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A comparative study of Bi_2WO_6, CeO_2, and TiO_2 as catalysts for selective photo-oxidation of alcohols to carbonyl compounds

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ABSTRACT

Several semiconductors based on ceria or bismuth tungstate were tested for selective oxidation of alcohols to carbonyl compounds in a search for photocatalysts more selective than TiO_2. Gas-phase selective photo-oxidation of propan-2-ol to acetone and liquid-phase transformation of 2-buten-1-ol (crotyl alcohol) to 2-butenal (crotonaldehyde) were studied as test reactions. In both processes the highest selectivities were achieved with Bi_2WO_6-based solids. Further studies on crotyl alcohol transformation evidenced the lower adsorption of the aldehyde on these systems which could minimize the decrease in crotyl alcohol yield observed for TiO_2 or CeO_2 at high conversions. Incorporation of titania (5% molar) to the Bi_2WO_6 system increased the reaction rate significantly whereas the aldehyde yield remained high.

1. Introduction

Partial oxidation of alcohols is an important process for the production of fine and specialty chemicals. The process can be carried out in different ways: (i) with strong oxidizing agents, for instance Jones reagent (a solution of chromic and sulfuric acids in water) which can oxidize primary allylic alcohols to aldehydes. Special care must be taken to prevent further oxidation of aldehydes to carboxylic acids. One possibility is distillation of aldehyde as it is produced. Alternatively, there are some other selective oxidizing reagents such as dimethyl sulfoxide or pyridinium chlorochromate, just to cite some of them. (ii) A second approach is the use of dehydrogenation catalysts, typically copper chromite. (iii) A third alternative is the utilization of the Oppenauer oxidation in which a ketone (typically acetone, butanone or cyclohexanone) in the presence of a base is used as the oxidizing reagent (and it is reduced to a secondary alcohol). (iv) Using TEMPO and related reagents. (v) Utilizing hypervalent iodine reagent, and (vi) resorting to N-bromosuccinimide or in the case of primary alcohols N-chlorosuccinimide [1].

Nevertheless, when talking about environmentally-benign oxidants, H_2O_2 and specially O_2 are preferred to the above-mentioned oxidants since they give either no byproduct or water as byproduct. However, the use of oxygen as oxidant in heterogeneous catalyzed organic reactions is typically associated with substrate total oxidation and/or to the formation of byproducts [2].

One alternative is the use of heterogeneous photocatalysis which can provide a new synthetic method since it requires milder conditions with respect to thermal activation and allows shorter reaction sequences minimizing side processes [3]. Several selective photo-oxidation processes have been reported in the literature (e.g. aromatic hydroxylation, hydrocarbon oxidation, alkene epoxidation, and alcohol oxidation) [4–10]. Focusing on alcohols, the most studied substrates are aromatic, typically benzyl alcohol. One interesting example is oxidation of 4-methoxybenzyl alcohol to the corresponding aldehyde of application in organic synthesis and Fine Chemistry [11]. In comparison to aromatic alcohols, aliphatic require longer irradiation times. The heterogeneous

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catalyst of choice is TiO_2 typically, though some other such as ZnO [12], CdS/TNTs nanocomposites [13], Fe-g-C_3N_4, and titanium silicate zeolite hybrid materials [14] or encapsulated polyoxometalate [15] have been described.

In a previous paper [16] 24 different titania-based systems were tested for gas-phase selective photo-oxidation of propan-2-ol to acetone and liquid-phase transformation of 2-buten-1-ol (crotyl alcohol) to 2-butenal (crotonaldehyde). In general, selectivities to acetone with all the systems were very similar (ca. 50–60%) and quite constant with conversion, the exception being platinum-containing solids which showed quite high selectivity values to acetone (in the 78–80% range at 22–28% conversion). As for the crotyl alcohol transformation, the catalysts differed on the time required to achieve a certain conversion level but for the same conversion values all systems exhibited similar selectivities to crotonaldehyde, the highest crotonaldehyde yield being, under our experimental conditions, ca. 35%. This suggests that selectivity is somehow associated to the semiconductor of choice. With a view to increase the carbonyl compound yield, in the present manuscript the study is expanded to two other semiconductors: Bi_2WO_6 and CeO_2. Though comparatively less explored than TiO_2, both systems have been successfully used in photocatalytic processes. Therefore, for instance, Bi_2WO_6 has been described in photocatalytic mineralization of rhodamine B [17–19], methyl orange [20] or 4-chlorophenol [21] as well as selective photo-oxidation of glycerol to dihydroxyacetone [22] or several benzylic alcohols to the corresponding carbonyl compounds [23]. As for CeO_2, some examples of its photocatalytic application include degradation of halogenated herbicides [24], organic acids [25] or dyes [26], propylene epoxidation [27], and selective oxidation of benzyl alcohols [28,29].

2. Experimental

2.1. Synthesis and characterization of the solids

The synthesis and characterization of the different bismuth tungstate solids was described previously [17,18]. Briefly, the Bi_2WO_6 solids were obtained from a mixture of a solution of $Bi(NO_3)_3$ in glacial acetic acid and an aqueous solution of Na_2WO_4 at pH 2. The resulting suspension was submitted to hydrothermal treatment (140 °C for 20 h) followed by filtration, washing, and drying overnight at 120 °C. The solid was then calcined at 300 °C for 4 h, thus obtaining the system labeled as Bi_2WO_6 (2). Solid named as Bi_2WO_6 (9) was synthesized in a similar way but adjusting the pH of the $Bi(NO_3)_3$–Na_2WO_4 mixture at a value of 9. Incorporation of titanium was carried out through addition of TiO_2 sol (formed from titanium isopropoxide in isopropanol) [17] before the hydrothermal method at the required level as to obtain a final composition 5% molar TiO_2/Bi_2WO_6.

The incorporation of gold was carried out by a photodeposition method. For this purpose, solutions of $HAuCl_4$ in isopropanol (0.3 M) with the corresponding Au content were prepared (0.25 wt% nominal). Suspensions of 1 g of catalyst in 250 mL of the previous solution were prepared and sonicated, after which the pH value was adjusted to 9 by KOH addition. Then, the suspensions were irradiated by visible light for 2 h, under a N_2 atmosphere and, finally, the powder material was filtered, repeatedly washed, and dried overnight.

Catalyst nomenclature includes the pH of the synthesis in brackets. Moreover, when applicable, a suffix indicates the presence of gold (Au) or the incorporation of 5% molar TiO_2 (Ti5).

As regards ceria-based systems, they were prepared from a CeO_2 sample supplied by Rhodia with ≥99.5% and 118 as purity and BET specific surface area, respectively. This ceria was previously studied in [30]. It was separated in three portions and submitted to three different calcination treatments at 500 (2 h), 800 (2 h) or 900 °C (4 h), respectively, with the aim of obtaining samples with different textural properties. Platinum was then incorporated for obtaining different nominal loadings (0.02%, 0.04% or 0.06%, respectively) by incipient wetness from an aqueous solution of $[Pt(NH_3)](OH)_2$. Solids were dried at 105 °C for 12 h and finally calcined at 500 °C for 4 h. Nomenclature includes a suffix (5, 8 or 9) referring to ceria calcination temperature (500, 800 or 900 °C, respectively) and the Pt weight % in the case of the metalized samples.

Finally, Degussa P25 titania was used as a common reference material for photocatalysis.

Some of the features concerning characterization of the solids are given in Table 1.

2.2. Photocatalytic experiments

2.2.1. Gas-phase selective photo-oxidation of propan-2-ol to acetone

Experimental device and reaction conditions were described elsewhere [16]. Basically, 15 mL min^{-1} of O_2 previously bubbled through propan-2-ol at 0 °C was allowed into the photocatalytic reactor, in which 30 mg of catalyst had been placed. The fix bed of the catalyst was in contact with the gas flow. UV light (UV Spotlight source LightningcureTM L8022, Hamamatsu, maximum emission at 365 nm) was focalized on the sample compartment through an optic fiber. Radiant flux in the catalyst compartment was measured to be 1 W cm^{-2} (Newport UV-meter 818P-015-19 Model) and the spot area 1.33 cm^2. Reactor was on-line connected to a HP6890 chromatograph equipped with a six-way valve, a HP-PLOTU column (30 m long, 0.53 mm ID, 20 mm film thickness) and a Ni methanator (Agilent Part Number G2747A) which allowed us to determine the percentage of CO_2 resulting from mineralization. Temperature at the photoreactor was controlled by water thermostated at 10 °C. The reaction lasted for 5 h.

2.2.2. Liquid phase selective photo-oxidation of 2-buten-1-ol (crotyl alcohol) to 2-butenal (crotonaldehyde)

Experimental device and optimization of reaction conditions were described in a previous study [16]. Under standard conditions, 3 mL of a stock solution 0.01 M of crotyl alcohol (97% *trans*) in acetonitrile was introduced in the 30 mL double-mouthed heart-shaped reactor. After 5 min bubbling through the solution pure oxygen (10 mL min^{-1}), 0.15 mL were sampled, filtered, injected in the GC and taken as initial concentration (C_0). The catalyst 18 mg (6 g/L) was then added, the system closed and stirred (900 rpm) and after 15 min of adsorption in the dark, light was allowed into the reactor. UV light (UV Spotlight source LightningcureTM L8022, Hamamatsu, maximum emission at 365 nm) was focalized on the sample compartment through an optic fiber. Radiant flux in the catalyst compartment was set up at 500 mW cm^{-2} (measured with a Newport UV-meter 818P-015-19 Model) and the spot area on the liquid surface was 2.54 cm^2. Water used for cooling was thermostated at 10 °C. Reaction profiles were obtained for the same stock solution, each point corresponding to one individual reaction. Once the system had been irradiated for the selected time, the whole suspension was filtered (15 mm diameter, 0.45 μm pore size, Sartorius re. 17559) and analyzed by GC (HP6890 chromatograph equipped with an automatic injector and a HP-PLOTU column −30 m long, 0.53 mm ID, 20 mm film thickness). The main reaction products identified in the liquid phase were crotonaldehyde (*cis* and *trans*) and acetaldehyde. Moreover, some other very minor species (e.g. formaldehyde and methanol) were detected at trace levels.

Table 1
Some of the main features concerning characterization of the solids used in the present study.

Catalyst	BET surface (m^2/g)	Band gap (eV)	Crystal size (nm)	Modifier content (%)[a]
TiO_2 (Degussa P25)	55	3.2	21	–
CeO_2 5	113	3.5	11	–
CeO_2 5 Pt 0.02	110		12	0.02
CeO_2 8 Pt 0.04	45		25	0.04
CeO_2 9 Pt 0.06	23		42	0.06
Bi_2WO_6 (2)	25	2.8	10	–
Bi_2WO_6–Ti5 (2)	52	2.9	9	5.8% Ti
Bi_2WO_6–Au (5)	25	2.5	11	0.25% Au
Bi_2WO_6–Ti5–Au (2)	41	2.9	9	5.8% Ti, 0.25% Au
Bi_2WO_6 (9)	20	2.8	23	–
Bi_2WO_6–Au (9)	13	2.8	27	0.25% Au

[a] Weight % for Pt and Au. Molar content (as determined by XRF) for Ti.

2.3. Study of superficial adsorption of crotyl alcohol and crotonaldehyde on the catalysts

Adsorption studies of crotyl alcohol and crotonaldehyde on TiO_2 and Bi_2WO_6 were carried out by DRIFT on an ABB Bomen MB 3000 Series IR spectrophotometer equipped with a SpectraTech P/N 0030-100 environmental chamber including a diffuse reflectance device capable of performing 256 scan at 8 cm^{-1} resolution at an adjustable temperature. Catalysts were submitted to an atmosphere saturated in the substrate at room temperature for 30 min. DRIFT spectra were then registered at different time intervals on application of a cleaning N_2 flow of 30 mL min^{-1}. Spectra of the untreated catalysts were used as the reference.

For monitoring of photocatalytic degradation of the substrates, the saturated solids were submitted to UV irradiation (UV Spotlight source LightningcureTM L8022, Hamamatsu, maximum emission at 365 nm) at different time intervals and then transferred to the DRIFT equipment. Again, untreated solids were used as the reference.

For the sake of comparison, infrared spectra of pure crotyl alcohol and crotonaldehyde were carried out on the ABB Bomen MB 3000 Series IR spectrophotometer using in this case a Pike Miracle single reflection ATR.

3. Results and discussion

3.1. Gas-phase selective photo-oxidation of propan-2-ol to acetone

All catalysts based on Bi_2WO_6 and CeO_2 as well as the reference material TiO_2 (Degussa P25) were tested for gas-phase selective photo-oxidation of propan-2-ol to acetone. Results found for initial and final (5 h on stream) conversion as well as final selectivity to acetone and CO_2 are depicted in Fig. 1A. In terms of conversion, the highest values corresponded to the reference TiO_2 material followed by CeO_2-based solids, the Bi_2WO_6 systems exhibiting the lowest conversion values. It is also worth noting that in the case of ceria-containing samples the incorporation of Pt at a very low content (0.02% by weight) resulted in conversion values being doubled (from 16% to 32%) whereas selectivity to acetone hardly changed (ca. 46% for $t = 5$ h). This could be explained in terms of the metal decreasing the electron–hole recombination rate [31,32]. In the case of the CeO_2 8 Pt 0.04 and CeO_2 9 Pt 0.06 samples their significantly lower surface area values (see BET data in Table 1) may explain the decrease observed in the conversion parameter.

As regards Bi_2WO_6 solids, it is worth noting their high selectivity to acetone (85–92%). It could be argued that this is just the result of

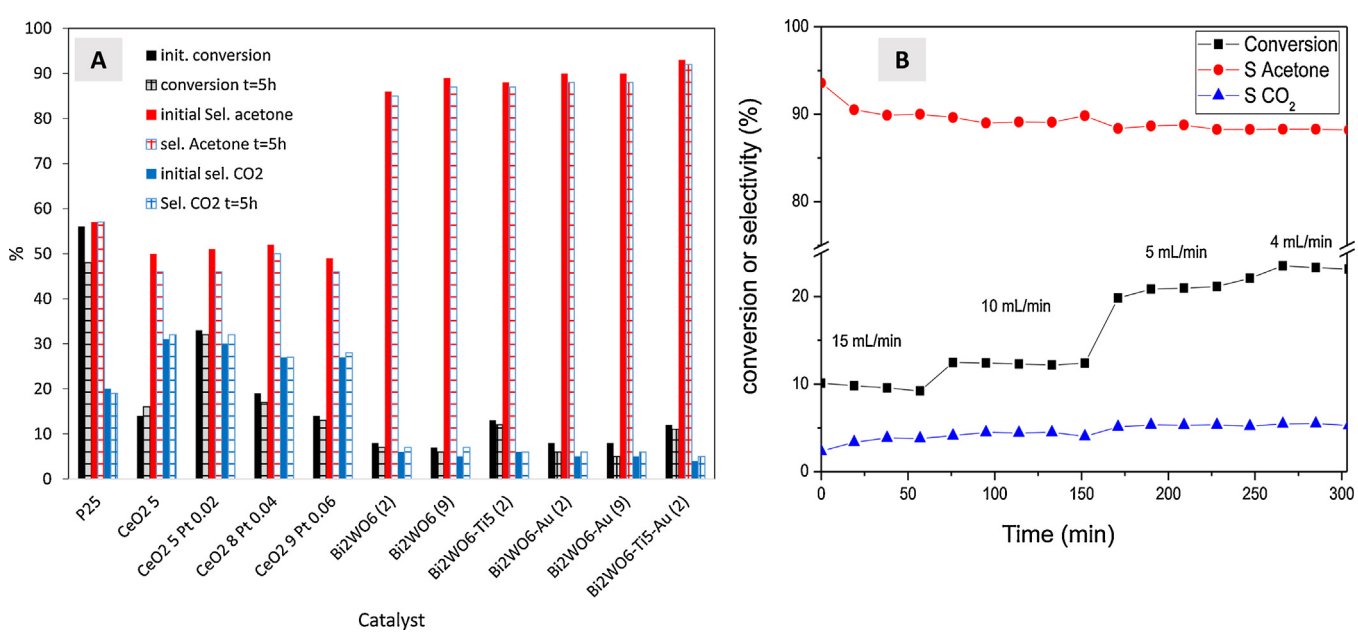

Fig. 1. (A) Gas-phase selective photo-oxidation of propan-2-ol to acetone on all the systems described in the present study under standard conditions. (B) Further studies on Bi_2WO_6–Ti5 (2) using different oxygen flows.

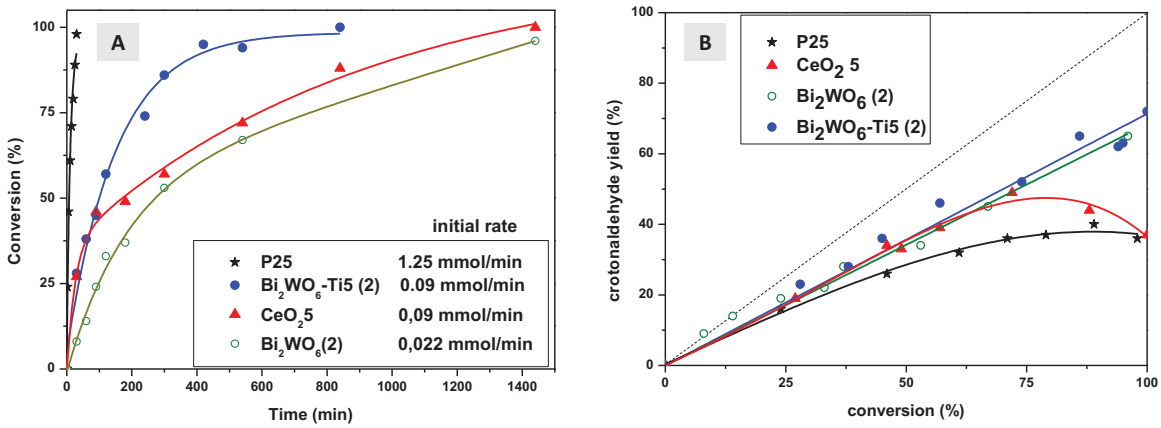

Fig. 2. Liquid-phase selective photo-oxidation of 2-buten-1-ol (crotyl alcohol) to 2-butenal (crotonaldehyde). (A) Evolution of conversion on several solids with irradiation time and (B) crotonaldehyde yield as a function of conversion.

their low conversion values (6–12%). However, a decrease in oxygen flow (Fig. 1B), in order to increase contact time, resulted in conversion of acetone on Bi_2WO_6 Ti5 (2) increasing up to 23% for $t = 5$ h, selectivity to acetone remaining in the 88–90% range. Therefore, Bi_2WO_6 solids seems to be intrinsically more selective to acetone than those based on TiO_2 or CeO_2. Interestingly, incorporation of titania into Bi_2WO_6 led to a significant increase in conversion (from 7% to 12% for $t = 5$ h) whereas selectivity hardly changed. Incorporation of gold also resulted in an increase in selectivity to acetone (from 85–88% to 87–92%).

All in all, given the comparatively high conversion levels obtained with Degussa P25, the yield to acetone for $t = 5$ h followed the sequence Degussa P25 (27%) > CeO_2 5 Pt 0.02 (14.8%) > Bi_2WO_6–Ti5 (10.4%) > Bi_2WO_6–Ti5–Au (10.1%). Studies for Bi_2WO_6–Ti5 (2) at lower oxygen flows resulted in acetone yield of 20.6% for $t = 5$ h.

3.2. Liquid-phase selective photo-oxidation of crotyl alcohol to crotonaldehyde

This second test reaction incorporates an additional challenge: the presence of a C=C bond which can also be oxidized. Moreover, unlike propan-2-ol, crotyl alcohol is a primary alcohol thus leading on oxidation to an aldehyde which tends to oxidize to the carboxylic acid.

Initially, direct photolysis (no catalyst) and catalysis in the dark experiments were performed on crotyl alcohol. In the first case, there was only a conversion of ca. 5% after 5 h of irradiation. In the latter case, the most active photocatalytic system, Degussa P25, did not exhibit any conversion in the dark. Therefore, disappearance of the substrate with the irradiation time in the presence of the catalyst can be attributed to photocatalytic phenomena, mainly.

Reaction profiles under standard conditions for the different systems expressed in terms of conversion and crotonaldehyde yield are depicted in Fig. 2. Similarly to gas-phase selective photo-oxidation of propan-2-ol to acetone, the most active bare system for liquid-phase crotyl alcohol transformation is Degussa P25 (100% conversion after 30 min) followed by ceria and Bi_2WO_6 solids. In terms of selectivity to crotonaldehyde, for similar conversion data, the highest values corresponded to Bi_2WO_6 (decreasing from 81% to 65% as reaction proceeds) followed by Degussa P25 (from 65% down to 35%) and CeO_2 (72–37%). This results in the highest crotonaldehyde yield values being achieved with Bi_2WO_6 solids (Fig. 2B). Interestingly, the significant increase in Bi_2WO_6 conversion achieved upon incorporation of 5%TiO_2 (Fig. 2A) was not detrimental to crotonaldehyde selectivity (Fig. 2B). Bi_2WO_6–Ti5 (2) exhibits higher selectivity to crotonaldehyde especially at high conversion values than a physical mixture containing 95% Bi_2WO_6 (2) and 5% TiO_2 (see Fig. S1). This could be explained in terms of a synergistic effect between TiO_2 and Bi_2WO_6 upon accommodation of titania within the Aurivillius structure, between the perovskite WO_6 layer and near $(Bi_2O_2)^{2+}$ sheets [17].

The above-described results seem to suggest a lower adsorption of crotonaldehyde on Bi_2WO_6 solids whereas for CeO_2 and TiO_2 this substrate could adsorb stronger thus favoring subsequent degradation to the detriment of crotonaldehyde yield.

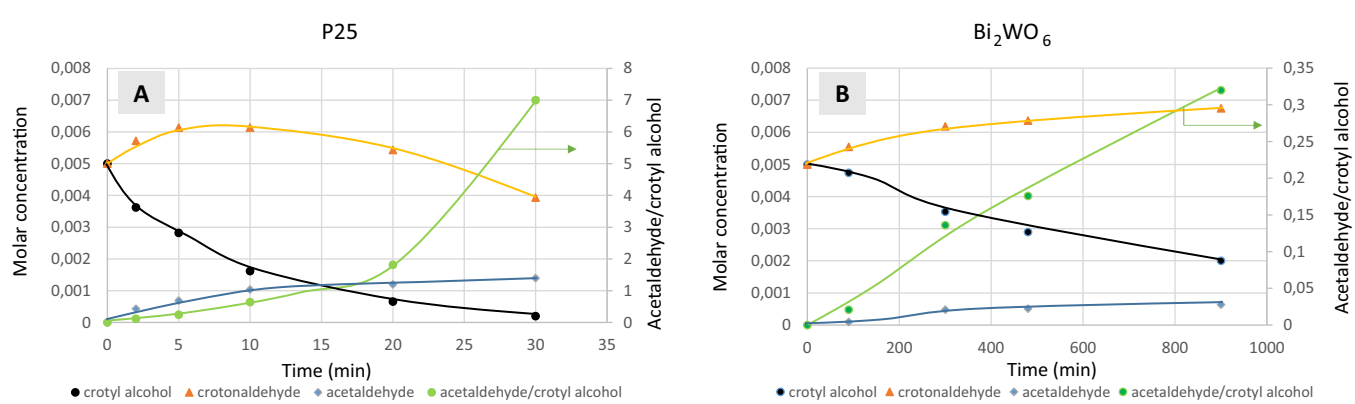

Fig. 3. Liquid-phase photo-oxidation of an equimolecular mixture of 2-buten-1-ol (crotyl alcohol) and 2-butenal (crotonaldehyde), 0.005 M each, on Degussa P25 (A) or Bi_2WO_6 (B).

In order to cast further light on the reason for the higher selectivity values to crotonaldehyde on Bi_2WO_6 solids, several experiments were performed.

Firstly, a competitive photocatalytic experiment starting from an equimolecular mixture of crotyl alcohol and crotonaldehyde (0.005 M each) was carried out on both Degussa P25 and Bi_2WO_6. Reaction profiles are given in Fig. 3. As can be seen, in both cases there is one point when concentration of crotonaldehyde (which can result from photo-oxidation of crotyl alcohol) is higher than initial value (0.005 M). This is an evidence of the faster degradation of the alcohol as compared to the aldehyde. However, as reaction proceeds there are some other side reactions such as oxidative cleavage through C=C bond which can lead to acetaldehyde. In the case of Degussa P25, acetaldehyde to crotyl alcohol ratio is significantly higher than that for Bi_2WO_6 which again is indicative of the higher selectivity to crotonaldehyde on bismuth tungstate. For instance, for a crotyl alcohol conversion of ca. 40%, acetaldehyde to crotyl alcohol ratio is 0.24 and 0.17 for Degussa P25 and Bi_2WO_6, respectively.

Secondly, some reactions starting with crotonaldehyde were carried out (not shown). Unlike crotyl alcohol, crotonaldehyde undergoes a significant direct photolysis, its conversion being ca. 21% after 5 h of irradiation. These values are similar to those achieved on Bi_2WO_6–Ti5 (2) or a photocatalytically inert material such as alumina (Fig. S2). On the contrary, CeO_2 and TiO_2 exhibited higher conversions (50% for $t = 5$ h or 33% for $t = 30$ min, respectively), Again, this is supportive of the lower adsorption of crotonaldehyde on Bi_2WO_6 systems. An additional evidence pointing towards this direction is evolution of *trans* to *cis* isomerization of crotonaldehyde on the different catalysts. As commented in the experimental section, crotyl alcohol used in the experiments had a *trans*/*cis* ratio of ca. 97/3%. This alcohol keeps a similar isomers ratio with irradiation time whereas crotonaldehyde undergoes some *trans* to *cis* isomerization [16,33] towards the equilibrium composition which seems to be around 72:28 (*trans*/*cis*). Fig. 4 shows evolution of *trans* crotonaldehyde percentage with crotyl alcohol conversion. As can be seen, for similar conversion values, *trans* to *cis* isomerization followed the order Bi_2WO_6 (2) > CeO_2 5 > Bi_2WO_6–Ti5 (2) > Degussa P25. One could think that this is just the result of the conversion rates depicted in Fig. 2A. Therefore, in order to achieve similar conversion values, the least active solids (i.e. Bi_2WO_6) require longer irradiation times, this light exposure being responsible for the isomerization to a higher extent. However, the values highlighted with the circle correspond to the same irradiation time (30 min) and confirm the higher isomerization when Bi_2WO_6 was used as the catalyst. Results are interpreted in terms of crotonaldehyde adsorption strength on the different solids. The stronger the adsorption the more hindered the *trans* to *cis* isomerization. The star symbols in Fig. 4 correspond to direct photolysis, 76/24% *trans*/*cis* ratio (quite close to equilibrium) being achieved within ca. 15 min irradiation time.

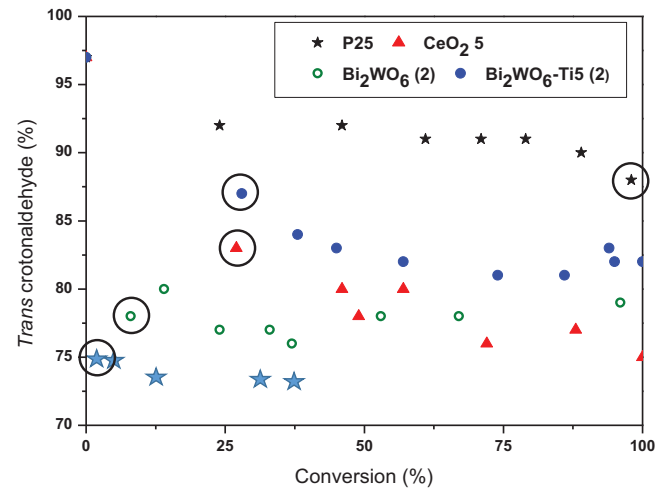

Fig. 4. Evolution of the percentage of *trans* crotonaldehyde in liquid-phase selective photo-oxidation of 2-buten-1-ol (crotyl alcohol) to 2-butenal (crotonaldehyde) starting from 97/3% *trans*/*cis* crotyl alcohol. The stars correspond to direct photolysis (no catalysts) of 97% *trans* pure crotonaldehyde. The values highlighted with a circle were obtained for 30 min irradiation time.

More experimental evidences on the different adsorption of crotyl alcohol and crotonaldehyde on the solids are given by DRIFT studies performed using Bi_2WO_6 and TiO_2 as the catalysts. Results are depicted in Figs. 5–7. In all cases (except for pure substrates), spectra of catalysts were used as the reference.

Spectra of Bi_2WO_6 and Degussa P25 TiO_2 submitted to an atmosphere saturated in crotyl alcohol or crotonaldehyde for 30 min are shown in Fig. 5. For comparative purposes, spectrum of liquid crotonaldehyde and crotyl alcohol are also represented. As can be seen, adsorption of both substrates results in the appearance of some negative bands in the 3600–3700 cm^{-1} region which suggests the adsorption onto the catalysts through surface OH groups. Those negative bands are sharper for Degussa P25 which suggests a higher adsorption on this solid. As regards crotyl alcohol (Fig. 5A), adsorption on both solids also results in the shift of the C=C stretch band from 1672 to ca. 1625 cm^{-1}, thus suggesting similar adsorption strength through this group in both cases. As for crotonaldehyde (Fig. 5B), its adsorption results in a shift of C=O stretch band from 1685 cm^{-1} to 1660 or 1650 cm^{-1} (for Bi_2WO_6 and TiO_2,

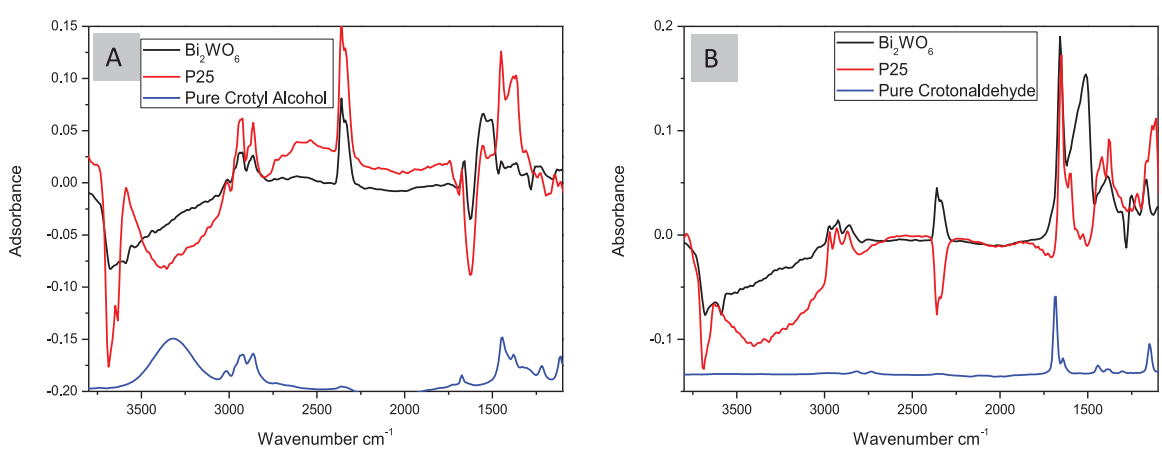

Fig. 5. DRIFT spectra of crotyl alcohol (A) or crotonaldehyde (B) on Bi_2WO_6 or Degussa P25 catalysts. For the sake of comparison, the ATR spectra of liquid substrates have also been included.

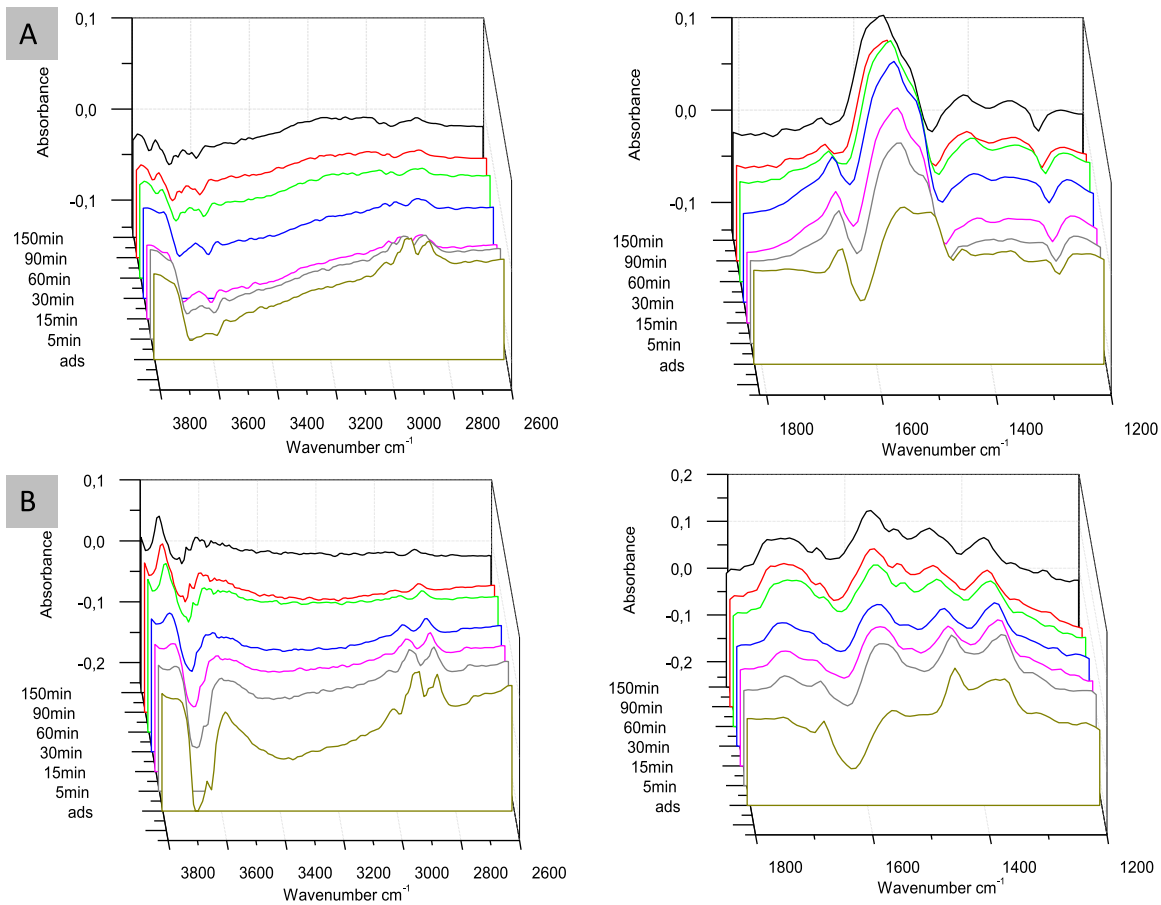

Fig. 6. Photo-oxidation of crotyl alcohol preadsorbed on Bi_2WO_6 (a) or P25 (b) for different irradiation times.

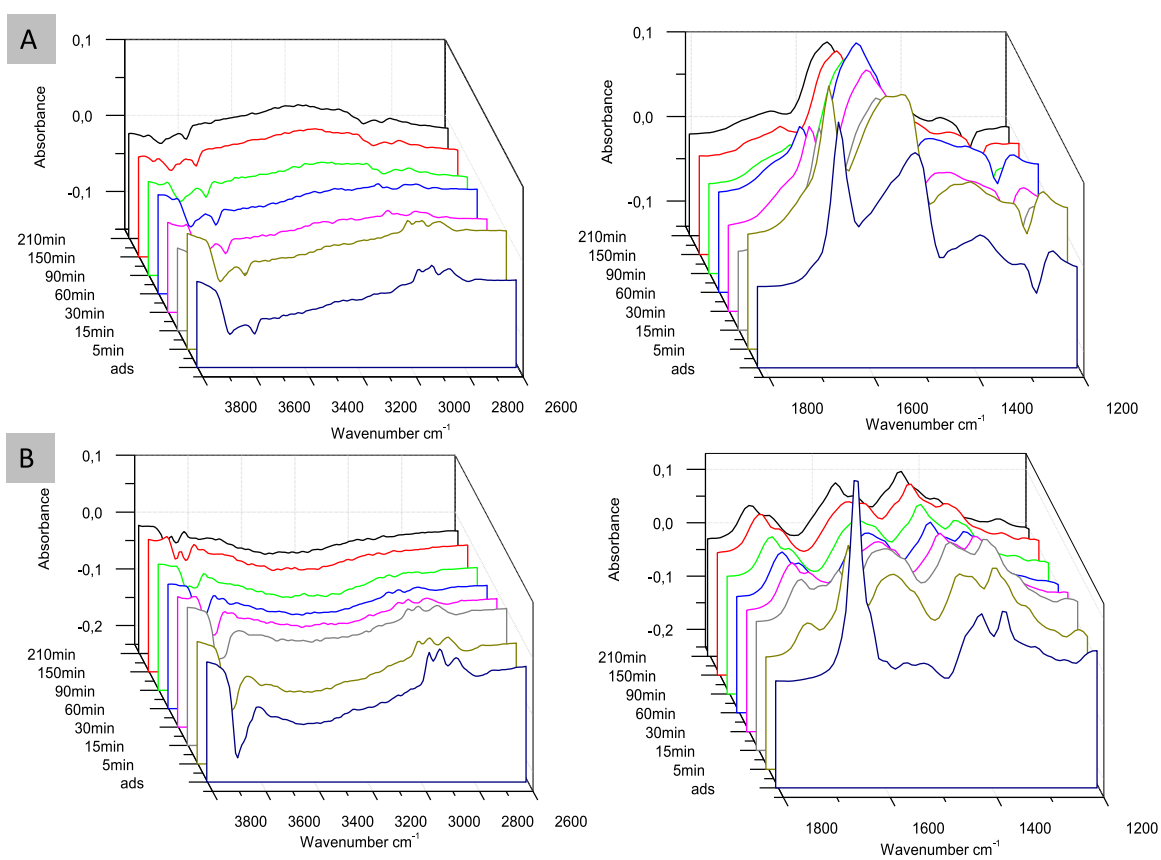

Fig. 7. Photo-oxidation of crotonaldehyde preadsorbed on Bi_2WO_6 (a) or P25 (b) for different irradiation times.

respectively). This could be indicative of a stronger interaction of crotonaldehyde through the C=O bond on TiO_2.

The above-mentioned experiments on adsorption of crotyl alcohol and crotonaldehyde were completed with photocatalytic studies by irradiation of samples with UV light. In the case of photocatalytic degradation of crotyl alcohol on Bi_2WO_6 (Fig. 6A) there is an increase in the intensity of bands at 1658 and 1550 cm^{-1} (C=O and C=C in crotonaldehyde, respectively) [34] up to t = 15–30 min. For longer irradiation times, all bands decrease thus suggesting desorption of all reaction products. In the case of P25 (Fig. 6B), there is a continuous increase in bands at 1560 and 1730 cm^{-1}. The former band is indicative of conjugated C=C whereas the latter could be ascribed to acetaldehyde or acetic acid [34]. Results obtained for photocatalytic degradation of crotonaldehyde on both catalysts (Fig. 7) confirm the quicker degradation on TiO_2 (as evidenced by the sharp decrease in C=O band) as well as the appearance of a small shoulder at ca. 1708 cm^{-1} in Bi_2WO_6 (probably indicative of acetaldehyde) and a well-defined band at ca. 1720 cm^{-1} in Degussa P25 (oxidation to a further extent, probably to acids). Therefore, these results are also supportive of the stronger adsorption of crotonaldehyde on TiO_2 as compared to Bi_2WO_6. The longer residence time of crotonaldehyde onto TiO_2 favors its subsequent photo-oxidation (to acetaldehyde through oxidative cleavage of C=C and/or to acids) thus accounting for the lower selectivity obtained for Degussa P25 as compared to Bi_2WO_6.

4. Conclusions

Different solids based on titania, ceria, and bismuth tungstate were tested for two selective oxidation processes: gas-phase selective photo-oxidation of propan-2-ol to acetone and liquid-phase selective photo-oxidation of crotyl alcohol to crotonaldehyde. In both processes, Bi_2WO_6 solids were intrinsically more selective to the carbonyl compound. Different experiments on crotyl alcohol photocatalytic reaction evidenced that the higher selectivity to crotonaldehyde on bismuth tungstate is the result of the lower adsorption of this chemical. Interestingly, the incorporation of a small amount of titania (5% molar) to Bi_2WO_6 increased reaction rate considerably while keeping the selectivity to crotyl alcohol high. This could be the result of the balance between the presence of some titania which would be detrimental to crotonaldehyde yield and the lower irradiation times required thus resulting in the photolysis of crotonaldehyde to a lower extent. This opens the possibility to the synthesis of new hybrid (e.g. Bi_2WO_6–TiO_2) photocatalytic materials highly active and selective for oxidation of alcohols to carbonyl compounds.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.08.013.

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