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The kinetics of ethanol adsorption from the aqueous phase onto zeolite NaZSM-5

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Abstract The kinetics of the isothermal adsorption of ethanol from an aqueous solution onto a hydrophobic zeolite of the NaZSM-5 type in the temperature range 298–333 K was investigated. Specific shape parameters of the adsorption degree curves were determined. The changes in the specific shape parameters of the adsorption degree curves with temperature were determined. The kinetic parameters of ethanol adsorption (E_a, $\ln A$) were determined by the initial rate, the saturation rate and the maximum rate methods as well as from the Johnson, Mehl and Avramy equation. The kinetic model of ethanol adsorption $kt = [1 - (1-\alpha)^{1/3}]$ was determined by the "model fitting" method.

Ethanol adsorption from aqueous solution onto NaZSM-5 is a kinetically controlled process limited by the rate of three-dimensional movement of the boundary layer of the adsorption phase. A model for the mechanism of ethanol adsorption onto NaZSM-5 is suggested on the basis of the kinetic model. Ethanol molecules in aqueous solution are associated in clusters. The activation energy of the adsorption process corresponds to the energy required for the detachment of an ethanol molecule from a cluster and its adsorption onto the zeolite.

Keywords Kinetics · Ethanol · Aqueous phase · NaZSM-5

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Abbreviations

C_0	ethanol concentration in aqueous solution before adsorption (wt%)
C	ethanol adsorption in aqueous solution after infinite adsorption time (wt%)
m_s	mass of solution (g)
m	mass of zeolite (g)
α	degree of adsorption
x	specific adsorption capacity (g/g)
$x_{\max}$	experimentally determined maximal value x at given temperature (g/g)
t_L	period of linearity (min)
t_s	saturation adsorption time (min)
v_{in}	initial adsorption rate (%/min)
v_s	saturation adsorption rate (%/min)
$v_{\max}$	maximal adsorption rate (%/min)
$E_{a,\max}$	activation energy determined by maximal adsorption rate (kJ/mol)
$\ln A_{\max}$	pre-exponential factor determined by maximal adsorption rate (min^{-1})
n_A	kinetics constant Johnson–Mehl–Avrami equation
k	kinetics constant Johnson–Mehl–Avrami equation
$E_{a,A}$	activation energy determined applying JMA equation
$\ln A_A$	pre-exponential factor determined applying JMA equation
t_N	normalized adsorption time
$t_{0.9}$	adsorption time at which $\alpha = 0.9$ at given temperature
$f(\alpha)$	analytical expression describing the kinetic model
$g(\alpha)$	$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt$ integral form of kinetic model
k_M	model constant of adsorption rate
$E_{a,M}$	activation energy determined by model-fitting method

$\ln A_M$	pre-exponential factor determined by model-fitting method
R_0	initial effective zeolites pores radius (cm)
V_0	specific zeolite adsorption volume before adsorption (cm^3/g)
R_t	effective pore radius at adsorption time t
V_t	pore volume of zeolite at adsorption time t
S_t	effective surface area of boundary phase at adsorption time t
k_a	adsorption rate constant shrinking-core model
$k^* = k_a/R_0$	
R	linear regression coefficient
ΔH_c	ethanol condensation enthalpy

1 Introduction

One of the main problems that needs to be solved in order to economically produce anhydrous ethanol and biogasoline is a reduction in the energy consumption in the process of dehydration of aqueous ethanol solutions obtained from fermentation broths. When distillation is used to obtain dehydrated ethanol, 50% of the total energy is consumed during this process (Carmo and Gubulin 1997). Selective ethanol adsorption onto hydrophobic zeolitic materials is an alternative to dehydration via distillation, which is presently the most promising procedure for anhydrous ethanol production (Flanigen et al. 1978; Milestone and Bibby 1981; Pitt et al. 1983; Luong 1982; Robert et al. 1983).

Lin et al. (1989) determined the adsorption isotherms of different alcohol–water systems on a hydrophobic zeolite, type silicalite-1. Einicke et al. (1989, 1991, 1995, 2004) investigated the influence of the molar ratio SiO_2/Al_2O_3 on the selectivity and adsorption characteristics of a zeolite for ethanol from an ethanol-water mixture. Farhadpour et al. (1996) examined the separation of an ethanol-water mixture on a bi-dispersion of a hydrophobic zeolite, silicalite, and observed that diffusion had a dominant influence on the kinetics and selectivity of the separation. Falamaki et al. (2001) studied the kinetics of ethanol adsorption from an aqueous solution onto a zeolite of the (Na-1,6-hexanediol)-ZSM-5 type and proved that micropore diffusion had a major influence on the kinetics of the adsorption. Selective ethanol removal from an ethanol/water mixture was investigated using various hydrophilic membranes. Adnadjevic et al. (1997) investigated the effects of different physico-chemical properties of different hydrophobic zeolites and pervaporation properties of composite PDMS-zeolite membranes. Lin et al. (2003) reported that a silicalite-1 membrane is the best membrane so far for this separation. Their membrane had a 14 mol/m^2 h flux and ethanol/water separation factor of 106 for a 5 wt% ethanol/water feed at T = 333 K. Matsuda et al. (2002) used a silicone-coated silicalite-1 membrane on a stainless support to obtain a higher separation factor (125), but a significantly lower flux (3.7 mol/m^2 h) for 4 wt% ethanol/water feed at T = 303 K. Li et al. (2002) reported a 34 mol/m^2 h flux and a separation factor of 96 for a 1 wt% ethanol/water feed using B-ZSM-11 membrane. Bowen et al. (2003) found that adsorption selectivity for linear alcohols/water increases as the alcohol carbon number increases because the alcohol adsorption strengths increase in this order. In the work of Bowen et al. (2004) a review on the physico-chemical properties of different types of zeolites and pervaporation properties of zeolites membranes is given.

Bearing in mind the lack of information concerning the kinetics of ethanol adsorption from water solution by hydrophobic zeolites, in this paper the kinetics of ethanol isothermal adsorption on zeolite type NaZSM-5 was investigated in detail. The aim of this investigation was to determine the kinetics model of the adsorption process; the kinetics parameters (activation energy and pre-exponential factor) and to determine the required parameters for theoretical modeling and optimization of the adsorption separation of ethanol from an ethanol/water mixture.

2 Materials and methods

NaZSM-5 zeolite was synthesized from a reaction mixture at the Faculty of Physical Chemistry, Belgrade (Adnadjević 1997).

For the zeolite synthesis, the following materials were employed: commercial silicasol (30 wt% SiO_2), aluminum sulphate (Merck, GR grade), sodium hydroxide (Merck, p.a), tetrapropylammoniumbromide (TPABR) and distilled water. Zeolite crystallization was conducted in a stirred stainless steel autoclave, having V = 200 mL volume, at temperature T = 493 K in duration of t = 2 h. A reaction mixture, with the following molar content, $10Na_2O\cdot Al_20_3\cdot 92SiO_2\cdot 36H_20$, was formed by mixing NaOH solution with the silicasol and aluminum sulfate solution. Into the reaction mixture during the crystallization, the crystallization nucleus (5 wt%) having the following molar content: $0.2Na_2O\cdot 0.05TPABR\cdot 2SiO_2\cdot 10.5H_20$, was introduced at T = 298 K for a duration of t = 48 h. After the crystallization was completed, the reaction mixture was cooled and mother liquor and zeolite cake were separated by filtration. Zeolite cake was washed with distilled water and dried at T = 343 K. The basic physico-chemical properties of the synthesized zeolite are given in Table 1.

The zeolite was thermally activated at 623 K for 6 hours, then cooled and kept in a desiccator before using it. Aqueous solutions of ethanol (10 wt%) were prepared from 99.5% ethanol p.a. (Hemos, Belgrade) and bidistilled water.

Table 1 Basic physico-chemical properties of NaZSM-5 zeolite

Physico-chemical property	Value
Degree of crystallinity (%)	≥99
SiO_2, wt%, anhydrous basic	94.70
Al_2O_3, wt%, anhydrous basic	3.22
Na_2O, wt%, anhydrous basic	2.08
SiO_2/Al_2O_3, molar ratio	90
Surface area BET, m^2/g	420
Crystal size SEM, µm	0.2–1

2.1 Determination of the specific adsorption capacity of zeolite to ethanol

Zeolite powder (5 g) was added to 50 g of a 10 wt% aqueous ethanol solution and the adsorption vessel was placed in the thermostat at a pre-determined temperature. During the adsorption process, the adsorption system was homogenized by stirring at 400 rpm Samples were taken from this adsorption system at regular time intervals. After centrifugation, the concentration of ethanol remaining in the supernatant was determined by measuring its refractive index using a Reichart-Jung Auto Abbe refractometer.

The specific adsorption capacity of zeolite for ethanol (x) at a given temperature after certain adsorption period can be calculated from the equation:

$$x = \frac{(C_0 - C)}{m} \times m_s \qquad \text{(g/g)} \tag{1}$$

where: C_0—the initial concentration of the ethanol solution before adsorption (wt%), C—the concentration of the ethanol solution after a certain adsorption time (wt%), m_s—the mass of the solution (g), m—the mass of zeolite (g).

The adsorption degree of ethanol (α) was calculated from equation:

$$\alpha = \frac{x}{x_{\max}} \tag{2}$$

where: $x_{\max}$ = the maximum specific adsorption capacity of zeolite for ethanol at a given temperature (see Fig. 1).

2.2 Kinetics model of ethanol adsorption at zeolite type NaZSM-5

Assume that ethanol adsorption from the ethanol/water mixture by zeolite type NaZSM-5 at all the investigated temperatures takes place by an identical mechanism and that the zeolite pore system (adsorption volume) consists of a great number of identical spherical pores with equal effective diameter. Those pores become occupied by the adsorbed ethanol at same time. The main stages of the adsorption mechanism are the following:

1. Instantaneous ethanol adsorption in the outer adsorption centers (pores) of the zeolite particle.
2. Formation of a continuous adsorbed-phase in the zeolite, which consists of already adsorbed ethanol molecules.
3. Controlled three-dimensional (spherical) growth of the adsorbed layer, i.e. at the phase boundary, within the adsorbent particle.
4. Slowing down of the rate of uptake due to the saturation of the zeolite's pores with ethanol molecules.

Let us assume that the value of the zeolite's specific pore volume before adsorption is V_o and the value of the effective pore radius is R_o. The specific occupied pore volume of the zeolite at adsorption time (t) has a value of V_t and it has penetrated to an effective pore radius of R_t, then:

$$1 - \alpha = \frac{V_t}{V_0} = \frac{\frac{4}{3}\pi R_t^3}{\frac{4}{3}\pi R_0^3} = \frac{R_t^3}{R_0^3} \tag{3}$$

i.e.

$$R_t = R_0(1-\alpha)^{1/3} \tag{4}$$

According to this model, the adsorption rate is given by the expression (5):

$$\frac{d(1-\alpha)}{dt} = \frac{k_a S_t}{V_0} = k_a\left[\frac{4\pi R_t^2}{\frac{4}{3}\pi R_0^3}\right] \tag{5}$$

where S_t is the effective surface area of the phase-boundary interface and k_a is the rate constant of the shrinking-core rate model, i.e.

$$\frac{d\alpha}{dt} = \frac{3k_a(1-\alpha)^{2/3}}{R_0} \tag{6}$$

By variable separation and integration of (6), taking into account the conditions $t = 0$, $\alpha = 0$, (7) representing the kinetics model for ethanol adsorption on zeolite is obtained:

$$1 - (1-\alpha)^{1/3} = k^* t \tag{7}$$

where $k^* \approx k_a/R_0$.

3 Results and discussion

The temperature dependence of specific adsorption capacity of the zeolite for ethanol vs. adsorption time (kinetic curve) is shown in Fig. 1.

The isothermal changes of the degree of ethanol adsorption with adsorption time (adsorption degree curves) are shown in Fig. 2.

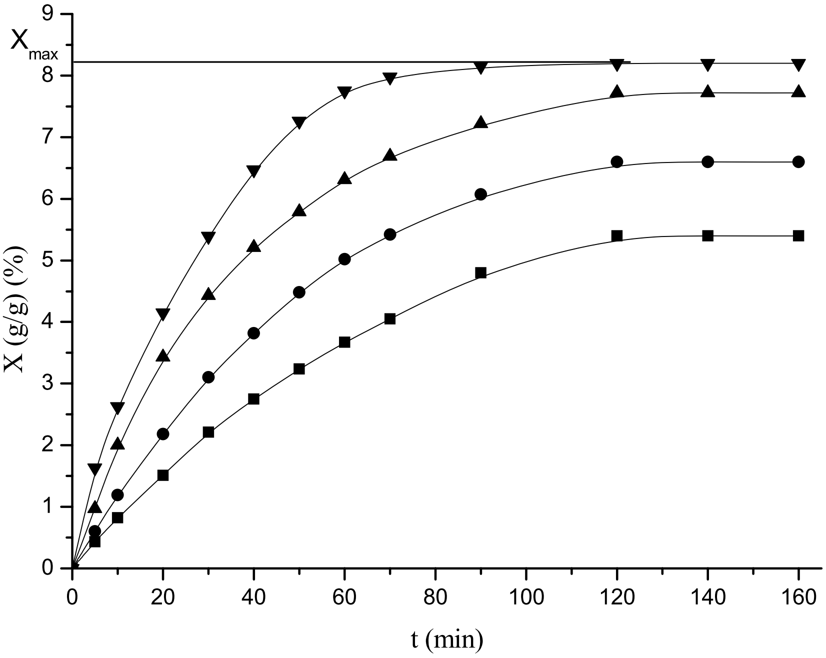

Fig. 1 Isothermal specific adsorption capacity curves of ethanol adsorption (■ 298 K, ● 308 K, ▲ 313 K, ▼ 333 K), $x_{\max}$—the maximum specific amount of ethanol adsorbed on NaZSM-5 at a given temperature

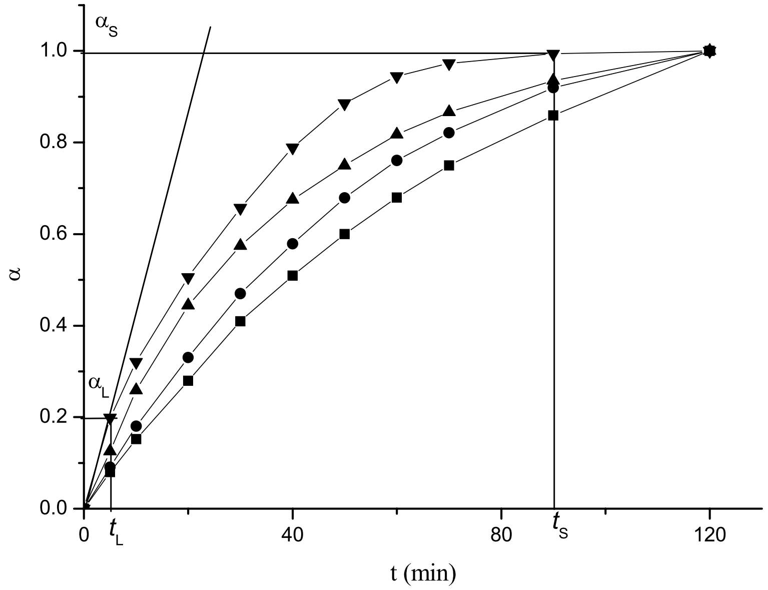

Fig. 2 Isothermal adsorption degree curves of ethanol adsorption on NaZSM-5 (■ 298 K, ● 308 K, ▲ 313 K, ▼ 333 K); *straight line* marks period of linearity; t_L—period of linearity, t_S—saturation time, α_L—the degree of ethanol adsorption at t_L, α_S—the degree of ethanol adsorption at t_S

Three distinct regions of adsorption kinetics can be clearly seen from the adsorption degree curves, i.e., linear, non-linear and saturation regions.

In order to determine the temperature influence on the shape of those adsorption degree curves the so called shape parameters are defined: period of linearity (t_L, see Fig. 2), initial adsorption rate (v_{in}), saturation time (t_s) and saturation adsorption rate (v_s).

The period of linearity is the time interval within which the degree of adsorption increases linearly with the adsorption time. The initial adsorption rate is defined as the adsorption rate during this linear region of the adsorption curve. The saturation time represents the adsorption time required to achieve $x_{\max}$(as shown in Fig. 1). The saturation adsorption rate can be calculated from the equation:

$$v_s = \frac{x_{\max}}{t_s} \tag{8}$$

The adsorption curve parameters at different temperatures are given in Table 2.

According to the results given in Table 2, it can easily be seen that the values t_L and t_s decrease while those of v_{in} and v_s increase with increasing temperature. Since the increases of v_{in} and v_s with temperature are exponential, the kinetic

Table 2 Change of shape parameters of the adsorption curve with temperature

T (K)	t_L (min)	v_{in} (min^{-1})	t_s (min)	v_s (%/min^{-1})	$x_{\max}$ (%)	$E_{\mathrm{a,in}}$ (kJ/mol)	$\ln(A_{\mathrm{in}}/\mathrm{min}^{-1})$ (kJ/mol)	R	$\mathrm{E_{a,f}}$	$\ln(A_s/\mathrm{min}^{-1})$	R
298	28.38	0.014	144.99	0.035	5.07	25.6 ± 0.3	6.15 ± 0.05	0.993	22.1 ± 0.2	5.95 ± 0.05	0.993
308	12.54	0.022	140.97	0.050	7.07						
313	10.00	0.025	127.57	0.061	7.74						
333	4.62	0.043	87.33	0.092	8.07						

R—linear regression coefficient

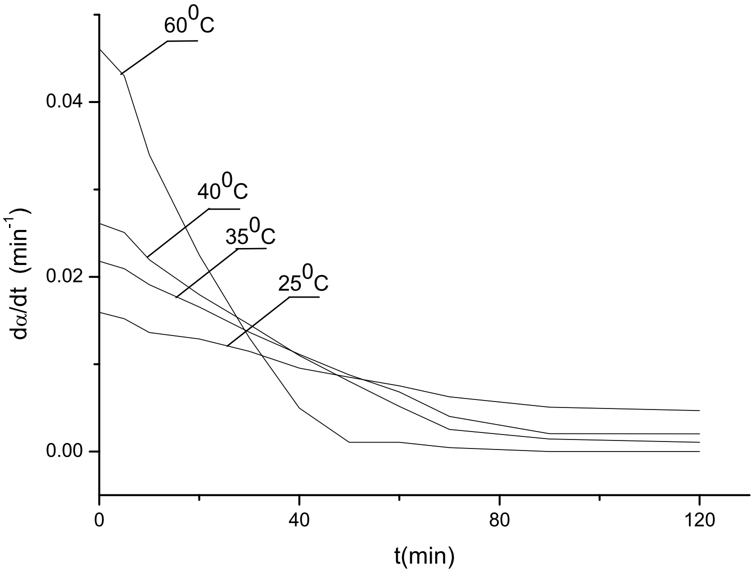

Fig. 3 Isothermal dependance of ethanol adsorption rate on adsorption time

parameters of the initial and saturation stage of the adsorption of ethanol onto NaZSM-5 ($\mathrm{E_{a,in}}$, $\ln \mathrm{A_{in}}$, $\mathrm{E_{a,s}}$, $\ln \mathrm{A_s}$) can be determined by applying the Arrhenius equation. The results are given in columns 6 to 9 of Table 2.

The kinetics parameters of adsorption were also determined by the maximal rate method (Day et al. 1989), based on the experimentally determined isothermal adsorption degree curves. Accordingly, ethanol adsorption rates were determined as a function of the adsorption duration at various fixed temperatures.

The ethanol adsorption rates as a function of the adsorption time, at various temperatures, are presented in Fig. 3.

At all the investigated temperatures, the adsorption rate significantly decreased with the adsorption time, while the maximal adsorption rate was achieved at the initial stage of the adsorption. The observed changes in adsorption rate with the adsorption duration were characteristic of the so called decelerator processes and the kinetics models related to them (F1, R2 and R3) (Brown and Galwey 1989).

The change in the maximum rate of adsorption ($v_{\max}$) with temperature is given in Table 3.

Since the increase of $v_{\max}$ with temperature is exponential, the kinetic parameters of ethanol adsorption, $\mathrm{E_{a,max}}$ and $\ln \mathrm{A_{max}}$, can be determined using the Arrhenius equation. The results are given in columns 3 and 4 of Table 3.

Table 3 Change of maximum adsorption rate with temperature

T (K)	$v_{\max}$ (min^{-1})	$E_{\mathrm{a,max}}$ (kJ/mol)	$\ln(\mathrm{A_{max}}/\mathrm{min}^{-1})$	R
298	0.0162	25.5 ± 0.3	6.10 ± 0.05	0.977
308	0.0181			
313	0.0262			
333	0.0462			

Because the process of ethanol adsorption on zeolite type NaZSM-5 appears to take place at the interface of a shrinking core, the kinetics of this process can be well–described by the Johnson–Mehl–Avrami equation (JMA) (Johnson and Mehl 1939; Avrami 1939)

$$\alpha = 1 - \exp[-kt^{n_A}] \tag{9}$$

where k is overall rate constant and n_A is kinetics constant, the so called Avrami's exponent, which depends on the mechanism and on the region in which the process takes place.

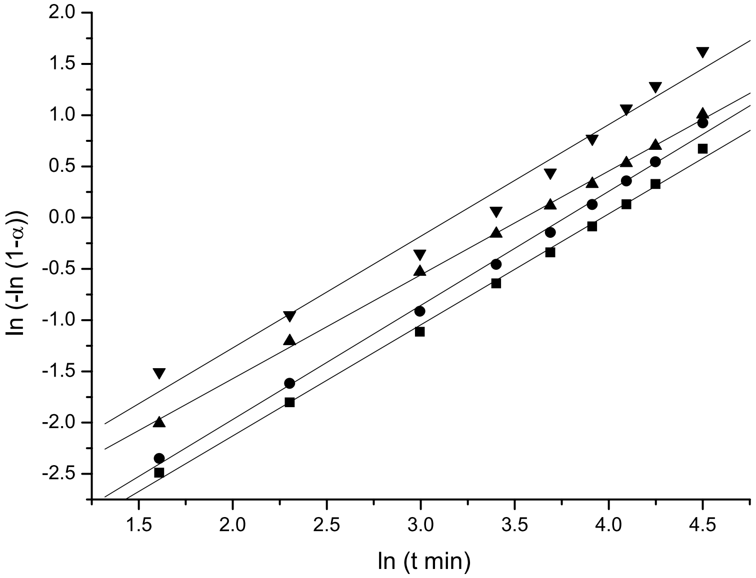

Fig. 4 Isothermal dependence of $\ln[-\ln(1-\alpha)]$ vs $\ln t$ at different temperatures (■ 298 K, ● 308 K, ▲ 313 K, ▼ 333 K)

Table 4 Change of parameters of JMA equation (n and k) with temperature

T (K)	n	k_{A} (min^{-1})	$E_{\mathrm{a,A}}$ (kJ/mol)	$\ln(\mathrm{A_A}/\mathrm{min}^{-1})$	R
298	1.08	0.014	20.6 ± 0.2	4.05 ± 0.05	0.897
308	1.11	0.015			
313	1.10	0.027			
333	1.09	0.032			

The kinetics of the ethanol adsorption was modeled using the JMA equation and the kinetics parameters were determined, i.e., by the Johnson–Mehl–Avrami (JMA) method in which plots of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ for different temperatures are made, and are given in Fig. 4.

The isothermal dependence of $\ln[-\ln(1-\alpha)]$ on $\ln t$ are linear over almost the whole range of adsorption.

The constants of the JMA equation (n_A and k) at different temperatures are given in Table 4.

The temperature of the adsorption process has a little influence on the Avrami's exponent. The calculated values of n_A were 1.07 to 1.10, which was in accordance with previous work by Sharp et al. (1966), and also supports the validity of the ethanol adsorption kinetics model: $[1-(1-\alpha)^{1/3}] = kt$.

The Avrami's kinetics constant (k) increased exponentially with the adsorption temperature. Bearing that in mind, applying Arrhenius equation the kinetics parameters $\mathrm{E_{a,A}}$ $\ln \mathrm{A_A}$ of the adsorption process by JMA methods were determined and listed in Table 4.

Bearing in mind the generality of the JMA equation and the differences in values of the kinetic parameters obtained by different methods (the initial rate, saturation rate, and maximal rate methods), the "model-fitting procedure" (Vyazovkin and Wight 1999) was used to determine the kinetics parameters for the various kinetics models. The "model-fitting procedure" is widely used to determine the suitability of various kinetic reaction models for solid state reactions. The kinetic reaction models are classified in 5 groups according to the reaction mechanism: (1) power law reactions, (2) phase-controlled reactions, (3) reaction order, (4) reactions described by the Avrami equation, and (5) diffusion controlled reactions.

Accordingly, the model-fitting method was used to determine a suitable kinetic model of these adsorption experiments. Specifically, the models were compared graphically and analytically with the experimentally obtained function $\alpha_e = f(t_N)$, and using theoretical functions for different reaction models (Brown et al. 1980), $\alpha = f(t_N)$, where t_N is the so-called normalized time:

$$t_N = \frac{t}{t_{0.9}} \tag{10}$$

where $t_{0.9}$ is the adsorption time at $\alpha = 0.9$.

The kinetic models used to determine the model best describing the kinetics of ethanol adsorption are shown in Table 5.

Figure 5 shows the plot of $\alpha = f(t_N)$ for the theoretical reaction models presented in Table 5 (solid curves in Fig. 5) and the experimental plots of $\alpha_e = f(t_N)$ for the ethanol adsorption process at different temperatures.

Experimentally determined normalized isothermal adsorption degree curves, at all of the investigated temperatures are identical in shape and they all conform to a single model. According to the results shown in Fig. 5, with great confidence, it can be stated that the kinetics of ethanol ad-

Table 5 Set of kinetic reaction models used for determination of model of ethanol adsorption kinetic; f(α)—analytical expression describing the kinetic model; g(α)—$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = kt$ integral form of kinetic model

Model	Reaction mechanism	f(α)	g(α)
P1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
P2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
R1	Zero-order (Polany-Winger equation)	1	α
R2	Phase-boundary controlled reaction (contracting area, i.e., bidimensional shape)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
R3	**Phase-boundary controlled reaction (contracting volume, i.e., tridimensional shape)**	$\mathbf{3(1-\alpha)^{2/3}}$	$\mathbf{[1-(1-\alpha)^{1/3}]}$
F1	First-order (Mampel)	$(1-\alpha)$	$-\ln(1-\alpha)$
F2	Second-order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
F3	Third-order	$(1-\alpha)^3$	$0.5[(1-\alpha)^{-2}-1]$
A2	Avrami-Erofe'ev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami-Erofe'ev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami-Erofe'ev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
D1	One-dimensional diffusion	$1/2\alpha$	α^2
D2	Two-dimensional diffusion (bidimensional particle shape)	$1/[-\ln(1-\alpha)]$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	Three-dimensional diffusion (tridimensional particle shape) Jander equation	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
D4	Three-dimensional diffusion (tridimensional particle shape) Ginstling-Brounshtein	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

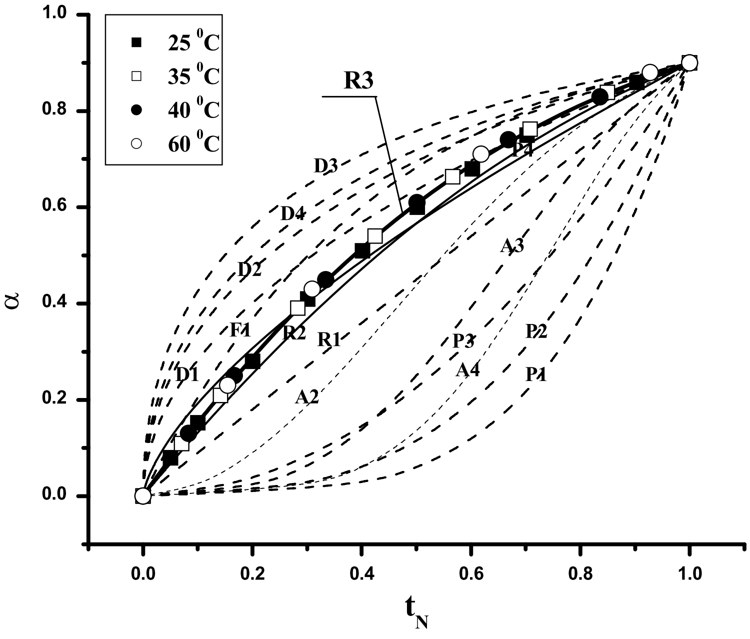

Fig. 5 Plot $\alpha = f(t_N)$ for theoretical kinetics models of ethanol adsorption at different temperatures

sorption onto NaZSM-5 at all the investigated temperatures can be best described by the kinetic reaction model:

$$[1-(1-\alpha)^{1/3}] = k_M t \tag{11}$$

where k_M is kinetic model constant.

The isothermal dependences of $1-(1-\alpha)^{1/3}$ vs. adsorption time are shown in Fig. 6.

Over the whole range of adsorption degree, the dependences $1-(1-\alpha)^{1/3}$ on the adsorption time are linear, which confirms that the correct model was se-

Fig. 6 Isothermal dependances of $1-(1-\alpha)^{1/3}$ vs adsorption time (■ 298 K, ● 308 K, ▲ 313 K, ▼ 333 K)

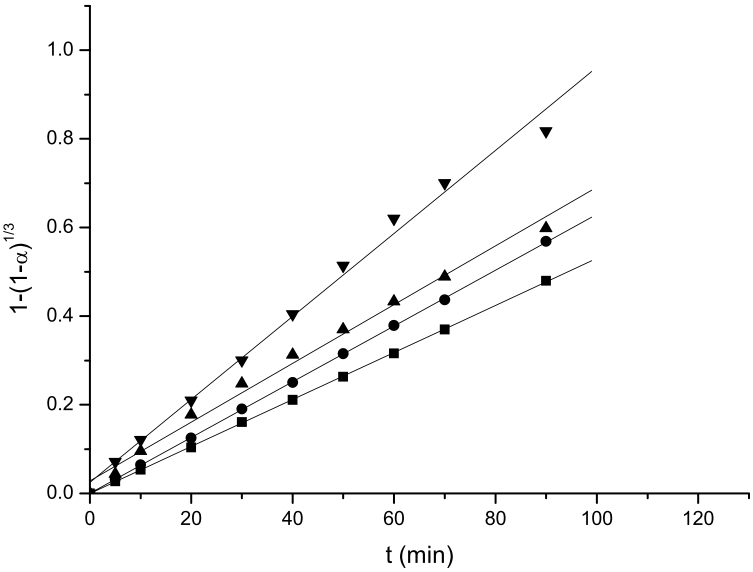

Table 6 Change of model constant of ethanol adsorption rate with temperature

T (K)	k_M (min^{-1})	$E_{a,M}$ (kJ/mol)	ln(A_M/min^{-1})	R
298	0.053	26.7 ± 0.3	8.90 ± 0.06	0.999
308	0.076			
313	0.090			
333	0.170			

lected for describing the adsorption of ethanol onto zeolite NaZSM-5.

The values of the kinetic model constant for the rate of ethanol adsorption at different temperatures are given in Table 6.

Since the increase k_M with temperature is exponential, the model parameters ($E_{a,M}$ and $\ln A_M$) of ethanol adsorption can be determined by applying the Arrhenius equation. The obtained results are given in columns 3 and 4 of Table 6.

The kinetics model of the adsorption process, which is validated in this paper, as well as the determined values of the kinetic parameters and the constants of JMA equation indicate that ethanol adsorption onto NaZSM-5 zeolite is not a diffusion controlled process, but a process controlled by an apparent shrinking core, described by the rate of the movement of the interface.

The values of the kinetic parameters obtained by the different methods differ significantly. The maximum values of the kinetic parameters were obtained on the basis of the kinetic reaction model ($E_{a,M} = 26.7$ kJ/mol; $\ln A_M = 8.9$), while the minimum values were obtained by applying the JMA equation ($E_{a,J} = 20.6$ kJ/mol; $\ln A_J = 4.05$).

The values of the kinetic parameters obtained by application of the initial rate and maximal rate methods were very similar to one another. This is logical since the initial rate and maximal rate were practically identical. The other differences in the values of the kinetic parameters obtained by the different methods are the consequence of the limitations of the considered method at one or several parts (initial, saturation, etc.) of this adsorption process.

The kinetic model of the adsorption process determined by the "model fitting" procedure is identical with the theoretically obtained function of the adsorption process, which validates the starting point, i.e., the mechanism of ethanol adsorption on zeolites.

The determined values for E_a, are significantly lower than those of the enthalpy of ethanol condensation ($\Delta H_c = 38.27$ kJ/mol) which indicates that the ethanol molecules in aqueous solution are associated in small groups, i.e., clusters (Brown et al. 1980; Einicke et al. 1988), which are in a different phase to that of liquid ethanol and the value of E_a corresponds to the energy required for an ethanol molecule to be detached from a cluster and adsorbed onto the zeolite.

4 Conclusions

Ethanol adsorption from aqueous solution onto NaZSM-5 is a kinetically controlled process limited by the rate of three-dimensional movement of the boundary layer of the adsorption phase and can be described by the following kinetic model: $[1-(1-\alpha)^{1/3}] = kt$. The ethanol molecules in aqueous solution are associated in clusters, and the activation energy for the adsorption process corresponds to the energy which is required for the detachment of an ethanol molecule from a cluster and its adsorption onto the zeolite.

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