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Carbon nanotubes, silica and titania supported heteropolyacid $H_3PW_{12}O_{40}$ as the catalyst for ethanol conversion

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ABSTRACT

The new catalyst: heteropolyacid $H_3PW_{12}O_{40}$ (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.

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 $H_3PW_{12}O_{40}$ (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 ($H_6P_2W_{18}O_{62}$ and $Ag_6P_2W_{18}O_{62}$) supported on CNTs. However the authors were not interested in the catalytic properties of their samples. Similarly the investigation of MWCNT supported $H_3PW_{12}O_{40}$ 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 $H_3PW_{12}O_{40}$, 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 SiO_2, 100 mesh, A.R. Mallinckrodt, BET specific surface area 517 m^2/g
- titanium dioxide TiO_2 anatase with small amount (~6 wt.%) of rutile, Chemical Factory Police, Poland, BET specific surface area 264 m^2/g

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