Transport of Isopropanol in H-ZSM5 by Impedance Spectroscopy

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Abstract

Gas diffusion mechanisms and diffusion coefficients in microkinetic system of solid materials characterize the different performance of chemical and transport processes. These factors should be evaluated with respect to the range of diffusion coefficients based on the number of experimental methods. Here, impedance spectroscopy which is a powerful tool for understanding transport phenomena of gases in nanostructured porous solids is used. In this work, we developed a new approach to compare and evaluate diffusion coefficients of isopropanol in the zeolite H-ZSM5. Furthermore, FTIR spectroscopy was used to study the adsorption of isopropanol in H-ZSM5 at different temperatures to support the interpretation of diffusion regimes. The combination of EIS with FTIR enables to illustrate preferred interaction sites and their influence on transport processes. The activation energy for transport of molecules in the channels is also calculated. Results are compared to literature data and suggest improved applications of EIS to characterize transport processes.

Keywords: Isopropanol, Zeolite H-ZSM5, EIS, FTIR, diffusion coefficient

1. Introduction

The transport of gases or liquids in mesopores and micropores of solid materials is the first important step in the microkinetic catalysis cycle. For instance, in molecular sieves diffusion processes play an important role with respect to their catalytic activity and selectivity [1]. According to Kouva S. et al. [2] the sorption of molecules and their shape selective transport were chosen as a key characteristic of zeolites.

The well-known diffusion of isopropanol in H-ZSM5 may serve here as an example to illustrate EIS as a tool while using a system which has been shown previously of great relevance [1,3,4]. In other studies, the results for diffusion coefficients of isopropanol mostly resulted in self-diffusion coefficients. Several methods have been employed so far to determine transport characteristics as for instance NMR, temporal analysis of products (TAP) or frequency response (FR). All data differed according to the method used, thus, no general view to describe the transport behavior of isopropanol is available. Therefore, electrochemical impedance spectroscopy (EIS) is suggested here to establish an easy and reproducible determination of transport characteristics for gases in porous networks.

EIS is a powerful tool for characterizing materials with respect to their electric behavior, permittivity, and is able to describe pore structures by using small perturbations of sinusoidal potentials on a wide range of frequencies [5,6]. The method can be extended to analyze chemical processes, e.g., adsorption, diffusion, and reaction of mobile species. It has been applied in various fields of material sciences such as fuel cells, batteries, and gas sensors [5]. However, usage for a determination of transport coefficients of gases has not been shown so far.

In the following, a short introduction into EIS-background is given. The complex impedance is separated into real and imaginary parts according to the following equation:

$$Z^*(\omega) = Z^{'}(\omega) - j.Z^{''}(\omega) \qquad (1)$$

with ω is the angular frequency and $j = \sqrt{-1}$.

Impedance is generally represented on a Nyquist diagram by plotting the imaginary part $Z^{''}(\omega)$ versus the real part $Z^{'}(\omega)$. For analyzing data, impedance spectra will be fitted by an equivalent circuit with appropriate models such as: parallel (Maxwell), hierarchical ladder (Randles) and series (Voigt)

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[6]. In most cases, the series model is used first, it can simulate effects of grain, grain boundary or electrode interfaces as a semicircle on a Nyquist plot.

Generally, two elements, a resistor (R) and a capacitor (C) are connected in a parallel way. Theoretically, the change of the capacitance depends on the dielectric change by gas adsorption. On this view, Coehlo [7], and later Bandara and Mellander [8] developed a model for the dielectric change during a charged polarization to estimate the diffusion coefficients of mobile species. Impedance spectra with arcs or small angle lines at considerably low frequency ranges are characterized by a diffusion Warburg impedance of the gas on the interface of the electrode which has been shown in [9,10,11]. To classify two kinds of diffusion coefficients, the detailed approach used here will be shown in part 2 below in more detail.

Other applications have become a well-accepted fundamental tool for characterizing ionic conductivities, electrode polarization and the activation energy of adsorption/diffusion. Generally, the conductivity increases gradually with increasing temperature suggesting a thermally activated process in a material. This would give access to activation energy data. The ac conductivity, σ_{ac}, has been therefore determined from the impedance data using the Arrhenius equation afterwards. The value of the activation energy of diffusion, E_a, can be defined by the slope of $\ln(\sigma_{ac})$ versus the temperature.

The aim of the present work was to examine the adsorption process of isopropanol in mesopores and micropores of the zeolite H-ZSM5 at low temperature by FTIR spectroscopy and to explain the diffusion process in the zeolite channels as well. To estimate diffusion coefficients, we demonstrate, for the first time, how to calculate two values of diffusion coefficients for molecular and pore surface diffusion simultaneously for isopropanol in the zeolite H-ZSM5 derived from impedance spectroscopy. The results are compared to literature data.

2. Determination of diffusion coefficients

The transport of species (atoms, molecules, ions) in an electrolyte between two electrodes can be evaluated by the change of the dielectric or impedance in the material responding to the frequency. As mentioned above, an approach given by Bandara and Mellander [8] was developed from a model of Coelho [7] by separating the function of the effective dielectric into two components: a real and an imaginary part. Consequently, the transport coefficients of carriers in an electrolyte can be assumed in our case as values of molecular diffusion coefficients.

According to these authors, in an electrochemical cell with two blocking electrodes, the following model has an equivalent circuit with capacitances of the double-layer, capacitance of bulk geometry, and resistance of bulk; see equations (2)-(4) as following:

$$C_{dl} = \frac{\varepsilon_r \varepsilon_o A}{\lambda} \tag{2}$$

$$C = \frac{\varepsilon_r \varepsilon_o A}{2d} \tag{3}$$

$$R = \frac{2d}{\sigma A} \tag{4}$$

The effective permittivity ε^* of an ionic conductor can be given as:

$$\varepsilon^* = \varepsilon_o \varepsilon_r \left((1 + \frac{\delta}{1 + (\omega \tau_1 \delta)^2}) - j \frac{\omega \tau_1 \delta^2}{1 + (\omega \tau_1 \delta)^2} \right) \tag{5}$$

where, $\delta = d/\lambda$ and τ_1 is the characteristic time constant corresponding to the maximum in $Z''(\omega)$ at high frequencies.

The loss tangent is defined as a function of the frequency and a time constant τ. In experiments, the value of the loss-tangent can be determined as follows:

$$\tan(\phi) = \frac{\varepsilon''}{\varepsilon'} \approx \frac{\omega \tau_1 \sqrt{\delta}}{1 + (\omega \tau_1)^2 \delta} \tag{6}$$

$$\tan(\phi) = \frac{\varepsilon''}{\varepsilon'} = \frac{Z'(\omega)}{Z''(\omega)} \tag{7}$$

The function is given by equation (6) peaks at a defined point and corresponds to the transition point at the end of the first semicircle and the remaining impedance at low frequency. τ_2 is a time constant corresponding to the maximum in the dissipative loss curve (see Fig. 1).

$$\tan(\phi)_{max} = \left.\frac{\sqrt{\delta}}{2}\right|_{at\ \tau_2} \tag{8}$$

Hence, the diffusion coefficient of charge carriers can be defined by the following equation:

$$D_m = \frac{\lambda^2}{\tau_2} = \frac{d^2}{\tau_2\delta^2} \tag{9}$$
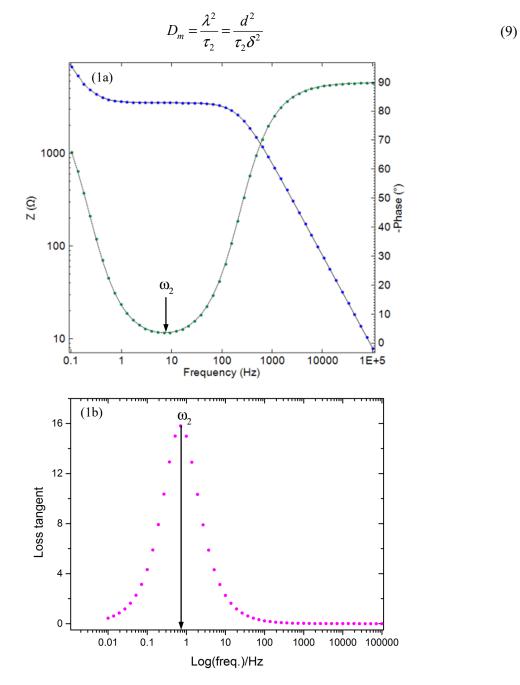

Figure 1: Representation of the peak point of relaxation time constant τ_2 shown as a) Bode phase and b) the loss tangent plot

On the other hand, impedance theory enables to determine diffusion coefficients derived from the Warburg impedance. The Warburg diffusion impedance for infinite length is given as following:

$$Z_W(\omega) = \frac{R_D}{\sqrt{j\omega\tau_D}}\tanh\left(\sqrt{j\omega\tau_D}\right) \tag{10}$$

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An example of the dielectric loss tangent including a Warburg diffusion impedance element in an equivalent circuit is shown in Fig. 2.
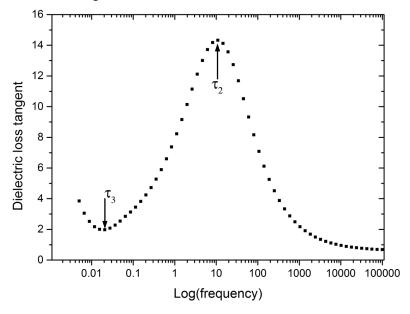

Figure 2: Determination of the life-time of molecular diffusion as a second peak at very low frequency

It can be seen that there are two peak points, the highest point corresponds to the relaxation time, τ_2 (similar Fig. 1b and Fig. 2) and the lowest point can be characterized as life-time of molecules on the surface of the pore, τ_3, see Fig. 2. Therefore, the diffusion length of molecules on the surface of the pore can be extracted from the value of D_m and τ_3, as follows:

$$l_D = \sqrt{D_m . \tau_3} \tag{11}$$

Generally, the diffusion time constant is derived by fitting impedance data at low frequencies with the Warburg impedance. However, in this study the value of the diffusion time constant is extracted by comparing each data point of the impedance spectra with theoretical values which are calculated by equation (10). The value of τ_D will be chosen as the smallest deviation between experimental and simulated data without using any curve fitting.

The new approach was applied to the transport of isopropanol molecules over acid sites on a porous material in the surface gas diffusion phenomenon described in [12,13]. Here, the surface diffusion coefficient will be determined as following:

$$D_s = \frac{l_D^2}{\tau_D} \tag{12}$$

3. Experimental and Methods

3.1 Sample preparation

The zeolite sample H-ZSM5 with a Si/Al ratio of 12 was provided by AlSi-Penta Zeolithe GmbH Schwandorf. Before carrying out the adsorption, the powder was dried at 250ºC (sample 1) and at 400ºC (samples 2 and 3) for 3 hours in air flow (0.05 Nl/min) to remove adsorbed water.
After that, the powder was cooled in air in a closed bottle for 2 hours. The sample was then placed in a desiccator which contains isopropanol for the adsorption process occurring at ambient conditions. The adsorption of isopropanol in H-ZSM5 was carried out 68h for sample 1 and 48h for sample 2, 3.

The dried powders were pressed into a tablet of 13 mm diameter and 0.62 and 0.97 mm of thickness at a pressure of 200 MPa; the details are given in Table 1. The tablets were finally connected to a small amount of conductive silver paste on their two faces and placed at room temperature in a bottle before carrying out the impedance measurements.

Table 1. Experimental details for sample preparation and treatment

Sample	No.1	No.2	No.3
Thickness (mm)	0.97	0.62	0.63
Adsorption time for isopropanol	68	48	48
Heat treatment (°C) for 3 hours	250	400	400
Tablet pressing pressure (MPa)	180 (with ∅ 13mm)	220 (with ∅ 13mm)	220 (with ∅ 13mm)

3.2 IR Measurements

70mg of zeolite H-ZSM5 (Si/Al = 12) were placed in a DRIFTS cell (Bruker Vertex 80v) and treated in situ at 450°C with flowing nitrogen 0.1Nl/min for 1hour.

The cell was then cooled to room temperature at 1 bar. The spectra were recorded at room temperature, 50°C, 100°C and 150°C; 32 scans were averaged at a nominal resolution of 2 cm^{-1}.

For each measurement, about 1.6 µl isopropanol were injected into the cell followed by time dependent measurement. The overall time for observation of the kinetics is approximately 30 min for each temperature. Final spectra were refined using background spectra of the sample.

3.3   Electrochemical measurements

A schematic drawing of the setup used for the impedance measurements is shown in Fig. 3. The sample was placed in a small chamber of the aluminium block between two copper electrodes on a cartridge heater (Roth, Germany). As electric collector silver paste was used on the two faces of the sample. Impedance spectra were recorded at 50°C in the closed chamber by Autolab PGSTAT 302N (Metrohm) during isopropanol desorption at constant temperature. The potentiostatic mode with AC amplitude 0.25 V and the range of frequency 0.01 Hz to 100 kHz were chosen. The transport coefficients of isopropanol in the zeolite channels are estimated based on impedance data for two levels of adsorption time (48 and 68h).
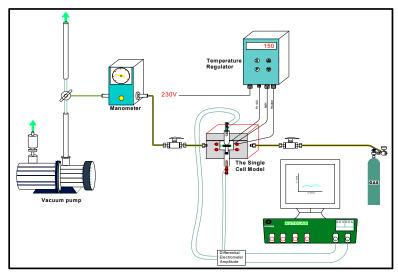

Figure 3: Schematic view of the experimental set-up for the single-cell model

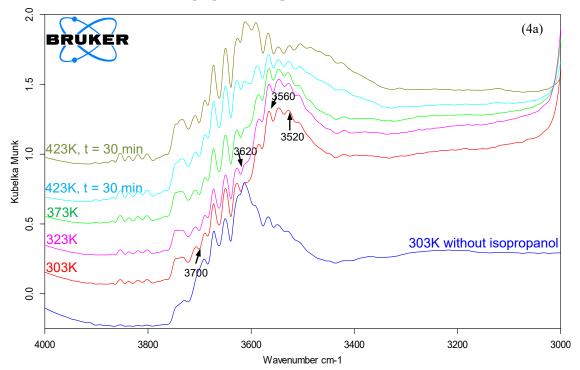# 4. Results and discussion

4.1 IR spectroscopy

Fig. 4a-c show DRIFT spectra that were recorded isopropanol adsorption at increasing temperature up to 150°C. As reference, the spectrum of pure H-ZSM5 without adsorbed isopropanol is given.
At room temperature, isopropanol adsorption changes the spectra as follows: strong adsorption bands of 2982 and 2940 cm^{-1} appear with high intensities (Fig. 4b). These bands are attributed to C-H stretching vibrations (CH$_3$-groups) of isopropanol molecules. Moreover, one can observe the IR-band

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at 1390 cm^{-1} which corresponds to the C-H bending vibrations (see Fig. 4c) which is also represented in [1,3]. In the range of bands between 3500-3600cm^{-1}, the intensities of the bands increase after adsorption of isopropanol indicating an interaction with the OH-groups of the zeolite (O-H stretching) (Fig. 4a). Likewise, the O-H stretching also appears with higher intensities after isopropanol adsorption in the region of 3800-3860 cm^{-1} (Fig. 4a). According to Glazneva et al. [1], the bands at 3620 and 3740 cm^{-1} are assigned to OH-groups in the zeolite channels and to the OH-groups in the mesopores. Thus, IR spectra reveal the strong interaction of isopropanol with OH-groups in the zeolite channels (3620 cm^{-1}) and in the mesopores (3700 cm^{-1}), see Fig. 4a.

Measurements at 50 and 100°C result in an increase of intensities for the band at 1333 cm^{-1} which characterizes the vibration of CH$_3$-groups in isopropanol. At these temperatures, the dehydration process of the alcohol occurs with a small rate that is proved by the increase of the band at 1650 cm^{-1} by formation of hydrogen bond between OH-group of the zeolite. This is in coherence with the study of Glazneva et al. [1] that the dehydration starts at the range of temperature 60-90°C.

At 150°C, Fig. 4b visualizes a complete variation in the C-H stretching region between 2850 and 3000 cm^{-1}. Particularly, the one at 2982 cm^{-1} shifted at 2957 cm^{-1}, giving decline of methyl groups in isopropanol molecules, apparently developing CH$_3$ stretching vibrations band at 2940 cm^{-1}. In addition, the rise of bands at 2867 and 2915 cm^{-1} (C-H stretching vibrations in the CH$_2$-groups) indicates that structure of propylene products is formed in the reaction between isopropanol and the surface of the zeolite. With increasing temperature, the band at 1390 cm^{-1} vanished, and the band at 1300 cm^{-1} gets a high peak which ascribes the rise of dehydration of alcohol by CH$_2$ bending vibrations on the hydrogen bond of OH-groups in the zeolite, see dehydration mechanism by de Miguel [4]. The accumulation of compounds were characterized by the lower band at 1510 cm^{-1} which was also recommended in [1] as isopropanol adsorption on zeolite at 190°C.
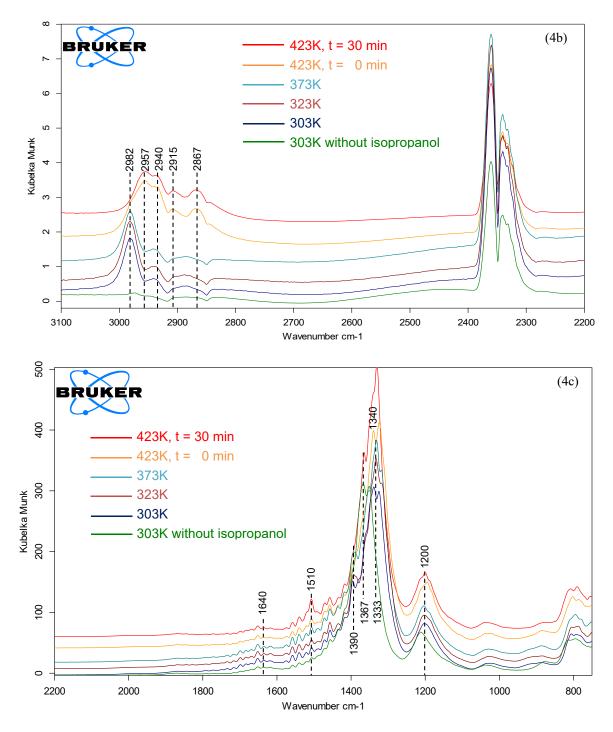
Figure 4a-c: IR spectra of isopropanol adsorption on zeolite H-ZSM5

According to Gorte et al. [3] the existence of bands at 2982 and 2940 cm^{-1} shows that the reaction of isopropanol molecules and zeolites has not yet occurred at temperature lower than 150°C. However, the band at 2982 cm^{-1} shifted at 2957 cm^{-1} at 150°C which indicates the accumulation of oligomeric propylene structures at the surface [1] by C-H stretching vibration in the CH$_2$-groups.

In order to assess the amount of water adsorption (see Fig 4a, c), one can observe at band 1200 cm^{-1} is characterization water adsorption on the surface of the zeolite. The intensities for the spectra (at room temperature to 150°C) are quite similar for this band showing small amount of adsorbed water. Others is the formation of water during dehydration supporting ionic transport that is shown in the range of 3520 - 3560 cm^{-1}.

4.2 Impedance spectroscopy of isopropanol in H-ZSM5

The impedance spectra of three samples are shown in Fig. 5a, b as Nyquist plots. In general, impedance spectra have two characteristics: one arc at high and intermediate frequencies and a line with small angle at low frequencies. It can be seen that the disappearance of points in the transition region between intermediate and low frequency leaves a space between the first arc and the line at low frequency. Hence it is not easy to fit those data. Here, we propose an assumption to interpret the noisy impedance spectra at intermediate frequencies. Actually, those points are situated in the same range of frequencies 1÷100 Hz for all three samples with different adsorption time 48h or 68h. The reason suggests that the large diameter of isopropanol is three orders of magnitude higher than zeolite pores, d_{iso}=16.05Å of isopropanol diameter size comparison with 5.5 Å of pore size of zeolite channels. Therefore, it is difficult for isopropanol molecules to permeate inside channels. These can only go inside channels under the "radius of gyration" phenomenon and interact on the Brønsted acid sites of OH-groups. Otherwise, as results of IR spectroscopy, a small intensity of the peak at 3620 cm^{-1} shows a few number of isopropanol species on the surface of the zeolite channels. Consequently, the interior of pore is still not full isopropanol molecules adsorption on hydrogen bond of OH-groups at the surface. That is a reason why there are many unstable points during measuring in the transition region.
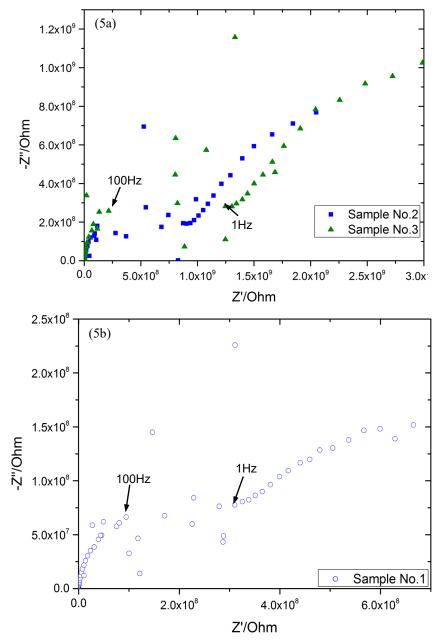

Figure 5: Impedance spectra of a) sample 2, 3 and b) sample 1 at 50°C in range of frequencies 0.01Hz ÷ 100 kHz

In Fig. 6a, the noisy points were removed by the NOVA program at frequencies 1÷100 Hz. It is clearly seen that the first semicircle is attributed to the bulk geometry of the sample and the line is characterized by isopropanol diffusion in channels. The equivalent circuit is illustrated in Fig. 6b. It can be fitted for the first arc by a resistance parallel with a constant phase element (CPE) and series the Warburg diffusion impedance as a line at low frequencies. The complex impedance of the CPE is given by [6]:

$$Z_{CPE} = 1/Y_o(j\omega)^n \qquad (13)$$

At low frequency the Warburg impedance with O-element is characterized as a diffusion of species on the surface of channels. O-element represents the finite length Warburg and the complex impedance by Eq. (10).
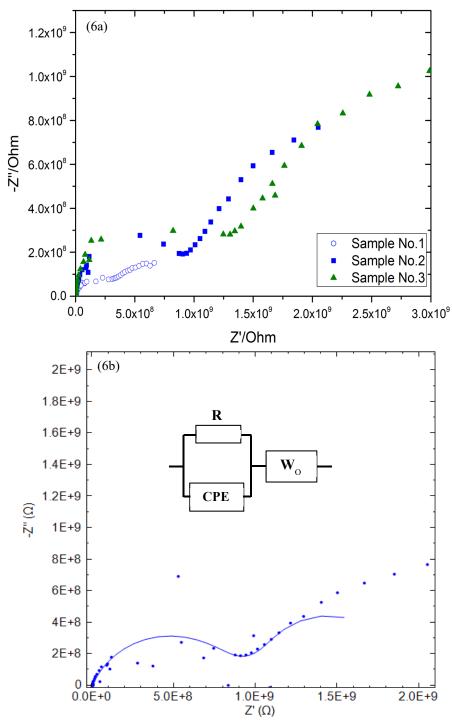

Figure 6: Nyquist plot after (a) remove the noisy points and (b) physical model of equivalent circuit

4.3 Diffusion coefficients

In solid catalyst pellets, two values of diffusion coefficients can be discussed: the bulk gas/liquid (or molecular diffusion) and the pore surface diffusion coefficient [14]. The diffusion processes occur in both external (mesopores) and internal (micropores) surface of the zeolite. References for adsorption and reaction of gases/liquids on zeolite H-ZSM5 were given in [1,3,15,16].

As was mentioned above the major existence of isopropanol is on the external pore of the zeolite. Generally, the bulk gas and Knudsen diffusion are parallel resistances in mesopores. However, Glazneva et al. [1] concluded that diffusion in the mesopores limited the dehydration process. As a result, the bulk gas diffusion is mainly concerned as isopropanol adsorption in mesopores. In the zeolite channels, the adsorption of isopropanol to the surface of zeolites is slow due to the size of the molecules. Moreover, the diffusion process depends on the partial density of surface coverage by absorbed isopropanol molecules in channels. According to Williford et al. [12], in case of low partial pressure of the bulk gas, pore surface diffusion process would be a significant mechanism before occurring adsorption or reaction of gas to the site occupancy.

In order to determine the molecular diffusion coefficient, the model of dielectric polarization by [7,8] was applied to peak points on the loss-tangent plot (Fig. 7). The value of molecular diffusion coefficient is calculated from Eqs. (7) - (9) for all three samples. The results are given on Table 2. Molecular diffusion coefficients of sample 2 and 3 are analogous and lower than that of sample 1. It can be understood that the concentration of isopropanol on the surface of the zeolite depends on the adsorption time, which was different.
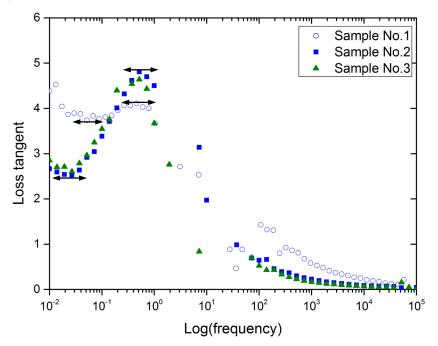

Figure 7: The peak point on the loss-tangent plot for 3 samples

In comparison to literature, these values of molecular diffusion coefficients is in good agreement with values of self-diffusion coefficients of isopropanol in H-ZSM5 giving by Glazneva et al. [1] by using the SEM data with crystallite size $5 \div 7$ μm (D = 10^{-7} cm^2/s). Another, the diffusion coefficient value of isopropanol in Pd electrode defined 1.04 x 10^{-6} cm^2/s in both methods: linear sweep voltammetry and chronoamperometry [17]. Furthermore, the bulk pore diffusion coefficient of isopropanol in mesoporous Pd/Al$_2$O$_3$ catalyst pellet was determined as 4.0 x 10^{-6} cm^2/s [14] by using PFG NMR.

As a second value, the pore surface diffusion coefficient has been reported by literature that is consistently 2 to 3 orders of magnitude lower than the molecular diffusion coefficient [13]. On the Nyquist plot, the calculated data were considered in the low range of frequency represented by the Warburg impedance. The value of pore surface diffusion coefficient is calculated by Eqs. (10)- (12) based upon the new approach which can determine the diffusion time constant from impedance data, and not use fitting curves. The detailed values of pore surface diffusion coefficients for each sample

are given in Table 2. It could be referenced by Weber et al. [14] that the value of pore surface diffusion coefficient of isopropanol in Pd/Al$_2$O$_3$ catalyst pellet is 0.99 x 10^{-7}cm^2/s.

Table 2. Average diffusion coefficients of isopropanol in H-ZSM5 at 50°C by EIS

	Molecular diffusion coefficients D_m(cm^2/s) $_{\tau 2}$	Pore surface diffusion coefficients D_s(cm^2/s) $_{\tau D}$
Sample 1	2.4 x 10^{-6}	9.2 x 10^{-7}
Sample 2	4.7 x 10^{-7}	1.9 x 10^{-7}
Sample 3	5.8 x 10^{-7}	1.9 x 10^{-7}

4.4 AC conductivity

The dependence of electric conductivity and temperature for isopropanol in H-ZSM5 for all three samples was studied in the range of temperature 50 to 250°C. To evaluate these temperature dependent data, the Arrhenius equation was applied. The experimental data indicate that the conductivity is enhanced with increasing temperature in range of 50 to 200°C (see Fig. 8) and reduced with the temperature higher than 200°C. This can be understood as follows: the increase of temperature is the cause of the protons jump into the neighborhood and there are always two hydrogen cations for each site [3]. However, at temperature above 200°C, the OH-groups declines and only one hydrogen cation jump appears, leading to a decrease in the ionic concentration. According to Glazneva et al. [1], in the zeolite channels the adsorption proceeds through a diffusion mechanism. In addition, the activation energy, E$_a$, which is a combination of defect formation and motion energy by diffusion, can be observed from the slope of the plot ln(σ_{ac}) versus 1000/T by the Arrhenius equation. The value was calculated for all three samples in range of 26 kJ/mol to 39 kJ/mol derived from the bulk resistance of the first arc on Nyquist plot. These in this work are within range of reported ones: the activation energy of isopropanol diffusion inside channels (22 kJ/mol) and on the external surface (18 kJ/mol) by Glazneva et al. [1]; the activation energy for reaction of 2-propanol in SAPO-5 (55 kJ/mol) by [18].
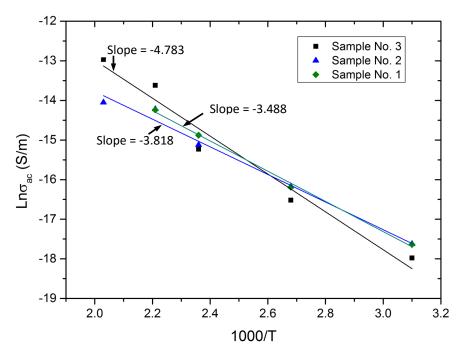

Figure 8: Temperature dependence of bulk conductivity for isopropanol in H-ZSM5

5. Conclusion

The new approach based on the analyzing of EIS data was developed and used for isopropanol adsorption and diffusion in the zeolite H-ZSM5. It can determine two values of diffusion coefficients of isopropanol in the zeolite H-ZSM5: bulk/molecular and pore surface diffusion coefficient even without using curve fitting. The phenomena of adsorption and diffusion of isopropanol on the external and internal surface of zeolite were studied by FTIR spectroscopy. It shows that the main adsorption

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of isopropanol is on the Brønsted acid sites in H-ZSM5 in both mesopores and micropores of the zeolite. In addition, EIS method is also used to explain the noisy phenomenon at frequency range $1 \div 100$ Hz in the transition region during isopropanol transport into the channels of zeolite. It indicates that isopropanol can go inside the channels to the Brønsted acid sites under the "radius of gyration" phenomenon. The values of diffusion coefficients and kinetics of adsorption/diffusion are appropriate to literatures and that explores the high ability in new applications of EIS method.

List of Symbols

A	The electrolyte/electrode contact area, m^2
C_{dl},	The double-layer capacitance, F
C	Bulk capacitance, F
D_m	Molecular diffusion coefficient, cm^2/s
D_s	Surface diffusion coefficient, cm^2/s
2d	The thickness of the sample, cm
E_a	Activation energy, kJ/mol
j	Complex number
l_D	The diffusion length, cm
n	The frequency power
R	The bulk resistance, Ω
R_D	The diffusion resistance, Ω
T	Absolute temperature, K
Y_o	CPE constant, s/Ω
Z^*	Complex impedance, Ω
Z'	Real part of impedance, Ω
Z"	Imaginary part of impedance, Ω
Z_{CPE}	Complex impedance of CPE, Ω
Z_W	The Warburg impedance, Ω

Greeks

ε_r	Dielectric constant of electrolyte
ε_o	Vacuum permittivity, $\varepsilon_o = 8.854 \times 10^{-12}$ F/m
ε'	Real part of dielectric constant
ε''	Imaginary part of dielectric constant
ε^*	Effective permittivity
λ	Mean thickness of double-layer, cm
σ_{ac}	ac conductivity, Sm/cm
ω	Radial frequency, rad
τ_D	The diffusion time constant, s
τ_2	Characteristic time constant, s
τ_2	Relaxation time constant, s
τ_3	Life-time constant, s
ϕ	Phase angle (shift), degree

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