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Keggin heteropolyacids supported on TiO_2 used in gas-solid (photo)catalytic propene hydration and in liquid-solid photocatalytic glycerol dehydration

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ABSTRACT

(Photo)catalytic propene hydration to 2-propanol and glycerol dehydration to acrolein were carried out by using Keggin heteropolyacids (HPAs) supported on TiO_2. Binary materials have been prepared by impregnation of $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, on TiO_2 Evonik P25. Moreover, a binary material consisting of $H_4SiW_{12}O_{40}$ and TiO_2 was prepared via a hydrothermal treatment and tested for the same reactions. All the materials were characterized by X-ray diffraction (XRD), scanning electron microscopy observations (SEM) coupled with energy dispersive X-ray (EDX) measurements, diffuse reflectance spectroscopy (DRS), Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). The supported Keggin HPA species played a key role both for the catalytic and for the photo-assisted catalytic reactions due to their strong acidity and ability to form strong oxidant species under UV irradiation.

1. Introduction

Polyoxometalates (POMs) are a wide class of discrete nano-sized transition metal-oxygen clusters that can be divided in three classes: heteropolyanions (HPA), isopolyanions (IPA) and Mo-blue and Mo-brown reduced HPA centers [1]. The most explored POM materials are the HPAs and it is convenient to classify them starting from the symmetrical 'parent' polyanion, for instance the Keggin or Wells-Dawson structures among others [2]. The Keggin anion $\{XM_{12}O_{40}\}^{y-}$ contains a heteroatom X in the XO_4^{y-} centre as PO_4^{3-} or SiO_4^{3-} and the so-called addenda atoms, commonly W or Mo. For instance, the structure of the $PW_{12}O_{40}^{3-}$ anion consists of a PO_4 tetrahedron surrounded by four W_3O_9 groups formed by edge sharing octhaedra. This cluster has a diameter of ca. 1.2 nm [3]. The heteropolyacids with the Keggin structure are strongly acidic and are remarkably stable particularly when deposited onto an oxide surface. They are widely used in catalysis and homogeneous photocatalysis because are very soluble in polar solvents. Heteropolyacids have been used as homogeneous photocatalysts because their ground electronic state (the solubilized HPA) absorbs light producing a charge transfer-excited state HPA*. HPA materials, when excited by light to HPA*, act as better oxidant and reductant species with respect to the corresponding ground states [4]. Indeed, HPA* can easily become HPA^-, a "heteropolyblue" specie by means of one (or more) electron transfer from other species [5]. Heteropolyblue species HPA^- are relatively stable and are readily re-oxidized. Enhanced degradation of organic compounds in the UV/TiO_2 process has been reported in the presence of supported Keggin-type HPAs [6]. In a previous paper the catalytic and catalytic photo-assisted activity of $H_3PW_{12}O_{40}$ supported on TiO_2, ZrO_2 or WO_3 was studied and a beneficial role of the photo-catalytically active support on the reaction rate was reported [7]. The significant increase of reactivity was justified by considering the ability of the semiconductor to transfer electrons from the conduction band to the activated HPA^* species. TiO_2, in fact, directly transfers photo-generated electrons from its conduction band to the interfacial HPA with empty d orbitals and consequently the electron-hole charge-pairs recombination is delayed [8]. Moreover, the dispersion of HPAs on solid supports with high surface area, is generally useful for improving the accessibility to their acid sites and the (photo)catalytic activity increases.

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In this paper catalytic photo-assisted activities of $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ supported on TiO_2 have been investigated for two kinds of reactions: i.e. the propene hydration and the glycerol dehydration in gas-solid and in liquid solid regimens, respectively. These reactions are of great interest from the industrial point of view, particularly when carried out under experimental mild conditions. The industrial propene hydration to 2-propanol is carried out at moderate temperatures (ca. 150–200 °C) and under pressure (2 MPa) in the presence of phosphoric acid supported on silica, strong acid resins or zeolites but also heteropolyacids are industrially used for this reaction [9]. Conversely, the dehydration of 2-propanol to form propene is accepted to be a good reaction to probe the acid character of a catalyst [10]. In a gas-solid regime propene and/or propanone are formed at ambient pressure and moderate temperature (in the range 140–325 °C). The selectivity to propene or propanone strongly depends on the acidity-basicity of the solid catalyst. The propene hydration is not an easy reaction to be carried out, because thermodynamically limited by the reverse reaction at high temperature. Intensive research efforts have been also devoted to find new outlets for the high amount of glycerol produced from the biodiesel process [11]. The finding of novel conversion processes to transform glycerol into other chemicals includes scientific efforts in the glycerol dehydration to form acrolein. 3-hydroxypropionaldehyde is obtained after the direct glycerol loss of one water molecule. A further loss of a water molecule gives rise to acrolein. Acrolein is an important chemical used as a feedstock to produce acrylic acid, pharmaceuticals or to treat fibers, and it is also an herbicide which controls the growth of aquatic plants. It is currently produced by oxidation of propene by heterogeneous catalysis. A maximum yield of 80% at high propene conversion (90–95%) is reached by using commercial catalysts based on Bismuth molybdates [12]. Synthesis of acrolein from glycerol has been widely investigated since the 1960's but it has been mainly reported in patent literature. A strong catalyst acidity seems to be necessary to perform the dehydration of glycerol to acrolein in gas phase in the presence of zeolite [13] or in supercritical water [14] by using various solid acid catalysts including sulphates. Chai et al. reported the gas-phase dehydration of glycerol to produce acrolein at 315 °C by using Nb_2O_5 [15,16]. Glycerol conversion and acrolein selectivity of the Nb_2O_5 catalysts were dependent on the fraction of strong acid sites ($-8.2 \leq H_0 \leq -3.0$), where H_0 corresponds to the Hammet factor. The amorphous catalyst prepared by calcination at 400 °C, having the highest fraction of acid sites at $-8.2 \leq H_0 \leq -3.0$, showed the highest mass specific activity and acrolein selectivity (51 mol%). The other samples, having a higher fraction of either stronger ($H_0 \leq -8.2$) or weaker acid sites ($-3.0 \leq H_0 \leq 6.8$), were less effective for glycerol dehydration and formation of the desired acrolein. The highest selectivity was ca. 70 mol%. The catalysts having further stronger acid sites ($H_0 \leq -8.2$) produce a lower selectivity (40–50 mol%) due to a more severe catalyst coking. Authors evidenced that Brönsted acid sites presented better performance than Lewis acid sites. Chai et al. proposed a mechanism where the reaction was initiated by the dehydration involving either the central or a terminal —OH of glycerol which result in the parallel formation of two enol intermediates. The enols would undergo rapid rearrangement to 3-hydroxypropionaldehyde or 1-hydroxyacetone, respectively. The 3-hydroxypropionaldehyde would be very unstable at the reaction temperature (315 °C) and it can easily give rise to a further dehydration to acrolein. A secondary hydrogenation reaction of the acrolein product will lead to the formation of allyl alcohol. The unstable intermediate 3-hydroxypropionaldehyde would also decompose to acetaldehyde and formaldehyde, according to a reversed aldol condensation; a follow up hydrogenation or decomposition of formaldehyde would result in the formation of methanol or CO and H_2.

Tsukuda et al. investigated the production of acrolein from glycerol over silica-supported heteropoly acids [17]. In that study, silicotungstic acid supported on silica with mesopores of 10 nm showed the highest catalytic activity with the acrolein selectivity <85 mol% at 275 °C and at ambient pressure.

Shen et al. studied the catalytic activities of silicotungstic, phosphotungstic, and phosphomolybdic acids in the liquid phase dehydration of glycerol to acrolein in a semi-batch reactor [18]. Silicotungstic acid exhibited high catalytic activity and the maximum yield of 78.6% was achieved when glycerol was completely converted at the reaction temperature of 300 °C with the mole ratio of silicotungstic acid to glycerol of $1{\cdot}10^{-4}$:1. The order of catalytic activities toward the formation of acrolein was silicotungstic acid > phosphotungstic acid > phosphomolybdic acid, revealing that the reaction was affected by the acidity and the stability of the heteropolyacids. Hydroxyacetone and acetic acid were also detected with yields of less than 10%, respectively.

Liu et al. studied Al_2O_3 supported silicotungstic acid ($H_4SiW_{12}O_{40}/Al_2O_3$) samples prepared by impregnation and calcined at 350, 450, 550, 650 °C to study the structural evolution of the $H_4SiW_{12}O_{40}$ heteropolyacid and its effect on the catalytic performance during glycerol conversion to acrolein in gas-solid regime at 300 °C [19]. The glycerol conversion increased with acid center concentration under the specified reaction condition. As well, selectivity to acrolein increased with Brønsted/Lewis acid ratio, suggesting the crucial role of Brønsted acid sites.

In this paper some bulk and surface properties of three heteropolyacid clusters supported on TiO_2 materials have been studied along with their use as heterogeneous photocatalysts in two reactions, i.e. the propene hydration and the glycerol dehydration. The investigation focuses how the (photo)reactivity can depend on the type of HPA but also how the support-heteropolyacid interaction can be important. As far as the glycerol dehydration is concerned, it is worth nothing that, contrarily to what reported in studies on thermal catalysis, in our UV irradiated system the reaction proceeded at very low temperature (35 °C).

2. Experimental

2.1. Preparation of the binary HPA/TiO_2 samples

The binary materials HPA/TiO_2 were prepared by impregnating the support (commercial TiO_2 Evonik P25) with an aqueous solution containing the desired amount of the commercial HPA, i.e. $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ or $H_4SiW_{12}O_{40}$ (Aldrich) denoted hereafter as PW_{12}, PMo_{12} and SiW_{12}, respectively. During the preparation, each suspension was stirred at 50 °C for 1 h, and then water was evaporated until dryness. The binary materials prepared as above described are denoted hereafter as PW_{12}/TiO_2, PMo_{12}/TiO_2 and SiW_{12}/TiO_2. The HPA amount deposited was 50% in weight with respect to the support corresponding to a molar percentage of 14% of W and 86% of Ti (with respect to the sum W + Ti) in PW_{12}/TiO_2 and SiW_{12}/TiO_2 samples and 20% of Mo and 80% of Ti (with respect to the sum Mo + Ti) in PMo_{12}/TiO_2 sample.

The theoretical coverage of the support has been calculated by taking into account that the diameter of each anionic HPA cluster is equal to ca. 10 Å and, consequently, by considering a roundish shape of the heteropolyanion, its surface area results ca. 78.5 Å^2 [3].

An alternative binary material has been prepared starting from a selected HPA (SiW_{12}) and a TiO_2 precursor, by using the following methodology. A solution was prepared by adding 7.5 ml of titanium isopropoxide (TTIP) to 50 ml of 2-propanol, hence 6 ml of HNO_3 0.05 M and the appropriate amount of SiW_{12} (0.5440 g) were added under vigorous stirring to the Ti containing solu-

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