

Photocatalytic Synthesis of Acetaldehyde by Selective Oxidation of Ethanol on RuO_x-VO_x/TiO₂

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The gas-solid photocatalytic partial oxidation of ethanol to acetaldehyde on monometallic RuO_x/TiO₂ and bimetallic RuO_x-VO_x/TiO₂ catalysts has been studied in a fluidized bed photoreactor at high illumination efficiency. For RuO_x/TiO₂, by increasing ruthenium loading ethanol conversion decreased from 60 to 37 %, while acetaldehyde selectivity increased to about 97% at 0.4 wt % RuO₂ loading. With bimetallic RuO_x-VO_x/TiO₂ the selective yield to acetaldehyde by monometallic Ru based catalysts is enhanced by the highly active V species, resulting in higher photocatalytic performance. By increasing the vanadium loading, ethanol conversion increased up to 100 % with almost total selectivity to acetaldehyde.

1. Introduction

Aldehydes are important products and intermediates in the field of fine chemicals. A commonly used method for their preparation is the oxidation of the respective alcohols. As alternative to the use of the stoichiometric application of toxic inorganic salts, catalytic process with environmentally benign oxidants has been studied in the past years (Sheldon et al., 2000). For this purpose, molecular oxygen is particularly attractive. Ru based catalysts are well known to oxidize alcohols. For example, Ru species immobilized on different supports (Dalal and Ram, 2000) were studied. The most of these studies are carried out in liquid phase and discontinuous reactors, so it is necessary to separate the catalyst from reaction products after the oxidation. This operation can be avoided using a gas-solid continuous catalytic reactor. But generally, the gas phase process is carried out at high temperatures resulting in low selectivity towards aldehydes. For this reason, from an environmental and economic standpoint, the use of a photocatalytic system to carry out selective oxidation of alcohols is particularly attractive because photocatalytic reactions are often conducted at ambient temperature (Murcia et al., 2012a, Murcia et al., 2012b, Sannino et al., 2012b, Ciambelli et al., 2008). Among aldehydes, acetaldehyde is widely used as an intermediate in industrial organic synthesis. We have already demonstrated that acetaldehyde can be the product of gas-phase oxidative dehydrogenation of ethanol with high yield by means of a photocatalytic fluidized bed reactor and VO_x/TiO₂ powders as photocatalysts. (Ciambelli et al., 2009b, Sannino et al., 2012a). Photocatalytic tests gave evidence of the selective formation of acetaldehyde, even in the presence of low amounts of ethylene, carbon dioxide and crotonaldehyde as by-products. The highest value for acetaldehyde selectivity, depended by the vanadium loading, was 97 % (Ciambelli et al., 2009b, Ciambelli et al., 2011).

With the aim to further limit the formation of all the secondary reaction products, monometallic RuO_x/TiO₂ and bimetallic RuO_x-VO_x/TiO₂ catalysts, at different ruthenium and vanadium loading, have been studied in the gas-solid photocatalytic oxidative dehydrogenation of ethanol to acetaldehyde.

2. Experimental

2.1 Catalysts preparation and characterization

Anatase titania (PC105, 87 m²/g by Millennium Inorganic Chemicals) was used as support. Monometallic catalysts RuO_x/TiO₂ containing various amounts of ruthenium were prepared. by wet impregnation of the support

with a solution of $(C_5H_8O_2)_3Ru$ (Aldrich) in acetone, followed by drying at 120°C and calcination at 300°C for 3 hours. RuO_x/TiO_2 samples were treated with a second wet impregnation in distilled water with ammonium metavanadate (NH_4VO_3), dried at 120 °C and calcined in air at 300 °C for 3 h to obtain bi-metallic RuO_x-VO_x/TiO_2 catalyst samples. Physico-chemical characterisation of catalysts was performed by different techniques. Specific surface areas were obtained by N_2 adsorption measurement at -196 °C with a Costech Sorptometer 1040 after pretreatment at 150 °C for 30 min in He flow (99.9990 %).

Laser Raman spectra were obtained at room temperature with a Dispersive MicroRaman (Invia, Renishaw), equipped with 633 nm diode-laser, in the range 100-2500 cm^{-1} Raman shift.

UV-Vis reflectance spectra were recorded with a Perkin Elmer spectrometer Lambda 35. Equivalent band gap determinations were obtained from Kubelka-Munk theory (Ciambelli et al., 2007) by plotting $[F(R_\infty)*hv]^2$ vs hv and calculating the x intercept of a line through $0.5 < F(R_\infty) < 0.8$. X-ray diffraction (XRD) was carried out using an X-ray microdiffractometer Rigaku D-max-RAPID, using $Cu-K\alpha$ radiation and a cylindrical imaging plate detector. Diffraction data from 0 to 204 degree horizontally and from -45 to 45 degree vertically were collected. The incident beam collimators enable different spot sizes to be projected onto the sample.

2.2 Photocatalytic tests

Photocatalytic tests were carried out at 100°C and atmospheric pressure, feeding 30 (stp) L/h of a He stream containing 0.2 vol. % ethanol, with oxygen/ethanol ratio of 2, to a catalytic fluidized bed, whose geometrical characteristics are reported in (Palma et al., 2010, Ciambelli et al., 2009a). The reactor was illuminated by two UVA-LEDs (emitting at 365 nm) modules of 40 pieces each, positioned in front of the Pyrex windows. The light intensity was regulated at 100mW/cm². The catalyst (1.2 g), was loaded after physical mixing with 20g of glass spheres (Lampugnani, 70-110 μm range size). The outlet reactor gas composition was continuously measured by an on-line quadrupole mass detector (TraceMS, ThermoElectron) and a continuous CO-CO₂ NDIR analyser (Uras 10, Hartmann & Braun). Dark equilibrium data of ethanol adsorption on the catalyst surface were obtained by integration of alcohol concentration profiles obtained before the photocatalytic tests.

3. Results and discussion

3.1 Catalysts characterization

The list of catalysts investigated and their composition is reported in Table 1. The specific surface area of 0.3Ru is similar to the titanium dioxide (87 m²/g) used as support, while a slight progressive decrease was found for 0.4Ru, 0.6Ru and 1.2Ru samples. Further decrease in specific surface area was obtained by increasing the V amount of 0.4Ru catalyst.

Table 1: RuO_x/TiO_2 and VO_x-RuO_x/TiO_2 catalysts and characteristics

Catalyst	RuO_2 wt %	V_2O_5 wt %	SSA m ² /g	E_{bg} eV	Ethanol dark adsorbed mol/g	Ru/Ti*	V/Ti*
TiO ₂	-	-	87	3.4	894	-	-
0.3Ru	0.3	-	85	3.4	882	0.0046	-
0.4Ru	0.4	-	81	3.3	852	0.0066	-
0.6Ru	0.6	-	78	3.3	836	0.0151	-
1.2Ru	1.2	-	74	3.4	685	0.0279	-
0.4Ru-2V	0.4	2	76	3.2	-	0.0064	0.06
0.4Ru-5V	0.4	5	68	2.6	-	0.0062	0.15

No significant effect on the band gap energy value of TiO₂ was found for monometallic RuO_x/TiO_2 (Table 1), while UV-Vis DRS spectra of bimetallic catalysts showed that the presence of VO_x species caused a shift of the lowest energy transition absorption, as previously reported (Ciambelli et al., 2009b), with respect to the parent 0.4Ru catalyst (Figure 1). These differences in absorption properties are clearly shown by plotting $[F(R_\infty)*hv]^2$ vs hv (Figure 1); the corresponding decrease in equivalent band gap energies is evident from Table 1. The increase of vanadium content further decreases the band gap energy.

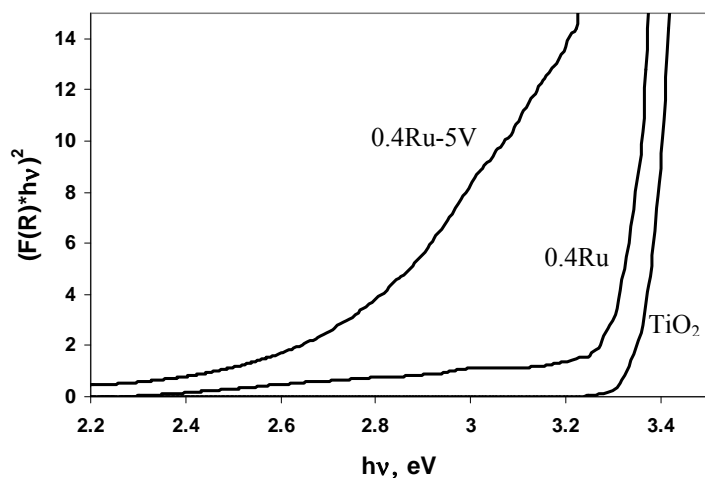


Figure 1: $[F(R_{\infty}) \cdot hv]^2$ vs hv for 0.4Ru-5V, 0.4Ru and TiO_2

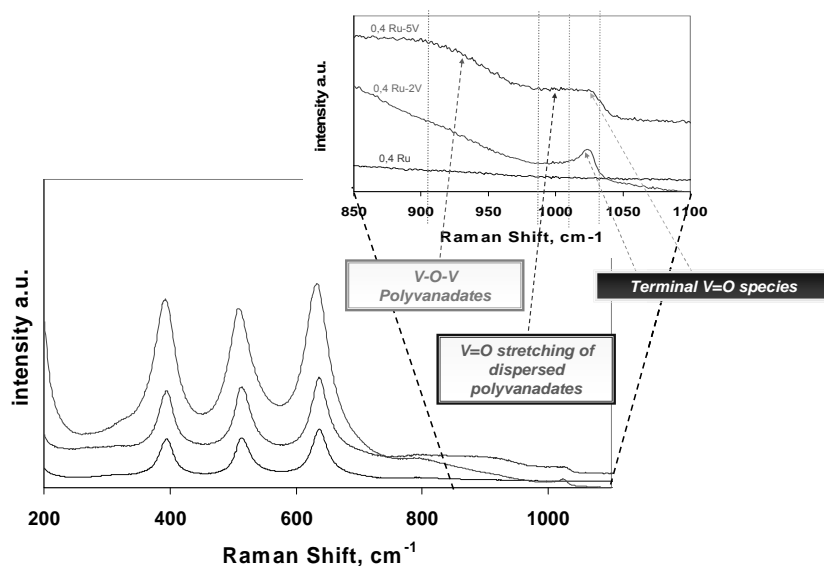


Figure 2: Raman spectra for VO_x - RuO_x / TiO_2 catalysts

Raman spectra of RuO_x / TiO_2 monometallic catalysts (not reported) do not show bands related to ruthenium species, but only signals related to the support, underlining that a very good dispersion of ruthenium species should be present on the titania surface. Also for RuO_x - VO_x / TiO_2 catalysts the high surface dispersion does not allow the description of the molecular structure of supported Ru species. As shown in Figure 2, some absorptions in the Raman spectra of the bimetallic catalysts can be attributed to the presence of polyvanadates: a broad band at about 940 cm^{-1} , assigned to V–O–V functionality (Burcham et al., 2000), a band at about 1016 cm^{-1} that occurs in the V=O stretching region, assigned to the corresponding mode of dispersed polyvanadates on the surface and a further signal at about 1030 cm^{-1} attributed to terminal V=O species (Went et al., 1992). As from Raman spectra, any conclusion on the ruthenium species can be drawn from XRD analysis (Figure 3), since no characteristic peaks related to ruthenium oxide, ($2\theta = 28.2, 35.2$ and 54) are detectable. The only signals present are related to the anatase phase of supporting titania, indicating that the calcination does not alter the crystallographic phase of the support.

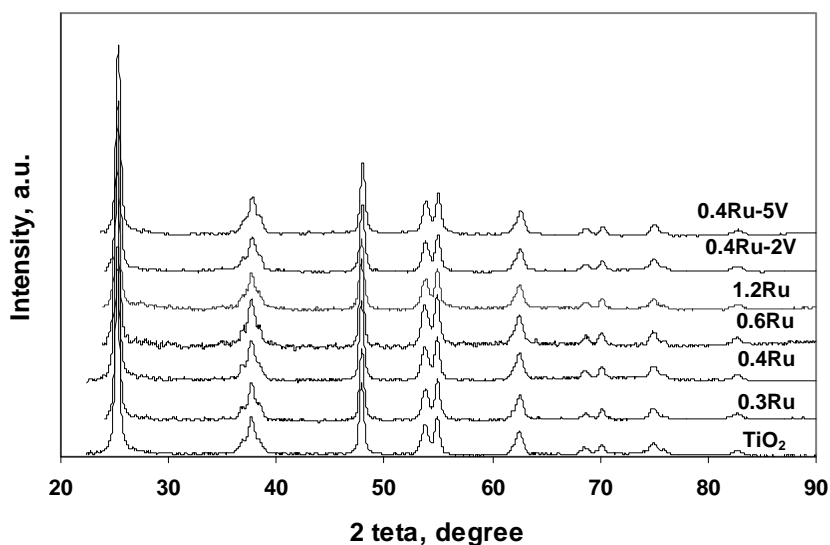


Figure 3: XRD spectra for $\text{RuO}_x/\text{TiO}_2$ and $\text{VO}_x\text{-RuO}_x/\text{TiO}_2$ catalysts

The same catalysts used in this work were characterized by XPS analysis (Mazzei, 2009) and the results showed that the ruthenium species are well dispersed on the catalyst support surface. Moreover, XPS analysis indicated that Ru species are present on the catalysts surface as Ru^0 and $\text{Ru}^{3+}/\text{Ru}^{4+}$ with an opposite and complementary trend of their surface percentage as function of RuO_2 nominal loading (Mazzei, 2009). Table 1 shows that by increasing the vanadium loading the V/Ti ratio (Mazzei, 2009) increased whereas the Ru/Ti ratio of the bimetallic samples is similar to that of 0.4Ru catalyst. This result indicates that vanadium species do not decorate Ru surface species unlike the case of sulphated $\text{MoO}_x/\gamma\text{-Al}_2\text{O}_3$ photocatalysts (Ciambelli et al., 2007, Ciambelli et al., 2009c).

3.2 Photocatalytic activity tests

Typically, the photocatalytic tests started feeding in dark the reaction gaseous mixture to the reactor, until the outlet ethanol concentration reached the inlet value. In the absence of light, no reaction products were observed during or after the ethanol dark adsorption. As a consequence, no selective ethanol oxidation occurred by thermal catalysis in the used operating conditions. After the establishment of the dark adsorption equilibrium of ethanol on the catalyst surface, and setting the reaction temperature, UVA-LEDs were switched on and, in the presence of light, ethanol begun to be selectively converted (Figures 4 – 6), moving to stable steady-state value. Ethanol steady-state conversion (Figure 4) decreased with RuO_2 content, reaching a maximum of about 60% at RuO_2 loading of 0.3 wt %. Beyond this value, the conversion decreased gradually up to 37 % with 1.2 RuO_2 wt%. Acetaldehyde as main product, together with low amounts of CO_2 and ethylene as by-products, formed on 0.3Ru, 0.4Ru, 0.6Ru and 1.2Ru catalysts, while crotonaldehyde was produced only on TiO_2 and 0.3Ru catalyst. The acetaldehyde yield (Figure 5) increased with irradiation time up to reach a steady state value after 25 minutes (a maximum value of 54% was obtained with 0.4Ru photocatalyst).

The results, in terms of ethanol conversion and products selectivity on $\text{RuO}_x/\text{TiO}_2$ catalysts, are summarized in Figure 6. On 0.4Ru selectivity to acetaldehyde was 97% at about 55% conversion, while on TiO_2 it was only 39%, at similar ethanol conversion. CO_2 selectivity showed an opposite trend: 34 % on TiO_2 decreasing to only 3.2 and 2.8% on 0.4Ru and 1.2Ru, respectively.

Moreover, with all catalysts ethylene selectivity never exceeded 1.6%. Selectivity to crotonaldehyde was 27 and about 28% on TiO_2 and 0.3Ru catalysts, respectively. Beyond 0.3 RuO_2 wt%, crotonaldehyde selectivity decreased to zero.

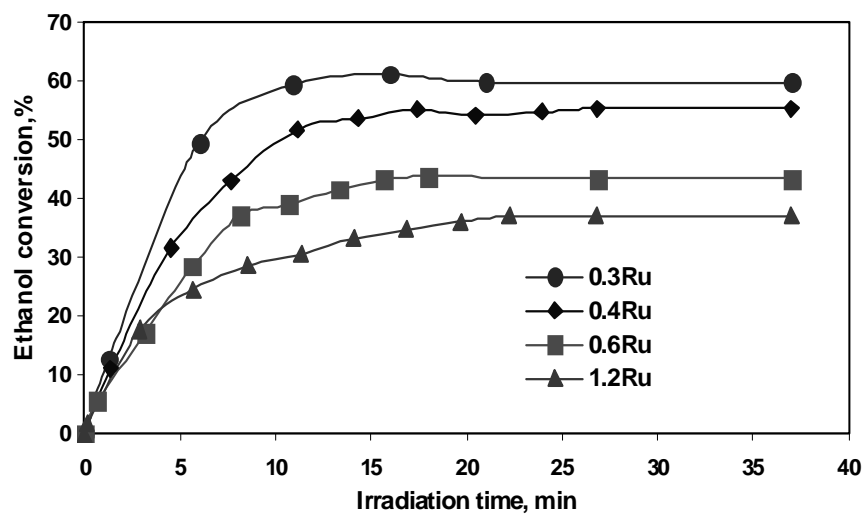


Figure 4: Ethanol conversion as a function of irradiation time on RuO_x/TiO_2

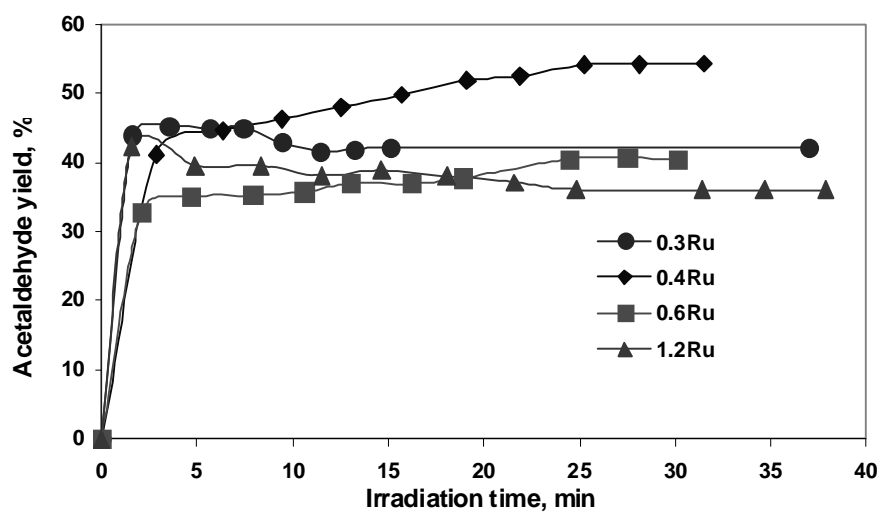


Figure 5: Acetaldehyde yield as a function of irradiation time on RuO_x/TiO_2

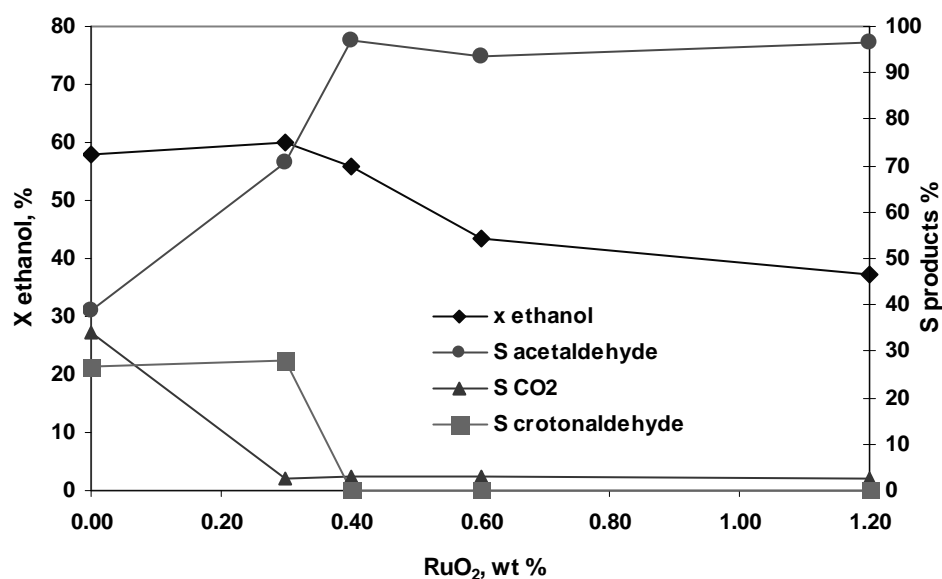


Figure 6: Ethanol conversion (X) and products selectivity (S) as a function of RuO_2 loading

The photoactivity of RuO_x/TiO_2 catalysts is associated to their different specific surface area, resulting in a decreased ethanol adsorption capacity, as reported in Table 1. In fact, a quite linear correlation between ethanol conversion and specific surface area has been found (Figure 7). This last result evidences that the overall photoactivity is due to the TiO_2 surface not covered by Ru species. These species, instead, play an essential role in addressing the selectivity to acetaldehyde. It has been reported that supported RuO_x is active and selective catalyst in thermal oxidative dehydrogenation of methanol and ethanol (Liu and Iglesia, 2005). The catalyst containing 0.4 wt% RuO_2 yields the highest selectivity to acetaldehyde and the lowest selectivity to by-products, together with a catalytic activity not so different with respect to the titania alone.

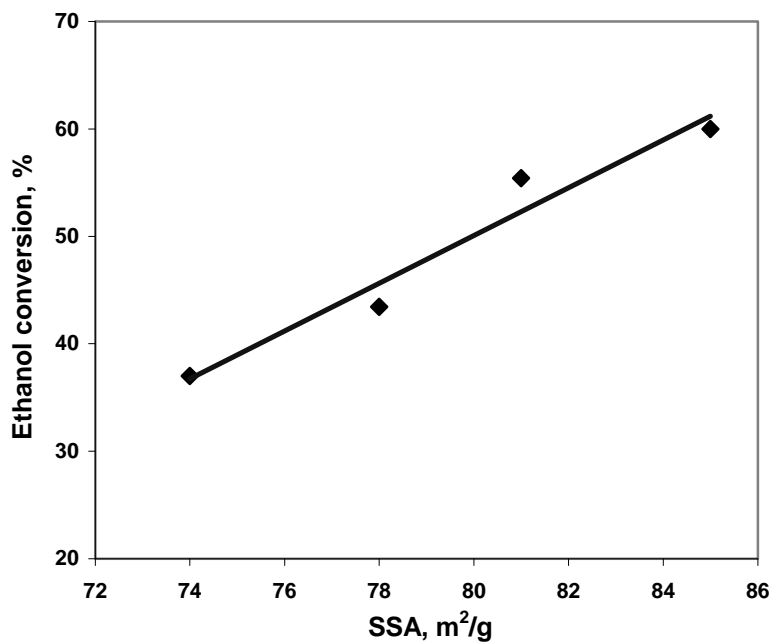


Figure 7: Ethanol conversion as a function of specific surface areas (SSA) for RuO_x/TiO_2 photocatalysts.

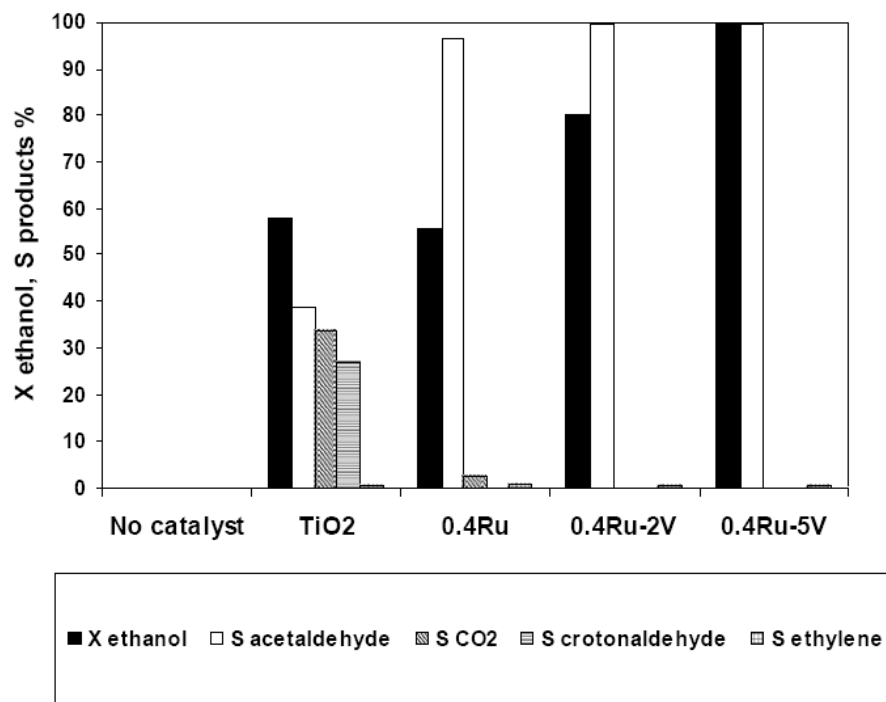


Figure 8: Ethanol conversion (X) and products selectivity (S) on TiO_2 , 0.4Ru, 0.4Ru-2V and 0.4Ru-5V

The catalyst 0.4Ru was chosen to investigate the influence of the addition of VO_x in the formulation on the photocatalytic performances. Figure 7 show a comparison of the photoactivity test results obtained with TiO₂, RuO_x/TiO₂ and RuO_x-VO_x/TiO₂ catalysts. Increasing V loading resulted in higher ethanol conversion, up to 80 and 100 % for 0.4Ru-2V and 0.4Ru-5V, respectively. On these latter catalysts, the production of CO₂ and crotonaldehyde was totally avoided, acetaldehyde selectivity being very close to 100 %. As previously found for different photocatalytic systems, the increase in photoactivity of RuO_x-VO_x/TiO₂ is correlated to the equivalent band gap energy values that decrease by increasing the V loading on 0.4Ru catalysts (Table 1) (Ciambelli et al., 2009b).

Like previously proposed for photoexcited surface vanadate (Ciambelli et al., 2009b) and molybdate (Ciambelli et al., 2008), and taking into account both characterization results and photocatalytic activity results, a comparison of reaction steps on TiO₂, RuO_x/TiO₂ and RuO_x-VO_x/TiO₂ in photocatalytic oxidation of ethanol is proposed (Figure 9).

As previously pointed out (Ciambelli et al., 2009b), on TiO₂ ethanol is adsorbed as ethoxy specie. Under UV irradiation hydroxyl can react with positive holes giving OH radicals that abstract hydrogen to the adsorbed ethoxy species to yield adsorbed acetaldehyde radicals. Ethoxy adsorbed species can give also a hydroxyls group and ethylene, which is desorbed. Acetaldehydes radicals may lose an electron and desorb as acetaldehyde, or undergo by to β-aldolization and dehydration to form crotonaldehyde, or subjected to further oxidation yielding adsorbed acetic acid, then transformed into CO₂ and water. A schematic representation of reaction steps is reported in Figure 8-a. In the presence of RuO_x species, TiO₂ sites that are able to transform ethanol to crotonaldehyde and to CO₂ and water are inhibited (Figure 8-b). No photoreactions occur on Ru site since the decrease in ethanol conversion was observed by increasing the Ru loading. For VO_x-RuO_x systems (Figure 8-c), we propose that the high acetaldehyde yield is due to the additional presence of surface polymeric vanadates possessing both V-O-Ti and V-O-V functionalities, as shown in Figure 2 (Ciambelli et al., 2009b).

4. Conclusions

The occurrence of photocatalysed heterogeneous oxidative dehydrogenation of ethanol with very high selectivity to acetaldehyde has been observed on RuO_x/TiO₂ and RuO_x-VO_x/TiO₂ catalysts. At the same mild reaction conditions ethanol was converted at very low extent to acetaldehyde, CO₂, crotonaldehyde and ethylene on TiO₂. We have found that both ethanol conversion and products selectivity depend on ruthenium content: by increasing ruthenium loading, ethanol conversion decreased from 60 to 37 % and acetaldehyde selectivity reached a maximum value of about 97% at 0.4 wt % RuO₂ loading. The overall photoactivity is likely due to the free TiO₂ sites not covered by Ru species, which instead, enhance the acetaldehyde selectivity inhibiting the crotonaldehyde formation. With bimetallic RuO_x-VO_x/TiO₂ the high activity of V species is coupled to the high selectivity to acetaldehyde of monometallic Ru/TiO₂ catalysts, resulting in a very high catalytic performance. In fact, by increasing the vanadium loading, the ethanol conversion increased up to 100 % with almost total selectivity to acetaldehyde: we attribute this enhanced performance to the presence of surface polymeric vanadates possessing both V-O-Ti and V-O-V functionalities. Moreover, the enhanced photoactivity of RuO_x-VO_x/TiO₂ is attributed to the equivalent band gap energy values that decrease at increased V loading.

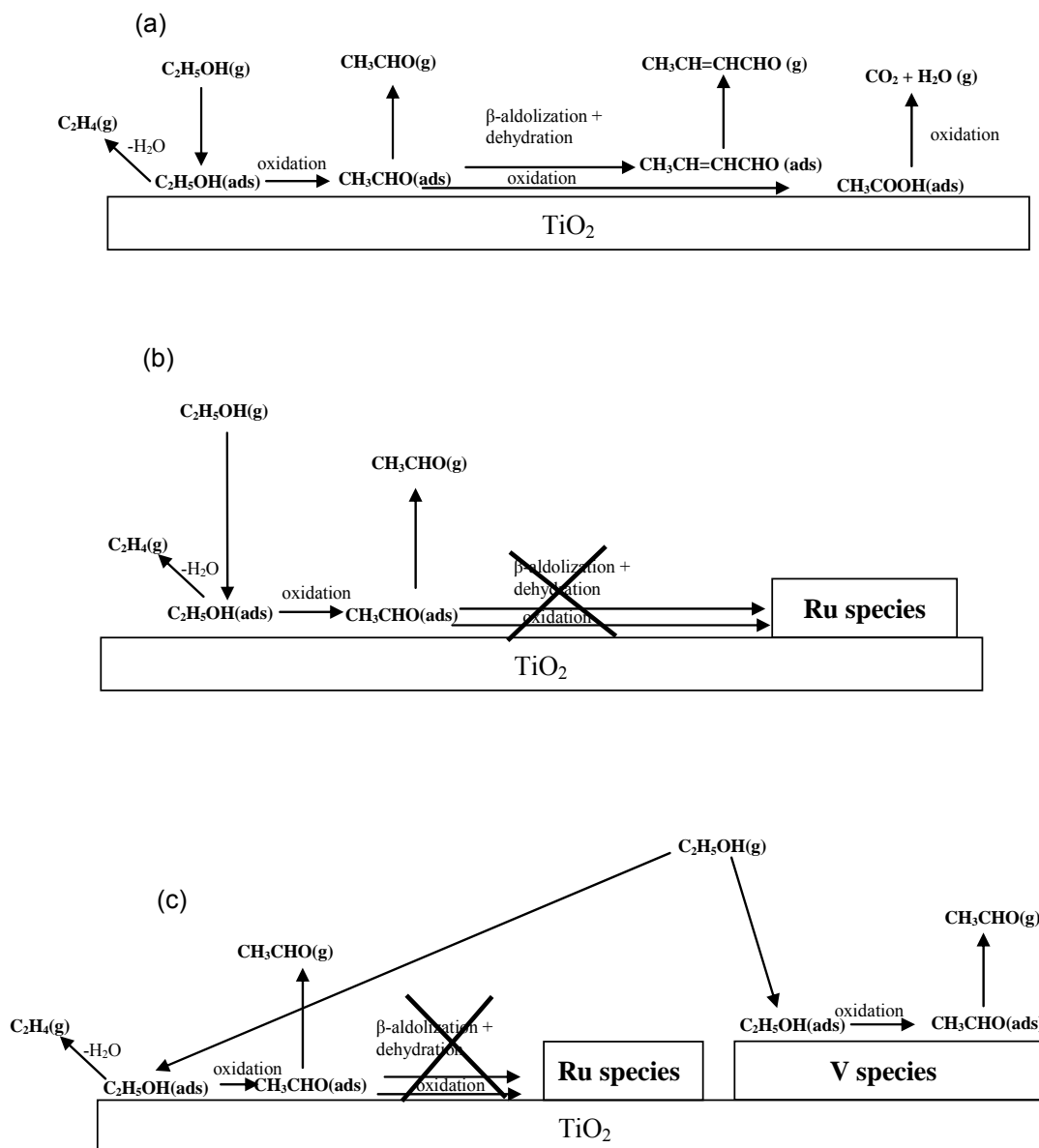


Figure 9: Schematic representation of photo-reactions of ethanol on TiO_2 (a) on RuO_x/TiO_2 (b) and VO_x-RuO_x/TiO_2 (c).

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