Physicochemical and catalytic properties of hybrid catalysts derived from 12-molybdophosphoric acid and montmorillonites

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ABSTRACT

The hybrid catalysts derived from 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$ denoted as HPMo) and montmorillonite (Na, H-exchanged montmorillonites derived from Polish bentonite denoted as Na-Mt, H-Mt and commercially available K10 montmorillonite denoted as Mt-K10) were prepared by conventional and modified impregnation routes. Conventional procedure based on the incipient wetness impregnation method involved stirring of the aqueous dispersion of HPMo and montmorillonite, followed by drying at elevated temperature. Modified preparation method employed ultrasonication as a means of the dispersion homogenization, followed by freeze-drying. Such prepared catalysts were characterized by means of powder X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen sorption, electron spin resonance (ESR), Fourier transform infrared (FT-IR), ultraviolet–visible (UV–vis) and ^{31}P solid-state magic-angle-spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. Acidic/redox properties of HPMo/montmorillonite systems were evaluated by catalytic conversion of ethanol and pyridine sorption.

The hybrid catalysts consist of two catalytically active components. In contrast to montmorillonite, especially acid-treated montmorillonite, which has mainly acidic sites, HPMo species in the final hybrid catalysts may offer both acidic and redox catalytic functions. Spreading HPMo on the surface of montmorillonites results in enhancement in the redox reactivity as a consequence of exposing the redox sites (Mo-containing species). The use of Na-Mt leads to the catalysts with dominating redox function as the acidic sites (coming from HPMo) may be obscured by replacement of protons by sodium ions coming from Na-Mt. In addition, the catalyst prepared by modified impregnation shows higher redox reactivity than that prepared by conventional impregnation.

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1. Introduction

Heteropolyacids with the Keggin-type structure have been of great interest in the field of catalysis owing to their acidic and redox properties [1,2]. They have been studied as catalysts in bulk or supported forms in both homogeneous and heterogeneous reactions. In liquid–solid and gas–solid heterogeneous reactions heteropolyacids are usually examined in a deposited form since they exhibit low specific surface areas. Besides a mechanical role, the support may modify the catalytic properties of heteropolyacids by

favoring growth of certain structures or by inducing different types of interaction.

Many porous materials such as silica, titania, carbon and alumina have been applied for the immobilization of 12-molybdophosphoric acid hydrate ($H_3PMo_{12}O_{40}$) [3–9]. Among them, clay minerals (e.g. montmorillonites) have been also explored as the supports for $H_3PMo_{12}O_{40}$ (HPMo). The motivation for choosing montmorillonites as components for the preparation of HPMo-containing catalysts is based on their high thermal stability, high specific surface area, beneficial interaction with HPMo species and their own catalytic properties. According to Ref. [10–12], acid-treated clays themselves can act as catalysts in the reactions such as ethylene polymerization, nitration of bromobenzene, esterification of fatty acids and fatty acid mixtures with methanol.

HPMo-containing catalyst derived from acid-treated clays were studied in many reactions catalyzed by acidic sites [13–16]. For instance, HPMo deposited on K10 montmorillonite with 20 wt% loading was tested in etherification of β-naphthol with alcohols such as methanol, ethanol, n-propanol, 2-propanol and n-butanol [13]. In this work, the activity of deposited HPMo was compared with other supported heteropolyacids, i.e. dodecatungstophosphoric acid (HPW) and dodecatungstosilicic acid (HSiW).

In other work [14], the catalyst prepared by mixing HPMo with K10 montmorillonite was examined in alkylation of benzene with 1-dodecene and its activity was also compared with the systems containing HPW or HSiW.

The catalytic performance of heteropolyacids (HPMo, HPW and HSiW) spread on K10 montmorillonite was also evaluated in transesterification of vegetable oils [15]. In this study, various edible/nonedible vegetable oils and alcohols were examined. Moreover, the effect of heteropolyacid loadings (5, 10, 15, 20 and 30 wt%) on clay was also evaluated.

The catalytic activity of HPMo (20 wt%) dispersed on acid-treated clay (bentonite from India) was tested in esterification of acetic acid with primary, secondary and tertiary butanol [16]. Its catalytic properties were compared with analogue catalysts containing HPW or HSiW.

Based on above-mentioned examples, the catalysts containing 20 wt% of HPMo deposited on acid-treated montmorillonite appeared to be active, selective and stable. According to Refs. [17,18], their catalytic performance may also derive from the synergy between heteropolyacid and montmorillonite.

In the present work we describe the hybrid catalysts derived from $H_3PMo_{12}O_{40}$ and various montmorillonites (Mt-K10, H-Mt or Na-Mt) prepared via a well-established and commonly applied impregnation procedure and by the method involving ultrasonication and freeze-drying. The conversion of ethanol was selected as a test reaction to evaluate the acidic/redox function of the composites and to demonstrate that not only the form (H- or Na-exchanged) of montmorilonite but also the preparation method affects the catalytic performance of the hybrid catalysts, in particular those derived from Na-Mt.

2. Experimental

2.1. Materials

12-Molybdophosphoric acid, $H_3PMo_{12}O_{40} \cdot xH_2O$ (denoted as HPMo) was purchased from Fluka. The number of structural water molecules (x) in HPMo was determined by thermogravimetric (TG) analysis. Based on TG results the formula of HPMo is the following $H_3PMo_{12}O_{40} \cdot 14H_2O$.

Polish bentonite (Milowice in Poland) was used as the raw material to prepare montmorilonite components, i.e. Na- and H-exchanged montmorillonites (denoted as Na-Mt and H-Mt, respectively). The preparation procedure was described in details in our previous publication [19].

Commercially available K10 montmorilonite (denoted as Mt-K10) was supplied by Fluka. According to [20], Mt-K10 is obtained from the raw material by treatment with mineral acid at high temperature which results in ion exchange and leaching the cations, i.e. aluminum, magnesium and iron.

2.2. Preparation of the hybrid catalysts

HPMo was deposited on Na-Mt, H-Mt and Mt-K10 according to either the conventional or the modified impregnation methods described in our previous publication [19]. For instance, the expressions HPMo/Na-Mt and HPMo/Na-Mt/m represent the samples prepared using HPMo and Na-Mt via conventional and modified impregnation methods, respectively.

The amount of HPMo used for the deposition (proportional to specific surface area of montmorillonite) was calculated assuming the formation of one HPMo monolayer coverage on both Na-Mt (HPMo content = 9 wt%) and Mt-K10 (HPMo content = 33 wt%), and a 0.7 monolayer on H-Mt (HPMo content = 9 wt%). This "monolayer coverage" model for the HPMo deposition was adopted from Ref. [21–23] in view to potentially achieve a uniform distribution of heteropolyacid species on the surface of montmorillonite.

2.3. Characterization of the physicochemical properties

Powder X-ray diffraction (XRD) patterns were obtained with a Philips X'Pert powder diffractometer using Cu-K_α radiation operating at 35 kV and 30 mA. The patterns were recorded from 2° to 72° 2θ with a scan step time of 2 s and a step size of 0.05°.

Nitrogen sorption analysis was carried out at −196 °C using an Autosorb-1 QUANTACHROME sorptometer. Prior to analysis, the samples were degassed at 200 °C over night. Adsorption/desorption of nitrogen was performed in the relative pressure range of $0.01 < p/p_0 < 1.00$, using ca. 0.2 g of sample. Nitrogen sorption measurements were carried out knowing that a similar set of the hybrid catalysts derived from heteropolyacid (HPW) and montmorillonites (Mt-K10, H-Mt and Na-Mt) appeared to be predominantly mesoporous [19]. Specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method based on adsorption data in the partial pressure of $0.1 < p/p_0 < 0.35$ [24] confirmed by satisfying correlation coefficients (>0.999). Total pore volume (V_{tot}) was determined by the amount of nitrogen adsorbed at $p/p_0 = 0.99$. Mesopore volume (V_{meso}) was calculated by using the method based on the non-local density functional theory (NLDFT), whereas micropore volume (V_{micro}) was estimated by the t-method. The pore size distribution (PSD) was calculated by the NLDFT method.

Scanning electron micrographs (SEM) were recorded by means of a Philips XL 30 microscope.

Ultraviolet–visible (UV–vis) reflectance spectra were recorded in the wavelength range of 200–800 nm using a Shimadzu 160A spectrometer equipped with a reflectance chamber with a 5 mm slit. The samples for analysis were prepared as pellets, and $BaSO_4$ was used as a reference for HPMo, whereas the appropriate montmorillonite was used as a reference for the hybrid catalysts.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 800 spectrometer using KBr disk technique.

Electron spin resonance (ESR) spectra were recorded at −196 °C with a Technical University of Wroclaw SE/X spectrometer operating in the X-band, at 100 mW microwave power, with a 100 kHz magnetic field modulation.

Solid state Magic-Angle-Spinning Nuclear Magnetic Resonance (MAS-NMR) spectra were measured on a Tecmag APOLLO pulse NMR spectrometer in the magnetic field of 7.05 T generated by a Magnex superconducting magnet. A Bruker HP-WB high-speed MAS probe equipped with a 4 mm zirconia rotor and a KEL-F cap was used to record the MAS spectra at the spinning speed of 8 kHz. The solid state ^{31}P MAS-NMR spectra were measured at 121.28 MHz, using a single 2 μs radio-frequency (rf) pulse, corresponding to $\pi/6$ flipping angle. The acquisition delay used in accumulation was 20 s. The ^{31}P chemical shifts were referenced using 85% H_3PO_4 solution (0 ppm).

Thermal stability of the hybrid catalysts was estimated by means of a STA 409PC (Netzsch) thermal analyzer. For comparison, thermal stability of pure HPMo and montmorillonites was also determined. Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves were recorded during heating the