu and Pd [34]. After these studies it was concluded that TiO_2 deactivation is inhibited by surfacial Pd and Cu oxides, which are able to avoid or reduce the formation of acetates on the catalyst surface. We also studied the gaseous propan-1-ol and butan-1-ol TiO_2-photocatalytic degradation. In this case the catalyst is not deactivated since carboxylates are not so readily generated on the catalyst surface [35]. In this paper, the propan-1-ol and butan-1-ol photocatalytic degradations by TiO_2 doped with Cu or Pd oxides have been studied. The main goal of these experiments was to determine whether the presence of these oxides on the catalyst surface avoids the formation of carboxylates, in addition to any other TiO_2 catalyst behaviour improving effect.

2. Experimental

2.1. Catalyst preparation

TiO_2 was Degussa P-25 (80% anatase). Doping was performed by impregnating TiO_2 with aqueous solutions of $PdCl_2$, or $CuSO_4$, according to the metal used by an incipient wetness impregnation method [36] 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 to obtain the corresponding metallic oxides. 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, X being the doping metal (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 already described in others papers [34,35]. This system consists of a continuously aerated vessel containing 2:1 (v/v) water–alcohol solutions at pH = 5. The obtained propan-1-ol and butan-1-ol fluxes were 4.2 and 3.3 μmol/min, respectively. The resulting gaseous mixture (air–water–alcohol vapours) was introduced into 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 [37] with a resulting 1.26×10^{-6} Einteins $l^{-1}\,s^{-1}$.

3. Results and discussion

3.1. Characterisation

3.1.1. Catalyst characterisation

The nature and distribution of TiO_2 surfacial OH group is often the catalyst behaviour determining factor [38–40]. This is why so much research has been devoted to the characterisation of these groups which are present on the surface of many metallic oxides, and especially on TiO_2 [39,41–44].

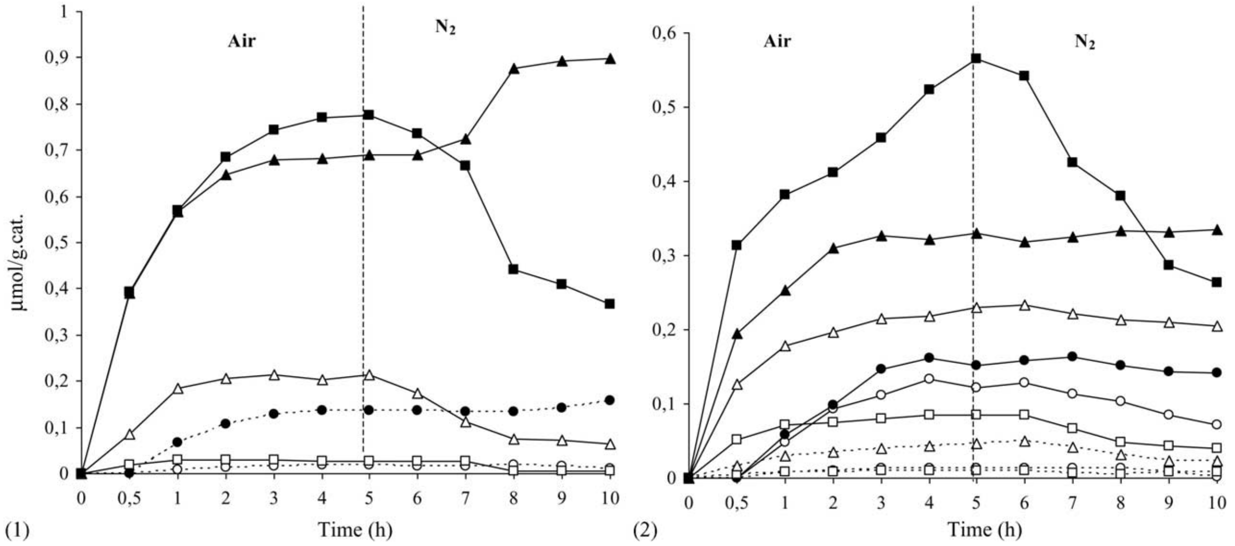


Fig. 1. Degradation results: (1) propanal (full symbol) and acetaldehyde (empty symbol) flow determined during propan-1-ol photocatalytic degradation with bare-TiO_2 (○, ●), Pd–TiO_2 (□, ■) and Cu–TiO_2 (△, ▲); (2) butanal (full symbol), propanal (empty symbol with continuous lines) and acetaldehyde (empty symbol with discontinuous lines) flow determined during butan-1-ol photocatalytic degradation with bare-TiO_2 (○, ●), Pd–TiO_2 (□, ■) and Cu–TiO_2 (△, ▲).

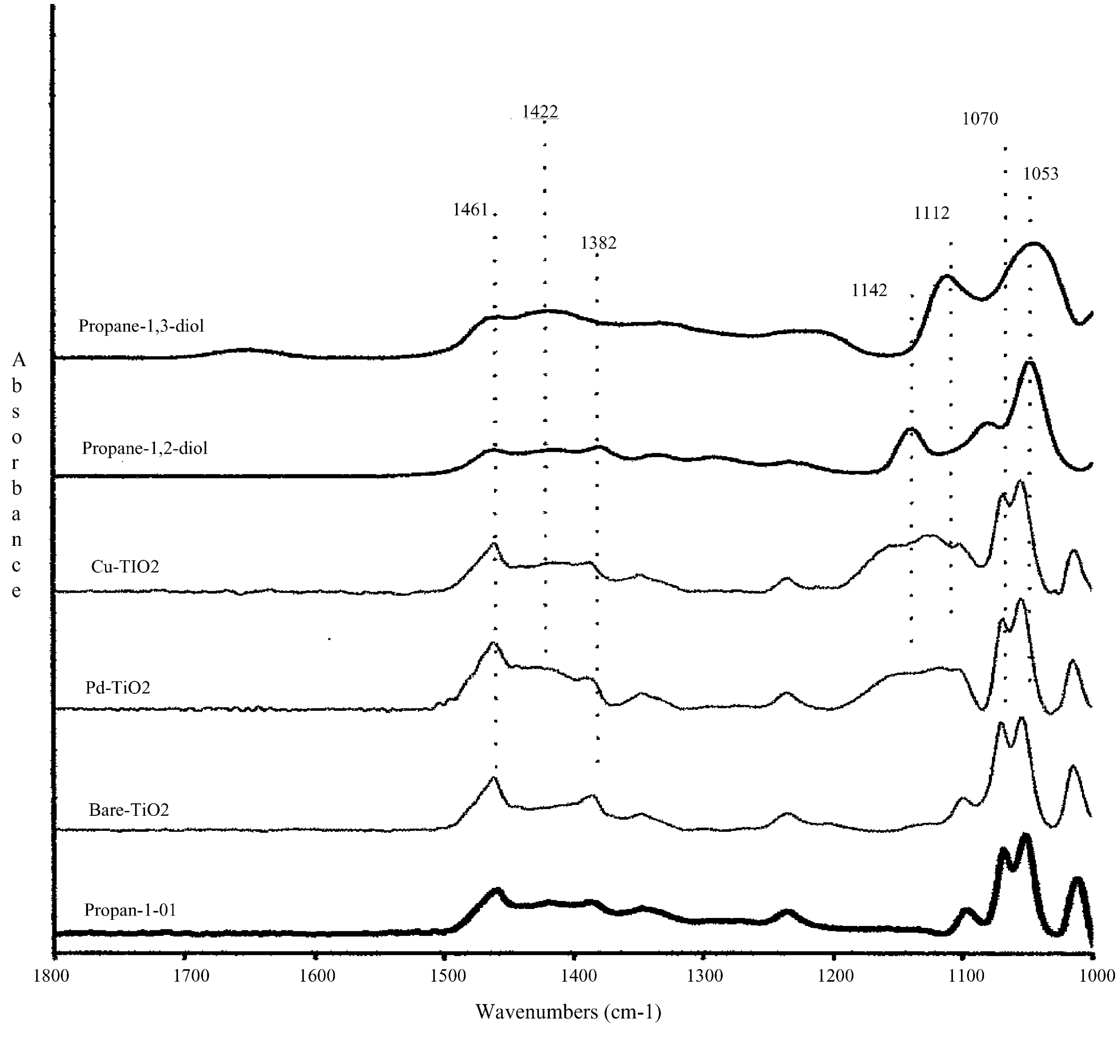


Fig. 2. FTIR spectra from propan-1-ol interaction with different catalysts in the regions between 1800 and 1000 cm^{-1}. Also propan-1-ol, propane-1,2-diol and propane-1,3-diol reference spectrun are showed.

Surfacial hydroxyl groups characterisation of catalysts studied in this paper and XRD analysis have already been described in a previous article [34]. Those studies showed that the catalyst bare-TiO_2 shows a much higher concentration of H-bounded hydroxyl groups (bands between 3500 and 3150 cm^{-1}) in comparison with those of Pd–TiO_2 and Cu–TiO_2. Additionally, XRD spectra from Cu–TiO_2 and bare-TiO_2 were identical. However, in Pd–TiO_2, deposits of PdO were also observed in addition to anatase and rutile phases [34].

3.1.2. Degradation study

Fig. 1(1) and (2) show the results obtained from the propan-1-ol and butan-1-ol degradation with bare-TiO_2, Pd–TiO_2 and Cu–TiO_2, respectivelly. During the first 5 h of reaction experiments were carried out in air, and later air was replaced by N_2.

These alcohols degradation by bare-TiO_2 did not result in the catalyst deactivation. Propanal (Fig. 1(1)) and butanal (Fig. 1(2)) flows are higher than those of other identified aldehydes. Also, the formation of propanoic and butanoic acids having similar flows to that of acetaldehyde has been observed.

When air is replaced by N_2, fluxes of the main aldehydes (propanal (Fig. 1(1)) or butanal (Fig. 1(2))) are slightly increased, while those of the other intermediates are considerably reduced.

In the propan-1-ol and butan-1-ol degradation by Pd–TiO_2 in air, a much higher propanal (Fig. 1(1)) or butanal (Fig. 1(2)) flux than that with bare-TiO_2 is observed. Nevertheless, the flux of other intermediates with this catalyst is very low. When air is replaced by N_2, propanal and butanal flux are notably reduced. In experiments with air this catalyst grew slightly darker, but in those with N_2 it became completely black.

In studies with Cu–TiO_2, the main aldehyde flux propanal (Fig. 1(1)) or butanal (Fig. 1(2)) was slightly lower than that with Pd–TiO_2, but significantly higher than that of bare-TiO_2. However, in this catalyst (Cu–TiO_2) the flux of other intemediates was notably higher than those obtained

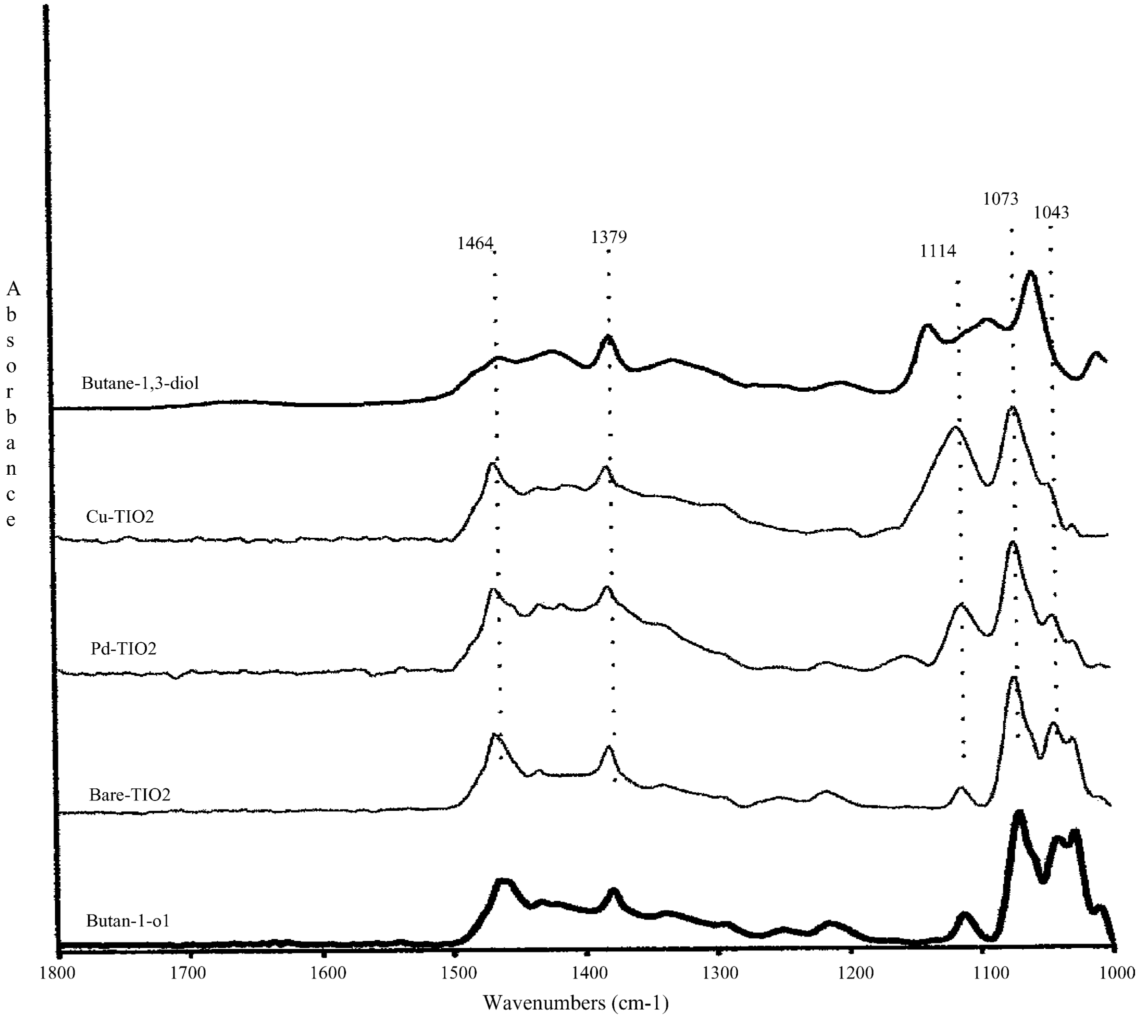


Fig. 3. FTIR spectra from butan-1-ol interaction with different catalysts in the regions between 1800 and 1000 cm^{-1}. Also butan-1-ol and butane-1,3-diol reference spectrun are showed.

with the other catalysts. The air substitution by N_2 gave a flux increment of the main aldehydes, while the flux of other intermediates was reduced. Also in these experiments the catalyst becomes darker, especially without air, though this color change is not so drastic as that observed with Pd–TiO_2.

In these degradation studies it has been observed that bare-TiO_2 is not deactivated by propan-1-ol and butan-1-ol degradations. The contrary was observed for methanol and ethanol [34]. It has been also observed that the presence of Pd or Cu oxides on the TiO_2 surface generates larger aldehyde fluxes.

To better understand these differences, FTIR studies have been performed on these alcohols interactions with the catalysts surfaces in presence and absence of irradiation.

3.2. FTIR study

Figs. 2 and 3 show the propan-1-ol and butan-1-ol interaction spectrum with different catalysts surface. In these alcohols interaction with bare-TiO_2, δOH vibration band (1422 cm^{-1}) disapears. This effect is not observed in the propan-1-ol or butan-1-ol interaction with the doped catalysts. Otherwise, in these catalysts the relative intensity of $\nu(CH_3)$ vibration band (1382 cm^{-1} (Fig. 2) and 1464 and 1379 cm^{-1} (Fig. 3)) is altered. Also new bands appear in the characteristic region of νC–O vibrations from secondary alcohols such as propane-1,2-diol and propane-1,3-diol (Fig. 2) or butante-1,3-diol (Fig. 3), between 1150 and 1112 cm^{-1}. FTIR studies from these catalysts and ethanol interactions indicated that H-bound hydroxyl group low concentration could favour the formation of similar compounds in catalysts doped with Pd and Cu [34].

After these catalysts were irradiated for 5 and 10 min (Figs. 4 and 5). After 5 min carboxylate (1590–1580 and 1440–1430 cm^{-1}) and aldehyde bands (1720–1710 and 1470–1460 cm^{-1}) are observed [41,45]. Adsorbed alcohol bands were also reduced. At larger irradiation times (10 min) the intensity of these bands is increased and that of alcohol is strongly diminished. Moreover, when the doped catalysts are irradiated, in addition to bands from aldehyde, carboxylates bands at different wavenumbers than those observed in bare-TiO_2 are observed. These bands could belong to carboxylates resulting from the oxidation of dihydroxilated or trihydroxilated alcohols, formed from the alcohol interaction with the catalysts. It must be also indicated that the relative intensity of these bands with respect to that from the determined aldehydes are much lower than those from bare-TiO_2.

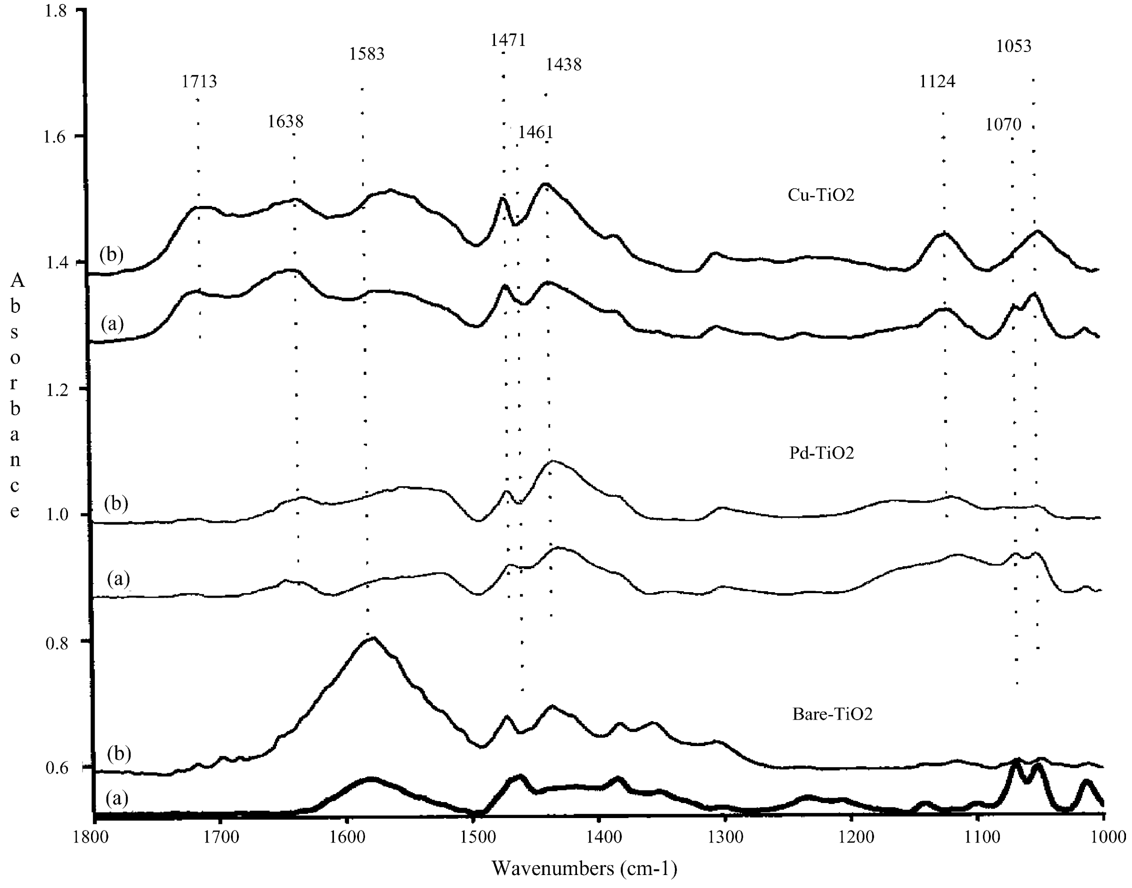


Fig. 4. FTIR spectra propan-1-ol interaction with different catalysts after irradiation for 5 (a) and 10 (b) min in the regions between 1800 and 1000 cm^{-1}.

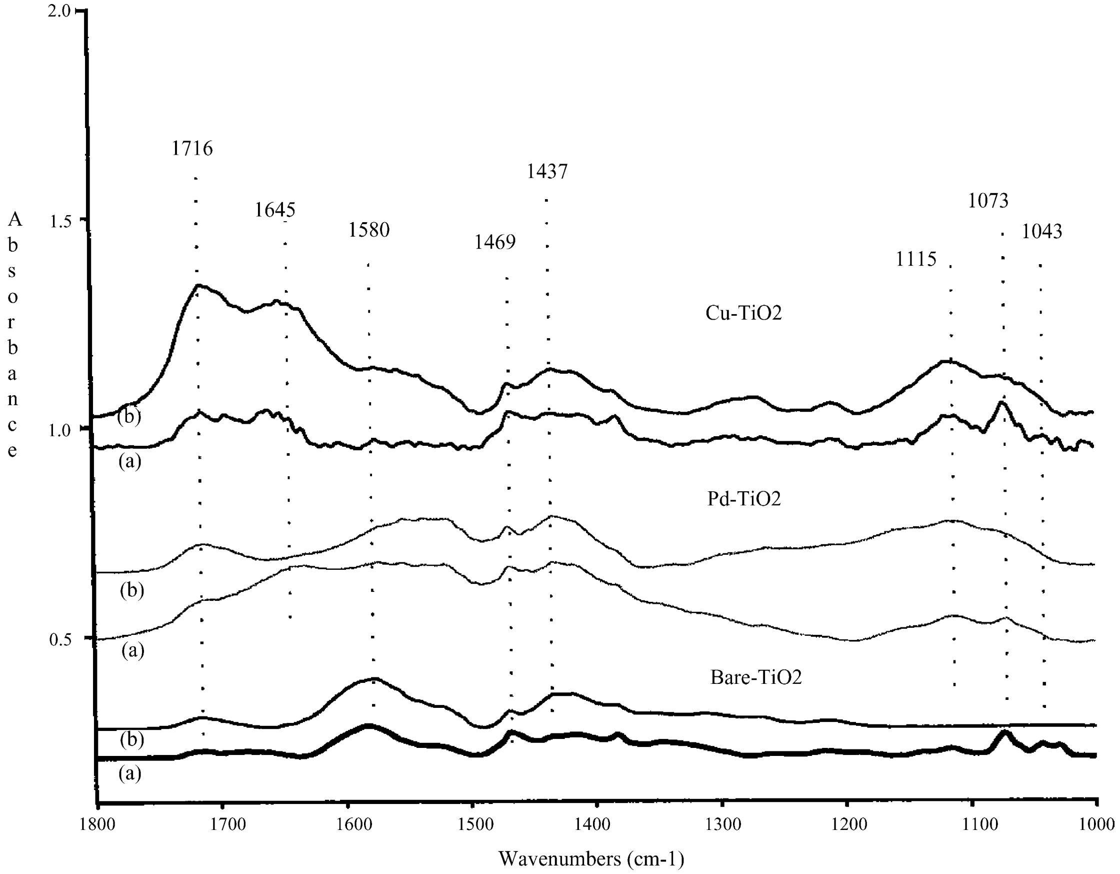


Fig. 5. FTIR spectra butan-1-ol interaction with different catalysts after irradiation for 5 (a) and 10 (b) min in the regions between 1800 and 1000 cm^{-1}.

3.3. Results discussion

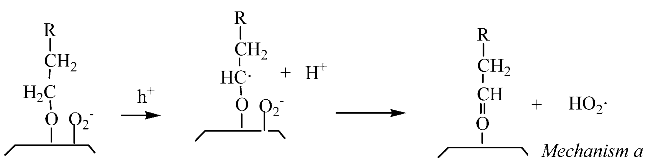
FTIR studies from propan-1-ol and butan-1-ol interactions with the indicated catalysts have shown important changes in their interaction and evolution under irradiation. Such changes depend on the presence of dopants on TiO_2 surface.

Furthermore, it has been observed that propan-1-ol and butan-1-ol interactions with bare-TiO_2 surface give the corresponding alcoholates, that under irradiation evolve to aldehyde and carboxylate. In this case, contrary to the one obtained with methanol and ethanol [34,35] the formation of carboxylates seems to not be so fast, thus possibly avoiding catalyst deactivation.

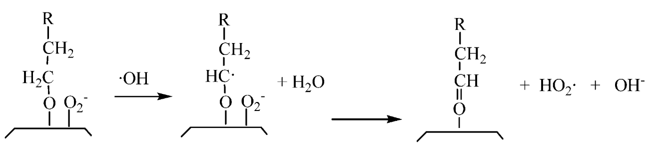
In studies with doped catalysts, the interaction of these alcohols with the catalysts surface seems not to yield the corresponding alcoholate, but an interaction between the methyl group closer to alcohol and catalyst surfacial hydroxylic groups. This interaction change may be, among others, one of the factors determining these catalysts different behaviour. Furthermore, FTIR studies have shown the formation dihydroxylated and trihydroxylated alcohols, in addition to aldehydes and carboxylates, which are different from those obtained with bare-TiO_2. Moreover, during degradation experiments the doped catalysts became darker under irradiation. This effect is attributed to the surfacial metallic oxides reduction. This darkening is stronger when air is substituted by N_2, particularly for Pd–TiO_2.

Results indicate that the photocatalytic degradation of aliphatic alcohols may occur by means of their direct reaction with holes or $^{\bullet}OH$ radicals to yield the corresponding aldehydes [46–50]:

$$TiO_2 \xrightarrow{h\nu} TiO_2\ (h^+, e^-)$$

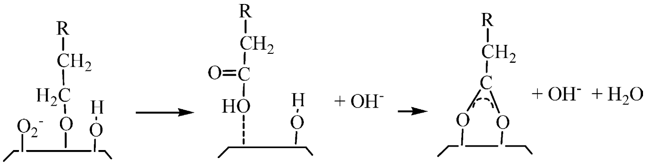


Mechanism a

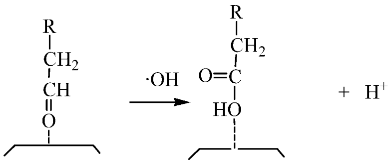


Mechanism b

Alcoholates or aldehydes generated in these reactions may respectively react with $O_2^{\bullet-}$ or $^{\bullet}OH$ radicals, to yield the corresponding carboxylates or carboxylic acids [34,51]:

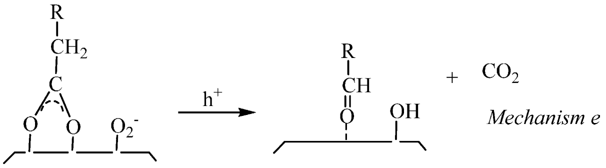


Mechanism c



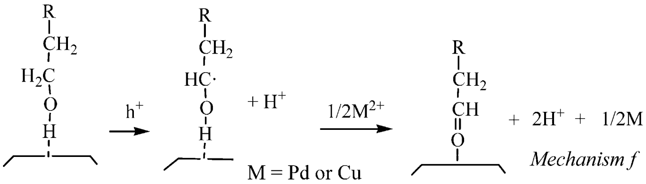
Mechanism d

Carboxylates located on the catalyst surface may react with holes to give the following aldehydes (Kolbe reaction):



Mechanism e

As indicated above, in the doped catalysts the formation of alcoholates has not been observed, but the alcohol molecule hydrogen bonding interaction with the catalyst surface. These species could also react with holes to generate radicals. Additionally, redox potentials of the formed radicals from propan-1-ol and butan-1-ol are high enough [52] to reduce Pd or Cu oxides present on the catalysts surface and give aldehydes, as well. Accordingly, mechanism a for doped catalysts may be illustrated as follows:



Mechanism f

These metallic oxides may also react with the photogenerated electrons, favouring the latter mechanism. Consequently, the high propanal and butanal concentrations determined in propan-1-ol and butan-1-ol degradation experiments, respectively, could be explained by means of this mechanism.

The reaction of photogenerated electrons with the surfacial metallic oxides would hamper the formation of $O_2^{\bullet -}$ radicals, thus inhibiting the formation of carboxylates through mechanism c. Consequently, FTIR determined carboxylates in the doped catalysts would be mainly generated through mechanism d. The low formation of carboxylates would also hamper reactions of mechanism e. This is why with the doped catalysts, propanal/acetaldehyde fluxes ratio in propan-1-ol experiments and that of butanal/propanal in those of butan-1-ol, are lower to fluxes determined with bare-TiO_2.

Reduced Pd or Cu atoms could be reoxidised by oxygen or holes, particularly Cu atoms [53–55]. This explains why in experiments without air almost no variation of intermediates concentrations is observed with Cu–TiO_2. However, with Pd such an oxidation is more difficult. Hence, the surfacial Pd oxides reduction in the absence of air would be fast, resulting in activity reduction.

4. Conclusions

The presence of dopants such as Pd or Cu oxides on the TiO_2 surface notably changes propan-1-ol and butan-1-ol degradation mechanisms. Thus, it has been observed that:

- these alcohols do not yield alcoholates as observed with bare-TiO_2;
- Pd and Cu oxides present on the catalyst surface may oxidise radicals formed from alcohol degradations, thus incrementing their degradation rates;
- these metallic oxides may also react with the photogenerated electrons, favouring the reaction of holes with the organics;
- the Pd or Cu oxides reaction with the photogenerated electrons avoids the formation of O_2^- radicals and the consequent generation of carboxylates;
- a lower carboxylate yield in the doped catalysts inhibits the formation of inferior aldehydes by means of the Kolbe reaction;
- the use of this combination may be particularly useful for treating gases with low O_2 contents or at high flow rates. In such cases, the reduction of the metallic oxides deposited on the catalyst surface would compensate the O_2 absence.

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