



# Dehydration of isopropyl alcohol used as an indicator of the type and strength of catalyst acid centres

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## Abstract

The subject of our studies was determination of the kind and strength of the catalyst acid centres on isopropyl alcohol conversion. The investigations were carried out for two groups of catalysts: typical Lewis acids  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{ZrO}_2$  and Brønsted acids:  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . Considerable differences between Lewis and Brønsted acids in the conversion of isopropyl alcohol were observed. The influence of Brønsted acid centres was studied for a group of catalysts with different strength: mixtures of two different heteropolyacids. It was observed that the increasing strength of Brønsted acids centres leads to higher catalytic activity but it does not significantly affect the activation energy of dehydration to propene.

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## 1. Introduction

Catalysts with acid properties are used in many industrial processes such as cracking, hydrocracking, isomerisation, polymerisation of alkenes and dehydration of alcohols. The knowledge of the type, number and strength of acid centres is very important when attempting to explain the mechanism of reactions, which proceed at the catalyst surface and to find optimum catalysts for specific reactions.

Numerous methods to determine the number, strength and type of acid centres (Brønsted and Lewis) have been developed [1]. They include titration methods [2], spectroscopy [3], temperature-programmed desorption of chemisorbed bases [4] and the use of test reactions [5,6]. Among all the methods the best ones are test reactions because they enable determination of the character of the surface under the catalytic reaction conditions. It is important as the acid properties of the surface can depend on temperature. The increase of temperature can change the strength of acid centres as a result of water desorption or changes in lattice distances in the structure of crystalline catalysts.

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The objective of our work was to determine the influence of the type and strength of acid centres of the catalyst on the conversion of isopropyl alcohol. This method is very often used to test acid–base properties of the catalyst surface. Two parallel reactions occur during the process: dehydration to propene over acid centres and dehydrogenation to acetone over basic or redox centres. In some cases di-isopropyl ether is formed as a result of dehydration of two molecules of isopropyl alcohol over acid centres.

Two kinds of catalysts were studied: (1) typical strong Brønsted acids, crystalline heteropolyacids:  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ; (2) typical Lewis acids  $\text{ZrO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$ . The influence of the acid centre strength on the isopropyl alcohol conversion was investigated for catalysts with linearly changed acidity:  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , mixture of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (molar ratio 3:1), mixture of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (molar ratio 1:1), mixture of  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (molar ratio 1:3), and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .

## 2. Experimental

Kinetic measurements were performed in a glass reactor with the inside diameter of 18 mm. The reaction substrate–isopropyl alcohol was diluted with nitrogen. During the measurements the mole fraction of isopropyl alcohol was 0.0179. The flow rate in the catalytic reactor was equal to 20 dm<sup>3</sup>/h. The measurements were carried out in the conversion range below 25%. Approximately 2 g of the catalyst was used in each catalytic test. Before the reaction all the catalysts were conditioned in the reactor at 130 °C for 1 h in the nitrogen flow. The products were analysed using a gas chromatograph with a flame-ionisation detector (FID).

The chemicals used were commercially available:  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (Aldrich)  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  (Fluka),  $\text{ZrO}_2$  (Hopkins & Williams Ltd.) and  $\gamma\text{-Al}_2\text{O}_3$  (Zakłady Azotowe Puławy), isopropyl alcohol (POCh). Before the catalytic reaction heteropolyacids were dispersed on the silicon carbide support. The 174 mg of heteropolyacid or the mixture of heteropolyacids was dissolved and an appropriate quantity of the support was added until all the solution was absorbed.

## 3. Results and discussion

Dehydration of isopropyl alcohol to propene shows significant differences in the properties of both groups of catalysts (Fig. 1). Strong Brønsted acids exhibit high activity at low temperatures (350 K), whereas Lewis acids catalyse dehydration to propene at much higher temperatures (450 K). The results suggest that the temperature at which the catalyst is active in the dehydration reaction can serve as an indicator of the type of acid centres present on the surface. The value of activation energy for Brønsted acids, in the kinetic region, is approximately 120 kJ/mol, while in the case of Lewis acids it exceeds 130 kJ/mol (Table 1). It suggests that the mechanism of dehydration to propene over Brønsted centres can be different than over Lewis centres. The reaction over Brønsted centres is probably a typical acid–base process, which begins with the formation of protonated alcohol, from which the elimination of water does not require high energy. On the contrary, the dehydration reaction over Lewis centres requires breaking the C–O bond without prior protonation of the OH group, for which more energy is necessary.

The reaction of dehydration to di-isopropyl ether is observed for both Brønsted and Lewis acids (Table 2). This fact suggests that it is not related to the presence of specific acid centres. This reaction seems to be preferred to dehydration to propene, which is confirmed by observations of dehydration of alcohols over heteropolyacids [7]. According to these results dehydration to di-isopropyl ether proceeds exclusively on the surface of heteropolyacids, while the reaction to propene takes place in the bulk of crystals. The ether cannot be formed in the bulk of crystals due to steric

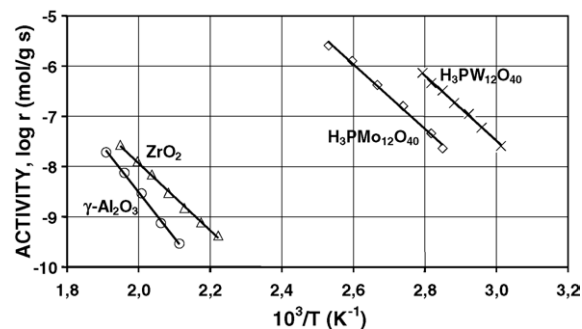


Fig. 1. Arrhenius plots of isopropyl alcohol dehydration to propene.

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