

The conversion of ethanol to acetone on a ZnO-CaO catalyst in the presence of water vapor

Konwersja etanolu do acetonu na katalizatorze ZnO-CaO w obecności pary wodnej

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ABSTRACT: The main product of the conversion of ethanol to acetone on a ZnO-CaO catalyst is acetone, the yield of which strongly depends on the composition of the reaction environment. When oxygen is present, the yield of products of destructive and complete oxidation increases greatly. In contrast, when water vapor is present, both the selectivity and conversion of ethanol increase. Therefore, the conversion of ethanol is the limiting step in the overall process, which determines the selectivity of the conversion of ethanol to acetone. In this regard, it appeared suitable to investigate the effect of introducing water to the contact zone. As experiments indicated, the addition of water caused a significant effect on the conversion, selectivity, and acetone yield on the ZnO-CaO catalyst. As the partial pressure of water vapor increases, the conversion of ethanol and the acetone yield increase, while the yield of carbon dioxide decreases. The decrease in carbon dioxide is associated not only with the inhibition of the conversion of ethanol to CO₂. In this study, the adsorption of water vapor and ammonia on the surface of the ZnO-CaO catalyst was examined by infrared spectroscopy method. It has been shown that water vapor at low temperatures is adsorbed on the catalyst surface in the molecular form, while at higher temperatures it is adsorbed in the dissociative form. Co-transformation reactions of ethanol with acetic acid, acetaldehyde with ethylene, and acetaldehyde with acetic acid have been studied. The obtained results indicated that acetone is formed mainly through the stage of complexation of acetaldehyde with ethylene. The isomerization reaction of 1-butene to 2-butene has been investigated. It was found that the yield of cis-2-butene in the absence of water vapor is higher, likely attributed to the molecular adsorption of water on Lewis centers. Based on these findings, a scheme for the vapor-phase conversion of ethanol into acetone on the studied catalysts was formulated.

Key words: catalyst, acetone, ethanol, adsorption, acetaldehyde, water, vapor, spectroscopy, method, 1-butene, 2-butene, Lewis centers.

STRESZCZENIE: Głównym produktem konwersji etanolu do acetonu na katalizatorze ZnO-CaO jest aceton, którego wydajność silnie zależy od składu środowiska reakcji. W obecności tlenu znacznie wzrasta wydajność produktów destrukcyjnego i całkowitego utlenienia. Natomiast w obecności pary wodnej wzrasta selektywność i konwersja etanolu. Dlatego konwersja etanolu jest etapem ograniczającym w całym procesie, który określa selektywność konwersji etanolu do acetonu. W związku z tym celowe wydawało się zbadanie wpływu domieszek wody do strefy kontaktu. Jak wykazały doświadczenia, dodatek wody miał istotny wpływ na konwersję, selektywność i wydajność acetonu na katalizatorze ZnO-CaO. Wraz ze wzrostem ciśnienia cząstkowego pary wodnej wzrasta konwersja etanolu i wydajność acetonu, podczas gdy wydajność dwutlenku węgla maleje. Spadek dwutlenku węgla jest związany nie tylko z hamowaniem konwersji etanolu do CO₂. W niniejszej pracy metodą spektroskopii w podczerwieni badano adsorpcję pary wodnej i amoniaku na powierzchni katalizatora ZnO-CaO. Wykazano, że para wodna w niskich temperaturach jest adsorbowana na powierzchni katalizatora w postaci cząsteczkowej, natomiast w wyższych temperaturach jest adsorbowana w postaci dysocjacyjnej. Zbadano reakcje kotransformacji etanolu z kwasem octowym, aldehydu octowego z etylenem i aldehydu octowego z kwasem octowym. Uzyskane wyniki wykazały, że aceton powstaje głównie na etapie kompleksowania aldehydu octowego z etylenem. Zbadano reakcję izomeryzacji 1-butenu do 2-butenu. Stwierdzono, że wydajność cis-2-butenu w nieobecności pary wodnej jest większa, co prawdopodobnie wynika z molekularnej adsorpcji wody na centrach Lewisa. Na podstawie uzyskanych wyników zaproponowano schemat przemiany etanolu do acetonu w fazie gazowej na badanych katalizatorach.

Słowa kluczowe: katalizator, aceton, etanol, adsorpcja, aldehyd octowy, woda, para, spektroskopia, metoda, 1-buten, 2-buten, centra Lewisa.

Introduction

One of the main monomers widely used in the petrochemical industry is acetone. The known methods of its production are multistage and are realized by high temperature and pressure (Anikeev et al., 2004). Owing to the development of the more economical and easily realized processes it is one of the current tasks in basic organic synthesis (Alalwan et al., 2021). Acetone is produced both by the cumene method and from isopropyl alcohol. Recently, ethanol is considered as a possible initial raw material for the production of acetone. Prospects for the use of ethanol as initial raw material is stipulated by large renewed resources for its production (Mohammed Ali et al., 2022). The growing interest in ethanol production through the processing of agricultural products and waste materials from the food and woodworking industries will undoubtedly encourage further advancements in the method of producing acetone from ethanol (Llorca et al., 2001). Research has shown that ethanol in the presence of zinc-containing catalysts is converted to acetone with high yield. This paper presents the results of research on the methods of converting ethanol to acetone on ZnO:CaO = 9:1 catalyst (Mustafayeva, 2022).

By altering the main process parameters, the composition of the tested catalysts, and the initial reagents, it is possible to significantly change the selectivity of the conversion of alcohols into ketones. As a result, due to the complex reaction, certain products are obtained. Both the absolute yield of each product and their relative proportions can undergo changes under the influence of the catalyst and the reaction medium (Mikayilova and Mustafayeva, 2020). The obtained experimental and literature data demonstrate that in contact oxidation, water plays a role as a source of hydrogen atoms and hydroxyl groups, thereby contributing to the formation of a new chemical composition of the catalyst surface. When adsorbed on certain areas of the catalyst surface, a water molecule forms proton-donor centers. These functions of water cause the oxidizing ability of the catalyst and the selectivity of its action to change (Salge et al., 2005). The positive effect of water vapor is due to a change in the surface properties of the catalyst. To determine the acid-base properties of the surface of the zinc oxide system in the presence of water vapor, we would use the IR spectroscopic and indirect method – the isomerization of butene-1 to butene-2 in the region close to the catalyst (Baghirova, 2021).

Problem statement

Zinc-calcium oxide catalyst was prepared using the co-precipitation method, involving the suspension of calcium

carbonate and zinc carbonate in water. The resulting mixtures were first evaporated and dried at 100–110°C. Subsequently, they underwent a stepwise calcination process, initially at 250–300°C, followed by a final calcination at 550°C for a duration of 10 hours. The activity of the catalysts was examined using a flow unit with a quartz reactor in the temperature range of 250–500°C. The research results indicated that the catalyst with a composition ratio of 9:1 exhibited the highest level of activity. The yield of acetone on it reached 86.9% at the full conversion of ethanol. The gaseous reaction products were analyzed on an LKhM-8 chromatograph. The ester of diethylene glycol and n-butyric acid deposited on INZ-600 was used as a sorbent. Liquid reaction products and starting materials were analyzed on a CHROM-5 chromatograph with a flame ionization detector using a column filled with polysorb. The adsorption of water vapor and ammonia on the catalyst surface was investigated using IR spectroscopy.

The catalytic activity of ZnO-CaO systems in the reactions of ethanol conversion in the presence of atmospheric oxygen, water vapor, and the conversion of 1-butene to 2-butenes was studied on a combined laboratory setup. The setup provides for the reaction of ethanol conversion and isomerization of 1-butene on a flow unit with an integral reactor, as well as kinetic studies on the conversion of ethanol to acetone on a Timoshenko-designed non-gradient reactor at atmospheric pressure. 1-butene was obtained directly at the plant at a temperature of 310–340°C by degradation of n-butyl alcohol on aluminium oxide, pre-treated with a solution of KOH (0.06% wt.) to suppress isomerization of 1-butane. The non-gradient part of the combined setup makes it possible to carry out kinetic studies of ethanol transformations. Ethanol with water vapor, passing through the evaporator, enters the non-gradient reactor, which is heated by an automatically controlled furnace. To prevent condensation of reaction products in the piston part of the reactor, nitrogen is supplied to this part. From the bottom of the reactor, the products enter the refrigerator, where liquid products are condensed, and gaseous products, after analysis, are released into the atmosphere.

Problem solution

The main product of the reaction of the conversion of ethanol to acetone on the ZnO-CaO catalyst is acetone, the yield of which strongly depends on the composition of the reaction environment. As the by-products – acetaldehyde, ethylene, and other hydrocarbons are formed (Baghirova, 2020). When oxygen is present, the yield of products of destructive and complete oxidation also increases greatly, while in the absence of oxygen and only when water vapor is present, selectivity,

conversion, and acetone yield increase. Based on physicochemical and kinetic studies, a probable pathway for the conversion of ethanol in the presence of water vapor can be suggested (Baghirova, 2021). It has been established that water, directly participating in the process of ethanol conversion, increases acetone conversion and yield. During the dissociation of water vapor on the catalyst surface, hydrogen likely plays a role in the slow stage, thereby accelerating the rate at which ethanol is converted to acetone. Furthermore, water vapor changes the acid-base properties of the surface, leading to an increased concentration of active centers.

Problem solution method

Considering that water vapor is directly involved in the reaction of acetone formation, we have studied the adsorption of water vapor and ammonia on the surface of the ZnO-CaO catalyst using the IR spectroscopic method. Water vapor adsorption at 100°C followed by its desorption is characterized by the emergence of absorption bands 1085 cm^{-1} (ν_{OH}), 1610 cm^{-1} ($\delta_{\text{H}_2\text{O}}$) and a wide band spanning the range of 2600–3700 cm^{-1} (ν_{OH}), with a peak at 3500 cm^{-1} , which suggests the presence of coordinated water molecules on the catalyst's surface. The adsorption of ammonia on a sample with pretreated water vapor leads to the emergence of specific absorption bands in the IR spectra. These bands include peaks at 1085, 1240, 1445, 1610, 1670 cm^{-1} , along with a broad absorption band spanning the range of 2600–3700 cm^{-1} , with a maximum at 3260 cm^{-1} and a shoulder at 3500 cm^{-1} . It is known that the absorption bands at 1240, 1610 cm^{-1} can be attributed to Lewis acid sites (MeNH_3), and the absorption bands at 1445 cm^{-1} can be assigned to Brønsted acid sites (NH_4^+). It is evident that the adsorption of water vapor at 300°C, followed by subsequent desorption, results in the appearance of absorption bands at 1085, 1610 cm^{-1} and a wide absorption band spanning the range of 2600–3700 cm^{-1} with a pronounced peak at 3500 cm^{-1} in the IR spectrum (Figure 1).

It should be noted that the intensities of the absorption bands change depending on the water vapor adsorption temperature. During the subsequent adsorption of NH_3 , absorption bands at 1085, 1240, 1445, 1610 cm^{-1} and a broad absorption band spanning the range of 2600–3700 cm^{-1} with a shoulder at 3500 cm^{-1} are observed in the IR spectra.

In addition to the emergence of a new absorption band 3270 cm^{-1} , the intensities of the absorption bands in the region of 1000–1700 cm^{-1} also change (Figure 1).

Water vapor is probably adsorbed on the catalyst surface in molecular form at low temperatures, while at higher temperatures dissociatively, that is, water as a donor of hydrogen

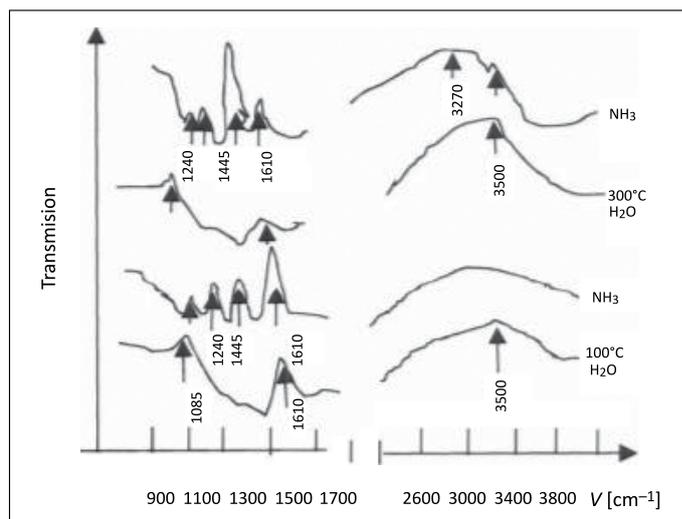


Figure 1. IR spectra of water vapor and ammonia adsorbed on the surface of the ZnO-CaO catalyst

Rysunek 1. Widma IR pary wodnej i amoniaku zaadsorbowanych na powierzchni katalizatora ZnO-CaO

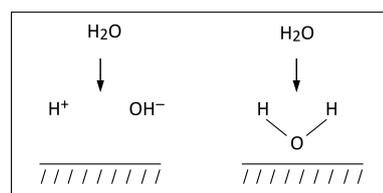


Figure 2. Schematic illustration of water vapor adsorption on the the catalyst surface

Rysunek 2. Schematyczna ilustracja adsorpcji pary wodnej na powierzchni katalizatora

atoms and hydroxyl groups contributes to the formation of a new chemical composition of the catalyst surface (Figure 2).

The influence of water vapor on the degree of conversion of 1-butene to 2-butenes on the ZnO-CaO catalyst was investigated (Table 1).

Table 1 shows that without water vapor, 1-butene turns into 2-butene at 150°C, and the yield of cis-2-butene is greater than that of trans-2-butene, and this trend persists as the temperature increases. At all temperatures, the ratio of trans-2-butene to cis-2-butene ranges from 0.6 to 0.65, and the total yield of 2-butene at 350°C is 34.5%.

The introduction of water vapor into the reaction zone changes both the total yield of 2-butene and the ratio of trans-2-butenes to cis-butenes-2. At low temperatures, the yield of cis-2-butene is less than without water vapor, and the total yield of 2-butene also decreases.

The data obtained confirm that, with increasing temperature, water vapor, being dissociatively adsorbed on the catalyst surface, contributes to an increase in the formation of the number of active centers, which ultimately affect the degree of isomerization.

Table 1. The degree of conversion of 1-butene to 2-butenes on the ZnO-CaO = 9:1 catalyst**Tabela 1.** Stopień konwersji 1-butenu do 2-butenu na katalizatorze ZnO-CaO = 9:1

T [°C]	The degree of conversion of 1-butene without water vapor 1-butene: air = 1:9 [% mass]			The degree of conversion of 1-butene with water vapor 1-butene : air : water vapor = 1:6:3 [% mass]			
	cis-2-butene	trans-2-butene	trans cis	cis-2-butene	trans-2-butene	trans cis	cis
150	0.95	0.56	0.59	0.49	0.50	1.02	
200	4.40	2.70	0.62	1.30	1.70	1.31	
250	7.30	4.70	0.63	3.10	4.70	1.50	
300	15.4	9.50	0.62	6.63	10.70	1.60	
350	20.9	13.6	0.63	9.40	17.20	1.80	

It is worth noting that the yield of cis butene-2 in the absence of water vapor is higher, likely due to molecular adsorption on Lewis centers. Consequently, in the presence of water vapor, the yield of cis butene-2 is reduced. At higher temperatures, the adsorption of water vapor in molecular form is not observed. Through adsorption, in the IR spectrums the spectral bands, characterize the coordinative connected water is appeared. At higher temperatures, water undergoes dissociative adsorption, leading to an increase in the concentration of Brønsted centers. This, in turn, accelerates the second pathway, which involves the formation of trans butene-2.

Changes of the acid-base properties of oxide catalyst surfaces in the presence of water vapor can be assessed using various physico-chemical methods. In the case of determining the acid-base properties of the ZnO-CaO catalyst, the isomerization reaction of 1-butene to 2-butenes in the presence of water vapor was used. It is established that the isomerization of 1-butene to 2-butene can take place in two ways: a mechanism involving hydrogen transfer (A) and a heterogenic- ion (B) mechanism (Figure 3).

It is known that pathway (A) occurs on Lewis centers, and pathway (B) on the Brønsted centers. Through molecular adsorption, water vapor tends to slow down the conversion of 1-butene in 2-butene (the first pathway (A)), and in the case of water vapor dissociation, it leads to an increase in the isomerization of butene-1 into trans butene-2 (the second pathway (B)).

There are suggestions in the literature that acetone is formed from two molecules of ethanol through the interaction of an intermediate acetic acid with a carbonate-carboxylate complex, with the further formation of acetone (Figure 4).

It is evident from the proposed mechanism that acetic acid should be found in the reaction products, and carbonate-carboxylate fragments should be present on the catalyst surface. However, a detailed examination of the existing experimental data shows that the mechanism outlined above fails to adequately account for the following facts:

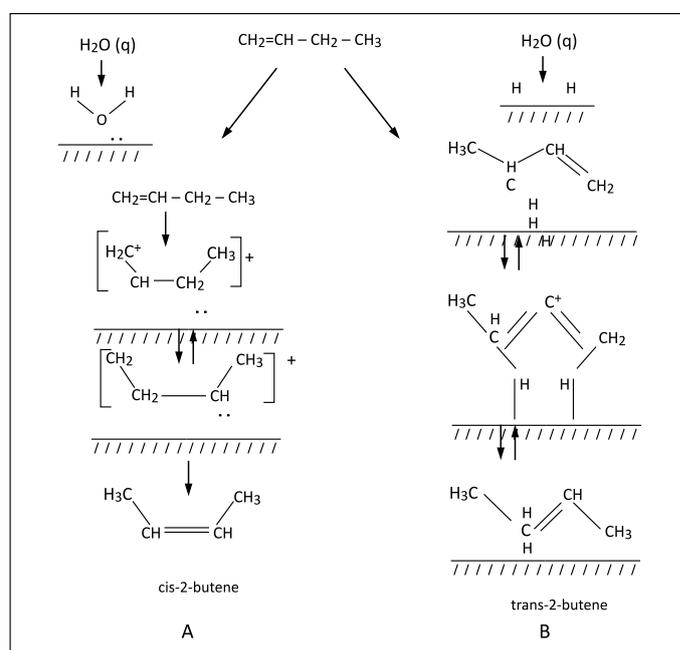


Figure 3. Conversion pathway of 1-butene in trans 2-butene
Rysunek 3. Przebieg konwersji 1-butenu w trans 2-buten

- the formation of acetic acid is not observed in the reaction products;
- in the presence of water vapor, the amount of carbonate-carboxylate complex on the catalyst surface decreases;
- when 1 molecule of acetone is formed, 1 molecule of CO₂ is not formed, i.e. at 86.5% yield of acetone, the CO₂ yield is no more than 5%.

In order to reveal the pathways for the formation of acetaldehyde, ethylene, and acetone on the ZnO-CaO catalyst from ethanol, we carried out a series of experiments on the joint gas-phase transformation of these products.

As evident from the data in Table 2, the reaction products of the co-conversion of ethanol with acetic acid are ethyl acetate, acetone and, in small amounts, ethylene and carbon dioxide. It can be seen that the ZnO-CaO = 9:1 catalyst does not show high activity in the reaction of the co-conversion of ethanol

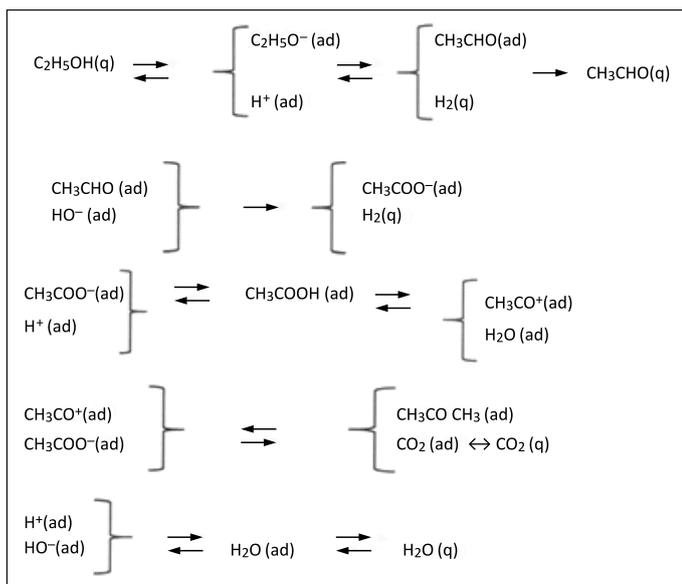


Figure 4. Acetone formation

Rysunek 4. Tworzenie się acetonu

Table 2. Study on the co-conversion of ethanol with acetic acid, acetaldehyde with ethylene and acetaldehyde with acetic acid on a ZnO-CaO catalyst ($P_{H_2O} = 20$ kPa; $V_{cat} = 5$ cm³)

Tabela 2. Badanie współkonwersji etanolu z kwasem octowym, aldehydu octowego z etylenem i aldehydu octowego z kwasem octowym na katalizatorze ZnO-CaO ($P_{H_2O} = 20$ kPa; $V_{cat} = 5$ cm³)

T [°C]	Yield of reaction products		
	CH ₃ COCH ₃	CH ₃ COOC ₂ H ₅	CO ₂
C ₂ H ₅ OH : CH ₃ COOH = 2 : 1			
300	1.1	3.1	0.2
350	4.3	5.8	1.4
400	8.2	10.2	3.2
CH ₃ CHO : C ₂ H ₄ = 2 : 1			
300	2.0	0	0.91
350	11.8	0	2.00
400	26.4	0	5.70
CH ₃ CHO : CH ₃ COOH = 2 : 1			
300	0.0	0.2	0.0
350	1.5	0.5	1.1
400	2.1	1.0	2.4

and acetic acid into acetone (the acetone yield does not exceed 10%), i.e. acetone is not formed as a result of the interaction of ethanol with intermediate complexes of acetic acid.

Based on previous research, it was assumed that acetone is formed through the stage of complexation of acetaldehyde with ethylene. Therefore, it was of interest to study the reaction of the co-conversion of acetaldehyde and ethylene on the ZnO-CaO = 9:1 catalyst. The results of these studies are presented in Table 2. This reaction shows that acetone is formed in sufficiently large quantities, and carbon dioxide in

small quantities, while the formation of ethyl acetate was not observed at all. At the same time, Table 1 illustrates that the zinc-calcium catalyst exhibits practically negligible activity in the production of acetone, ethyl acetate, and carbon dioxide during the co-conversion of acetaldehyde and acetic acid.

The conversion of ethanol to acetone in the presence of water vapor can be represented as follows. In the first stage, ethanol is converted at the Brønsted centers to acetaldehyde, and at the Lewis centers to ethylene. The number of Brønsted centers in the presence of water vapor is greater than the number of Lewis centers. Then, a complex is formed on the catalyst surface from two molecules of adsorbed acetaldehyde and ethylene, which decomposes into 2 molecules of acetone.

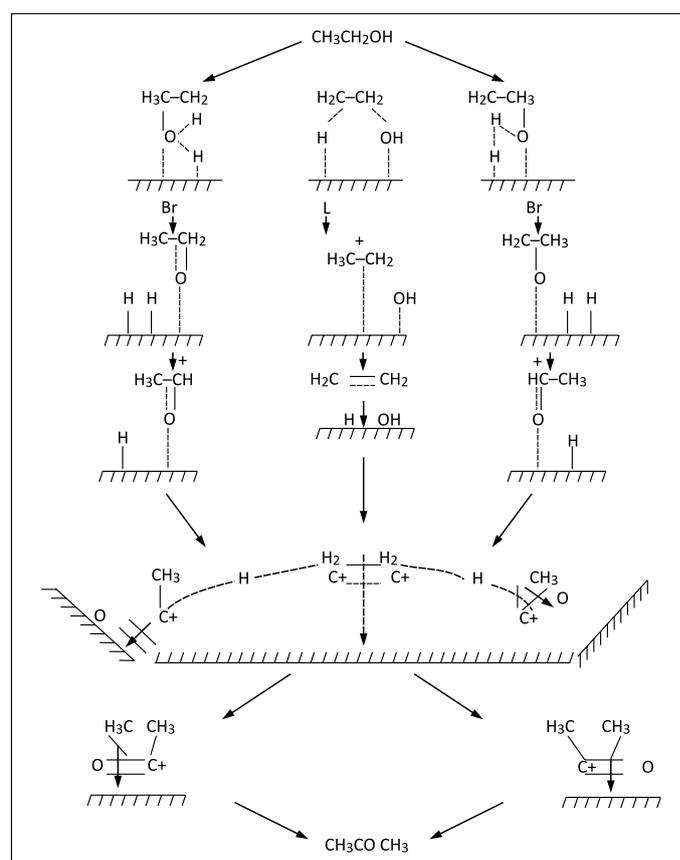


Figure 5. Supposed mechanism for the conversion of ethanol to acetone

Rysunek 5. Przypuszczalny mechanizm konwersji etanolu do acetonu

Conclusions

- In this study, the adsorption of water vapor and ammonia on the surface of the ZnO-CaO 9:1 catalyst was investigated by infrared spectroscopy methods. It is shown that water vapor at low temperatures is adsorbed on the catalyst surface in molecular form, while at higher temperatures in a dissociative form.

2. Based on the findings, a mechanism and scheme for the conversion of ethanol to acetone on the ZnO-CaO 9:1 catalyst was proposed. It is shown that acetone is formed through the stage of complexation of acetaldehyde with ethylene.

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