

Evaluation of oxide catalysts' properties based on isopropyl alcohol conversion

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ABSTRACT

The aim of this work was to verify the usefulness of isopropyl alcohol conversion as a test reaction to evaluate the properties of the surface of oxide catalysts. The results presented below suggest that this test reaction can be used not only to distinguish the type of active centres over which the reaction proceeds but also to determine the strength of active centres. The strength of active centres can be evaluated on the basis of the rates of respective parallel reactions. The type of active centres can be determined from the rates of parallel reaction at the given temperature and selectivity of these reactions. The possibility of formation of diisopropyl ether over Lewis acid centres depends on the distance between the adjacent cations, their accessibility for reactants and the acidity.

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1. Introduction

In studies on the properties of the surface of heterogeneous catalysts test reactions play an important role. A simple catalytic test, which does not require complicated equipment, can determine the properties of the catalyst surface under conditions of catalytic activity. It is known that an increase in temperature can change the number and strength of active centres [1,2], whilst most spectroscopic techniques show the properties of the surface at room temperature. Isopropyl alcohol conversion is the most popular amongst many proposed test reactions. Its wide application is due to the fact that this reaction can be used to determine both acid–base and redox properties of oxide catalysts [3–9]. Moreover, the reaction does not require complicated equipment and it is easy to carry out. During conversion of isopropyl alcohol three parallel reactions can proceed. The first reaction—dehydration to propene characterises acid [3–5] or acid–base properties of the catalyst [3,6]. The second reaction—dehydrogenation to acetone characterises basic properties [3–5,7,8] or redox properties of the catalyst [4,5]. The third reaction, which occurs rarely, is intermolecular dehydration of two alcohol molecules to diisopropyl ether. This reaction can characterise acidic properties of the surface [4,8].

Selectivity of these reactions is often used as a measure of acid–base and redox properties of the catalysts surface [3–9]. Some authors [7] write about acid–base properties of the catalyst when the reaction proceeds in an inert atmosphere and redox properties when the reaction proceeds in the presence of oxygen.

There are reports [3,7,10,11], which indicate certain problems or limitations associated with the application of this reaction to determine the properties of the surface of oxide catalysts. Correct interpretation of the results may be difficult as a result of:

- 1) the same reaction (dehydration or dehydrogenation) proceeding over various active sites [3,7], which is associated with changes in the mechanism of formation of a specific product;
- 2) various parallel reactions over the same active sites [3,7].

Therefore, the use of selectivity as an indicator of acidic and basic properties of the catalyst becomes doubtful. The selectivity depend not only on the nature of the catalyst, but also on the temperature [7,8,12,13]. Moreover, apart from three main reactions, there are several other possible consecutive and parallel-consecutive reactions in which the main products (propene and acetone) can be formed [7,10,12–15]. For example propene can be produced not only directly from isopropyl alcohol but also in a consecutive reaction from diisopropyl ether.

The objective of this work was to verify the problems associated with the use of isopropyl alcohol conversion to characterise the properties of the surface of oxide catalysts. An attempt was

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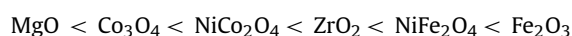
Table 1
Ranking of catalysts according to the type and strength of active centres [19,23–26].

Group of catalysts	Type of active centres	Catalysts in the order of increasing strength of acid centres
Acid–base	Lewis acid	MgO < SnO < ZrO ₂ < Fe ₂ O ₃ < TiO ₂ < SnO ₂ < ZrO ₂ < MoO ₃ < γ-Al ₂ O ₃ CuCo ₂ O ₄ < Co ₃ O ₄ < NiCo ₂ O ₄ < NiFe ₂ O ₄
	Basic	γ-Al ₂ O ₃ < SnO ₂ < TiO ₂ < Fe ₂ O ₃ < ZrO ₂ < SnO < MgO NiFe ₂ O ₄ < NiCo ₂ O ₄ < Co ₃ O ₄ < CuCo ₂ O ₄
Oxidation–reduction	Brønsted acid	MoO ₃ < H ₃ PMo ₁₂ O ₄₀ < H ₃ PW ₁₂ O ₄₀
	Oxidation–reduction	CuCo ₂ O ₄ , NiCo ₂ O ₄ , Co ₃ O ₄ , NiFe ₂ O ₄ , MoO ₃ , SnO ₂ , SnO, Fe ₂ O ₃ , H ₃ PMo ₁₂ O ₄₀

made to find which kinetic parameters of the reaction: specific rate of parallel reactions, selectivity or activation energy are most effective in determination of the type and strength of active centres. The additional aim of this work was to determine the conditions of formation of diisopropyl ether. Diisopropyl ether is formed as a result of condensation of two isopropyl alcohol molecules and it is often regarded as the intermediate in the formation of propene [7,12,13]. Several mechanisms of the reaction have been suggested. In most cases it has been assumed that the reaction involves two forms of isopropyl alcohol adsorbed at two types of active sites [3,12–14,16–18]. In our studies, it is assumed that the ether is formed (over catalysts with Lewis acid centres) in the reaction between the isopropoxy group attached the acid centre and the molecule of alcohol adsorbed at a different acid centre. The alcohol molecule adsorbed at an acid centre generates a carbocation, which in the next stage reacts with the nucleophilic isopropoxy group and the ether is produced. This mechanism is similar to mechanisms proposed by Knözinger [17] and Wang [16]. Consequently, the course of dehydration to diisopropyl ether should depend on the concentrations of both forms of chemisorbed alcohol as well as on the distance between these two species – the distance between the acid centres to which the both species are attached. Isopropoxy groups on the catalyst surface can also undergo transformation to acetone [14,15,19,20], whilst the carbocations formed at acid centres can be transformed to propene [3,6,14,15,19,21,22]. It is obvious that the rates of both reactions increase with temperature. This leads to a gradual decrease of concentrations of these forms of alcohol on the catalyst surface and hinders or even prevents the competitive slower formation of the ether. It is consistent with frequently observed decline in ether formation at higher temperatures [12,13]. Sometimes the decline in ether formation at high temperatures is explained by the increasing rate of decomposition of diisopropyl ether to propene [12,13]. The second factor mentioned earlier, which can affect the formation of diisopropyl ether is the distance between the two forms of chemisorbed alcohol. Longer distance between adsorbed species means that the probability of reaction is lower. The distance between two forms of chemisorbed alcohol is related to the arrangement of Lewis acid centres (cations). Therefore, additional experiments were carried out to check the dependence of the amount of the formed ether and the distance separating Lewis acid centres (metal cations) on the catalyst surface.

To solve the presented problems we chose a group of catalysts, which significantly change the properties of surface active sites. Several simple and mixed oxides (spinel) and heteropolyacids were used in our study because the properties of active sites on the surface were previously characterised [19,23–26]. Catalysts with Brønsted or Lewis acid centres (of different strength), basic centres (of different strength) and catalysts active in selective or full oxidation were studied. Qualification of simple oxides to the group of catalysts with Brønsted or Lewis acid centres or basic centres and the evaluation of the strength of these centres (Table 1) was done on the basis of IR studies of adsorption of specific molecules found in a review article by Busca [23]. The evaluation of strength of spinel acid centres was more complicated. With the exception

of Co₃O₄ the strength of acidic and basic centres of spinels has not been well determined and compared with the strength of such centres in simple oxides. Studies on complex oxides–spinel [23] indicate the presence of Lewis acid centres. To verify, whether the influence of the strength of acidic and basic centres on the rate of propene dehydration is the same as in the case of simple oxides, it was necessary to establish the probable order of increasing strength of acidic centres and compare it to simple oxides. Three simple oxides were selected: Fe₂O₃, ZrO₂ and MgO, which served as reference to compare properties of investigated spinels. Iron oxide Fe₂O₃ was chosen because it is a component of NiFe₂O₄. Zirconium oxide ZrO₂ was chosen as it exhibits the highest activity in the reaction of dehydration to propene amongst simple oxides with Lewis acid centres. Magnesium oxide MgO was selected because it is the most basic amongst simple oxides studied. IR measurements of pyridine and ammonia adsorption [23] show that the oxide Co₃O₄ has Lewis acid centres of slightly higher strength than MgO. Studies on spinels MAl₂O₄, MFe₂O₄ and MCr₂O₄ [23–25] suggest that their acid–base properties depend mainly on the nature of respective trioxides: Al₂O₃, Fe₂O₃ and Cr₂O₃, whilst the oxides MO only modify these properties. Therefore, nickel ferrite should exhibit weaker acidic properties than Fe₂O₃ because NiO is more basic than iron oxide. Nickel cobaltate NiCo₂O₄ should be more acidic than cobalt(II,III) oxide Co₃O₄, since nickel(II) oxide which modifies the properties of Co₂O₃ is more acidic than cobalt(II) oxide [23]. Hence, the most probable order of increasing acid centres strength of oxides is given below:



Qualification of the catalyst to the group with redox centres was done on the basis of knowledge about the tendency of elements to change the oxidation state and the literature data concerning reduction, especially with hydrogen [26–30].

2. Experimentals and methods

2.1. Catalyst preparation

CuCo₂O₄, NiCo₂O₄, NiFe₂O₄, Co₃O₄, were prepared by calcinations of respective co-precipitated hydroxides at 830 K for 8 h. Hydroxides were obtained by precipitation of aqueous solutions of respective nitrates (Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O: POCH, Pure P. A.) with 25% aqueous solution of ammonia (POCH, Pure P. A.). Fe₂O₃ was obtained in the reaction between ammonia (25% aqueous solution, POCH, Pure P. A.) and FeCl₃ (POCH, Pure P. A.) in solution and calcination of the product at 870 K for 6 h. SnO₂ was obtained by oxidation of metallic tin (POCH, 99.85%) with concentrated nitric acid (65%, POCH, Pure P. A.) and calcination of the precipitate at 870 K for 6 h. Other compounds used were commercial products: H₃PW₁₂O₄₀ (Aldrich, reagent grade), H₃PMo₁₂O₄₀ (Fluka, reagent grade), ZrO₂ (Hopkins & Williams Ltd, 99.5%), TiO₂ (POCH, 99%), SnO (POCH, 99%), MoO₃ (JMC LTD, spectrographically standardised), MgO (POCH,

spectrographically standardised) and γ -Al₂O₃ (Zakłady Azotowe "Puławy", 99%).

Heteropolyacids were deposited on the support (SiC) before the catalytic reaction. 174 mg of the heteropolyacid was dissolved in hot water, and subsequently the support was added to the solution until all the solution was absorbed.

2.2. Catalyst characterisation

The XRD analysis of obtained samples was performed using powder diffractometer type Siemens D5005 (AXS-Bruker) in Bragg–Bretano geometry (scan Θ – Θ). The measurements conditions: Cu K α radiation, wavelength $\lambda = 1.54184 \text{ \AA}$, graphite monochromator, lamp operating voltage $U = 55 \text{ kV}$, intensity of cathode current $I = 30 \text{ mA}$, scan range 10 – 90° (2Θ), step $0.01^\circ/\text{s}$.

The specific surface area of the sampler was determined using BET method, from nitrogen adsorption, at the boiling point of liquid nitrogen under normal pressure ($T = 77.4 \text{ K}$) (ASAP 2010V 400G).

2.3. Kinetic studies

Before the measurements all the catalysts were standardised in the flow of nitrogen for 1 h at 400 K.

Catalytic activity of the oxides was measured in a glass flow reactor with a fixed catalyst bed. Isopropyl alcohol (POCH, Pure P. A.) was diluted with nitrogen. The mole fraction of alcohol was 0.0179. The flow rate of the mixture was $20 \text{ dm}^3 \text{ h}^{-1}$. The contact time of the alcohol with the catalyst bed was the same in all measurements ($SV = 5000 \text{ h}^{-1}$). Measurements were carried out in the kinetic region of the reaction (conversion below 20%). The mass of the catalyst was about 1–2 g. The products were analysed using a gas chromatograph (GCHF 18.3) with a flame-ionisation detector (FID). Separation of products took place in an acid resistant steel column (3 m long and with internal diameter of 3 mm) packed with 4% Carbowax 20 M on Chromosorb G, AW, DMCS, 80/100 mesh. Two identical parallel columns were used.

2.4. Calculations of the distance between adjacent cations on the surface of oxides

Distances between adjacent cations on planes with low Miller indices (1 0 0), (0 1 0), (0 0 1) were calculated using CrystalMaker, version 1.4.3. The positions of cations in which the distances between them were lower than the sum of their ionic radii were ignored. The calculations were limited to three planes, because the surface of a solid consists of the faces with low indices. When calculating the average distance between cations, it was assumed that the share of the surface of planes is proportional to the period in the direction normal to the given plane. The appearance of a crystal depends on its internal lattice structure. It is well known that in crystals with lamellar or scaly habit, which exhibit very low growth rate in one direction, the unit cell has the longest period in this direction.

Since γ -Al₂O₃ has a defective structure in which the positions of aluminium atoms are not fully populated, for three non-equivalent positions (Al1, Al2 and Al3) the average distance from the neighbours was calculated as a weighted average, where the weights were the coefficients of population of neighbour positions. A similar procedure was applied to calculate distances between ions Fe³⁺ in NiFe₂O₄, where the population of octahedral (Fe1) and tetrahedral (Fe2) positions by this ion is not full. In calculations of distances between cations on the surface of spinels only distances between trivalent cations (or between tri- and divalent cations) were taken into account, since trivalent cations are more acidic.

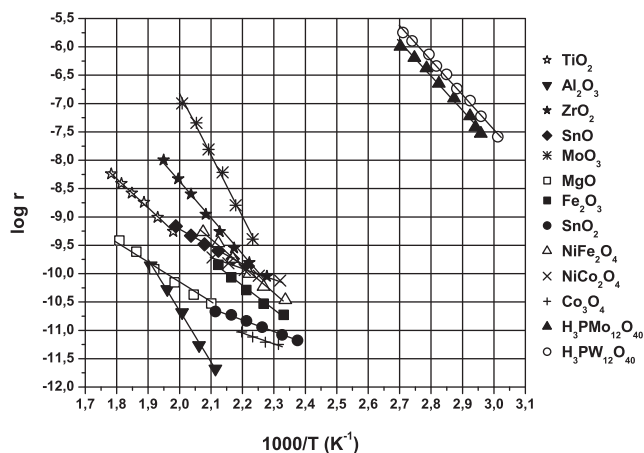


Fig. 1. Arrhenius plot for dehydration of isopropyl alcohol to propene. The rate of reaction unit is: $\text{mol m}^{-2} \text{ s}^{-1}$ for oxides and $\text{mol g}^{-1} \text{ s}^{-1}$ for heteropolyacids. $x_{\text{alc}} = 0.0179$, $SV = 5000 \text{ h}^{-1}$.

3. Results and discussion

3.1. Characterisation of oxides

The selected catalysts were analysed by X-ray diffraction to determine their phase composition. The knowledge of the phase type was necessary to calculate the distance between the cations on the surface of catalysts with Lewis acid centres. Specific surface area (BET) was measured because it is required for kinetic calculations. The results and parameters of unit cells of oxides are given in Table 2.

3.2. Choice of parameters for measurements

The choice of proper conditions for kinetic measurements of isopropyl alcohol conversion was necessary because of the reports concerning [3,7] the possibility of side reactions (consecutive and parallel-consecutive), which may hinder the analysis of results. Therefore, to limit or even exclude the undesired reactions, the measurements were performed at high flow rate of reactants ($20 \text{ dm}^3 \text{ h}^{-1}$), which guaranteed short contact time ($SV = 5000 \text{ h}^{-1}$) of reactants and products with the catalyst surface. Moreover, low conversion was maintained in order to keep the reaction in the kinetic region, which also helped limit undesired side reactions. The temperature in which the process was carried out depended on the activity of the catalyst and was chosen to obtain the desired conversion.

3.3. Dehydration of isopropyl alcohol to propene

Dehydration to propene is considered a good measure of acidic or acid–base properties of the catalyst surface. Evaluation of these properties is based on selectivity of propene formation. In our study influence of the type and strength of active centres on specific reaction rate, selectivity and activation energy were determined for dehydration of isopropyl alcohol to propene.

3.3.1. Lewis acid centres

Fig. 1 shows the Arrhenius plot for dehydration of propene over all studied oxides, active in this reaction. The oxides with Lewis centres exhibit activity in this reaction at higher temperatures, i.e. above 420 K. Comparison of activity of oxides apparently does not reveal any correlation between the strength and the reaction rate. The least active is aluminium oxide, which has the strongest acid centres. Magnesium oxide, which has the weakest acid centres,

Table 2
Specific surface area and structural data of oxide catalysts.

Catalyst	S_{BET} (m ² /g)	Structure name	Phase purity	Space group	Unit cell parameters
Al ₂ O ₃	145.6	γ -Al ₂ O ₃	Fine-crystalline	Fd-3 m	$a = 7.911 \text{ \AA}$
SnO ₂	15.0	Cassiterite	Pure	P4 ₂ /mnm	$a = 4.738 \text{ \AA}, c = 3.187 \text{ \AA}$
TiO ₂	0.9	Rutile	Pure	P4 ₂ /mnm	$a = 4.592 \text{ \AA}, c = 2.957 \text{ \AA}$
Fe ₂ O ₃	13.4	Hematite	Pure	R-3c	$a = 5.025 \text{ \AA}, c = 13.736 \text{ \AA}$
ZrO ₂	2.7	Baddeleyite	ca. 3% trigonal ZrO ₂	P2 ₁ /c	$a = 5.159 \text{ \AA}, b = 5.200 \text{ \AA}, c = 5.313 \text{ \AA}, \beta = 99.16^\circ$
SnO	1.5	Romarchite	Pure	P4/mnm	$a = 3.802 \text{ \AA}, c = 4.838 \text{ \AA}$
MgO	15.2	Peryclase	Pure	Fm3 m	$a = 4.217 \text{ \AA}$
MoO ₃	3.1	Molybdite	Pure	–	–
NiFe ₂ O ₄	7.7	Spinel	ca. 5% Fe ₂ O ₃ (hematite)	Fd-3 m	$a = 8.337 \text{ \AA}$
NiCo ₂ O ₄	2.5	Spinel	Pure	Fd-3 m	$a = 8.114 \text{ \AA}$
Co ₃ O ₄	37.4	Spinel	Pure	Fd-3 m	$a = 8.084 \text{ \AA}$
CuCo ₂ O ₄	33.0	Spinel	ca. 3% CuO (tenorite)	Fd-3 m	$a = 8.133 \text{ \AA}$

is more active than Al₂O₃. Zirconium oxide exhibits the highest activity and its acidic centres are of medium-weak strength.

The relationship between the rate dehydration and the strength of acidic and basic centres was studied at two temperatures (Fig. 2). As it is shown in the plot the rate of dehydration increases with the strength of basic centres up to zirconium oxide (average-strong basic centres), and then decreases (tin(II) oxide and magnesium oxide). This type of relationship indicates that the rate of dehydration to propene is determined by the strength of basic and not acidic centres. It means that the reaction proceeds over Lewis acid centres according to elimination mechanism E2. A strong base is necessary for this reaction, to proceed according to this mechanism; after co-ordination of the alcohol molecule by the acidic centre the base can attack it before dissociation which could produce a carbocation. Since the course of reaction is determined by the strength of basic centres (which attack the molecule in a rate-limiting stage), the rate of reaction increases with the strength of basic centres. The decrease of the rate over oxides with strong basic centres and very weak acidic centres can be associated with weak co-ordination of the alcohol molecule by Lewis acid centres. It is possible that the reaction over these oxides can proceed according to a different mechanism, i.e. E1cB. This mechanism requires a strong base, which attacks the alcohol molecule and a carbanion is formed. However, this mechanism does not explain why the reaction is slower over a more basic oxide–MgO. It is possible that this mechanism is valid only in the case of MgO and tin oxide is too weak base and cannot induce dehydration according to the E1cB mechanism.

Selectivity of the reaction (Table 3) does not depend on the strength of acidic and basic centres. However, it can depend on the

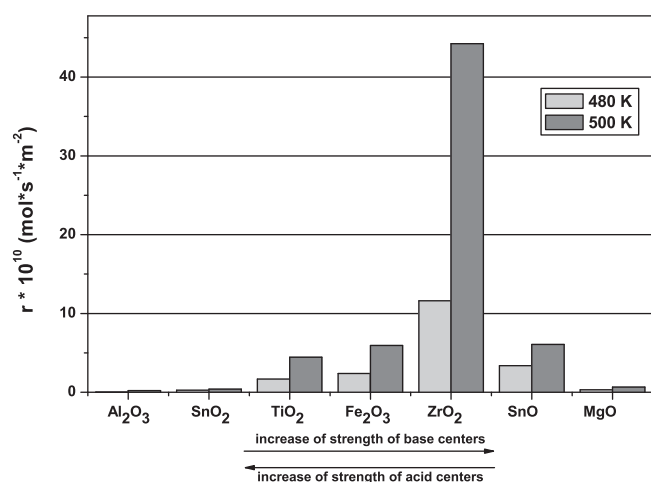


Fig. 2. Rate of dehydration of isopropyl alcohol to propene as a function of strength of acid and base Lewis centres at two temperatures for simple oxides. $x_{\text{alc}} = 0.0179$, $SV = 5000 \text{ h}^{-1}$.

number of accessible active centres. For example measurements of the number of Lewis acid centres on the surface of γ -Al₂O₃ and TiO₂ [1,23,31] revealed that titanium oxide has much more medium-strength Lewis acid centres than aluminium oxide. Aluminium oxide also has some strong acid centres, but the total number of acid centres is lower than in the case of titanium oxide. It can be explained by high hydration of the Al₂O₃ surface. Water on the oxide surface generates Brønsted acid centres, but their strength is too low to catalyse the dehydration reaction [1,23,31]. Their presence blocks Lewis acid centres. The results are confirmed by selectivity of dehydration over aluminium and titanium oxides (Table 3). Selectivity of propene formation at 465 K over aluminium oxide is much lower than over titanium oxide. Similar situation is observed at higher temperature (500 K) but the difference is lower. Significant increase in the selectivity of propene formation over aluminium oxide can be related to the dehydration of the oxide surface as a result of increasing temperature. Removal of water from the surface of aluminium oxide whilst increasing temperature leads to unblocking of Lewis acid centres (Al³⁺) and the number of accessible active sites increases. If the number of active sites increases with temperature, the reaction rate increases not only as a result of rising temperature but also due to the higher number of active sites. This phenomenon can explain high activation

Table 3

Selectivity of isopropyl alcohol conversion to propene, acetone and diisopropyl ether.

Catalyst	Selectivity (%)					
	465 K			500 K		
	Propene	Ether	Acetone	Propene	Ether	Acetone
Al ₂ O ₃	13.6	1.5	84.9	39.0	2.6	58.4
SnO ₂	0.2	–	99.8	0.03	–	99.97
TiO ₂	44.8	–	55.2	42.9	–	57.1
Fe ₂ O ₃	5.8	–	94.2	11.0	–	89.0
ZrO ₂	58.4	–	41.6	76.5	–	23.5
SnO	4.8	–	95.2	3.3	–	96.7
MgO	22.0	–	78.0	24.9	–	75.1
MoO ₃	56.8	39.8	3.4	87.9	9.9	2.2
	435 K			455 K		
	Propene	Ether	Acetone	Propene	Ether	Acetone
NiFe ₂ O ₄	2.2	0.3	97.5	3.5	0.7	95.8
NiCo ₂ O ₄	1.8	–	98.2	1.3	–	98.7
Co ₃ O ₄	0.3	–	99.7	0.2	–	99.8
CuCo ₂ O ₄	–	–	100	–	–	100
	345 K			370 K		
	Propene	Ether	Acetone	Propene	Ether	Acetone
H ₃ PMo ₁₂ O ₄₀	76.9	20.2	2.9	80.1	18.2	1.7
H ₃ PW ₁₂ O ₄₀	90.1	9.9	–	76.1	23.9	–

Table 4

Activation energy of isopropyl alcohol conversion to propene, acetone and diisopropyl ether.

Catalyst	Energy of activation (kJ mol ⁻¹)		
	Dehydration to propene	Dehydration to diisopropyl ether	Dehydrogenation to acetone
Al ₂ O ₃	173.0	157.8	92.3
SnO ₂	38.8	–	126.9
TiO ₂	98.2	–	102.4
Fe ₂ O ₃	91.0	–	52.3
ZrO ₂	133.4	–	67.3
SnO	58.4	–	79.7
MgO	74.2	–	65.1
NiFe ₂ O ₄	90.8	127.6	51.5
NiCo ₂ O ₄	43.3	–	71.8
Co ₃ O ₄	36.4	–	57.0
CuCo ₂ O ₄	–	–	47.9
MoO ₃	208.0	120.5	167.0
H ₃ PMo ₁₂ O ₄₀	115.9	111.0	84.2
H ₃ PW ₁₂ O ₄₀	124.6	161.8	–

energy (Table 4) of dehydration to propene over aluminium oxide. The opposite situation is observed for tin oxides—SnO₂ and SnO. The reactions over tin oxides proceed with low activation energy. In this case, the number of active centres decreases as a result of reduction of surface oxide layers. Reduction also decreases the number of acid centres (Sn⁴⁺ and Sn²⁺), which are converted to metallic tin (Sn⁰). The small increase in the rate of dehydration to propene is caused by the lower number of acid centres. Activation energy of dehydration over tin(IV) oxide is lower than over tin(II) oxide because SnO₂ is more easily reduced to the metal than SnO [26]. Higher rate of reaction can be caused not only by increasing temperature but also by changes in the number of active sites. Such changes can be caused by the removal of adsorbed water from the surface, reduction of the oxide, or presence of active centres with various strength. Their activity in the reaction can appear at various temperatures (strong centres are active at low temperatures and weak centres at higher temperatures).

It is noticeable that the rate of dehydration does not depend on the selectivity to propene (Table 3). It means that evaluation of strength of acidic and basic centres using the rate of reaction gives results independent on the number of these sites.

Apart from simple oxides, oxosalts with spinel structure: CuCo₂O₄, NiCo₂O₄, Co₃O₄ and NiFe₂O₄ were studied. Amongst spinel oxides only CuCo₂O₄ is not active in the dehydration to propene. These oxides are treated separately because the strength of acidic and basic centres cannot be exactly determined in relation to simple oxides.

For the established order of increasing strength of acidic and basic sites (see Introduction) the graph showing the rate of dehydration as a function of strength of active centres was prepared (Fig. 3).

The relationship is very similar to that obtained for simple oxides. The rate of reaction over cobalt oxide Co₃O₄ is slightly lower than over magnesium oxide. It can be caused by reduction of the surface, which leads to lower activation energy (Table 4). Cobalt oxide Co₃O₄ is active at lower temperature than magnesium oxide, so if activation energy over Co₃O₄ were higher its activity should be higher than in the case of magnesium oxide. A similar situation can be observed for NiCo₂O₄, which could be more active than ZrO₂, if the activation energy were higher.

All spinels studied exhibit low activity in the dehydration to propene (Table 3). Special attention should be paid to the activation energy of the reaction (Table 3). In the case of spinels with the same trioxide, e.g. NiCo₂O₄ and Co₃O₄ the values of activation energy of dehydration to propene are similar. The same situation occurs in the case of NiFe₂O₄ and Fe₂O₃ (91.0 kJ mol⁻¹). These

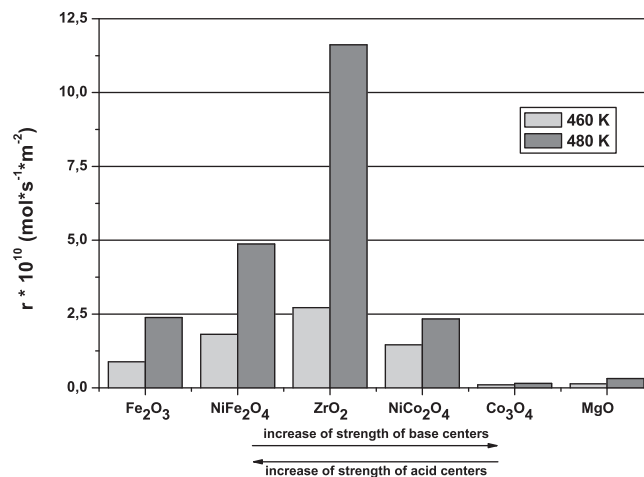


Fig. 3. Rate of dehydration of isopropyl alcohol to propene as a function of strength of acid and base Lewis centres at two temperatures for spinels and selected simple oxides. $x_{alc} = 0.0179$, $SV = 5000 \text{ h}^{-1}$.

results suggest that dehydration over spinels proceeds mainly with the participation of the component trioxide. The course of reaction with participation of the cation with higher valency confirms higher acidity of this cation.

A big difference in activation energy between nickel ferrite and cobaltates is surprising. If low activation energy suggests reduction of the catalyst during measurements, nickel ferrite is reduced much less than cobaltates.

3.3.2. Brønsted acid centres

The relationship between the rate of dehydration to propene and the strength of Brønsted acid centres is completely different than in the case of Lewis acid centres (Fig. 1). The activity of catalysts increases with the strength of Brønsted acid centres: MoO₃ < H₃PMo₁₂O₄₀ < H₃PW₁₂O₄₀. This type of relationship suggests that the rate of dehydration to propene is determined by the strength of Brønsted acid centres. The reaction proceeds over these centres according to elimination mechanism E1. In the first stage the alcohol molecule is adsorbed and protonated at Brønsted acid centre. In the second stage slow dissociation to a carbocation takes place. The carbocation does not have to be co-ordinated by a basic centre, which in the following stage co-ordinates the proton abstracted from the carbocation with the formation of propene. The last stage is fast and its rate does not depend on the strength of the basic centre.

In the same way as for Lewis acids selectivity observed for Brønsted acids does not depend on the strength of active centres (Table 3). Lower selectivity to propene over molybdenum oxide and phosphomolybdic acid is not associated with lower strength of acidic centres but is due to formation of acetone over centres active in this reaction at low temperatures. This type of centres is not present in phosphotungstic acid.

Activation energy of propene formation (Table 4) is higher than 100 kJ mol⁻¹ for all Brønsted acids studied. The activation energy of propene formation over molybdenum oxide is 208.0 kJ mol⁻¹. Brønsted acid centres on the surface of this oxide are formed as a result of dissociation of water. Standardisation procedure could remove some water from the catalyst. During dehydration a water molecule is removed, but it can be adsorbed at the surface and the conditions favour dissociation of water. Moreover, reduction of the molybdenum oxide surface is accompanied by an increase in the specific area, which is proportional to the reduction time and also to the degree of reduction [27,28]. In this way, new active centres can

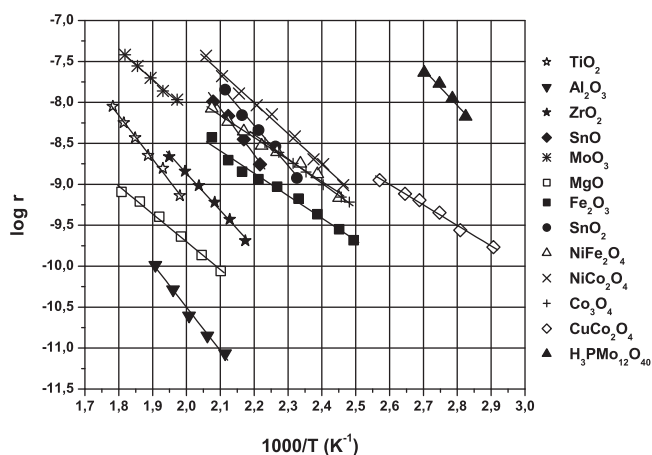


Fig. 4. Arrhenius plot for dehydrogenation of isopropyl alcohol to acetone. The rate of reaction unit is: $\text{mol m}^{-2} \text{s}^{-1}$ for oxides and $\text{mol g}^{-1} \text{s}^{-1}$ for heteropolyacids. $x_{\text{alc}} = 0.0179$, $\text{SV} = 5000 \text{ h}^{-1}$.

be generated, which leads to high activation energy of dehydration to propene.

3.3.3. Comparison of Brønsted and Lewis acid centres

As it was shown above, the rate of dehydration to propene is determined by the strength of acid and basic Lewis centres and Brønsted acid sites, and the influence of these centres on the rate of reaction determines the type of acid centres. Another parameter which can be used to distinguish Lewis and Brønsted acid centres is the activity of the catalyst in the dehydration at a given temperature. The Arrhenius plots for all the catalysts studied (Fig. 1) reveal that catalysts with Brønsted acid centres are more active than catalysts with Lewis acid centres. It is also clear that changes in strength of Brønsted acid centres have a greater influence on the rate of dehydration to propene than changes in strength of Lewis acid centres. Hence, evaluation of strength of Brønsted acid centres on the basis of the rate of dehydration is more exact. The evaluation of strength of Lewis acid centres is more complicated due to the lower rate of reaction and changes of its mechanism in the case of strong bases. It means that the strength of Lewis centres can be evaluated but with the support of other techniques.

3.4. Dehydrogenation of isopropyl alcohol to acetone

Dehydrogenation to acetone is treated as an indicator of basic and redox properties of the catalyst. The majority of authors treat the reaction only as an indicator of basicity of the surface, and mention redox properties of the surface only in the oxidation of isopropyl alcohol by molecular oxygen. The reason is the fact that only the strength of basic centre is easy to determine using an independent method, e.g. temperature-programmed desorption of acidic molecules.

The most important questions asked in this part of our studies were: (1) Is it justifiable to mention only basic properties when analysing the conversion of isopropyl alcohol to acetone? (2) If the reaction proceeds not only over basic centres, is it possible to distinguish them from redox centres? and (3) Is there a relationship between the strength of the centres and the rate of dehydrogenation to acetone?

The results of activity of all catalysts studied in the dehydrogenation to acetone are presented as Arrhenius plots in Fig. 4. Oxides with constant valency of cation Al_2O_3 , MgO , TiO_2 and ZrO_2 exhibit the lowest activity in this reaction. All oxide catalysts with cations of variable valency are more active. Therefore, we cannot expect for all the catalysts studied that the reaction of dehydrogenation

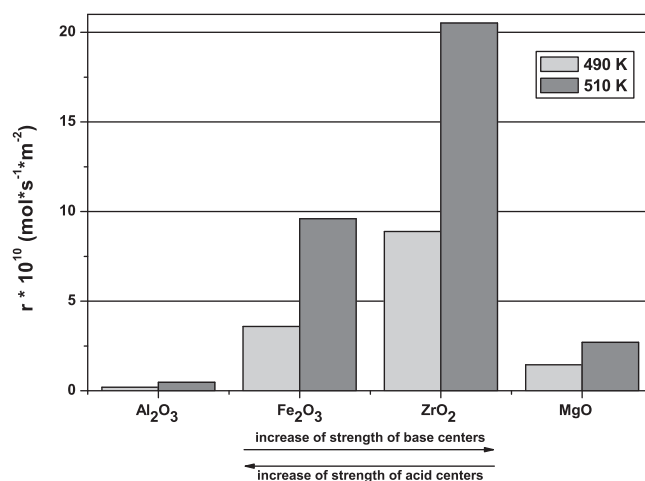


Fig. 5. Rate of dehydrogenation of isopropyl alcohol to acetone as a function of strength of acid and base Lewis centres at two temperatures for oxides with constant valency of metals. $x_{\text{alc}} = 0.0179$, $\text{SV} = 5000 \text{ h}^{-1}$.

to acetone will be determined by the strength of basic centres. In further parts of this work the groups of catalysts will be discussed separately.

3.4.1. Oxides with constant stable valency and basic Lewis centres

In the case of oxides with stable valency of cations (Al_2O_3 , MgO , TiO_2 i ZrO_2) dehydrogenation to acetone can proceed over basic centres. Fig. 5 shows the dependence of rate of dehydrogenation to acetone on the strength of basic centres and Lewis acid centres. The relationship is similar as in the case of dehydration to propene over a couple of acid and base Lewis centres. It suggests that over this group of oxides dehydrogenation also proceeds with the participation of a pair of acid and basic centres. The reaction rate is determined by the strength of basic centres and lower reaction rate over magnesium oxide can be caused by too low acidity of magnesium cations. Mechanisms presented in the literature indicate abstraction of a hydrogen anion from carbon atom near the OH group as the limiting step of the process [20,32,33]. In this case the reaction rate should depend on the strength of acid centres. However, these results were obtained for more basic catalysts than zirconium oxide. The results suggest that for strong acid centres the reaction rate is determined by the strength of basic centres and for strong basic centres the reaction rate is determined by the strength of acid centres.

3.4.2. Oxides with variable cation valency and redox centres

Dehydrogenation to acetone can proceed over redox centres when catalysts with variable valency of the cation are used (SnO , Fe_2O_3 , SnO_2 , MoO_3 , CuCo_2O_4 , NiCo_2O_4 , Co_3O_4 , NiFe_2O_4 , $\text{H}_3\text{PMo}_{12}\text{O}_{40}$).

When the reaction proceeds over redox centres an increase in the oxidising and reducing properties of the catalyst should give higher rates of dehydrogenation to acetone. This assumption is confirmed by comparison of reducing properties of various oxides with their activity in dehydrogenation reaction. Hence, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is easily reduced by hydrogen at low temperature whilst MoO_3 , which has the same redox centre (Mo^{6+}), undergoes reduction at much higher temperatures. $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was found to be much more active in dehydrogenation to acetone than MoO_3 (Fig. 4). Similar situation is observed for SnO_2 and SnO . SnO_2 is reduced at lower temperatures than SnO [26] and its activity is higher than the activity of SnO .

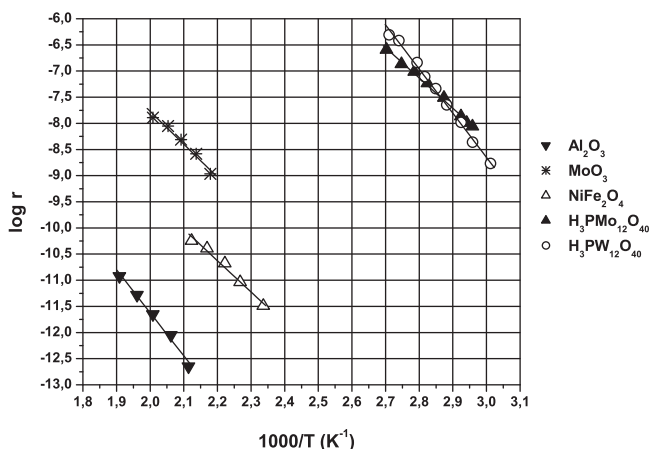


Fig. 6. Arrhenius plots for dehydration of isopropyl alcohol to diisopropyl ether. The rate of reaction unit is: $\text{mol m}^{-2} \text{s}^{-1}$ for oxides and $\text{mol g}^{-1} \text{s}^{-1}$ for heteropolyacids. $x_{\text{alc}} = 0.0179$, $\text{SV} = 5000 \text{ h}^{-1}$.

3.4.3. Selectivity and activation energy

Comparison of selectivity to acetone over two groups of catalysts (Table 3) suggests that the contribution of dehydrogenation over catalysts with redox centres is much higher than over catalysts with acid–base centres. There are two exceptions: $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and MoO_3 which give low selectivity to acetone. This behaviour is caused by Brønsted acid centres, which start to be active at lower temperature than redox centres. Other redox catalysts with Lewis acid centres are active at higher temperatures. Moreover, Lewis acid centres are situated in the same places as redox centres (metal cations M^{n+}). Since the cation with variable valency is more active as a redox centre, the preferred reaction after adsorption of alcohol is dehydrogenation.

In the case of catalysts with acid–base centres, dehydrogenation to acetone proceeds over the same pair of centres as dehydration to propene. As the centres are active in both reactions at the same time, the direction of the process depends on how the molecules are adsorbed at the centres, and this is determined by physico-chemical properties of active centres.

Activation energy of dehydrogenation to acetone is usually below 100 kJ mol^{-1} . The exceptions are two oxides with redox centres: molybdenum(VI) oxide and tin(IV) oxide. High activation energy can be associated with intensive reduction of the surface of oxides during measurements. The surface of tin(IV) oxide was reduced so quickly that after reaching the temperature of 443 K its activity decreased and the colour of the catalyst changed from light green to black. Molybdenum oxide also changed colour from pale green to black, which suggests its reduction.

3.5. Formation of diisopropyl ether

Dehydration of isopropyl alcohol to diisopropyl ether occurs in measurable quantities over all catalysts with Brønsted acid centres ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and MoO_3) and over two catalysts (Al_2O_3 and NiFe_2O_4) with Lewis acid centres. Traces of ether were found after the reaction at higher temperatures over titanium, iron, tin(IV) and zirconium oxides. The reaction rate is not sensitive to the strength of acid centres (Fig. 6). Both heteropolyacids show the same activity in ether formation despite the fact that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is a stronger acid. Nickel ferrite is much more active than aluminium oxide even though Al_2O_3 has stronger acid centres. These data suggest that strength of acid centres has a very weak or even no influence on the rate of reaction.

Selectivity of diisopropyl ether formation (Table 3) is much higher over catalysts with Brønsted acid centres (more than 40%)

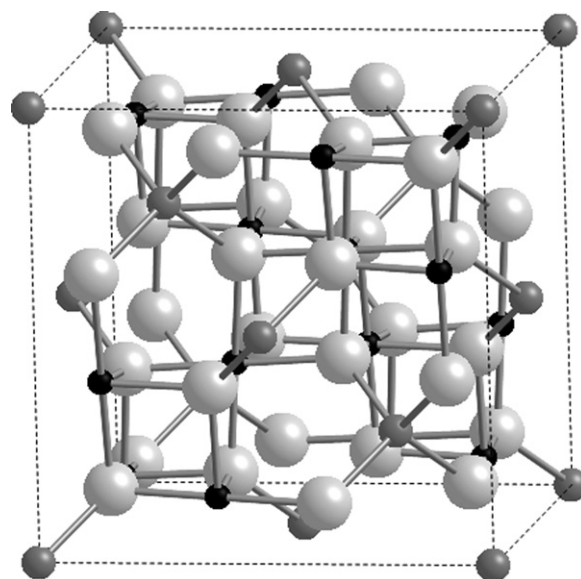


Fig. 7. Structure of spinel AB_2O_4 . Bright gray ball-oxygen ion O^{2-} , dark gray ball-metal ion A (Ni^{2+} , Cu^{2+} , Co^{2+}), black ball-metal ion B (Co^{3+} , Fe^{3+}).

when compared to catalysts with Lewis acid centres (a few per cent). This situation may be caused by the effect of higher concentration and accessibility of Brønsted acid centres. Two Brønsted acid centres-OH groups or protons on the surface are not separated by obstacles such as large O^{2-} anions present on the surface of oxides. A large ion can hinder the reaction between two molecules of alcohol (or alkoxy groups) attached to adjacent Lewis acid centres. Moreover, the oxygen ion is a basic centre, which can attack the alcohol molecule attached to an acidic centre and cause the formation of propene. Therefore, dehydration to propene is a preferred reaction over Lewis acid centres.

Activation energy of dehydration to diisopropyl ether (Table 4) is high and exceeds 100 kJ mol^{-1} . It should be noted that in the case of catalysts which do not exhibit redox properties the activation energy is about 160 kJ mol^{-1} and is much higher than in the case of redox catalysts, where the typical value is 120 kJ mol^{-1} . The reason for lower activation energy of redox catalysts can be the same as observed for the dehydration reaction – lower number and/or strength of acid centres.

Dehydration to diisopropyl ether proceeds only over two catalysts with Lewis acid centres. As the reaction practically does not occur over oxides with similar or higher strength of acid centres than nickel ferrite, i.e. iron(III), titanium and tin(IV), the course of ether formation cannot be related to acidity of the catalyst. Intermolecular dehydration of alcohol requires the presence of acid centres. If the reaction proceeds according to Langmuir–Hinshelwood mechanism, i.e. the ether molecule is formed during the reaction of two alcohol molecules adsorbed at adjacent acid centres, the possibility of reaction between two molecules depends on the distance between the acid centres. To verify this assumption average distances between cations on the surface of all studied catalysts with Lewis acid centres were calculated (with the exception of CuCo_2O_4 , which is inactive in dehydration and MoO_3 , which is treated as a Brønsted acid). The results of calculations are presented in Table 5.

The lowest average distances between cations (2.9 and 3.2 \AA) were found for Al_2O_3 and all spinels. For other oxides the distances are above 3.5 \AA and in the case of acidic oxides (SnO_2 , TiO_2 , Fe_2O_3) above 4.0 \AA . The difference between average distances in aluminium oxide and spinels compared to acidic oxides (over which dehydration to ether does not occur) is around 1.0 \AA (33.3%). In the

Table 5
Distances between cations on the surface of oxides.

Metal oxide	Plane	Distance between adjacent cations (Å) ^a	Number of adjacent cations/occupation ^b	Average distance between cations on a given plane (Å)	Average distance between cations on the surface (Å)	
γ -Al ₂ O ₃	100,010,001	Al1	2.797	2/0.58	3.032	2.907
			2.822	4/0.17		
			3.280	2/0.84		
		Al2	3.273	4/0.58	3.127	
			2.086	2/0.17		
			2.822	2/0.58		
		Al3	2.086	2/0.84	2.421	
			2.830	2/0.17		
			2.188	1/0.17		
SnO ₂	100,010	4.738	2	3.962	4.178	
		3.187	2			
	001	4.738	4	4.738		
TiO ₂	100,010	2.957	2	3.775		3.952
		4.592	2			
	001	4.592	4	4.592		
Fe ₂ O ₃	100,010	2.843	1	4.228	4.601	
		4.011	1			
		5.028	2			
	001	5.028	4	4.875		
		4.567	2			
		4.019	2			
ZrO ₂	100	3.446	2	3.483	3.638	
		3.581	1			
	010	3.485	1	3.733		
		3.331	1			
		4.534	1			
		3.468	2			
001	3.920	2	3.694			
	3.799	2				
	4.841	2				
SnO	100,010	3.799	2	4.320	4.117	
		4.841	2			
	001	3.799	4	3.799		
MgO	100,010,001	2.982	4	3.599		3.599
		4.217	4			
NiFe ₂ O ₄	100,010,001	Fe1	2.960	2/0.89		3.079
		Fe2	3.344	2/0.40		
			3.344	4/0.89	3.344	
NiCo ₂ O ₄	100,010,001	Co	2.918	2	3.099	3.190
			3.280	2		
		Ni	3.280	4		
Co ₃ O ₄	100,010,001	Co1	3.244	4	3.244	3.156
			2.891	2		
		Co2	3.244	2		

^a If the plane contains various cations, distances to all neighbours were calculated.^b Given if the occupation is not full.

case of spinels the average distance between cations is similar. It means that some other factors must determine the course of dehydration to diisopropyl ether. The answer can be found by analysing the structure of spinels (Fig. 7). Normal spinel structure is characteristic of NiCo₂O₄ and Co₃O₄. In this structure tetragonal positions are occupied by divalent ions (Co²⁺ and Ni²⁺) and octahedral positions by trivalent ions (Co³⁺). The faces of a unit cell and as a result the surface of oxides contain mainly divalent ions. Trivalent ions are situated below the surface of the faces. NiFe₂O₄ has an inverse spinel structure in which 9 of 10 tetragonal positions are occupied by Fe³⁺ ions and only 1 of 10 is occupied by the ion Ni²⁺. In this spinel the surface contains mainly Fe³⁺ ions and positions below the surface of the faces are occupied by Fe³⁺ and Ni²⁺ ions. As it was shown above more acidic trivalent cations take part in dehydration to propene. It means that in nickel ferrite the ions capable of catalysing dehydration (trivalent) are more accessible than in cobaltates. Since the ether is not formed over cobaltates, adjacent trivalent cations Co³⁺ found below the plane surface separated by around 2.9 Å, and the pair of ions Co³⁺–Ni²⁺(Co²⁺) separated by around 3.25 Å

cannot catalyse the formation of ether. It is likely that diisopropyl ether is formed over the pair of ions Fe1–Fe2 separated by 3.344 Å. The ion Fe1 is on the surface (tetragonal co-ordination) and the ion Fe2 slightly below the surface (octahedral co-ordination). In the same way over cobaltates the reaction is not catalysed by the ion pair Fe2–Fe2 (situated slightly below the surface) nor by the pair Fe1(2)–Ni, because divalent ions are weak acids. The reaction cannot be catalysed by the pair Fe1–Fe1 situated on the surface as the distance between them is 5.92 Å. Traces of ether were observed during alcohol conversion over iron, tin(IV), titanium and zirconium oxides. These oxides contain one or two pairs of cations situated at a distance lower than 3.35 Å. Comparatively low number of cation pairs, which can catalyse intermolecular dehydration, on the surface of oxides can be responsible for low quantities of ether in the products. Low distance between cations is characteristic of MgO. Lack of ether formation over this oxide can be caused by low acidity of magnesium cations, which is associated with weak co-ordination of alcohol molecules. The molecules of alcohol are mainly attacked by bigger than Mg²⁺ and strongly basic oxygen ions (formation

of propene according to E1cB mechanism and dehydrogenation to acetone).

Therefore, the possibility of dehydration of isopropyl alcohol to diisopropyl ether is determined by the distance between adjacent cations, their accessibility for reactants and acidity.

4. Conclusions

The results presented above show that the test reaction of isopropyl alcohol conversion can be used not only to determine the type of centres over which the reaction proceeds, but also to evaluate the strength of active centres.

- 1) It was demonstrated that Brønsted and Lewis acid centres in oxide catalysts can be distinguished on the basis of catalytic activity in the reaction of dehydration to propene. It is possible because the dehydration to propene proceeds over Brønsted acid centres according to a different mechanism than over Lewis acid centres. As a result the rate of reaction over Brønsted acid centres is significant at lower temperatures than over Lewis acid centres.
- 2) It was also found that the rate of dehydration to propene is a measure of the strength of acid and basic centres participating in the reaction. In the case of catalysts with Lewis acid centres the rate of dehydration increases when the strength of basic centres is higher. In the case of catalysts with Brønsted acid centres the rate of dehydration increases with the strength of acid centres. It is important that the evaluation of the strength of Lewis and Brønsted acid centres on the basis of the rate of dehydration to propene does not depend on the amount of formed propene, therefore it is independent of the number of active centres participating in the reaction.
- 3) It was found that the value of activation energy of dehydration to propene can indicate changes in the number of active centres during catalytic measurements. If at higher temperatures an increase in the number of active centres occurs, the obtained activation energy of dehydration to propene is comparatively high (over 150 kJ mol^{-1}). If higher temperature and the course of reaction decrease the number of active centres the activation energy is very low (ca. 40 kJ mol^{-1}).
- 4) It was proved that in the case of dehydrogenation to acetone not only basic properties of the surface should be taken into account, because the reaction can also proceed over redox centres. Distinction of these active centres can be achieved on the basis of the rate of dehydrogenation to acetone at a given temperature. In this reaction redox centres are active at lower temperatures than basic centres.
- 5) It was also discovered, that the rate of dehydrogenation to acetone is a measure of the strength of active centres participating in the reaction. If the catalyst contains Lewis basic centres of low and medium strength, the rate of dehydrogenation to acetone increases with the strength of basic sites, whilst for strongly basic catalysts the rate of reaction is determined by the strength of acid centres. If the catalysts contain redox centres, the rate of reaction increases with their reducibility.
- 6) It was found that the selectivity to propene, diisopropyl ether and acetone depends mainly on the type of active centres on the surface. Brønsted acid centres are active in dehydration reactions at lower temperatures than Lewis acid and basic centres. Redox centres are active in dehydrogenation at lower temperatures than acid and basic Lewis centres. Therefore, if the

catalyst contains Brønsted acid centres, the reaction products are mainly propene and diisopropyl ether. If the catalyst contains redox centres and it does not contain Brønsted acid centres, the main reaction product is acetone. For catalysts with Lewis acid and basic centres the amounts of propene and acetone are similar.

- 7) The conditions of diisopropyl ether formation over Lewis acid centres were determined. The possibility of this reaction is determined by:

- the distance between adjacent cations (Lewis acid centres). If the distance is higher, the probability of dehydration to diisopropyl ether decreases,
- accessibility of the centres for the substrate (isopropyl alcohol), and
- strength of acid centres and adjacent basic centres, which can interact with alcohol molecules chemisorbed at acid centres and direct its transformation to propene or acetone.

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