

Research Paper

Catalytic properties of carbon nanotubes-supported heteropolyacids in isopropanol conversion



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ABSTRACT

The technique of catalytic flow microreactor has been combined with the gas flow-through microcalorimetry to correlate the catalytic activity of supported heteropolyacids with both the acid strength of protons as well as the protons' accessibility. Multiwall carbon nanotubes (CNT) were used as a support for Keggin ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and Wells-Dawson ($\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$) structured heteropolyacids, in order to produce catalysts combining high acidity from the parent acids with the inherent microporosity of the support. Prior to the catalytic tests, the obtained materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and Raman spectroscopies as well as by the nitrogen adsorption-desorption analysis (BET). The latter technique confirmed overall improved porosity of the obtained materials. Upon testing for activity in the isopropyl alcohol dehydration, the supported Wells-Dawson catalysts turned out to be superior to both the Keggin-based materials, as well as to the unsupported $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$. It has been found that the improvement of catalytic performance in the isopropanol conversion is mostly related to the increase of the accessibility of protons, rather than to the changes in the acid strengths.

1. Introduction

The mobility of protons in the heteropolyacids (HPAs) is fundamental for their performance in catalytic conversion of alcohols, making possible the activation of the organic molecule by addition of the H^+ species to the oxygen atom and forming methoxonium and ethoxonium ions [1,2]. Using HPAs in the form of supported catalysts can improve the accessibility of protons to the alcohol molecules, due to increased porosity resulting from high surface area of the supporting materials. However, there appears to be a trade-off between the accessibility of protons and their acidity in the supported HPAs, since the interaction between the HPA and the support can in some cases reduce acidity of the former.

The use of alcohols as reactive probe molecules to investigate acidic properties has been developed since the 1970s [3–8]. It was reviewed by Lauron-Pernot in [9], describing the catalytic data of alcohols conversion on various catalysts. The use of 2-propanol as a probe molecule in gas phase over solid supported catalysts containing heteropolyacids (HPA) as active phase has been described in [10]. The authors noticed that heteropolytungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ exhibited high catalytic activity and selectivity when it was loaded onto activated carbon. They investigated a broad series of activated carbon supports with large surface areas of 920–1656 m^2/g . These investigations were continued

by Chimienti et al. [11]. The authors used both the commercial wood-based activated carbon with a surface area of 960 m^2/g and the silica gel impregnated with either $\text{H}_3\text{PW}_{12}\text{O}_{40}$ or $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ heteropolyacids. They found a dependence of their respective content on the activity in isopropanol dehydration at 150 °C, for samples containing less than ca. 25%wt. of HPA. However, further increase of the HPA content did not improve the dehydration activity (constant 2-propanol conversion). The authors of [8] concluded, that the reaction was catalyzed mainly by the surface protons of heteropolyacid crystallites, rather than those located deeper in the bulk of crystals, thus confirming the accessibility of protons to be an important factor for the catalytic activity of supported HPAs.

Arguably, the latter may also be a function of structure of the HPA being used. While there is a profusion of data reporting catalytic activity of the Keggin-type HPAs, the Wells-Dawson-type HPAs seems to have been receiving relatively less attention. In this paper we attempt to compare catalytic properties of the Wells-Dawson-type $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ (HP2W) with the Keggin-type $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW), pure and supported on the carbon nanotubes (CNT), and to correlate textural properties of these catalysts, as well as their microcalorimetrically measured acidity, with their activity for the isopropanol dehydration. HPW is considered to be the strongest acid among all known HPAs [12]. In spite of this fact, the Wells-Dawson-type catalysts (HP2W/support) are considered

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to be more effective in the acid–base type reactions, compared to the Keggin-type, in both the gas and the liquid phase reactions [13]. In particular, they appear to be very good and selective catalysts for tertiary ethers synthesis by alcohol addition to olefins [14].

The CNT may be considered as a useful support in heterogeneous catalysis because, first, they are inert enough to avoid strong interaction with active phase and to remain catalytically inactive themselves, and secondly, because of their high surface area combined with porous structure. There have been only a handful of reports describing the application of carbon nanotubes as supports for heteropolyacids, against the prevalence of active carbon materials or carbon fibers [15] having been used for the purpose. The catalysts comprising a heteropolyacid and CNT or CNT modified with nitrogen atoms were investigated only by Timofeeva [16] in esterification of *n*-butanol with acetic acid, by Qi [17] in ester hydrolysis reactions and by the present authors [18] in ethanol conversion. A CNT-supported $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ was investigated as potential material for NO_x capture [19]. To our best knowledge, the Wells-Dawson-type HPA supported on CNT has not been investigated yet. The aim of the present study is to confirm the potential of carbon nanotubes as supports for Wells-Dawson-type heteropolyacid as an active phase and the comparison of these systems with the Keggin-type heteropolyacid supported on CNT.

2. Experimental

2.1. Materials

The Keggin-type heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) has been provided by Aldrich p.p.a. The Wells-Dawson type $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ (HP2W) was prepared in our lab according to [20]. In order to maintain a constant content of crystallization water, the obtained HP2W was stored over saturated solution of $\text{Mg}(\text{NO}_3)_2$ prior to its use in experiments. The samples so treated had the compositions corresponding to the formulas: $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 26.6\text{H}_2\text{O}$ and $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}\cdot 28.8\text{H}_2\text{O}$. The commercial multi-wall carbon nanotubes (Sunnano[®], China) were formed by CVD process, resulting in a material of purity > 80% and the outer diameter of nanotubes ranging, according to the producer's information, from 100 to 300 Å. As for the inner diameter, our own estimation has been made using a dedicated software (ImageJ 1.51p) for analysis of our SEM images. The results of a separate estimations at twenty eight selected points turned out to be falling into three ranges: 38–60 Å, 77–92 Å and 110–123 Å (cf. Fig. 1A). The XRF analysis shows mainly Fe and Ni impurities, with traces of Zn (cf. Fig. 1B). The former are likely resulting from using spinels in the synthesis of CNT [21]. The Fe content was determined based on analysis of a series of three samples prepared by adding various amounts of iron citrate to the original CNT. Using the Ni peak as an internal standard to obtain a calibration curve, the calculated Fe content was less than 1.2% wt. The BET specific

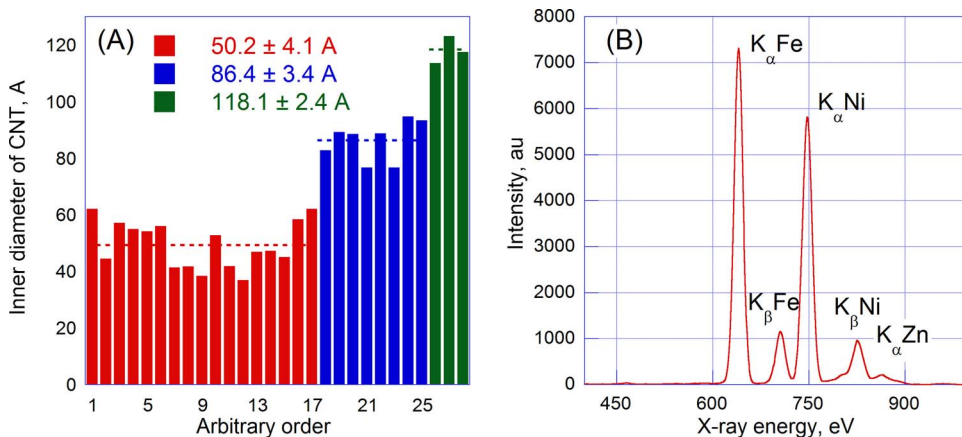


Fig. 1. Characteristics of the CNT support: A) the inner diameters estimations (mean values shown for each range); B) XRF spectrum.

Table 1
Characterization of CNT and modified HPA/CNT catalysts.

Sample	HPA (% wt.)	BET (m ² /g)
CNT	–	136
0.5HPW/CNT	27.0	58
1.0HPW/CNT	42.5	33
0.5HP2W/CNT	30.2	71
1.0HP2W/CNT	46.4	32

surface area of 136 m²/g has been measured basing on the N₂ sorption.

Two series of catalysts were synthesized: HPW/CNT and HP2W/CNT in which CNT were used as a support. The appropriate amounts of heteropolyacids HPW and HP2W were dissolved in absolute ethanol (10–30 cm³) and mixed with carbon nanotubes. The suspensions were evaporated at room temperature and dried at 333 K for 2 h. The amount of heteropolyacid used corresponded to the coverage of support with approximately 0.5 or 1.0 of heteropolyacid monolayer. Hence, the samples were labeled as 0.5HPW/CNT or 1.0HP2W/CNT, etc. where the values 0.5 or 1.0 denote the coverage of the surface with heteropolyacid. Calculations of the number of layers were carried out based on the values: 11.7 Å [22] and 12.8 Å [23] as the dimensions of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ heteropolyanions, respectively, and the surface covered by a single molecule of HPW was assumed to be equal to 107 Å², while that covered by a HP2W molecule to 129 Å². Table 1 presents composition of the catalysts. Isopropyl alcohol (anhydrous, 99.5%, Sigma-Aldrich) was used as reagent in catalytic tests, whereas propylene (≥99%, Aldrich) and diisopropyl ether (analytical standard, Sigma-Aldrich) were used in calibration procedures in the catalytic experiments.

2.2. Methods

Powder X-ray diffraction (XRD) analysis was performed using a X'Pert PRO MPD (Pananalytical) powder diffractometer with Cu K_α radiation (40 kV, 30 mA). The measurements were conducted from 5 to 80° (2θ) at an average scanning rate of 0.02°. The XRF spectra were obtained using Skayray EDXRF 3600H spectrometer equipped with the tungsten lamp, with energy resolution of 135 ± 5 eV. The FTIR characterizations were carried out by Excalibur 300 Series Digilab spectrometer, equipped with DTGS detector and using the standard transmission KBr techniques (ca. 300 mg of KBr and 2 mg of sample, pellet diameter 2 cm). The spectra were recorded in the range of 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹. Spectra processing was performed using TotalChrom software package. Nitrogen adsorption/desorption analysis was carried out at –196 °C using an Autosorb-1 (Quantachrome) surface area/pore size analyzer. Prior to volumetric sorption measurement, the samples were preheated and degassed under

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