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Improved (photo)catalytic propene hydration in gas-solid system by using heteropolyacid/oxide composites: EPR, acidity and role of water

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Abstract: Binary materials composed by oxides as SiO_2, TiO_2 and N-doped TiO_2 and the Keggin heteropolyacid (PW_{12}) have been prepared and physico-chemically characterized. They have been used both as catalysts and photocatalysts for the hydration of propene to 2-propanol. The characterization of the samples, particularly the EPR results and the acidity properties, were useful to explain the key role played by PW_{12} in the composite materials, both in thermal and in photo-assisted catalytic processes.

The contemporary presence of heat and UV light improved the PW_{12} activity with respect to the thermal process, and the binary materials showed a better (photo)catalytic activity than the bare PW_{12} in almost all cases. This work, for the first time, evidenced by the EPR study that the increase of reactivity under irradiation could be attributed to the ability of photoexcited PW_{12} to trap electrons, particularly when it is supported. Moreover, the role of water on the reactivity was also studied.

Introduction

Polyoxometalates are molecular metal oxides with potential application in various fields. Heteropolyacids (HPAs) are a class of polyoxometalates with a heteroatom in the cluster structure which forms the oxo-metallic cluster with the addenda metal atoms [1]. Due to the tunable acid-base and redox properties, HPAs have been used as catalysts both for homogeneous and heterogeneous reactions. Many efforts have been devoted to the heterogeneization of HPAs [2]. In liquid-solid regime their separation and recovery are relevant problems for practical application because they are soluble in polar solvents. Moreover, due to the low specific surface areas (1÷10 m^2 g^{-1}) their dispersion on supports with high surface area can increase the accessibility of the reacting species to their acidic sites, and consequently their catalytic activity as Brönsted acid and oxidant catalysts [3]. These compounds have been also used as photocatalysts [2], as their ground electronic state can absorb light, producing a charge transfer-excited state HPA*; for instance tungstophosphoric acid, $H_3PW_{12}O_{40}$ (PW_{12}), absorbs at λ=260 nm (4.8 eV). The excited species can be easily reduced to form HPA^-, the so-called "heteropolyblue" species, by means of electron(s) transfer from another species [4]. By summarizing, HPAs have been used not only as acid catalysts for reactions such as esterification, transesterification, hydrolysis, Friedel-Crafts alkylation and acylation, Beckmann rearrangement, but also as oxidation catalysts for alkanes, aromatics, olefins, alcohols [5]. Moreover, the acidic properties of HPAs have been exploited to catalyse hydration and dehydration reactions [6]. For instance, propene hydration to obtain 2-propanol is a reaction carried out industrially at moderate temperatures (ca. 150-200°C) and pressure (2 MPa) in the presence of an acid catalyst and it has been the object of several patents [3]. The achievement of this reaction under mild conditions is of great interest and the use of HPAs could help to reach this scope. It is reported that HPA based materials showed a significant catalytic activity from ca. 100 °C, reaching a maximum effect at ca. 130°C Indeed, further increase of temperature induced a decrease of 2-propanol formation rate due to the significant occurrence of the reverse 2-propanol dehydration reaction [7]. Consequently, propene hydration is not an easy reaction to be carried out, because thermodynamically limited by the mentioned reverse reaction that, anyway, can occur also at temperatures lower than 130 °C.

2-Propanol dehydration reaction is frequently used to investigate on the acidic character of catalysts, as for instance the supported heteropolyacids [8]. In a previous work some of us reported a study on the role of the support of HPA in 2-propanol (photo)catalytic dehydration to propene [9], concluding that the type of support (semiconductor or insulator) differently affected the reactivity of the composite material. Also for propene hydration carried out both in catalytic and photocatalytic systems various insulator and semiconductor oxides have been used as supports of HPA, playing the semiconductor a role in the reaction mechanism when irradiated by light with appropriate wavelengths, but experimental evidence by EPR of the electron transfer to the HPA species had not been presented [10,11]. Indeed, charge carriers formation, stabilization and reactivity at the surface of semiconductor metal oxides strongly influence the heterogeneous photo-assisted reactions. EPR is an useful technique to monitor the charge separation processes; Grätzel and Howe [12,13] and Micic et al. [14] monitored for the first time both the excited electrons and holes upon irradiation of a colloidal suspension of TiO_2 in water. The same experiment can

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be performed under vacuum, though less efficiently, in the case of TiO_2 based photoactive solids [15,16]. The direct charge separation can be obtained by irradiating the solid in situ at the temperature of liquid nitrogen to avoid the rapid recombination of the carriers.

In this work some home-prepared TiO_2, SiO_2 and N-doped TiO_2 samples were coupled with the Keggin heteropolyacid (HPA) $H_3PW_{12}O_{40}$ (PW_{12}), forming mixed compounds. Two strategies have been used for the heterogenization of PW_{12}, i.e. the deposition by impregnation of the oxide surface with an aqueous PW_{12} solution and the formation of the PW_{12}-oxide composite under hydrothermal conditions. The research aimed to elucidate the role of PW_{12} as catalyst and photocatalyst along with that played by the type of support (insulator or semiconductor). The (photo)-catalysts have been characterized by various physico-chemical methods and the results used to explain the catalytic and photocatalytic activities. In particular, EPR measurements have been carried out in dark and under UV irradiation to demonstrate the ability of the supported PW_{12} to be (photo)-reduced. A correlation between activity and Brönsted acidity was found and the influence of the amount of water vapour on the catalytic activity was investigated.

Results and Discussion

Characterization of the (photo)catalysts

A physico-chemical characterization of the composites, reported in detail in the supporting information, gives information on some features of the (photo)catalysts. XRD measurements confirmed the crystalline structure of the home prepared TiO_2 and N-TiO_2 supports, the amorphous structure of SiO_2 and the good dispersion of the HPA in all of the composite materials (see Figure S1). Table 1 reports the size of the anatase crystallites estimated by applying the Scherrer equation to the XRD diffractograms along with the BET specific surface areas (SSA) of all of the binary materials, the bare supports and PW_{12}. As far as the molar ratio PW_{12}/oxide reported in Table 1 the choice 1/150 [mol/mol] was due to the fact that in this way, at least one supported catalyst (PW_{12}/N-TiO_2 in this case) resulted covered by a theoretical monolayer (see experimental section of the manuscript). Consequently, in order to compare the reactivity of the various samples we maintained the same PW_{12}/oxide molar ratio. We know that by changing the molar ratio PW_{12}/oxide the reactivity changes but the aim of this work was not to find the best catalyst but to better understand, by EPR study, how the presence of light could increase the reactivity of both bare and supported PW_{12}. SSA's of the PW_{12} impregnated samples decreased with respect to the bare commercial supports. This finding can be attributed to the fact that some pores of the supports were blocked, due to the presence of the PW_{12} clusters; indeed, the volume of the pores of the supported samples was always smaller with respect to that of the bare support. This phenomenon was evident in the case of PW_{12}/SiO_2 for which the SSA decreased from 121 to 73 $m^2 \cdot g^{-1}$, but also for PW_{12}/TiO_2 with a decrease from 171 to 134 $m^2 \cdot g^{-1}$. The SSA of N-TiO_2 did not significantly change after the deposition of PW_{12}, and only a slight decrease was observed. On the contrary, it is remarkable that the SSA of the materials prepared by mixing the Si or Ti alkoxydes with PW_{12}, i.e. the PW_{12}/SiO_2 ex A and PW_{12}/TiO_2 ex A samples, increased significantly compared with the correspondent hydrothermally prepared bare oxide, suggesting that the heteropolyacid was incorporated into the porous structure of the binary system without reducing the porosity of the support. Notably, the SSA of the PW_{12}/SiO_2 ex A sample was much higher than that of SiO_2, probably because during the hydrolysis of TEOS (SiO_2 precursor), the ethanol formed was dehydrated due to the presence of the PW_{12}, giving rise to the evolution of ethene which in turn favoured the formation of smaller mesopores on the sample which were responsible for a higher total volume (see Table 1).

The evolution of propene gas produced by dehydration of 2-propanol (deriving from hydrolysis of TTIP) in the presence of PW_{12} during the preparation of the PW_{12}/TiO_2 ex A sample, was also accountable for its higher SSA with respect to the bare TiO_2, and the obtained solid contained mainly small mesopores with size close to micropores.

All of the TiO_2 based samples were nanostructured (see Table 1) and the size of the crystallites was in the same magnitude order of the sample's pores.

The SEM microphotographs (Figure S2) indicate that the presence of the heteropolyacid did not affect the morphology of the support for the samples prepared by impregnation, however the hydrothermal preparation of the composites gave rise to different morphologies with respect to those of the bare support.

TABLE 1. Specific surface area (SSA), average pore size, anatase crystalline size, PW_{12}/oxide ratio and band gap value of the samples

Sample	SSA [$m^2 \cdot g^{-1}$]	Average pore size* [nm]	Anatase crystallite size [nm]	PW_{12}/oxide [mol/mol]	E gap [eV]
PW_{12}	15	-	-	-	3.1
SiO_2	121	25.0 (0.64)	-	-	-
TiO_2	171	7.5 (0.31)	7.5	-	3.2
N-TiO_2	87	23.4 (0.61)	9.9	-	3.2 and 2.4
PW_{12}/SiO_2	73	26.3 (0.47)	-	1/150	3.3
PW_{12}/TiO_2	134	6.2 (0.24)	7.1	1/150	3.2
PW_{12}/N-TiO_2	80	18.4 (0.36)	11.0	1/150	3.2 and 2.4
PW_{12}/SiO_2 ex A	338	8.9 (0.75)	-	1/150	3.2
PW_{12}/TiO_2 ex A	199	3.6 (0.18)	5.6	1/150	3.2

* Pore's volume [cm^3 g^{-1}] in brackets

Raman spectroscopy (Figure S3) evidenced that the structure of the PW_{12} Keggin cluster remained almost unchanged after the preparation of the impregnated composites: PW_{12}/SiO_2, PW_{12}/TiO_2, PW_{12}/N-TiO_2 and PW_{12}/SiO_2 ex A materials. The widening of some vibration modes can be attributed to a Hbonding interaction between the oxygen atom of the Keggin anion and the hydroxyl groups on the oxide surface. On the contrary, a strong modification of the Keggin structure was evidenced in the PW_{12}/TiO_2 ex A composite.

The optical absorption properties of the binary materials, related to their electronic structure, were investigated by UV-Vis diffuse reflectance spectra (DRS) (Figure S4). The obtained E_g values in the Tauc plots, reported in Figure S4 are reported in Table 1.

The acidic properties of the samples were evaluated by NH_3-TPD experiments carried out from room temperature up to 600 °C. Such high temperature was chosen in order to detect also the contribution of strong acid sites that are known to desorb NH_3 above 550 °C. According to the literature it seems that Keggin acid clusters still kept their heteropolyoxoanion structure at least up to 550 °C [17,18].

In order to known the fate of the PW_{12} structure of our samples treated at 600 °C, we recorded the Raman spectra after the TPD measurements. These results indicated that the heteropolyoxoanion structure was maintained only in the case of samples in which PW_{12} was supported on TiO_2.

Nevertheless, the PW_{12} structure instability at temperatures higher than 550 °C did not negatively affect the TPD results obtained for both bare and SiO_2 supported PW_{12} samples. Indeed, for these samples, the loss of the heteropolyoxoanion structure occurred between 550 °C and 600 °C. Consequently, the ammonia evolution observed at temperatures higher than 550 °C indicates, anyway, the presence of strong acid sites even if the heteropolyanion structure is damaged.

The NH_3-TPD experiments provided information on the total acidity of the catalysts without distinguishing between Brönsted acid sites (typical of bare PW_{12} and SiO_2) and Lewis acid sites, characteristic of defective TiO_2 support. The amount of desorbed NH_3 (ppm/g PW_{12}) allowed for a quantitative evaluation of the number of active sites, while the temperature of desorption is an indication of the strength of the acid sites. Figure 1 reports the NH_3-TPD profiles obtained for TiO_2 and SiO_2 supported PW_{12} samples (A and B, respectively), and for TiO_2 and SiO_2 bare supports (C and D, respectively). For the sake of comparison, NH_3-TPD profile of bare PW_{12} is also reported in Figure 1 (A and B). No NH_3 desorption occurred at temperature below 200 °C, suggesting the absence of weak acid sites [19,20]. According to our previous results, NH_3 desorption in the range 200-550 °C was attributed to medium strength acid sites, whilst desorption peaks observed at temperatures higher than 550 °C were assigned to strong sites. As far as the NH_3-TPD curves of the various TiO_2 supported PW_{12} samples are concerned, it can be observed that the ammonia desorption depended on the type of TiO_2 and on the preparation method of the catalyst. In particular, a broad peak centred between 350-410 °C was observed for the PW_{12}/TiO_2 ex A, PW_{12}/TiO_2 and $PW_{12}/N\text{-}TiO_2$ samples. In addition to such features, attributed mainly to the Lewis acid sites typical of TiO_2 (see Figure 1 (C)) [21], a shoulder probably due to the medium strength Brönsted acid sites of supported PW_{12} was detected at around 490 °C and 470 °C, for the PW_{12}/TiO_2 and $PW_{12}/N\text{-}TiO_2$ samples, respectively. Notably the peak at 600 °C corresponding to the strong Brönsted acid sites typical of bare PW_{12} was not observed for the previous samples, except for the $PW_{12}/N\text{-}TiO_2$ catalyst, for which such peak slightly shifted at lower temperature (590 °C). By summarizing, the only sample that did not show the presence of medium or strong strength Brönsted acid sites was PW_{12}/TiO_2 ex A which was the only inactive sample for the hydration of propene, as reported in the “catalytic and photocatalytic activity” section. For such sample some interaction between the forming TiO_2 and the PW_{12} during the hydrothermal preparation, can be hypothesized in order to explain the catalytic inactivity. Moreover, it cannot be excluded that during the formation of the PW_{12}-oxide composite under hydrothermal conditions, the active PW_{12} is somehow buried into the TiO_2 matrix.

For the bare SiO_2 support the main desorption occurred with a broad and intense peak centred at 600 °C but a less pronounced peak can be also observed at ca. 270 °C along with a pronounced shoulder at around 385 °C. NH_3-TPD profile recorded for PW_{12}/SiO_2 sample seems an overlap of the profiles of the two components, i.e. PW_{12} and SiO_2, indicating that the acidic sites characteristic of the two solids were maintained in the supported sample. On the contrary, for the PW_{12}/SiO_2 ex A only the peak at 600 °C, due essentially to PW_{12}, was observed more or less unchanged. Indeed, two intense peaks appeared at 255 and 430 °C where the first one could correspond to that at 270 °C and the other one to the shoulder at ca. 385 °C observed for the bare SiO_2. However, these two peaks are very intense and this finding strongly suggests that some interaction occurred between the forming SiO_2 and the PW_{12} during the hydrothermal preparation of PW_{12}/SiO_2 ex A. This hypothesis is supported by the Raman study.

EPR spectra of PW_{12}, the bare oxides and the mixed compounds based on TiO_2 are reported in Figure 2 A, while PW_{12}, the bare oxides and the mixed compounds based on SiO_2 are reported in Figure 2 B. In both figures, the first spectra are related to PW_{12} and the pure oxides. In particular, in Figures 2 A and 2 B spectrum (a) is related to the PW_{12} sample and it does not show any paramagnetic species.

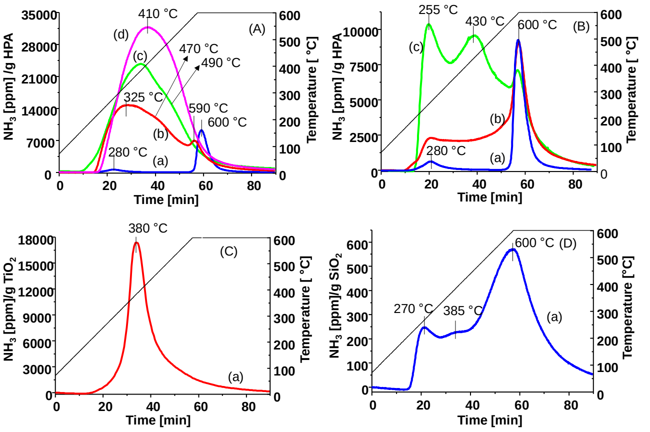

Figure 1. Temperature programmed desorption curves of ammonia (NH_3-TPD) for the as prepared samples: (A) PW_{12} (a); $PW_{12}/N\text{-}TiO_2$ (b); PW_{12}/TiO_2 (c); PW_{12}/TiO_2 ex A (d); (B) PW_{12} (a); PW_{12}/SiO_2 (b); PW_{12}/SiO_2 ex A (c); (C) TiO_2 (a) and (D) SiO_2 (a).

Spectra (b) and (c) in Figure 2 A are referred to $N\text{-}TiO_2$ and TiO_2

oxides, and in both cases paramagnetic species are present. In the case of N-TiO_2 the spectrum has been deeply described elsewhere [22] and the signal can be attributed to the presence of NO• trapped species adsorbed on the surface of the catalyst, due to some residual nitrogen compounds formed during the synthesis process. In the case of TiO_2 sample, the EPR signal is due to the presence of Ti^{3+} ions formed during the synthesis. PW_{12}/TiO_2 ex A (line d), PW_{12}/N-TiO_2 (line e) and PW_{12}/TiO_2 (line f) samples, show a signal in the region at $g > 2.0$ typical of holes stabilized on oxygen ions (i.e. O^- ions) in the solid [12,13]. In the case of line (e), the signal due to the hole is covered by the more intense signal due to the NO• species already described.

No signals are present in Figure 2 B for the PW_{12}, SiO_2, PW_{12}/SiO_2 and PW_{12}/SiO_2 ex A samples.

The spectra shown in Figure 3, obtained in the same conditions as those mentioned above, but after UV irradiation under vacuum, are more informative.

Indeed, in the case of a generic semiconductor oxide, the reaction occurring after irradiation is:

$$MeO_X + h\nu \rightarrow (MeO_x)^* + e^-_{(CB)} + h^+_{(VB)} \qquad (1)$$

If the two photo-promoted charge carriers are stabilized by the solid at different sites of the oxide, usually a cation for the electron and an oxide anion for the hole, the formation of a reduced form of the cation and the formation of the paramagnetic and EPR active O^- species ($O^{2-} + h^+ \rightarrow O^-$) can be observed.

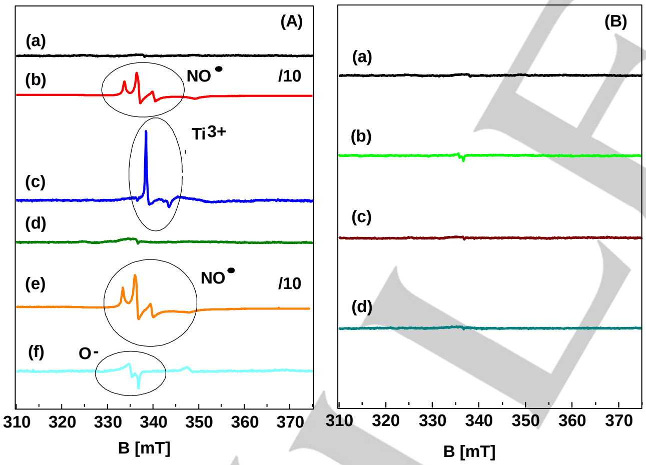

Figure 2. EPR spectra of the "as prepared" samples recorded at 77K: (A) PW_{12} (a); N-TiO_2 (b); TiO_2 (c); PW_{12}/TiO_2 ex A (d); PW_{12}/N-TiO_2 (e); PW_{12}/TiO_2 (f) and (B) PW_{12} (a); SiO_2 (b); PW_{12}/SiO_2 (c); PW_{12}/SiO_2 ex A (d).

Under irradiation it can be considered that also PW_{12} could be excited by forming the PW_{12}^* that is a very strong oxidant species which can easily trap electrons from other species present in the reacting medium [3].

We followed (Figures 3 A and B) the charge separation for all of the samples described before by irradiating with the full lamp spectrum (including UV frequencies) the solids kept under vacuum. Again, Figure 3 A is related to the samples PW_{12}, and the materials based on TiO_2, while Figure 3 B is related to materials based on SiO_2.

No effects upon irradiation was observed for the bare PW_{12} sample. In the case of N-TiO_2 (Figure 3 A, line b) the irradiation simply produced a lessening of the intensity of the original spectrum, indicating the desorption of the NO• species from the catalyst's surface. In the case of TiO_2 (Figure 3 A, line c) the irradiation did not bring to a deep change in the EPR spectra already present in the as prepared sample, but the Ti^{3+} signal increased in intensity, indicating the photo-formation of stabilized electrons.

For all of the other samples the effect of UV irradiation presented a common feature: the signal typical of holes (O^- ions) grew a little [23]. The formation of holes in all systems caused by irradiation with UV light indicated that a charge separation was actually induced in the solids by photons. In the case of PW_{12}/N-TiO_2, the presence of NO• species hindered the detectability of the O^- ions signal. Photo-promoted electrons, however, were produced in all cases but they were not observable in terms of reduction of Ti(IV) present in the solid. Anyhow, for the PW_{12}/N-TiO_2 and PW_{12}/TiO_2 (Figure 3 A, lines e and f) and PW_{12}/SiO_2 ex A (Figure 3 B, line d) samples, a huge signal at high field and $g_1=1.83/g_2=1.78$, $g_1=1.83/g_2=1.79$ and $g_1=1.87/g_2=1.80$ can be respectively observed. This signal that was observed also for PW_{12}/SiO_2 (in that case it was less intense) can be correlated to the change of colour (turning from white/yellow to blue) of the samples which occurred under irradiation and it is strictly connected to the presence of PW_{12} in the compounds. A possible interpretation of this behaviour is that the photo-excited PW_{12} (that is a very oxidant species) trapped electrons from the oxide anion of the solid reducing to form the heteropolyblue PW_{12}^- species ($O^{2-} + PW_{12}^* \rightarrow O^- + PW_{12}^-$). The photo-excited PW_{12}^* species, that in the reaction environment could also trap electrons from propene [19], was probably responsible for the photocatalytic activity as the samples showing this signal were the most active ones in the photocatalytic propene hydration experiments (*vide infra*).

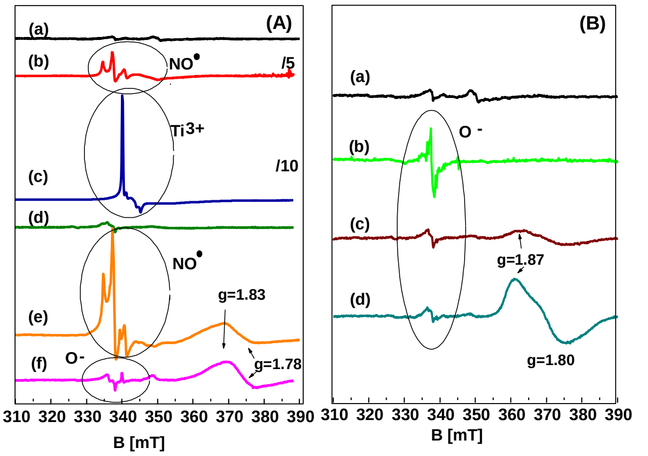

Figure 3. EPR spectra of samples after irradiation with UV light under vacuum, recorded at 77K: (A) PW_{12} (a); N-TiO_2 (b); TiO_2 (c); PW_{12}/TiO_2 ex A (d); PW_{12}/N-TiO_2 (e); PW_{12}/TiO_2 (f) and (B) PW_{12} (a); SiO_2 (b); PW_{12}/SiO_2 (c); PW_{12}/SiO_2 ex A (d).

Moreover, in the case of TiO_2 based materials, the electrons excited in the conduction band could be scavenged by PW_{12}, forming again the heteropolyblue PW_{12}^{-} species. Notably, each PW_{12}^{*} can trap more than one electron but this does not change our interpretation of the new EPR signal reported in Figure 3 A (lines e and f) and Figure 3 B (line d).

This insight can explain why the photo-promoted electrons are not available for reducing the metal oxide cations. Finally all of the samples were irradiated with UV light in the presence of 20 mbar of molecular oxygen, and in all cases, except for the bare oxides, the expected trace of the EPR signal of a superoxide anion (O_2^{-}) adsorbed on a surface metal cation and produced according to the following reaction $e^{-} + O_{2(gas)} \rightarrow O_2^{-}{}_{(ads)}$, was not observed [24,25]. The EPR spectra obtained after the irradiation with oxygen (not shown for the sake of brevity) are very similar to that reported in Figure 2 relative to the samples “as prepared”. It can be hypothesized the occurrence of a reaction between molecular oxygen and the reduced form of PW_{12} that gave rise to the formation of a diamagnetic, EPR inactive, species.

Catalytic and photocatalytic activity

Neither catalytic nor photocatalytic activity were observed in the presence of bare oxides, whilst PW_{12} was active both catalytically and photocatalytically. The presence of PW_{12} was in any case essential for the occurrence of propene hydration. Indeed, no reaction occurred in the presence of bare oxide samples, i.e. SiO_2, TiO_2 or N-TiO_2.

2-Propanol formation rate by using the binary materials as catalysts and photocatalysts, in the presence of 2 mM water vapour concentration is reported in Figure 4. The reaction rate is reported per gram of PW_{12}, which is the active catalyst/photocatalyst.

As far as the thermal catalytic activity is concerned, the bare PW_{12} material was the least active solid. When PW_{12} was dispersed on the support surface its performance improved. The PW_{12} impregnated on SiO_2 resulted the most active catalyst, followed by the PW_{12}/SiO_2 ex A sample which was prepared under hydrothermal conditions. The PW_{12}/TiO_2 was also active but, on the contrary, the PW_{12}/TiO_2 ex A sample which was hydrothermally prepared resulted completely inactive. The activity of PW_{12}/TiO_2-N was similar to that obtained by using PW_{12}/TiO_2. The different Lewis or Brönsted acidity accounts for the different catalytic activity of these materials (see NH_3-TPD results). The presence of the impregnated PW_{12} allowed a larger surface of contact between the inorganic cluster and the reagents which favoured the reactivity. The acidity is an important feature as propene hydration occurred by means of an acid-base mechanism involving dioxonium ions placed between PW_{12} anions [26]. In all cases, the binary materials showed higher catalytic and photocatalytic activities than the bare PW_{12}, with the exception of the PW_{12}/TiO_2 ex A. The hydrothermal conditions used to obtain the PW_{12}/oxide ex A composites determined significant differences between PW_{12}/SiO_2 ex A and PW_{12}/TiO_2 ex A. In fact, PW_{12}/SiO_2 ex A was one of the most active material, whilst PW_{12}/TiO_2 ex A was inactive. This finding can be justified by considering the strong Brönsted acidity of PW_{12} which, under hydrothermal conditions, dehydrated ethanol and 2-propanol deriving from hydrolysis of TEOS and TIIP (precursors for SiO_2 and TiO_2, respectively). The alcohol dehydration gave rise to ethene and propene, respectively, and their presence can explain the high pressure (ca. 10 and 25 bar for the PW_{12}/SiO_2 ex A and PW_{12}/TiO_2 ex A samples, respectively) reached in the autoclave during the preparation of the samples.

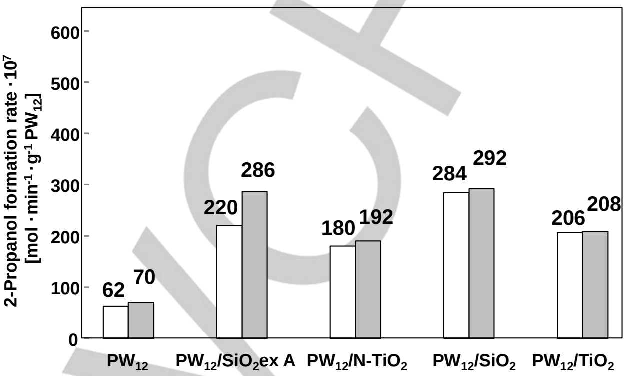

Figure 4. 2-Propanol formation rate per gram of PW_{12} present in the various solids, in the catalytic (white) and photocatalytic (grey) propene hydration reaction. Water concentration: 2 mM.

The presence of ethene and propene not only can account for the high specific surface area and porosity of these two composites, but also it produced effects on the nature of PW_{12}. The Keggin structure of PW_{12} was strongly compromised during the PW_{12}/TiO_2 ex A sample preparation, as evidenced by FTIR and Raman spectra, and the Brönsted acidity totally lost. On the contrary, both Keggin structure and Brönsted acidity were maintained in the case of PW_{12}/SiO_2 ex A sample. By considering the experiments carried out under irradiation, the activity slightly increased with respect to the catalytic runs with the exception of the run carried out in the presence of PW_{12}/SiO_2 ex A sample, for which, instead, a significant increase of 2-propanol formation rate was observed. Both catalytic and photocatalytic reaction rates were higher than those observed in a previous work [19].

An additional set of propene hydration experiments were carried out in the presence of higher amount of water vapour (10 mM instead of 2 mM). The reaction rate generally decreased when 10 mM water vapour was used (Figure 5) instead of 2 mM (Figure 4), both in the absence and in the presence of light. The abatement of the catalytic 2-propanol formation rates can be explained by taking into account the properties of the heteropolyacid (PW_{12}), used as bare or supported (photo)catalyst. It is well known the ability of the heteropolyacid species to absorb polar substrates giving rise to catalytic reactions in a peculiar phase known as “pseudo-liquid” phase, as extensively reported by Misono et al. [17,27]. Polar species, as 2-propanol, can be solubilized in the water molecules present in bulk PW_{12}. The heteropolyacid nanometric clusters (considered as the primary structures) can assemble to form a secondary structure which incorporates water molecules. The catalytic behaviour of PW_{12} strongly depends on the modifications of the secondary structure, and in particular on its Brönsted acidity which is influenced by water. The hydration state of the secondary structure determined not only the accessibility of the reacting molecules, but also the number and the strength of the surface acid sites, i.e. the $H_5O_2^+$ species [9, 18].

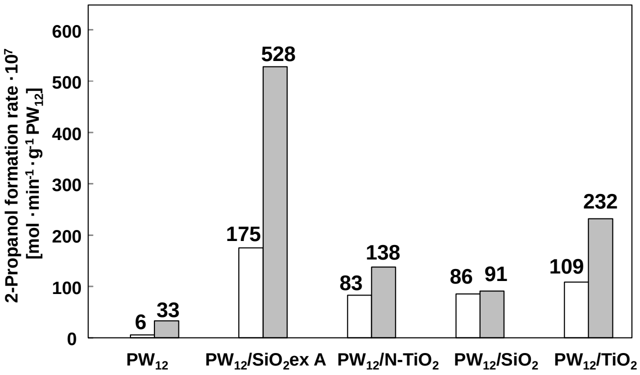

Figure 5. 2-Propanol formation rate per gram of PW_{12} present in the various solids, in the catalytic (white) and photocatalytic (grey) propene hydration reaction. Water concentration: 10 mM.

The presence of 2-propanol molecules in the pseudo liquid-phase, favoured by the increased amount of water vapour in the reacting stream (10 mM), appeared to be not beneficial because 2-propanol molecules could be subjected to dehydration on the PW_{12} acidic sites to form again propene.

As far as the photocatalytic experiments are concerned, it can be observed that the presence of light was beneficial, and the activity always increased, particularly when PW_{12}/TiO_2 and PW_{12}/SiO_2 ex A were used. Notably, the percentage of increase of reactivity observed under irradiation was higher when the concentration of water was 10 mM.

Probably the presence of light, in addition to the effect of exciting the PW_{12} species (responsible for the increase of reactivity as mentioned above) caused also a displacement of H_2O from the secondary Keggin structure to the support. In particular, this water displacement could be more important in the case of the samples with higher surface area, which can disperse water on its surface more easily. It has been reported that the amount of H_2O in the secondary structure is one of the key factors influencing the acidity, and hence the (photo)catalytic reactivity of PW_{12} [9]. It is possible to envisage that in the case of PW_{12}/TiO_2 and PW_{12}/SiO_2 ex A (samples possessing the highest surface areas) the amount of water reached an optimal concentration, causing a strong increase of 2-propanol production.

Conclusions

Composite materials of SiO_2-, TiO_2- and N-doped TiO_2 and the Keggin heteropolyacid (HPA) $H_3PW_{12}O_{40}$ (PW_{12}) have been prepared and physico-chemically characterized. They have been used both as catalysts and photocatalysts for the hydration of propene to 2-propanol in a gas-solid system at atmospheric pressure and 85°C. The characterization of the samples, particularly the EPR results and the acidity properties, were useful to explain the key role played by PW_{12} on SiO_2, TiO_2 and N-doped TiO_2, both in the thermal and photo-assisted catalytic processes. EPR spectroscopy indicated the likely occurrence of electron-hole transfer between the heteropolyacid and the oxide before and during the UV irradiation. As far as the acidity measurements are concerned, it seems that the presence of strong Brönsted acidic sites are needed for the occurrence of propene hydration and their amount is directly proportional to the reactivity of the catalysts.

The contemporary presence of heat and UV light improved the PW_{12} activity with respect to the thermal process, and the binary materials appeared in almost all cases to be more (photo)active than the bare PW_{12}. This work, for the first time, evidenced by the EPR study, that the increase of reactivity under irradiation can be attributed to the ability of photoexcited PW_{12} to trap electrons, particularly when it is supported. Moreover, the role of water on the reactivity was studied and it was observed that the rate of 2-propanol formation decreased by increasing the water content in the catalytic experiments while it increased under irradiation in the presence of PW_{12}/TiO_2 or PW_{12}/SiO_2 ex A samples.

Experimental Section

Preparation of the (photo)catalysts

SiO_2 was obtained by using tetraethylortosilicate (TEOS) as the precursor. An aqueous TEOS solution (0.101 mol of TEOS in 50 ml of water) has been hydrothermally treated (24 h at 200 °C) and the obtained solid filtered and dried overnight at 40 °C. TiO_2 was obtained by using titanium tetraisopropoxide (TTIP), that was hydrolysed in water (0.105 mol of TTIP in 50 ml of water). The resulting suspension was hydrothermally treated for 24 h at 200 °C, filtered and dried overnight at 40 °C. A N-doped TiO_2 (in the following N-TiO_2) was prepared via a sol-gel method, by mixing a solution of TTIP in isopropyl alcohol (7.5 ml + 7.5 ml) with an aqueous solution of 0.27 g of NH_4Cl in 7.5 ml of distilled water The mixture was kept under stirring at room temperature until the achievement of complete hydrolysis. The gel prepared in this way was left aging for 15 h at room temperature, subsequently dried at 70 °C for 4 h and then calcined in air at 500 °C for 2 h.

As far as the preparation of the composite materials is concerned, two sets of PW_{12}/support samples were prepared. The first set of composites were prepared by impregnating SiO_2, TiO_2 or N-TiO_2 with an aqueous solution containing $H_3PW_{12}O_{40}\cdot 26\ H_2O$ (Aldrich, reagent grade). The obtained slurries were therefore dried overnight at 70 °C. The PW_{12}:oxide molar ratio was 1:150 and these binary materials, where the theoretical PW_{12} coverage on the surface of the oxide was 0.4, 0.3 and 1.0, have been labelled as PW_{12}/SiO_2, PW_{12}/TiO_2 and PW_{12}/N-TiO_2, respectively. The theoretical coverage of the support was estimated by taking into account the value of its specific surface area and the diameter of the PW_{12} anionic cluster (ca. 10 Å) [27]. Consequently, the surface area of a roundish heteropolyanion can be considered equal to ca. 78.5 $Å^2$. The second set of materials was prepared by a hydrothermal treatment (24 h at 200 °C) of a solution obtained by dissolving the alkoxide precursor of SiO_2 (0.101 mol of TEOS) or TiO_2 (0.105 mol of TTIP) in 50 ml of an aqueous solution of PW_{12} (also in this case the molar ratio PW_{12}:oxide was 1:150). The solids obtained after the hydrothermal treatment of the suspensions were filtered and dried and they were labelled as PW_{12}/SiO_2 ex A and PW_{12}/TiO_2 ex A, respectively.

Characterization of the binary HPA/oxide samples

Bulk and surface characterizations were carried out to study some physicochemical properties of the composites. The crystalline structure of the samples was determined at room temperature by powder X-ray diffraction analysis (PXRD) carried out by using a Panalytical Empyrean apparatus, equipped with CuKα radiation and PixCel1D (tm) detector. Scanning electron microscopy (SEM) was performed using a FEI Quanta 200 ESEM microscope, operating at 20 kV on specimens upon which a thin layer of gold had been evaporated. An electron microprobe used in an energy dispersive mode (EDX) was employed to obtain information on the actual PW_{12} content in the samples and to evaluate its dispersion on the support. Specific surface area and porosity were determined in accordance with the standard Brunauer-Emmet-Teller (BET) method from the nitrogen adsorption-desorption isotherm using a Micromeritics ASAP 2020. Studies on the preservation of the structure of the PW_{12} cluster after the deposition and the (photo)reactivity experiments were carried out by vibrational spectroscopy. FTIR spectra of the samples in KBr (Aldrich) pellets were obtained by using a FTIR-8400 Shimadzu spectrometer with 4 cm^{-1} resolution and 256 scans. Raman measurements were performed on pure powdered samples. Spectra were recorded by a Reinshaw in-via Raman equipped with an integrated microscope and with a charged-coupled device (CCD) camera. A He/Ne laser operating at 632.8 nm was used as the exciting source. In order to calculate the band gap of the samples, diffuse reflectance spectra (DRS) were recorded in the range 250-600 nm by using a Shimadzu UV-2401 PC instrument with $BaSO_4$ as the reference sample.

The acidity of the (photo)catalysts was determined by temperature-programmed desorption of ammonia experiments (NH_3-TPD) by using a Micromeritics Autochem 2950 apparatus equipped with a thermal conductivity detector (TCD), a quadrupole mass (QM) spectrometer (Ther-mostar, Balzers) and an ultraviolet gas analyzer (ABB, Limas 11). An amount of 0.3 g of each catalyst sample was pre-treated in He flow at 100 °C for 30 min. Then, after cooling down to room temperature, ammonia adsorption was performed by admitting a flow of 5% NH_3/He stream (30 ml min^{-1}) for 1 h. In order to remove the physically adsorbed ammonia, the sample was purged by flowing 100 ml min^{-1} He at 100 °C for 1 h. Then, after cooling down to room temperature, ammonia desorption started by flowing He (30 ml min^{-1}) and heating up to 600 °C (rate of 10 °C min^{-1}). The temperature was held constant at 600°C for 30 min. Ammonia concentration profiles were recorded with the ultraviolet gas analyzer. TCD and QM data were used to qualitatively confirm the trends.

Electron Paramagnetic Resonance (EPR) spectra, recorded at liquid nitrogen temperature (-196°C), were carried out on a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation. The effect of light on the EPR spectra was investigated by irradiating the sample in the region of UV and Visible light, in the EPR resonant cavity by using a 1600 W Xenon lamp (Oriel Instruments) equipped with a IR water filter to avoid over-heating. For all of the samples the irradiation occurred at 196°C under high vacuum (10^{-5} mbar) or under oxygen atmosphere. For the latter experiment the samples were evacuated first and subsequently contacted with 20 mbar of O_2. Upon irradiation, residual oxygen was evacuated before performing the EPR measurements.

(Photo)-catalytic experimental set-up

(Photo)-catalytic activity of the materials was tested in a continuous Pyrex photoreactor which was horizontally positioned (diameter: 10 mm, length: 100 mm) and operated in gas-solid regime. The reactivity experiments were carried out with 0.5 g of (photo)-catalyst. The gas feeding consisted of propene (40 mM) and water (2 mM or 10 mM). A mass flow controller allowed to feed propene, whereas H_2O was mixed with propene by means of a home assembled infusion pump. The total flow rate of the gaseous stream was 20 cm^3·min^{-1}. All of the runs were carried out at atmospheric pressure and 85°C. The (photo)-reactor and all of the pipes of the set-up were heated by an electric resistance. K-type thermocouples allowed to monitor the temperature in the system. A pre-treatment of the catalysts was carried out under dry N_2 at 85°C for 1 h. The photo-assisted reactions were performed by illuminating the reactor by two UV LED IRIS 40 with an irradiation peak centred at 365 nm. The irradiance reaching the photoreactor was 0.50 W. The temperature of the photoreactor was held constant at 85°C also during the irradiation. Samples of the reacting fluid were analyzed by a Shimadzu 17A gas chromatograph equipped with a FID and an Alltech AT-1 column (30 m, 0.53 mm, 2.65 μm) operating at 40 °C.

Keywords: EPR, heteropolyacids, photocatalysis, propene, hydration, 2-propanol

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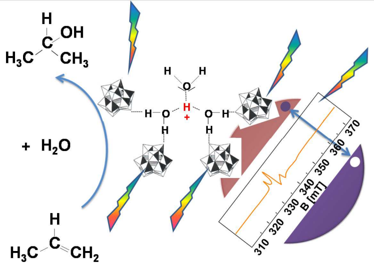
FULL PAPER

Heterogeneous photocatalysis by heteropolyacids.



(Photo)catalysis, hydration, heteropolyacids.

E. García-López, G. Marcì, F.R. Pomilla, L.F. Liotta, B. Megna, M. C. Paganini, C. Gionco, E. Giamello, L. Palmisano*

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Improved (photo)catalytic propene hydration in gas-solid system by using heteropolyacid/oxide composites: EPR, acidity and role of water

This work reports the preparation and characterization of binary materials composed by SiO_2, TiO_2 and N-doped TiO_2 and the Keggin heteropolyacid. The catalysts were used for the hydration of propene to 2-propanol and for the first time it was evidenced by an EPR study that the increase of the reactivity under irradiation can be attributed to the ability of photoexcited PW_{12} to trap electrons.