



Carbon nanotubes, silica and titania supported heteropolyacid H₃PW₁₂O₄₀ as the catalyst for ethanol conversion

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ABSTRACT

The new catalyst: heteropolyacid H₃PW₁₂O₄₀ (HPA) supported on carbon nanotubes (CNTs) for ethanol conversion was compared with silica and titania supported heteropolyacid. The ethanol conversion did not depend on the type of the support up to reaction temperature 403 K while above 423 K ethanol conversion was higher for HPA on CNTs than for unsupported HPA. Generally, the most active catalysts were obtained by using high surface area silica as the support.

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1. Introduction

Carbon nanotubes belong to the most interesting forms of elemental carbon. Due to their specific electronic, adsorption, mechanical and thermal properties they are expected to find in the future many applications. In particular Serp et al. [1] in their review article expected their use in catalysis as the catalyst support. Arunajatesan [2] express the same opinion. In fact the catalysts containing noble metals (Pd, Pt, Ru) and also nickel and iron supported on CNTs were investigated in [3]. Less frequently the catalysts with finely divided oxides on CNTs were investigated and only a few publications appeared dealing with CNTs supported heteropolyacids. Timofeeva et al. [4] were using H₃PW₁₂O₄₀ (HPW) on mesoporous multiwall carbon nanotube (MWCNT) supports for their study of liquid phase catalytic esterification of n-butanol with acetic acid. Kang et al. [5] studied the physicochemical properties of Wells–Dawson type polyoxometallates (H₆P₂W₁₈O₆₂ and Ag₆P₂W₁₈O₆₂) supported on CNTs. However the authors were not interested in the catalytic properties of their samples. Similarly the investigation of MWCNT supported H₃PW₁₂O₄₀ published by Skutnik et al. [6] was limited to the study of electrical capacitance of the obtained materials.

The aim of the present investigation was to compare the catalytic activity of catalysts containing H₃PW₁₂O₄₀, one of the

strongest heteropolyacids, supported on carbon nanotubes with the activity of the catalysts containing the same heteropolyacid supported on commonly used oxides: silica and titania. Conversion of ethanol in the gas phase has been chosen as the catalytic test reaction. The interest in this latter reaction is justified by the fact that it is important from the point of view of “green” chemistry. The conversion of alcohols by acid catalysts, e.g. ethanol obtained by the way of fermentation of different biological materials such as sugar and starch, may produce important industrial chemicals: ethylene, diethyl ether as well as lower and higher hydrocarbons. From this point of view catalyst’s selectivity to particular products, ethylene or diethyl ether, is of special interest for its potential application [7].

2. Experimental

2.1. Materials

Ethyl alcohol azeotrope (95.6 wt.%, p.p.a., supplied by POCh Gliwice), ethylene ≥99.5% (Sigma–Aldrich) and diethyl ether (p.p.a. supplied by POCh Gliwice) were used in catalytic experiments.

The following materials were used as the supports:

- silicon dioxide SiO₂, 100 mesh, A.R. Mallinckrodt, BET specific surface area 517 m²/g
- titanium dioxide TiO₂ anatase with small amount (~6 wt.%) of rutile, Chemical Factory Police, Poland, BET specific surface area 264 m²/g

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- multiwall carbon nanotubes MWCNT, Sun Nanotech Co. Ltd., BET specific surface area 138 m²/g

The catalyst containing heteropolyacid supported on MWCNT was prepared using the sample of carbon nanotubes and Keggin type heteropolyacid H₃PW₁₂O₄₀·6H₂O (HPW, Aldrich p.a.). Before synthesis both components of the catalyst, carbon nanotubes and heteropolyacid, were dehydrated by heating. The former were heated at 353 K for 1 h and the latter at 483 K for 2 h. The appropriate amounts of anhydrous H₃PW₁₂O₄₀ were dissolved in absolute ethanol (10–30 cm³) and mixed with the supports: carbon nanotubes, SiO₂ or TiO₂. The suspensions were evaporated at room temperature and dried at 333 K for 2 h; subsequently the samples were kept at room temperature in a desiccator over saturated solution of NaCl. Table 1 presents composition of the catalysts. The amount of heteropolyacid used corresponded to the coverage of supports with approximately 0.3 or 1.3 of heteropolyacid monolayer. Hence, the samples were labeled as HPW/0.3/SiO₂ or HPW/1.3/SiO₂, etc. where the values 0.3 or 1.3 denote the coverage θ of the surface with HPW. The size of the Keggin unit in dodecaheteropolyacid was given by Okuhara et al. [8] as 10–15 Å. In [9] unit cell of H₃PW₁₂O₄₀ was determined by X-ray diffraction as 12.5 Å. Song et al. [10] obtained the most recent value 11.7 Å. It was determined by scanning tunnelling microscopy of HPW deposited on a graphite surface. In our present research, we used the value 11.7 Å as the dimension of HPW unit cell and the surface covered by one molecule of HPW was equal to 137 Å².

2.2. Characterization techniques

The microstructures of MWCNT alone and MWCNT supported H₃PW₁₂O₄₀ were examined by means of scanning electron microscopy (SEM) using JEOL 7500F and also transmission electron microscopy (TEM) using FEI Tecnai G² microscope at 200 kV equipped with high angle annular dark-field (HAADF) and EDAX energy dispersive X-ray (EDX) detectors.

Specific surface area and porosity of the catalysts were determined with Quantachrome Autosorb Gas Sorption System using sorption of nitrogen at 77 K. The moisture analyzers MAC equipped with the heater up to temperature 523 K determined the content of water in the catalysts.

In order to characterize acid sites on the solid acid catalysts ammonia sorption-desorption cycles were carried out using a Microscal flow microcalorimeter model 4112 [11]. First the samples were placed in calorimetric cell and dehydrated at 423 K for 2 days in situ in a flow of He gas. Afterwards ammonia was sorbed by passing a gas mixture containing 1% NH₃ and 99% He (3 cm³ min⁻¹) at 423 K over the catalysts. A thermal conductivity downstream detector (DSD) was used for continuous monitoring the concentration of NH₃ in the gas leaving the cell. Switching back to pure helium carrier gas begins the desorption stage which lasts until the DSD base line comes back again to its original position. The results of calorimetric measurements allow obtaining the following sorption and desorption parameters:

- total heat of sorption Q_{total} and total heat of desorption Q_{des} [mJ(g_{sample})⁻¹]
- total amount of adsorbed ammonia $[(\text{NH}_3)_{\text{total}}] \mu\text{mol}(g_{\text{sample}})^{-1}$
- total release of ammonia upon desorption $[(\text{NH}_3)_{\text{des}}] \mu\text{mol}(g_{\text{sample}})^{-1}$

Using these calorimetric data the following values can be calculated (Table 2):

- irreversibly sorbed amount of ammonia $[(\text{NH}_3)_{\text{irrev}}] = [(\text{NH}_3)_{\text{total}}] - [(\text{NH}_3)_{\text{des}}] \mu\text{mol}_{\text{NH}_3} (\text{g}_{\text{HPW}})^{-1}$
- the enthalpy of irreversible ammonia sorption $\Delta H_{\text{irrev}} = (Q_{\text{total}} - Q_{\text{des}}) / [(\text{NH}_3)_{\text{irrev}}] \text{ kJ} (\text{mol}_{\text{NH}_3})^{-1}$
- the molar ratios of the amount of ammonia which was totally and irreversibly sorbed per one Brønsted acid center H⁺ in H₃PW₁₂O₄₀, denoted as $[(\text{NH}_3)_{\text{total}}] / [\text{H}^+]$ and $[(\text{NH}_3)_{\text{irrev}}] / [\text{H}^+]$ respectively.

FTIR spectra of the samples were recorded using Bruker Equinox 55 spectrometer equipped with an MCT detector (KBr technique), in the absorption mode, with a spectral resolution of 2 cm⁻¹. The wafers of the samples were activated in situ in the IR cell at 353 K in vacuum.

The ethanol conversion was used as a test reaction in a constant flow differential microreactor ($\varnothing = 10$ mm). The mixture of reactant was obtained by passing helium flow through an azeotropic ethanol saturator maintained at 298 K. The hydrated samples of catalysts (Table 1) were mixed with quartz grains ($\varnothing = 0.19$ mm) thus producing a catalyst layer of 0.5 cm thickness. Then catalysts were calcined in situ in a catalytic reactor (in helium flow 30 cm³ min⁻¹) at 473 K for 30 min. Weight of the catalyst samples was adjusted in such way that it always contained 0.025 g of anhydrous HPW. The mixture, ethanol and helium, rate was 50 cm³ min⁻¹. Catalytic reactor was connected on-line with Perkin-Elmer AutoSystem XL Gas Chromatograph equipped with a Porapak QS column and the composition of the feed before or after the reaction was determined automatically, by injection of the outflowing gas directly into the chromatographic column.

3. Results and discussion

3.1. Physicochemical properties of the catalysts

Fig. 1 shows typical shapes of MWCNT, not covered with heteropolyacid, registered in transmission electron microscope. Two kinds of carbon nanotubes can be distinguished in the figures. One of them with external diameter of the order of ca. 70 nm is shown in Fig. 1(left) and the other one, less abundant, with external diameter of the order of 20–40 nm in Fig. 1(right). In the centre of both kinds of carbon nanotubes the regions of increased transparency for electron beam can be seen along their axes, indicating the presence of internal empty channels.

Distribution of H₃PW₁₂O₄₀ over CNTs has been investigated using TEM and SEM techniques combined with EDX microanalysis. The examples of STEM-HAADF images are shown in Figs. 2 and 3. Different forms of heteropolyacid distribution are observed. The bright areas visible in both images are interpreted as distribution of tungsten (large Z value) contained in the catalyst H₃PW₁₂O₄₀. In Fig. 2 the concentration of tungsten is homogeneous over carbon nanotube and it corresponds well to the situation in which heteropolyacid covers uniformly the external surface of the tube. The distribution of elements (phosphorous, tungsten) along the line taken across the nanotube (Fig. 2b) confirmed almost homogenous distribution of phosphorous and tungsten. The EDX microanalysis in Fig. 3b showed tungsten enrichment in the bright area marked by point 1 in Fig. 3a as compared to grey point 2 in Fig. 3a with analysis in Fig. 3c (Cu signal results from the copper grid supporting the sample). The enrichment of tungsten around point 1 corresponds most probably to heteropolyacid agglomerating on the external surface of the tube. On the other hand in the case of HPW/0.3/CNT tungsten is concentrated along the axis of the tube in its centre (Fig. 4) which corresponds to the situation in which tungstophosphoric acid is concentrated in the internal channel of CNT. Both types of HPW distribution (predominant gathering of HPA inside

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