

# Liquid phase synthesis of ethyl-*tert*-butyl ether: The relationship between acid, adsorption and catalytic properties of zeolite catalysts

N.V. Vlasenko<sup>a</sup>, Yu.N. Kochkin<sup>a</sup>, A.M. Puziy<sup>b,\*</sup>

<sup>a</sup> Institute of Physical Chemistry National Academy of Sciences of Ukraine, Prospect Nauki 31, 03039 Kiev, Ukraine

<sup>b</sup> Institute for Sorption and Problems of Endoecology National Academy of Sciences of Ukraine, Naumov St. 13, 03164 Kiev, Ukraine

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## Abstract

The role of acid centers of natural zeolites in synthesis of ethyl-*tert*-butyl ether (ETBE) was investigated. The method for calculation of desorption energy distribution from stepwise desorption experiment was proposed. The method allows to calculate continuous desorption energy distribution of surface sites using different probes (ammonia, ethanol, *iso*-butylene, etc.).

The correlation between rate of ETBE synthesis and concentration of weak acid sites ( $E_{\text{NH}_3} = 70\text{--}75 \text{ kJ mol}^{-1}$ ) was found. It has been shown that during ETBE synthesis *iso*-butylene is activated mainly on medium and strong acid centers and forms one type of surface complex, while ethanol forms two types of adsorbed complexes. Low energy surface ethanol complexes ( $E = 53\text{--}60 \text{ kJ mol}^{-1}$ ) located on weak acid centers of zeolites were found to be active in ETBE synthesis. These complexes govern the catalytic activity of catalyst in ETBE synthesis.

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**Keywords:** Ethyl-*tert*-butyl ether; *iso*-butylene; Ethanol; Ammonia; Acidity

## 1. Introduction

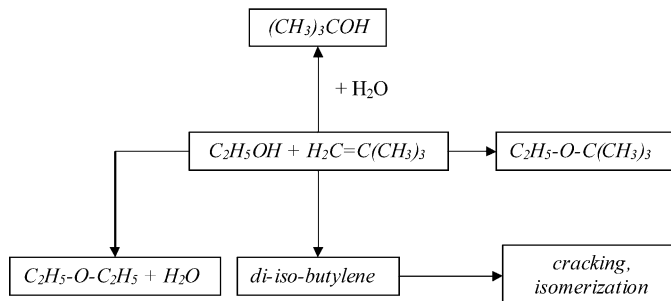
The key characteristic of catalysts used in numerous processes, proceeding by acid–base mechanism, is their acidity distribution (the nature of acid centers, their concentration and acidity) [1–7].

The matching of acidity strength of catalyst to the basic strength of the substrate requires an evaluation method of acid strength of the catalyst. The adsorption of ammonia is commonly used for evaluation of surface acidity of catalysts [1,8–12]. High basicity and low size of ammonia molecule allow characterizing all acid centers independently from their nature, localization and strength.

It is generally believed that the activity of catalyst in acid catalyzed processes is connected with total amount of surface acidic sites having heat of ammonia desorption higher than  $80\text{--}90 \text{ kJ mol}^{-1}$  [13–15]. Recently, the significance of weak acid surface groups in some catalytic reactions occurring in soft conditions was reported [16–18]. Nonetheless, so far the unified approach to the role of weak and strong acid sites in transfor-

mation on catalyst's surface is not yet developed. Due to this, the understanding of experimental data is often troublesome, especially when main reaction is accompanied by several simultaneous side reactions.

One such process is heterogeneous catalytic synthesis of ethyl-*tert*-butyl ether (ETBE) from ethanol and *iso*-butylene. The main reaction is accompanied by several side reactions, namely, dimerization of *iso*-butylene, dehydration of ethanol etc. In presence of water in reactants the *tert*-butanol is formed:



Due to complex nature, the process is a suitable model to reveal the role of different acid sites of catalyst in reaction pathways. Moreover, the adsorption of reactants is of interest for elucidation of the mechanism of the reaction.

\* Corresponding author. Tel.: +38 44 4529328; Fax: +38 44 4529327.  
E-mail address: [alexander.puziy@ispe.kiev.ua](mailto:alexander.puziy@ispe.kiev.ua) (A.M. Puziy).

To investigate the effect of acid surface sites on reaction pathways the catalysts with similar structure and nature but having different acid characteristics are required. In present study, the catalysts obtained by calcinations of ammonia form of natural mordenite–clinoptilolite at different temperatures have been used. The present study was aimed at elucidation of relationship between acid, adsorption and catalytic characteristics of zeolite catalysts in reaction of synthesis of ethyl-*tert*-butyl ether (ETBE) from ethanol and *iso*-butylene.

## 2. Experimental

HCMK catalysts were prepared from mordenite–clinoptilolite rocks of Transkarpatian deposits (Ukraine). The composition of raw mordenite–clinoptilolite was investigated elsewhere [19]. The preparation included ion exchange of naturally occurring cations ( $\text{Na}^+$ ,  $\text{K}^+$ ) with  $\text{NH}_4^+$  in ammonia aqueous solution followed by calcination for 4 h at different temperatures ranging from 250 to 600 °C. The heat treatment temperature (in °C) is indicated in the name of sample.

Stepwise thermodesorption of ammonia experiments were carried out at 50–500 °C under vacuum (constant pressure 0.133 Pa was maintained by vacuum pump) using thermogravimetric apparatus with quartz spring balance of McBain type. Prior to experiment, the sample was outgassed at its calcination temperature until constant weight was attained (typically 1.5–2 h). Then temperature was lowered to ambient conditions and ammonia was admitted into sample stepwise (10–20 Torr) until no uptake was observed. Finally, excess of ammonia was evacuated at 50 °C. Then the temperature was raised stepwise (5 °C  $\text{min}^{-1}$  between steps, step size 50 °C) with holding at constant temperature until constant weight was achieved (typically 10–15 min). Thus, experimental conditions corresponded to desorption at constant pressure, i.e. desorption isobar.

Stepwise thermodesorption of ethanol and *iso*-butylene were obtained at the same apparatus at temperature range from 80 to 180 °C corresponding to the temperature range of investigated catalytic reaction.

Catalytic activity of HCMK catalysts was investigated in flow reactor with fixed bed. Sample loading was 1.5  $\text{cm}^3$ , grain size 1–2 mm. Molar ratio ethanol/*isobutylene* was 1.5, LHSV 1  $\text{h}^{-1}$ , carrier gas helium. The pressure was 1.0 MPa, temperature range 80–180 °C.

Reaction products were analyzed using gas chromatograph Agat (“Mashpriborkomplekt”, Russia) equipped with Chromaton N-AW column with 10% Carbowax 600 (3 mm i.d., 2 m length) and catharometer.

### 2.1. Theoretical model

Desorption energy distribution from solid adsorbent can be written in the form of integral equation:

$$\Theta_{\text{exp}}(P, T) = \int_{Q_{\text{min}}}^{Q_{\text{max}}} \Theta_{\text{loc}}(P, T, Q) f(Q) dQ \quad (1)$$

where  $\Theta_{\text{exp}}$  is experimentally measured adsorption,  $\Theta_{\text{loc}}$  the kernel function describing local adsorption on surface center with energy  $Q$  at pressure  $P$  and temperature  $T$ , and  $f(Q)$  distribution energy function. The distribution function is a sought-for quantity that characterizes the catalyst surface.

For experiments carried out under constant pressure at different temperatures (stepwise thermodesorption), the local adsorption is described by isobar of adsorption. The isobar can be deduced from Langmuir equation taking into account the temperature dependence of constant  $K$ :

$$\Theta = \frac{KP}{1 + KP} \quad (2)$$

where constant  $K$  according to kinetic theory of gases [20,21] is:

$$K = \frac{N_A \sigma_0 \tau_0}{\sqrt{2\pi MRT}} \exp\left(\frac{Q}{RT}\right) \quad (3)$$

where  $N_A$  is Avogadro’s number,  $\sigma_0$  area of adsorbed molecule,  $\tau_0$  period of oscillation of the adsorbed molecule perpendicular to surface of adsorbent,  $M$  mass of adsorbed molecule,  $R$  and  $T$  have their usual meaning and  $Q$  energy of interaction of adsorbed molecule with surface of adsorbent, i.e. heat of adsorption. Period of oscillation,  $\tau_0$ , could be estimated as [20]:

$$\tau_0 = \frac{h}{kT} \quad (4)$$

Adsorption integral Eq. (1) have been solved with respect to distribution function  $f(Q)$  using CONTIN method [22–24].

## 3. Results and discussion

### 3.1. Surface acidity

Stepwise thermodesorption of ammonia gives quantitative information on energy of desorption from surface sites. Depending on the nature of adsorbed molecule, the method can probe different surface sites. Ammonia thermodesorption is often used for determination of acid surface sites. Fig. 1 shows desorption energy distributions calculated from ammonia thermodesorption experiments. The distributions show heterogeneous character of surface of HCMK catalysts. Depending on calcination temperature, catalysts exhibit from one to three types of surface groups, which may be classified into three groups: weak (50–100  $\text{kJ mol}^{-1}$ ), medium (100–135  $\text{kJ mol}^{-1}$ ) and strong (>135  $\text{kJ mol}^{-1}$ ) acid sites.

With the increasing heat treatment temperature the surface of catalyst becomes more energetically heterogeneous. Zeolite HCMK-250 exhibits only weak acid centers with mean energy about 72.3  $\text{kJ mol}^{-1}$ , while sample heat treated at 400 °C (HCMK-400) shows two types of acid sites (weak and medium). Further increase of heat treatment temperature brings into existence additional strong acid surface sites with energy 141–146  $\text{kJ mol}^{-1}$ . Acid characteristics of HCMK catalysts are listed in Table 1.

With the increase in calcination temperature the total amount of acid surface groups first increases at 400 °C and then steadily

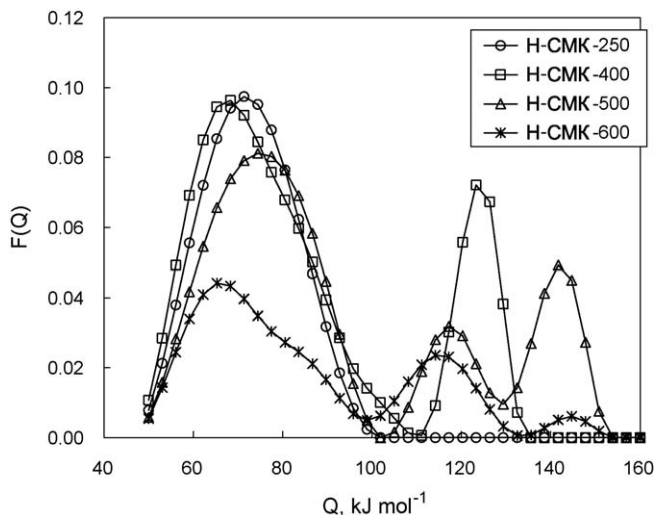
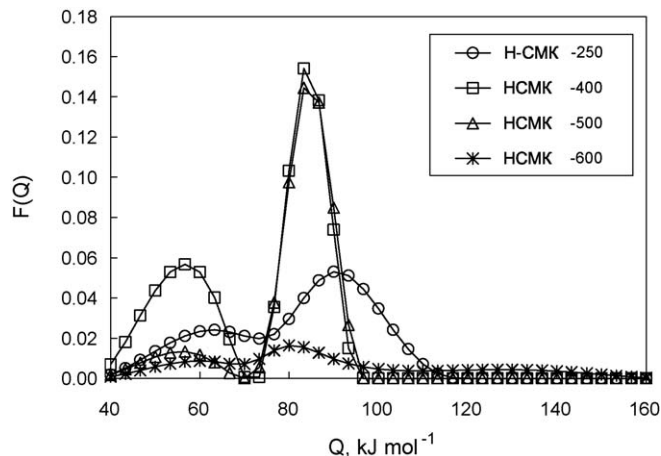
Fig. 1. NH<sub>3</sub> desorption energy distributions.

Fig. 2. Ethanol desorption energy distributions.

decreases. The density of weak acid surface sites follows the same trend—slight increase at 400 °C and then steadily decreases. Medium acid groups emerged at 400 °C, their concentration decreased at 500 °C and remained the same at 600 °C. Strong acid groups emerged at calcinations temperature 500 °C, their quantity decreased at 600 °C.

### 3.2. Adsorption of reactants

#### 3.2.1. Ethanol

C<sub>2</sub>H<sub>5</sub>OH-desorption energy distributions (Fig. 2) shows that two types of surface complexes are formed on surface of HCMK catalysts at 80–250 °C experimental range having mean heat of desorption 54–60 kJ mol<sup>-1</sup> and 84–90 kJ mol<sup>-1</sup>.

Average desorption energies and amount of each type of surface complexes with ethanol are listed in Table 2. Total amount of adsorbed ethanol decreases in the same manner with total amount of acid sites as follows:

$$\text{HCMK-400} > \text{HCMK-500} > \text{HCMK-250} > \text{HCMK-600}$$

This result indicates that adsorption of ethanol occurs on all acid centers of catalysts. The concentration of low energy ethanol complexes decreases in the same manner with weak acid site concentration as follows:

$$\text{HCMK-400} > \text{HCMK-250} > \text{HCMK-500} > \text{HCMK-600}$$

Table 1  
Surface acidity characteristics of HCMK catalysts

Parameter	Type	Heat treatment temperature (°C)			
		250	400	500	600
Mean desorption energy (kJ mol <sup>-1</sup> )	Weak (w)	72.3	72.9	74.8	71.8
	Medium (m)	–	122.9	117.6	115.5
	Strong (s)	–	–	140.6	145.5
Site density (mmol g <sup>-1</sup> )	Weak (w)	2.77	2.94	2.51	1.27
	Medium (m)	0.00	0.89	0.45	0.46
	Strong (s)	0.00	0.00	0.68	0.05
	Total	2.77	3.83	3.64	1.78

Table 2  
Ethanol adsorption characteristics of HCMK catalysts

Parameter	Type	Heat treatment temperature (°C)			
		250	400	500	600
Mean desorption energy (kJ mol <sup>-1</sup> )	Weak	59.4	54.5	53.8	57.7
	Strong	90.6	84.3	84.3	85.9
Surface concentration (mmol g <sup>-1</sup> )	Weak	0.59	1.07	0.24	0.20
	Strong	1.25	1.74	1.78	0.48
	Total	1.84	2.81	2.02	0.68

Obviously, such dependence suggests that low energy ethanol complexes are located on weak acid centers of zeolites.

#### 3.2.2. *iso*-Butylene

Fig. 3 shows desorption energy distribution calculated from desorption of *iso*-butylene in temperature range of 80–250 °C. Table 3 lists parameters of *iso*-butylene desorption energy distribution. The distributions show only one peak suggesting that *iso*-butylene is adsorbed on sole type of surface sites. Desorption energy increases with increasing heat treatment temperature of the catalyst, while the concentration of adsorbed complexes of *iso*-butylene is at maximum for sample HCMK-500 obtained at 500 °C.

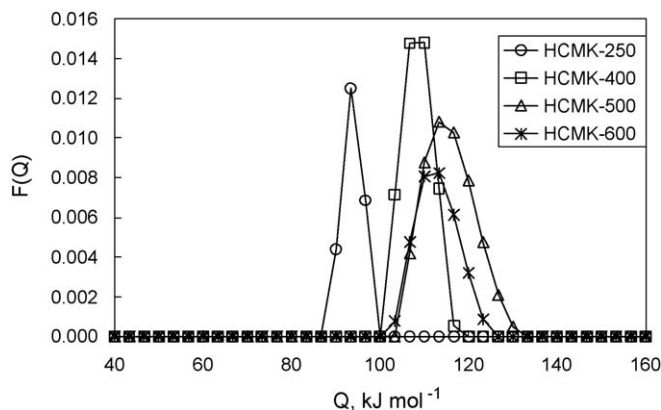
Fig. 3. *iso*-Butylene desorption energy distributions.

Table 3  
*iso*-Butylene adsorption characteristics of HCMK catalysts

Parameter	Heat treatment temperature (°C)			
	250	400	500	600
Mean desorption energy (kJ mol <sup>-1</sup> )	96.3	109.2	119.5	123.0
Surface concentration (mmol g <sup>-1</sup> )	0.08	0.15	0.16	0.11

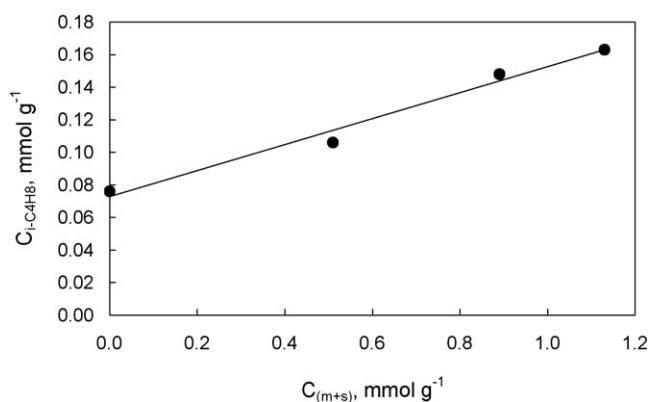


Fig. 4. Dependence of concentration of *iso*-butylene surface complexes on total amount of medium and strong acid sites on surface of zeolites.

*iso*-Butylene exhibits higher desorption energies (90–125 kJ mol<sup>-1</sup>) than ethanol. This fact could be explained by higher basicity of *iso*-butylene ( $\pi$ -base) as compared to ethanol ( $n$ -base). The higher basicity of organic substance the more strongly acidic surface sites required for stabilization of surface complexes. Indeed, the concentration of adsorbed *iso*-butylene does correlates with total medium and strong acid centers (Fig. 4).

Table 4  
Catalytic characteristics of HCMK catalysts

Catalyst	$T$ (°C)	$X_{iso-C_4H_8}$ (%)	Selectivity ( $S$ ) (%)				Yield ( $Y$ ) (%)			
			ETBE	<i>tert</i> -BuOH	DEE	Di- <i>iso</i> -C <sub>4</sub> H <sub>8</sub>	ETBE	<i>tert</i> -BuOH	DEE	Di- <i>iso</i> -C <sub>4</sub> H <sub>8</sub>
HCMK-250	100	8.62	66.68	33.32	0	0	5.75	2.87	0	0
	120	19.68	69.18	30.82	0	0	13.61	6.06	0	0
	140	25.72	83.85	16.15	0	0	21.57	4.15	0	0
	160	20.78	85.08	9.59	5.33	0	17.68	1.99	1.10	0
	180	15.78	66.03	9.94	24.03	0	10.42	1.56	1.56	0
HCMK-400	100	8.04	67.25	25.67	7.08	0	5.40	2.06	0.56	0
	120	27.31	74.60	23.98	1.41	0	20.37	6.54	0.38	0
	140	30.78	74.52	15.78	9.70	0	22.94	4.85	2.98	0
	160	24.72	65.93	12.46	21.61	0	16.30	3.08	5.34	0
	180	24.19	24.67	7.88	58.87	8.57	5.97	1.90	14.24	2.07
HCMK-500	100	4.48	69.19	30.81	0	0	3.10	1.38	0	0
	120	7.44	70.56	29.44	0	0	5.25	2.19	0	0
	140	16.68	83.14	16.86	0	0	13.87	2.81	0	0
	160	17.67	76.49	15.70	7.79	0	13.51	2.77	1.37	0
	180	21.10	53.66	10.52	22.95	12.86	11.32	2.22	4.84	2.71
HCMK-600	100	2.81	67.55	32.45	0	0	1.90	0.91	0	0
	120	2.58	68.51	31.49	0	0	1.77	0.81	0	0
	140	7.27	79.48	20.52	0	0	5.78	1.49	0	0
	160	12.11	87.72	12.23	0	0	10.62	1.48	0	0
	180	11.64	82.32	13.96	3.71	0	9.58	1.62	0.43	0

Free from medium and strong acid centers catalyst HCMK-250 exhibits the lowest amount of surface complexes of *iso*-butylene. However, the fact that adsorption of *iso*-butylene on HCMK-250 is in evidence suggests at least partial contribution of weak acid centers having desorption energy close to energy of medium acid centers. Desorption energy of *iso*-butylene for catalyst HCMK-250 is lowest among others.

### 3.3. Catalytic characteristics of HCMK catalysts

All catalysts were active in synthesis of ethyl-*tert*-butyl ether. Experiments showed the presence of all possible reaction products: ethyl-*tert*-butyl ether, diethyl ether, di-*iso*-butylene and *tert*-butyl alcohol (Table 4).

Temperature dependence of *iso*-butylene conversion goes through maximum for all samples (Fig. 5). With the increase of calcinations temperature the maximum conversion temperature increases from 140 °C for HCMK-250 and HCMK-400 to 160–180 °C for HCMK-500 and HCMK-600.

The highest conversion of *iso*-butylene was observed on catalyst HCMK-400. However, this catalyst is least selective since in all temperatures the formation of di-ethyl ether was observed and at 180 °C di-*iso*-butylene was formed.

Dependence of total conversion rate of *iso*-butylene on its desorption energy (Fig. 6) shows that the most active surface sites are those having energy of 100–110 kJ mol<sup>-1</sup>. The correlation was made for 140 °C where the maximum yield of ETBE was observed. Interesting enough is the fact that the most active catalysts are free from strong acid sites (catalysts HCMK-250 and HCMK-400). It is likely that strong acid sites cause the increase of desorption energy of *iso*-butylene, which is not optimal.

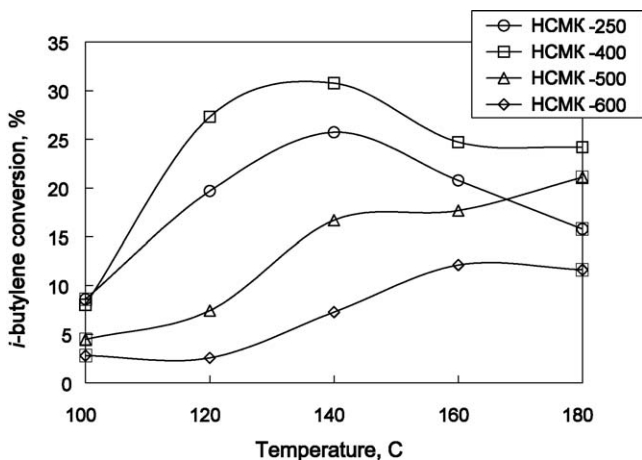


Fig. 5. Temperature dependence of *iso*-butylene conversion on HCMK catalysts.

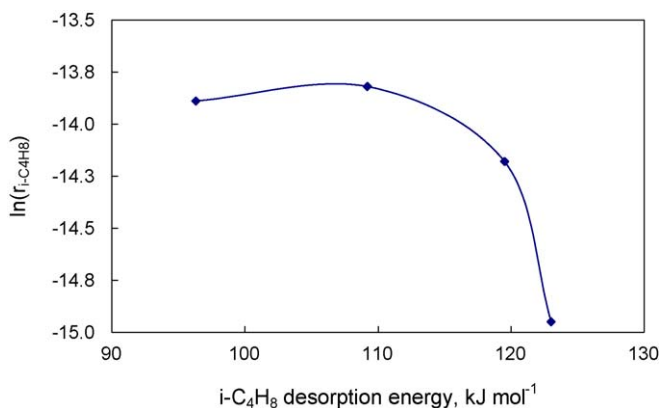


Fig. 6. Dependence of log conversion rate ( $r$ ,  $\text{mol s}^{-1} \text{g}^{-1}$ ) of *iso*-butylene at  $140^\circ\text{C}$  on *iso*-butylene desorption energy.

### 3.3.1. Synthesis of ethyl-*tert*-butyl ether

Synthesis of ethyl-*tert*-butyl ether is target reaction pathway. Contrary to wide-spread opinion that activity of catalyst is determined by total acidity of surface such dependence was not observed in our experiments. Instead, the strict correlation between the rate of formation of ethyl-*tert*-butyl ether and density of weak acid sites was found (Fig. 7). Correlation was made for  $140^\circ\text{C}$  where maximum yield of ETBE was observed. Con-

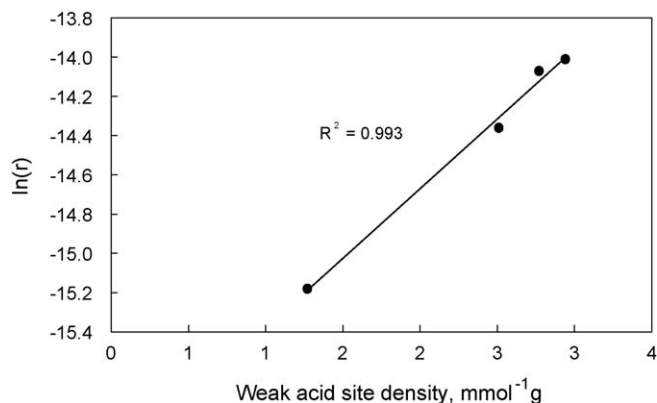


Fig. 7. Relationship between log rate of ETBE synthesis ( $r$ ,  $\text{mol s}^{-1} \text{g}^{-1}$ ) at  $140^\circ\text{C}$  and weak acid sites density.

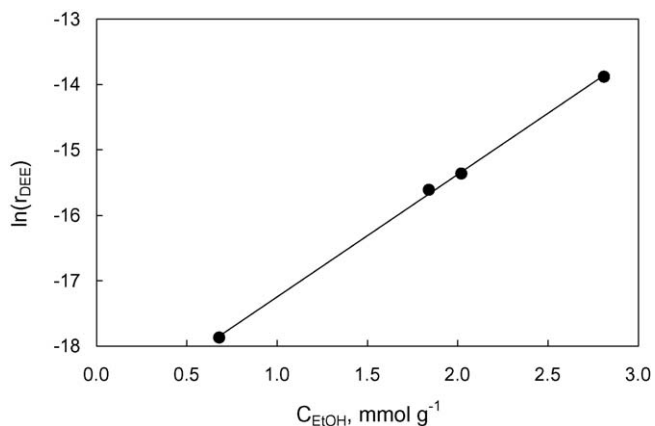


Fig. 8. Dependence of DEE formation log rate ( $r$ ,  $\text{mol s}^{-1} \text{g}^{-1}$ ) at  $180^\circ\text{C}$  on surface concentration of ethanol.

sidering the fact that weak acid site density is proportional to weakly bound ethanol ( $E = 54\text{--}60 \text{ kJ mol}^{-1}$ ) it is safe to believe that the rate of ETBE formation is determined by adsorption of ethanol on weak acid sites.

### 3.3.2. Formation of di-*iso*-butylene and di-ethyl ether

At elevated temperatures the synthesis of ETBE is accompanied by formation of condensation products of the same molecules—*iso*-butylene with formation of di-*iso*-butylene and ethanol with formation of di-ethyl ether (DEE). It would appear reasonable that these processes require increased concentrations of corresponding reactants. Indeed, the formation of di-*iso*-butylene was observed only for samples HCMK-400 and HCMK-500 which show the highest concentrations of *iso*-butylene adsorbed complexes (Table 3). Catalyst HCMK-500 with the highest concentration of *iso*-butylene complexes shows the highest selectivity to di-*iso*-butylene.

The same dependence observed for DEE formation—the higher adsorption of ethanol the higher is rate of DEE formation (Fig. 8). Correlation was made for  $180^\circ\text{C}$  where selectivity to DEE was at maximum. The dependence suggests the participation of all ethanol molecules adsorbed on the surface of catalyst. It can be inferred that the process proceeds through condensation of weak and strong surface complexes with ethanol.

### 3.3.3. Formation of *tert*-butanol

The formation of *tert*-butanol (*tert*-BuOH) from *iso*-butylene and water, introduced with ethanol (azeotrope) or formed via DEE pathway, was observed at all temperatures. Since *tert*-BuOH is formed from only one main reactant (*iso*-butylene), the dependence of activity of catalyst towards *tert*-BuOH on adsorption characteristics can be revealed. Selectivity to this product decreases with increasing temperature, so correlation was made for  $100^\circ\text{C}$ .

The existence of sole type of adsorption complexes with *iso*-butylene suggests the relationship between the rate of *tert*-BuOH synthesis and heat of desorption of *iso*-butylene. Fig. 9 shows that such linear relationship does exist. However, the sample HCMK-400 is out of the general trend observed. This can be explained by enhanced activity of HCMK-400 catalyst to DEE

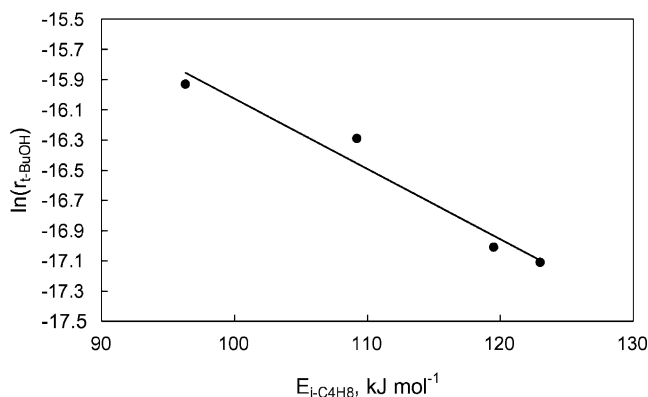


Fig. 9. Dependence of *tert*-BuOH formation log rate ( $r$ , mol s<sup>-1</sup> g<sup>-1</sup>) at 100 °C on surface concentration of *iso*-butylene.

synthesis at all investigated temperatures. The water released by this reaction increases the rate of *tert*-BuOH formation.

#### 4. Conclusions

The data obtained suggests the mechanism of transformations occurred in *iso*-C<sub>4</sub>H<sub>8</sub> + C<sub>2</sub>H<sub>5</sub>OH (+H<sub>2</sub>O) system in presence of zeolite catalyst. This gives an insight into the role of different acid centers in adsorption of reactants and thereby in catalytic characteristics of zeolites.

The method for calculation of desorption energy distribution from stepwise thermodesorption experiment was proposed. The method allowed calculating desorption energy of ammonia (probe molecule for acid characteristics) as well as ethanol and *iso*-butylene (reactants in ETBE synthesis).

Ammonia stepwise thermodesorption experiments allowed to reveal three types of acid surface groups, which may be classified as weak (50–100 kJ mol<sup>-1</sup>), medium (100–135 kJ mol<sup>-1</sup>) and strong (>135 kJ mol<sup>-1</sup>) acid sites.

Ethanol forms two types of surface complexes with energy 55–60 kJ mol<sup>-1</sup> and 80–90 kJ mol<sup>-1</sup>. Comparison of concentration of ethanol surface complexes with acid site concentration suggests that low energy ethanol complexes are located on weak acid centers of zeolites. Ethanol surface complexes located on weak acid sites are active in synthesis of ETBE. For this reason, the activity of catalyst in ETBE synthesis is determined by concentration of weak acid sites.

*iso*-Butylene is adsorbed mainly on medium and strong acid centers in the form of surface complex of sole type though differing in strength. The most reactive are surface complexes with desorption energy of 100–110 kJ mol<sup>-1</sup>. The rate of interaction

of *iso*-butylene with both ethanol (ETBE synthesis) and with water (formation of *tert*-BuOH) is determined by adsorption of second reactant.

High surface concentration of reactants causes condensation of molecules of the same type – diethyl ether from ethanol and di-*iso*-butylene from *iso*-butylene.

The present investigation showed that effective catalyst for ETBE synthesis must have high concentration of weak acid surface centers ( $E_{NH_3} = 50\text{--}100$  kJ mol<sup>-1</sup>) for selective activation of ethanol and minimum amount of strong acid centers ( $E_{NH_3} > 135$  kJ mol<sup>-1</sup>).

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