
Heteropolyacids with Keggin structure supported on silica-alumina

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Abstract: The behaviour of molybdophosphoric acid, with Keggin structure, supported on different silica-alumina mixtures, obtained by sol-gel method, was studied. Different techniques were used to synthesise the supports. In one of them, commercial alumina was added to a tetraethyl orthosilicate (TEOS) solution, and then this was hydrolysed. In the other preparations, TEOS and aluminium tri-sec-butoxide were hydrolysed, simultaneously or with TEOS prehydrolysis. The catalysts were prepared by incipient wetness impregnation, and different thermal treatments were applied after their leaching with toluene. The specific surface area of the solids was measured, and the nature of the Keggin heteropolyacid species present in the catalysts was characterised by diffuse reflectance spectroscopy and X-ray diffraction. In addition, their acidic properties were evaluated by potentiometric titration with n-butylamine.

Keywords: Keggin heteropolyacids; molybdophosphoric acid; silica-alumina; sol-gel synthesis; leaching with toluene.

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1 Introduction

The increasing use of catalyst-based production methods in the emerging industries has been favoured by the continuous innovation observed over the last decade for the different catalytic processes. Among the emerging industries, those involved in the synthesis of fine chemicals are at the leading edge in this class of catalytic processes. Currently, there is considerable interest in exploiting both the structure of catalyst precursors and the multicentre active sites to facilitate catalysis by polyoxometalates, as mentioned by Nomiya et al. (2000). It has been stressed by Okuhara et al. (1996) that it is important to discover more reliable and efficient procedures before the exploration of possible new reactivity patterns. Thus, it is very important to use fully characterised and more reliable catalyst precursors for catalytic reactions.

Polyoxometalates are well known as oxidation and acid catalysts in which the redox and acid-based properties can be tuned by variation of the structure type, the central heteroatom and addenda or transition-metal-substituted atoms. The catalytic function of the Keggin family has attracted much attention, particularly because these compounds provide a good basis for the molecular design of mixed oxide catalysts and high capabilities in practical uses. The free acids are less stable than the salts but can be obtained in structurally better-defined samples.

In 1826, Berzelius reported the preparation of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$, and, in 1864, Marignac observed two isomers, now designated α and β isomers. The structure of $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}$ was solved by Keggin in 1933, as noted by Weinstock et al. (1999). The Keggin heteropolyacids (HPA), constituted by a close-packed framework of metal-oxygen octahedra MO_6 ($\text{M} = \text{Mo}$ or W) surrounding a central PO_4 tetrahedron, exhibit stronger acidity than conventional acids. Advantages to be highlighted of using supported HPA as catalysts are their easiness of recovery and recycling after carrying out liquid phase reactions, and the easier product isolation, when they are compared to that of the homogeneously catalysed reactions. The preparation of supported catalysts from molybdophosphoric acid (MPA) on different carriers has been previously studied, as MPA on silica catalysts were used, obtaining high conversion and selectivity, in cyclisation reactions among others (Villabrille et al., 2002, Vázquez et al., 2001, 2002).

Usually, conventional mixed oxide preparation techniques do not lead to molecularly homogeneous, high-surface-area materials. In contrast, the sol-gel synthesis of mixed oxide aerogels allows excellent mixing control while stabilising considerable textural characteristics, most notably high surface area and pore volume. Within the sol-gel

process, relative precursor reactivity can be used to control the homogeneity. Sol-gel chemistry offers four main strategies for controlling relative precursor reactivity.

- For most metal atoms, more than one alkoxide precursor can be used. Taking into account some factors, such as the inductive capability and steric hindrance of various alkoxy groups, it would be expected that different alkoxides of the same metal display different reactivity.
- An unreactive precursor can be given a head start in the reaction sequence by allowing it to prereact with water. This technique, known as prehydrolysis, is the most common scheme used in sol-gel syntheses for matching reactivities.
- A reactive precursor can be slowed down by replacing some of their alkoxy groups by different ligands in a technique known as chemical modification.
- When the reactivity of the precursors responds differently to temperature, a change in the synthesis temperature might be made, to keep their reactivities alike (Miller et al., 1994).

The aim of this paper is to study the acidic behaviour of supported MPA, when different silica-alumina mixtures obtained by sol-gel method are used as carriers. The nature of the HPA species present in the catalysts was determined by different techniques. Their acidic properties were evaluated by potentiometric titration, before and after performing a leaching with toluene, and also after different thermal treatments.

2 Experimental procedure

Support preparation

Three different techniques were used to prepare the silica-alumina samples.

- Tetraethyl orthosilicate (TEOS) solution in ethanol (EtOH) was prepared. Then, commercial alumina Aldrich, 10 μm particle size, was added. The hydrolysis of TEOS, by means of water addition at 45°C, led to the gel of silica by sol-gel technique (Woignier and Phalippou, 1992). The molar ratio of $\text{H}_2\text{O}:\text{TEOS}:\text{EtOH}$ was 4:1:1. After 24 hours, the solid and solution were separated by decantation. Then the solid was dried at 60°C for 24 hours, and at 100°C for 2 hours. This support is named SiAl.
- The mixed oxide was prepared starting from TEOS, aluminium tri-sec-butoxide (TSBAI), EtOH and water by partial hydrolysis method, described by Hench and West (1990). First, TEOS was hydrolysed for 2 hours in the same conditions mentioned above. Then TSBAI solution in ethanol was added. The reaction time and drying conditions were the same as that described previously. The support is named SiAlPH.
- The carrier was prepared from TEOS, TSBAI, EtOH and water. Here, the support was prepared with the operative conditions same as that of SiAlPH preparation; however, both alkoxide ethanol solutions were simultaneously hydrolysed. This support is named SiAlSH.

Catalyst preparation

The synthesised supports were impregnated using the incipient wetness method with ethanol-water solutions (50% v/v) of MPA Fluka ($\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$), and two different MPA contents were used: low amount (0.07 mmol MPA/ml) and high amount (0.14 mmol MPA/ml). The samples were dried at room temperature for 24 h.

Leaching of catalysts with toluene

The catalysts were leached with toluene under continuous stirring, at room temperature, for two periods of 24 h. Later, the solids were dried at room temperature and calcined at 150°C, 250°C and 400°C.

Characterisation of catalysts

- *Textural analysis.* The specific surface area (S_{BET}) of supports and catalysts was determined by nitrogen adsorption/desorption technique using a Micromeritics Accusorb 2100E equipment.
- *Diffuse reflectance spectroscopy (DRS).* DRS spectra of solid samples were recorded, in the range 200–600 nm, using a UV-visible Varian Super Scan 3 equipment, fitted with a diffuse reflectance chamber with inner surface of BaSO_4 . Samples were compacted in a Teflon sample holder to obtain a sample thickness of 2 mm.
- *X-ray diffraction (XRD).* XRD patterns of representative solid samples were recorded by means of a Philips PW-1732 device, with built-in recorder, using the following conditions: Cu K_α radiation; Ni filter; 30 mA and 40 kV in the high voltage source; scanning angle (2θ) from 5° to 50° and scanning rate, 1° per minute.
- *Acidity measurements.* Acidity of solid samples was measured by means of potentiometric titration. A known mass of solid suspended in acetonitrile Baker was stirred for 3 hours. Then, the suspension was titrated with a solution of 0.05 N n-butylamine Carlo Erba in acetonitrile, at a flow rate of 0.05 ml/min. The electrode potential variation was measured with an Instrumentalia digital pH meter, using a double junction electrode.

3 Results and discussion*3.1 Textural properties*

As a consequence of the carrier preparation methods, different behaviour for supported MPA was observed. The specific surface area of three systems catalysts are shown in Table 1.

Table 1 Specific surface area (m^2/g) of MPA on SiAl(I), SiAlPH (II) and SiAlSH (III) catalysts

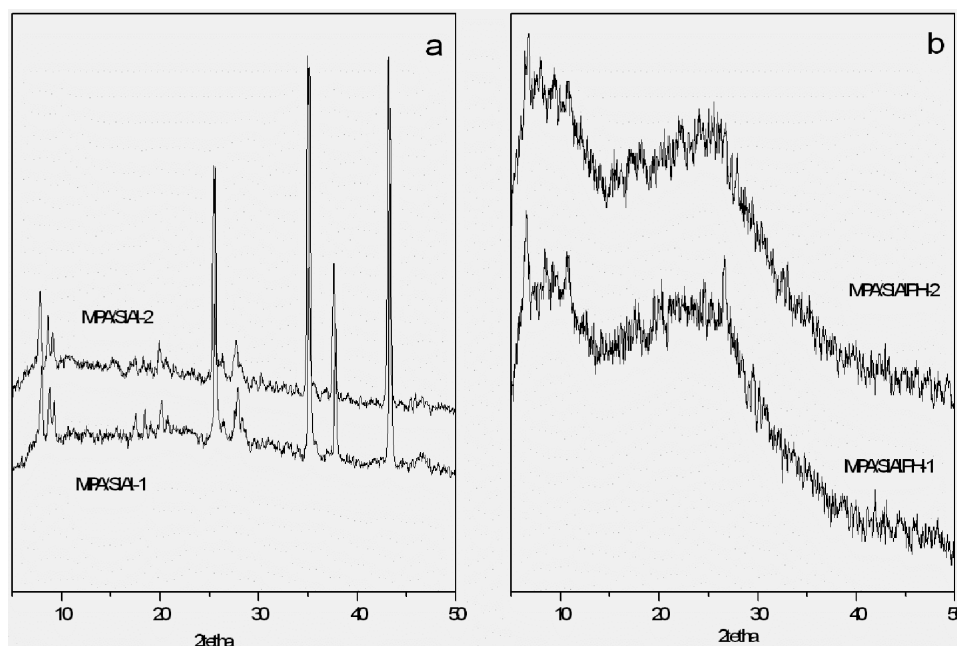
<i>Catalyst</i>	<i>I</i>	<i>II</i>	<i>III</i>
High content	3.0	185.3	220.2
Low content	2.4	246.5	291.2

SiAl-based catalysts presented very low S_{BET} values ($2.4\text{--}3\text{ m}^2/\text{g}$). In the synthesis of SiAl support, TEOS ethanol solution filled the pores of alumina particles. Then, TEOS was hydrolysed and, as a consequence, silica precipitated and blocked the pores. This behaviour led to the low surface area, observed in the catalysts prepared using this support. In turn, surface area was higher when SiAlPH and SiAlSH were used as support. The catalysts prepared with SiAlPH, synthesised by prehydrolysis of TEOS, showed slightly lower surface area ($185.3\text{--}246.5\text{ m}^2/\text{g}$) than those based on SiAlSH ($220.2\text{--}291.2\text{ m}^2/\text{g}$). For all carriers, S_{BET} decreased when MPA concentration increased owing to higher pore obstruction.

3.2 X-ray diffraction

Some remarkable differences between the catalysts prepared on different supports were found by XRD. While MPA/SiAl-1 (dried at room temperature) and MPA/SiAl-2 (calcined to 150°C) patterns showed the main diffraction lines of the bulk heteropolyacid (Figure 1(a)); diffraction lines corresponding to crystalline structures were not observed in the patterns of MPA/SiAlPH-1 and MPA/SiAlPH-2 (Figure 1(b)). This behaviour is related to the textural properties of the supports, mainly to their surface area. SiAl support presented a low surface area ($5\text{ m}^2/\text{g}$), thus leading to a poorly dispersed MPA on the support surface. In turn, SiAlPH support ($332\text{ m}^2/\text{g}$) let to obtain better-dispersed MPA, as it is suggested by the absence of defined lines assigned to bulk MPA.

Figure 1 XRD patterns of MPA catalysts dried at room temperature (1) or calcined at 150°C (2) on SiAl (a) and on SiAlPH and (b) supports

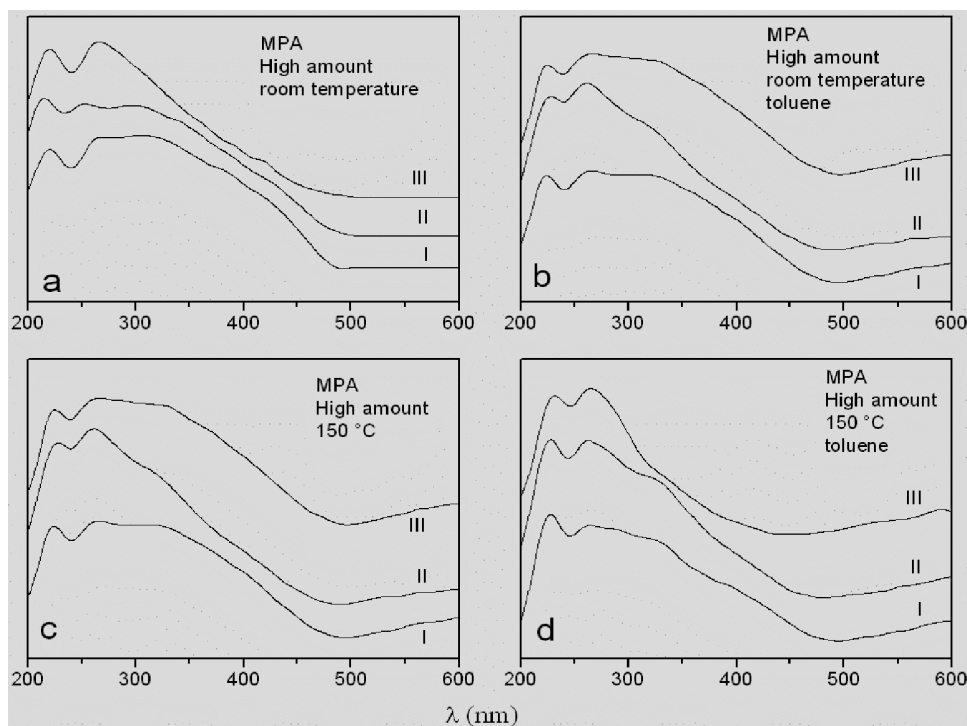


3.3 Diffuse reflectance spectroscopy

The spectra of the MPA on SiAl, SiAlPH and SiAlSH, for high amount, before and after the leaching with toluene, dried at room temperature and 150°C, respectively, are shown in Figure 2(a–d). All of them were indicative of the presence of the primary Keggin structure. The absorption spectra of most non-reduced polyanions appear in the 200–500 nm region, and consist of bands, which may be ascribed to oxygen-to-metal transfers. Nevertheless, an absorbance increase in the region near 600 nm, assigned to reduction of Mo^{VI} to Mo^{V} , was observed in the spectra of MPA-based catalysts over the three supports, though MPA reduction proceeded without a substantial change of its structure. The catalysts based on MPA were greenish as a consequence of a partial formation of the so-called heteropoly blues produced on MPA reduction (Pope and Muller, 1991).

In relation to the leaching with toluene, the MPA amount removed from the catalysts, at 20°C, was less than 0.1% of the initial content. This result corroborates the insolubility of MPA in toluene, when it is impregnated on silica-alumina supports.

Figure 2 DRS spectra of MPA-based catalysts on the studied supports: before (a) and (c) and after leaching with toluene (b) and (d) for three used supports: SiAl (I), SiAlPH (II) and SiAlSH (III)



3.4 Potentiometric titration with *n*-butylamine

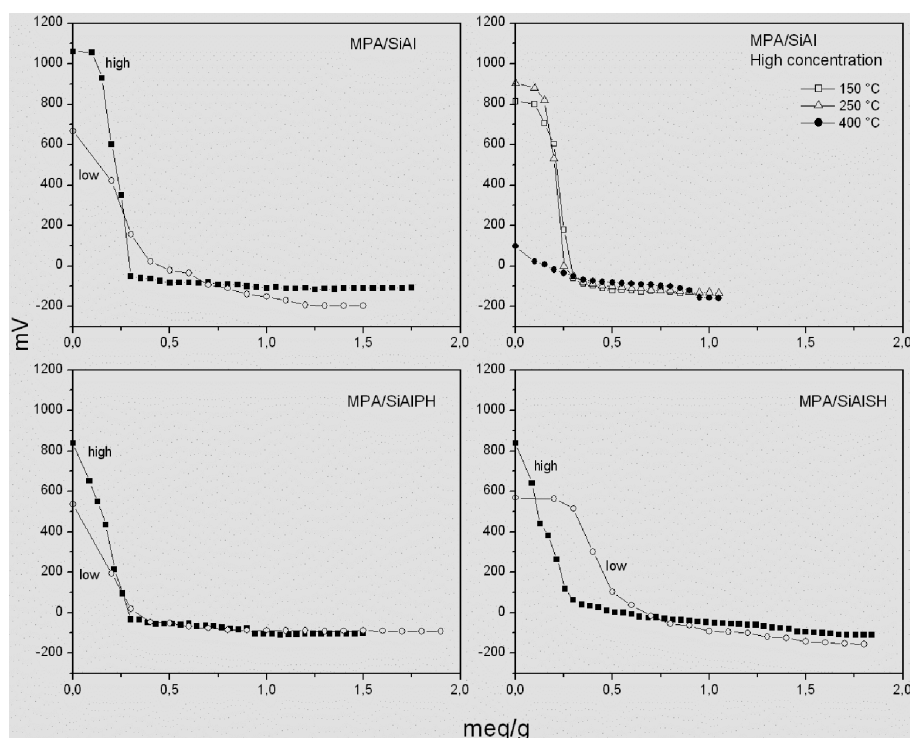
The acid strength of a solid is defined as the ability of the surface to transform an adsorbed neutral base into its conjugated acid. The use of an indicator test to assay the

Hammett acidity is considered a reference method, but it is difficult to apply to coloured solids, especially if they are weak acids. For these cases, a potentiometric method was developed; the measured potential difference is mainly determined by the acidic environment, which is around the electrode membrane. The measured electrode potential is an indicator of the bulk acidic properties of the dispersed solid particles. Use of an aliphatic amine such as n-butylamine, whose basic dissociation constant is approximately 10^{-6} , allows carrying out a potentiometric titration of a strong acid, being applicable to these systems.

The potentiometric titration enables the evaluation of the total number of acid sites and their acidic strength. The initial electrode potential (E) indicates the maximum acid strength of the surface sites, and the value (meq/g solid) where the plateau is reached indicates the total number of acid sites. The acidic strength of the surface sites can be assigned according to the following ranges: very strong site, $E > 100$ mV; strong site, $0 < E < 100$ mV; weak site, $-100 < E < 0$ mV and very weak site, $E < -100$ mV.

The potentiometric titration curves of MPA on different silica-alumina supports are shown in Figure 3. The curves for both high and low MPA concentration for three studied supports are shown. In the cases of high concentration of MPA on SiAl, SiAlPH and SiAlSH, the E values were 1060 mV, 840 mV and 840 mV, respectively. The supported MPA acidity using the same supports, for low concentration, was 667 mV, 535 mV and 567 mV, respectively.

Figure 3 Potentiometric titration curves of MPA catalysts supported on SiAl, SiAlPH and SiAlSH for high and low concentration. For MPA/SiAl system, potentiometric titration curves at different thermal treatments (150°C, 250°C and 450°C)



The acidic properties for MPA/SiAlSH are comparable to MPA/SiAlPH, perhaps owing to similar surface properties of SiAlPH and SiAlSH supports. These supports have greater surface area and then a higher number of surface groups compared to the SiAl carrier, increasing the MPA-carrier interaction, leading to well-dispersed MPA phase, but to a decrease of the acidic strength.

In addition to the study of acidic properties, from function to concentration, we studied the influence of calcination temperatures on the acidity of supported MPA. The potentiometric curves for MPA on SiAl carrier are presented also in Figure 3, for 150°C, 250°C and 400°C. For MPA-based catalysts, the E values are 815 mV, 903 mV and 98 mV for the temperatures 150°C, 250°C and 400°C, respectively. This behaviour could be explained assuming that different number of water molecules were retained by these samples, as previously reported by Serwicka et al. (1991), that acidity features depend on the extent of hydration. Mention can be made that the acid strength of MPA/SiAl catalyst, calcined up to 400°C, was lower than that of all the other samples, which were thermally treated at lower temperatures. This behaviour may be related to the supported HPA, which was partially decomposed at 400°C, as suggested by Vázquez et al. (1999).

4 Conclusions

Molybdophosphoric acid supported on different silica-alumina carriers, obtained by means of sol-gel method, was studied. The synthesised supports displayed different textural properties according to the preparation technique, e.g., the use of preformed alumina, prehydrolysis of the silica precursor or simultaneous hydrolysis of the silica and alumina precursors. These support properties significantly influenced the characteristics of the catalysts prepared by impregnation of the different carriers. The MPA catalysts presented the characteristic features of the Keggin primary structure, but their acidic properties varied according to the used support that led to different MPA-support interaction and dispersion.

These results show that the MPA supported on silica-alumina may be promissory solids to be used as heterogeneous catalysts, in liquid phase for acidic reactions, for example, in organic synthesis that occurs at a low temperature by means of an environmental benign technology.

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