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TiO_2-supported heteropoly acids for low-temperature synthesis of dimethyl ether from methanol

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ABSTRACT

The production of dimethyl ether via methanol dehydration with TiO_2-supported $H_3PW_{12}O_{40}$ (HPW) or $H_4SiW_{12}O_{40}$ (HSiW) catalysts has been studied. Both supported heteropoly acids (HPAs) exhibit superior performances in terms of methanol conversion rate and selectivity toward dimethyl ether at significantly lower temperatures than benchmark Al_2O_3- and ZSM-5-based catalysts. Both supported and unsupported heteropoly acids have strong Brønsted acid sites; however, the TiO_2-supported HPAs have a lower amount of acid sites than the bulk HPA. In addition, upon HPA deposition on TiO_2, the water of crystallization molecules, located between neighboring Keggin structures, becomes adsorbed more weakly, so they can be easily replaced by methanol molecules. As a result of the higher accessibility of methanol to the active acid sites of the supported heteropoly acids, both $H_3PW_{12}O_{40}/TiO_2$ and $H_4SiW_{12}O_{40}/TiO_2$ exhibit higher normalized rates for methanol conversion and total DME production than unsupported HPAs.

1. Introduction

Dimethyl ether (DME) is a versatile compound currently used as high-grade propellant or for the production of chemical intermediates. It is foreseen that DME could become an important actor within different energy sectors such as power generation in gas turbines, domestic use as LPG blend, and, because of its high cetane number (55–60) for the transportation sector as diesel blending or substitute [1,2]. DME is also a promising candidate as H_2 source for fuel cell applications [3–5]. DME is obtained by methanol dehydration reactions using solid acid catalysts such as γ-Al_2O_3, silica-modified alumina, TiO_2—ZrO_2, and zeolite materials (HZSM-5, HY, $AlPO_4$, SAPOs, etc.) [6–10]. The operation temperature range at the industrial level lies between 250 and 360 °C (depending on the H_2O content of the reactor feed) at atmospheric pressures, and the conversion levels obtained with these catalysts range between 70% and 85% [11]. Due to the high operation temperatures, the formation of undesired by-products, such as light hydrocarbons and coke, is a great concern because it decreases productivity, and more importantly, it leads to catalyst deactivation.

Heteropoly acids (HPAs) display high Brønsted acidity, and as a consequence, they are used for fundamental studies as well as for industrial applications involving acid-catalyzed processes, such as alkanols dehydration reactions [12–14]. HPAs may exhibit different molecular structures; among them, the Keggin and the Dawson structures are the most used HPA for catalytic applications. The Keggin structure consists of a central tetrahedron (XO_4) surrounded by four octahedral MO_6 units stabilized by protons [15,16]. Keggin HPA is represented by the formula $H_{8-n}[X^{n+}M_{12}O_{40}]$, where X is the central atom (P^{5+}, Si^{4+}, Al^{3+} ,Co^{2+}, etc.), n is its oxidation state, and M is the metal ion (W^{6+}, Mo^{6+}, etc.) [14,15,17,18].

For the correct understanding of the catalytic performance of HPA catalysts, it is necessary to take into account that solid HPAs combine two types of acid catalysis: surface-type and bulk-type catalytic processes [19,20]. Surface-type catalysis refers to the conventional heterogeneous catalysis, which takes place on the surface of solid catalysts, including pore walls. In bulk-type or pseudo-liquid catalysis, reactant molecules are absorbed within the interpolyanion space (not intrapolyanion) of the ionic crystal and actually react in there; *i.e.*, the actual catalytic sites lie in between Keggin units [15,16,20,21]. In this latter case, the solid HPA behaves, in some respects, as a liquid. The polarity and the size of reactants as well as the reaction conditions determine which type of catalysis dominates in each process. Accordingly, small polar molecules such as water and low molecular weight alcohols tend to be readily absorbed into solid HPA, and as a consequence, catalytic reactions often proceed via bulk-type catalysis.

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On the other hand, reactions involving nonpolar molecules proceed on the surface of solid HPA, *i.e.* surface-type catalysis.

The specific surface areas of bulk HPAs such as $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (HSiW) are lower than 10 $m^2\ g^{-1}$. As a consequence, the number of acid sites located at the surface of bulk HPAs accounts only to a minor fraction of the total number of acid sites. It is well documented, however, that HPAs exhibit very high catalytic activities for alcohol dehydration reactions [12,22–24]. This is because these reactions proceed through the bulk-type (pseudo-liquid) catalysis, and all of the protons, including those at the surface and within the bulk, do actually participate in the acid catalysis process. It has been also reported that HPW/TiO_2 and HSiW/SiAl exhibit high activity for alcohol dehydration reactions [12,25]. The superior performance of TiO_2-supported HPW has been explained in terms of the increasing dispersion of the TiO_2-supported HPW, providing a higher number of HPW protons to participate in ethanol conversion reactions along with a better accessibility of the reactant molecules to the protons into the HPA. It has been also reported that the catalytic performance of SiO_2-supported HPAs changes with the HPA loading, which seems to have influence on the amount and strength of the acid sites [19]. The coexistence of both Brønsted and Lewis acid sites on low-loaded supported HPW catalysts has been observed. Thus, the amount of Lewis acid sites decreases while the amount of Brønsted ones increases with the increasing HPA loading [26]. On the contrary, because of the low surface area of the bulk HPA, the participation of the bulk protons in unsupported HPA is very much limited.

We report here an extensive characterization study of the structure and acidity of TiO_2-supported $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (HSiW) by several technique, as well as, their performance for the synthesis of DME *via* methanol dehydration reaction at significantly lower temperatures (413–453 K) than those required by the benchmark catalysts (523–633 K). In addition, *in situ* spectroscopic experiments allow us to understand the origin of the higher DME production and normalized rates for methanol conversion exhibited by the TiO_2-supported HPAs.

2. Experimental

2.1. Preparation of catalysts

Phosphotungstic acid ($H_3PW_{12}O_{40}{\cdot}xH_2O$; Sigma–Aldrich, reagent grade) and tungstosilicic acid ($H_4SiW_{12}O_{40}{\cdot}xH_2O$; Sigma–Aldrich, ⩾99.9%) were supported on TiO_2 (Degussa P25, 20% rutile, 80% anatase, 53 $m^2\ g^{-1}$) by incipient wetness impregnation with ethanol solutions at room temperature. The ethanol solution concentrations were estimated to obtain heteropoly acid surface densities of 4.5 Keggin units per nm^{-2} (53 wt.% HPA). Samples were held at room temperature for 24 h after impregnation in order to reach a uniform distribution of the HPA clusters onto TiO_2, and dried in ambient air at 333 K for 24 h. The TiO_2-supported $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were referred to as HPW/TiO_2 and HSiW/TiO_2, respectively. Bulk phosphotungstic acid (HPW) and tungstosilicic acid (HSiW) were dried at 333 K in air and taken as reference materials.

Commercially available γ-Al_2O_3 (Condea, Puralox NWa-15, 147 $m^2\ g^{-1}$) and ZSM-5 (Akzo Nobel, Si/Al = 19, 342 $m^2\ g^{-1}$) were used as reference catalysts for the DME production.

2.2. Characterization techniques

The BET surface areas were determined by recording the nitrogen adsorption–desorption isotherms at 77 K with a Micromeritics ASAP 2010. Prior to the physisorption measurements, all samples were outgassed at 413 K during 16 h.

The thermogravimetric analysis (TGA) was made with thermogravimetric TGA/SDTA851 (Mettler Toledo) instrument using a 20%/80% O_2/N_2 mixture and a heating rate of 10 K min^{-1} from r.t. to 1250 K.

In situ X-ray diffraction (XRD) patterns were recorded with a Seiffert 3000 Xpert X-ray diffractometer using Cu Kα radiation equipped with a XRK 900 reactor chamber under synthetic air (20 vol.% O_2/N_2). Data were acquired at $2\theta = 15°$ and 90°, and phase identification was carried out by comparison with patterns from the International Centre for Diffraction Data (ICDD) database.

The molecular structure of the supported heteropoly acids was determined by Raman spectroscopy under ambient conditions and after dehydration at 373 K (10 vol.% O_2/N_2, 0.5 h). A Renishaw in via Raman Microscope spectrometer equipped with a laser beam emitting at 532 nm at 100 mW output power was used to collect the Raman spectra. The photons scattered by the sample were dispersed by an 1800 lines/mm grating monochromator and simultaneously collected on a CCD camera; the collection optic was set at 50× objective. The spectral resolution is 1 cm^{-1}.

A Micromeritics TPR/TPD 2900 instrument were used to obtain the ammonia desorption profiles. About 35 mg of the sample under study was introduced into a quartz U-tube microreactor with He as carrier gas and pretreated at 473 K for 1 h. The temperature was set at 373 K, and 50 mL min^{-1} of NH_3 (5 vol.%) in He was flown for 30 min. Physisorbed NH_3 was removed by flowing He at 373 K during 30 min. before recording the desorption experiments. Experimental runs were recorded by heating the sample in a flow of 50 mL min^{-1} of pure He from 373 to 1123 K at a heating rate of 15 K min^{-1}.

NH_3 adsorption isotherms were recorded at 100 °C with a ASAP 2010/2000 Micromeritics equipment. Before NH_3 adsorption, the samples were treated at 473 K under vacuum for 12 h.

A FTIR-6300 JASCO Fourier transform spectrophotometer equipped with a Harrick diffuse reflectance accessory (HVC-DRP cell) was used to record the DRIFT spectra. Before all the experiments, the catalysts were pretreated at 493 K in a current of He (20 mL min^{-1}) during 30 min. During the NH_3 adsorption experiments, the catalysts were treated at 373 K with a current of 5 vol.% NH_3 in He (total flow 20 mL min^{-1}) for 15 min. Then, the DRIFT cell was purged with He flow (20 mL min^{-1}) for 30 min before recording the spectra at increasing temperature (from 373 to 773 K; 15 K min^{-1}). For methanol adsorptions, the methanol was introduced into the DRIFT cell by bubbling He (20 mL min^{-1}) through a glass saturator filled with methanol at room temperature during 30 min. After methanol adsorption/reaction, the samples were treated in He flow at increasing temperatures from 413 to 673 K at 10 K min^{-1}.

Solid-state NMR measurements were carried out on Bruker AV-400-WB spectrometer, at ^1H NMR frequency of 400.13 MHz, using a 2.5 mm double-resonance MAS probe. Spinning speed was set at 25 kHz. Single-pulse experiments used a 3 μs $\pi/2$ pulse, spectral width of 35 kHz, and a relaxation delay of 2 s. All measurements were taken at room temperature using H_2O as secondary external reference at 4.77 ppm relative to TMS as primary external reference. All samples were kept at 373 K before the NMR experiments and rapidly transferred to the analysis chamber to avoid further hydration.

2.3. Catalytic tests

The catalytic conversion of methanol was measured in a fixed bed reactor, and the reaction temperature was measured with a K-type thermocouple directly placed in the catalytic bed. The catalytic bed consists of 0.2 g of the catalyst diluted with 2.0 g of SiC