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Immobilizing heteropolyacids on zirconia-modified silica as catalysts for oleochemistry transesterification and esterification reactions

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ABSTRACT

A new method of chemical immobilization of Keggin heteropolyacids (HPAs) was suggested. $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ were immobilized on the silica which was previously grafted with zirconium butoxide. The immobilization method promoted strong interaction HPA-support and yielded 25 wt.% of well-dispersed HPAs, so increasing the density of acid sites. The catalysts were active in the reaction of transesterification of methyl stearate with n-butanol and esterification of oleic acid with trimethylolpropane. We demonstrate that, contrary to the immobilized $H_3PMo_{12}O_{40}$, the $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$-based catalysts are stable toward leaching in a non-polar oleic acid medium. A discussion on circumventing the leaching in non-polar versus polar media is proposed in terms of interaction strength HPA-support. The stronger interaction (i.e., better resistance for leaching) between the support and $H_3PW_{12}O_{40}$ (or $H_4SiW_{12}O_{40}$) is referred to the lower difference of electronegativity between Zr and W and the lower polarizability of the bonds Zr–O–W compared to Zr–O–Mo.

1. Introduction

Considering the field of oleochemistry, acid catalysts are of big interest for the biofuel-dedicated transesterification and esterification reactions as well as biolubricant productions. Contrary to the alkaline synthetic paths, acidic catalysts can catalyze simultaneously both above-mentioned reactions while avoiding soap formation when low oil quality is employed [1]. Different studies showed that heteropolyacids (HPAs) are active acidic catalysts for both esterification and transesterification [2–6]. However, bulk heteropolyacids (HPAs) are soluble in polar media that make their recovery difficult. Moreover, if used in non-polar medium, the HPAs are not soluble and marginally active due to low accessibility of their active sites. In order to circumvent these penalties, different approaches were attempted to heterogenize HPA as for instances: impregnation into porous supports [7–9], entrapment in solid matrices via sol–gel [10,11], grafting on functionalized surfaces [12], and so forth. Nevertheless, the preparation of stable heterogeneous HPAs that do not leach in polar media while being well dispersed in non-polar media still remains a challenge. Particularly, some studies showed that zirconia is able to interact and stabilize dispersed HPAs [13,14]. However, due to high crystallinity of ZrO_2 and often low specific surface area, the accessibility of active sites remains limited. In order to limit this drawback, the combination of ZrO_2 with an amorphous support could be advantageous as the high surface area support would provide good accessibility of active species and the zirconia would chemically stabilize heteropolyacids.

In this work, we demonstrate an alternative approach to immobilize chemically HPAs on zirconia/silica support. The novelty of the suggested immobilization method relies on the use of zirconia as a linker between silica and HPA. Within the limit of our knowledge, the attempts to combine silica and zirconia with HPAs were done so far only by impregnation method or by sol–gel technique [15,16]. The difference in the HPAs immobilization may contribute positively or negatively to the catalyst texture, stability, and number of active sites. Moreover, we studied the stability of prepared materials toward leaching considering two reactions bearing industrial applications. First, we studied the stability of the prepared catalyst toward leaching in a model reaction for biofuel production, namely the methyl stearate transesterification with n-butanol. This reaction allowed us both to make screening tests and justify the efficiency of the suggested synthetic HPAs immobilization. Second, we tested the catalysts activity for the

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clean "solvent-free" synthesis of biolubricants by oleic acid esterification with trimethylolpropane. This reaction has not been extensively studied so far, where only few reports addressed some issues to be overcome [17,18]. The reaction possesses technical and scientific difficulties among which is the intrinsic molecular hindrance of the reaction components, being furthermore very difficult to analyze analytically. Besides, the mass transfer and diffusion limitations, due to high viscosity of the reaction medium, undoubtedly minimize the reaction kinetics. In this work, we report the successful preparation of stable heterogeneous catalysts appearing as good candidates when employed for the above-mentioned complex industrial processes.

2. Materials and methods

2.1. Chemicals

Silica (Merck 60, 333 m^2/g), 80% zirconium butoxide solution in n-butanol (Sigma), pentadecane (Sigma, TCI), acetonitrile, ethanol, n-butanol, toluene, hexane (all used solvents were of analytical grade or HPLC grade). Keggin HPAs ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$) were used as such without any previous treatment (Sigma). Other chemicals were as follows: N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Sigma, Alfa Aesar), oleic acid 90% (Alfa Aesar), trimethylolpropane (Alfa Aesar), methyl stearate 96% (Sigma), butyl stearate 95% (TCI).

2.2. Silica grafting with zirconium n-butoxide (Step I, Fig. 4)

22 g of commercial SiO_2 (pre-dried in vacuum at around 200 mbar, 150 °C and for 2 h) was dispersed in 180 ml of toluene. 10 ml of zirconium n-butoxide (ca. 1 mmol/g of SiO_2) was then added to the silica suspension under inert atmosphere and vigorous stirring. The mixture was stirred overnight (16 h in total) at 105 °C under reflux. Then, the reaction mixture was cooled down to room temperature, and the final product was washed four times with toluene. The obtained material – denoted ZrO_2/SiO_2 – was stored under a layer of toluene.

2.3. Immobilization of HPA on the ZrO_2/SiO_2 (Step II, Fig. 4)

2.5 g of corresponding Keggin HPA was dissolved in 100 ml of acetonitrile. Then, 5 g of ZrO_2/SiO_2 (pre-dried in vacuum at 40 °C for 1 h) was added to the HPA solution. The mixture was stirred at 80 °C for 15 h. Finally, the materials were filtered and washed with acetonitrile in a Soxhlet apparatus to remove unreacted HPA. The so-obtained catalysts were dried in air at 110 °C overnight. Depending on the corresponding HPA used for the synthesis, the materials were denoted PW–ZrO_2/SiO_2, SiW–ZrO_2/SiO_2, and PMo–ZrO_2/SiO_2.

2.4. Characterization

2.4.1. Elemental analysis

The content of Zr, P, W, and Mo was measured by inductively coupled plasma-atomic emission spectroscopy (ICP AES) on an Iris Advantage apparatus from Jarrell Ash Corporation. The amount (wt.%) of immobilized HPA was calculated by using the formula $H_nXM_{12}O_{40}$ (for X = P, n = 3 and for X = Si, n = 4; M = W or W).

2.4.2. Acidity measurements

The acidity of prepared materials was measured by potentiometric titration with n-butylamine as described elsewhere [19].

2.4.3. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded in transmission mode using an IFS55 Equinox spectrometer (Bruker) equipped with a DTGS detector. The spectra were recorded with 100 scans between 400 and 4400 cm^{-1} with a resolution of 4 cm^{-1}. The samples were analyzed after dilution in KBr (Janssens Chimica 99%) by a weight factor of 50.

2.4.4. NMR spectroscopy

^{31}P magic angle spinning (MAS) NMR measurements were performed at 202.47 MHz with a Bruker ASX 500 NMR spectrometer operating in a static field of 11.7 Teslas. The chemical shift was referenced with respect to external 85% H_3PO_4.

2.4.5. X-ray diffraction (XRD)

XRD was used to check the crystallinity and dispersion of the active phase in the synthesized catalysts. Measurements were performed with a Siemens D5000 diffractometer equipped with a 1.6 kW source and using the Kα radiation of Cu (λ = 1.5418 Å). The 2θ range was scanned between 5° and 75° at a rate of 0.02°/s. As a control sample, SiO_2 was mechanically mixed with the corresponding HPA (18–25 wt.%) and the XRD profile was recorded as described above.

2.4.6. N_2 physisorption

Specific surface area and pore size were obtained through nitrogen adsorption–desorption experiments in the Micromeritics Tristar 3000. Before analysis, the samples were degassed overnight under vacuum (0.67 Pa) at 150 °C. The measurements were performed at −196 °C and with relative pressures in the range of 0.01–1.00 (P/P_0). The specific surface area was calculated from the adsorption isotherm in the P/P_0 range of 0.05–0.30 using BET method, and denoted afterward S_{BET}.

2.5. Catalytic studies

Before each catalytic study, the catalysts were pre-dried at 80 °C in vacuum for 2 h to keep them in the same conditions before the catalytic tests. All catalytic studies were repeated at least twice to ascertain the reproducibility of the results.

2.5.1. Transesterification reaction of methyl stearate (MS) with n-butanol (BuOH)

Previously, pre-dried catalyst (0.1 g) was weighed into the reactor. Then, n-butanol (3 ml) and methyl stearate (0.5 g) were added. The start of the reaction was considered after all components were mixed and the reactor placed into an oil bath at 100 °C. The reaction was performed under magnetic agitation (400 rpm) in a batch closed reactor connected to a reflux. Pentadecane was used as internal standard for the GC analysis. For sampling, 20 µl of the reaction mixture was taken at certain time intervals and extracted with 2 ml of hexane and 2 ml of water. The organic phase was analyzed by GC. The standard deviation of the detection of butyl stearate was in the range of 0.2–0.9 (%), as calculated from three parallel tests for each GC injection of kinetic measurements.

2.5.2. Control tests

All catalytic studies were compared to a "blank" test where the reaction was carried out at the same conditions as described above but without any catalyst and to the reactions catalyzed by the supports (0.1 g) – SiO_2 and ZrO_2/SiO_2.

2.5.3. Leaching tests

The leaching tests were performed similar as described elsewhere [20] with some modifications. The catalysts were treated with hot butanol (100 °C, 2 h, reflux). The ratio catalyst/butanol