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Study of acid–base properties of supported heteropoly acids in the reactions of secondary alcohols dehydration

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ABSTRACT

The dehydration of secondary alcohols (propan-2-ol and 4-methylpentan-2-ol) was catalyzed by heteropolyacids (HPAs) supported on different solids. Catalysts prepared with 20 wt.% of HPAs were calcined at 400 °C and characterized by X-ray diffraction, Raman spectroscopy, XPS and N_2 adsorption measurements. Stability of the Keggin structure of supported HPAs and changes in textural properties of catalysts were analyzed. The catalytic conversion of alcohols to olefins and ethers has been studied over the catalysts prepared. All catalysts presented activity in the reactions, but only molybdophosphoric acid supported on ZrO_2 (MoP-Z) showed selectivity in the formation of acetone and methyl isobutyl-ketone (MIBK). Catalysts with tungstosilicic acid (WSi) and Tungstophosphoric acid (WP) were active in the formation to DIPE. The acid–base properties of the catalysts play a key role in route of the reaction mechanism.

1. Introduction

The acidity and basicity of solid catalysts are two influential factors in their activity and selectivity, not only in typical acid–base reactions, different authors reported on the importance of acid–base pair site in many catalytic processes [1,2]. The acid–base properties of the solids are involved in the catalysis of the dehydration reaction producing olefins and ethers that can be accompanied too by alcohol dehydrogenation to the corresponding ketone. Indications as to an application can be found in the patent literature: secondary alcohols were reported to give α-alkenes over thorium and cerium oxides supported on alumina [3] and zirconium oxide catalysts were found to be very selective toward alk-1-ene formation [4,5]. Ether synthesis from alcohol is known to be an acid catalyzed reaction; however, one of the undesirable products is hydrocarbons. Extensive studies on methanol dehydration, mainly over Al_2O_3, have been carried out to address the reaction mechanism. Knözinger and co-workers [6] have proposed that the ether formation takes place via a surface reaction between the adsorbed alcohol molecule on an acidic site and an adsorbed alkoxide anion on a basic site. Other authors have suggested that a Lewis acid-basic pair is responsible for ether formation [7].

4-Methylpent-1-ene is the starting material for manufacturing thermoplastic polymers of interest for their technological properties. This valuable alkene can be prepared through the dehydration of 4-methylpentan-2-ol. The acid–base properties of the solid are evaluated in the dehydration reaction, which can be accompanied by alcohol dehydrogenation to the corresponding ketone.

Heteropolyacids (HPAs) constitute a alternative for the dehydration reactions and others, as they are characterized by a strong acidity, fundamentally of the Brönsted type, comparable to that of fluorhydric and sulfuric acids; some of the more interesting HPAs show the Keggin structure. The Keggin HPAs comprise heteropoly anions of the formula $[XM_{12}O_{40}]^{n-}$, where X is the heteroatom (P^{5+}, Si^{4+}, etc.) and M the addendum atom (Mo^{6+}, W^{6+}, etc.). The structure of the heteropoly anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6 [8]. The HPAs are the usual catalyst of choice because of their acidic strength and relative thermal stability. A serious problem associated with the use of this type of materials as heterogeneous catalysts is their low surface area (~5–8 m^2 g−1) [9]. The use of HPA in supported form is preferable because of its high surface area compared to the bulk material. Acidic o neutral solids, which interact weakly with HPAs such as silica, active carbon and acidic ion-exchange resin, have been reported to be suitable as HPA supports [10]. Bielánski et al. reported tertiary ether synthesis using WSi on different supports as catalysts [11]. Recently, we had shown that zirconia-supported WP acts as an efficient catalyst for isomerization reaction [12,13].

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Tungstophosphoric acid ($H_3PW_{12}O_{40}$), tungstosilicic acid ($H_3SiW_{12}O_{40}$) and molibdophosphoric acid ($H_3PMo_{12}O_{40}$) are the most representative of the family of heteropoly acids (HPAs), and their structure is Keggin type [14]. These compounds show high catalytic activity as much in acid–base reactions and oxide–reduction. On the other hand, the HPAs have other special properties, which are very useful in catalysis, such as high solubility in water and in some polar organic solvents, a high thermal stability in solid state and ability to form pseudo-liquid phases. All these properties make possible their use in homogeneous and heterogeneous catalysis [15,16].

The objective of the present study is the evaluation of various solid acid catalysts for alcohols dehydration, mainly 4-methylpentan-2-ol and propan-2-ol. A correlation between catalytic activity and the acid–base properties of the catalysts were investigated.

2. Experimental

2.1. Preparation of catalysts

SiO_2-Gel (Merk-7734), ZrO_2/SiO_2 (Grace 18301-14 with 13 wt.% of ZrO_2), ZrO_2 (prepared in laboratory by precipitation pH = 10) [12,17] and ZrO_2 thermal treatment at 400 °C (Z*) for 4 h is used as support. These supports are referred like S, ZS, Z and Z*, respectively. The HPAs are supported by the impregnation method by the following way: First, solutions of HPAs/ethanol are prepared. Later, the necessary volume of these solutions is added in the different supports, to obtain 20 wt.% of HPAs, the solvent is evaporated using a rotavapor. Finally, the catalysts are dried at 120 °C and calcined at 400 °C for 4 h. The prepared catalysts were denoted as ***X-Y***, where ***X*** is the corresponding HPA (WP, MoP or WSi) and ***Y*** is for S, ZS, Z and Z*, respectively.

2.2. Characterization of catalysts

The specific surface area, pore volume and pore size distribution of the samples were measured in an automatic adsorption instrument (Quantachrome Autosorb 1C) using low-temperature N_2 adsorption–desorption isotherms. Prior to the measurements, the samples were evacuated in situ at 300 °C for 3 h under vacuum. The surface area was calculated from these isotherms using the multi-point Brunauer–Emmett–Teller (BET) method based on the adsorption data within the partial pressure P/P_0 range from 0.05 to 0.35. The pore size distribution was determined by BJH method from the desorption part of isotherm, the pore volume was determined from total volume of nitrogen adsorbed at $P/P_0 = 0.98–0.99$. All the diffraction patters (XRD) of the samples were obtained with an Siemens D 5005 apparatus equipped with monochromator of secondary beam for K-radiation $\alpha = 1{,}5406$ Å (anode of Cu). Raman spectra were recorded at room temperature on previously calcined samples in a nearly backscattering geometry using an ISA Labram micro-Raman apparatus. The excitation line was the 632.8 nm of a He-Ne laser. The laser power on the sample was kept low (about 1 mW) to avoid thermal effects. The samples were analyzed by X-ray Photoelectron Spectroscopy (XPS), the spectra were acquired with a THERMO Scientific K-Alpha spectrometer equipped with Al Kα X-ray source (1486.6 eV) and a hemispherical electron analyzer. Experimental peaks were decomposed into components using mixed Gaussian–Lorentzian functions and a non-linear squares fitting algorithm. Shirley background subtraction was applied. An intensity ratio of 2:3 and a splitting of 2.3 eV were used to fit the Mo 3d peaks. Binding energies were reproducible to within ± 0.2 eV and the C 1s peak at 284.6 eV was used as a reference from carbon.

Table 1
Surface area, pore volume and pore diameter of the different solids.

Sample	S_{BET} ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Average pore diameter (Å)
Z	204	0.24	47
Z*	132	0.29	69
S	220	1.05	191
ZS	207	0.95	184
MoP-Z	229	0.22	40
MoP-Z*	77	0.16	83
WP-S	227	0.86	151
WP-Z	272	0.22	32
WSi-Z	n.e.	n.e	n.e
WP-ZS	n.e	n.e	n.e

n.e. = not evaluated.
Z* stands for ZrO_2 calcined at 400 °C.

2.3. Activity test of catalysts

The catalytic activity of solids was evaluated on the reactions of dehydration of secondary alcohols (4-methylpentan-2-ol and propan-2-ol), these reactions were carried out in a fix-bed quartz tubular reactor. Previous to the reactions, the catalyst was activated at 350 °C with He flow (40 ml/min) during 1 h. On the propan-2-ol dehydration, 0.1 g of sample was used with 60 ml/min He flow as carrier gas (molar ration of He/propan-2-ol = 5). Dehydration of 4-methylpentan-2-ol was carried out with 0.05 g of catalyst and 165 ml/min He flow as carrier gas (molar ration of He/4-methylpentan-2-ol is 39). The products of the reactions were analyzed with a gas chromatograph Varian 3600 CX, connected to the outlet of the reactor and equipped with a Flame Ionization Detector (FID) and PONA capillary column. The reaction rate and conversion were calculated assuming a first order reaction. The following parameters were calculated as follows:

$$X_a \quad (\text{Conversion of secondary alcohol, mol\%}) = \frac{\sum_i^n Yi}{C_{out} + \sum_i^n Yi} \times 100,$$

Selectivity S_i to compound i:

$$S_i\,(\text{mol\,\%}) = \frac{Y_i}{\sum_i^n Y_i} \times 100,$$

where C_{out} is secondary alcohol mole percent in the outlet of reactor and Y_i are yields to the different products.

For a reaction of the type: A → products.

The reaction rate ($-r_a$) was determined using the following equation:

$$-r_a = \frac{F_{ao} X_a}{m}$$

where $-r_a$ = reaction rate [$mol\,g^{-1}\,s^{-1}$] F_{ao} = molar flow of A [$mol\,s^{-1}$]; X_a = Conversion of A; and m = catalyst mass [g].

3. Results and discussion

3.1. Physico-chemical characterization

In Table 1, the effects caused by the addition of the HPAs on the different supports on the specific area, pore volume and pore average diameter are shown. The ZrO_2 calcined at 400 °C (Z*), shows a surface area of 132 $m^2\,g^{-1}$. When Z was calcined at 300 °C, the area was 204 $m^2\,g^{-1}$. The reduction of area is due to the structural transformation by the effect of temperature. The presence of the HPAs produces a stabilization of the area in the supports. The SiO_2 (S) showed a high surface area of 220 $m^2\,g^{-1}$ and pore volume of 1.05 $cm^3\,g^{-1}$, when the support was impregnated with 20 wt % of WP, the surface area increases to 227 $m^2\,g^{-1}$. Similar effect happened with the samples WP-Z and MoP-Z, with areas of 272 and