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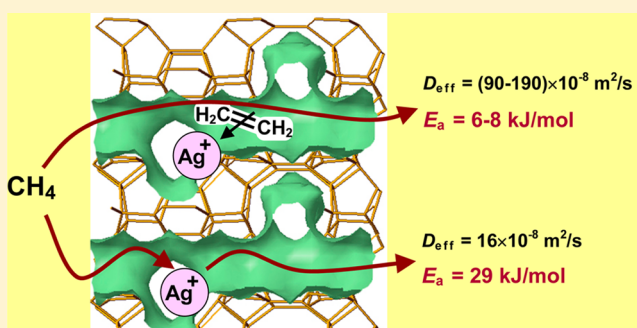
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ABSTRACT: With regard to the influence of methane on the reactivity of ethene on Ag/H-ZSM-5 zeolite, the diffusivities of methane in the presence of ethene coadsorbed on Ag/H-ZSM-5 has been analyzed by PFG ^1H MAS NMR spectroscopy. It is established that the diffusion of methane in the absence of ethene occurs more slowly (activation energy $E_a = 29 \text{ kJ mol}^{-1}$) than the diffusion of methane in the presence of coadsorbed ethene ($E_a = 6\text{--}8 \text{ kJ mol}^{-1}$). The higher value of E_a for the methane diffusion in the absence of ethene was related with some strong interaction of methane with Ag^+ cations located in the zeolite channel system. Acceleration of diffusion and a decrease of its activation energy in the presence of ethene were assigned to the shielding effect of ethene adsorbed on Ag^+ cations to form π -complexes. An absence of direct interaction of methane with Ag^+ cations was assumed to provide a significant decrease of activation energy and acceleration of methane diffusion. Two ensembles of methane molecules different by diffusivity have been assumed to exist in the zeolite in the presence of coadsorbed ethene. The presence of two ensembles of diffusing methane in the zeolite was rationalized in terms of the existence of two pathways of methane diffusion through the zeolite channel system. By one pathway, methane presumably diffuses over π -complexes of ethene with Ag^+ cations and the zeolite acid OH groups. The other pathway may include the methane diffusion in the zeolite channels exclusively over the zeolite OH groups.



1. INTRODUCTION

Methane is the most inert among alkanes, and its conversion to more valuable chemical products has been a real challenge in the last decades. One of the pathways of methane rational utilization represents an involvement of methane in the reaction with higher hydrocarbons to form olefins or aromatics on zeolites modified with Zn, Ga, In, Ag, etc.^{1–12} In particular, it has been reported on the methane conversion to propene by the reaction with ethene on Ag modified zeolite ZSM-5.^{7–12} Co-aromatization of methane with ethene on Ag/H-ZSM-5 zeolite was also reported, and the mechanism of methane activation and involvement in the reaction with ethene was clarified.¹³ In particular, it has been established that ethene forms the adsorption π -complexes with Ag^+ cations of Ag/H-ZSM-5. Because of the strong interaction with Ag^+ cations, ethene is not involved in chemical transformation on Brønsted acid sites of the zeolite even at temperatures as high as 673 K, although it is well known that ethene easily oligomerizes on pure acid form zeolite H-ZSM-5 already at room temperature.^{14–17} Only at a temperature of 823 K does ethene transform to aromatics on Ag/H-ZSM-5.¹³ Methane, similar to ethene, transforms to aromatics on Ag/H-ZSM-5 at 823 K.¹³ The transformation of methane occurs through the stages of

intermediate formation of methoxy species and ethene. It has been found, however, that in the presence of methane, the transformation of ethene to the aromatics starts at significantly lower temperature, at 673 K.¹³ This could imply that methane competes with ethene for the active sites, Ag^+ cations, providing decomposition of π -complexes and expulsion of ethene molecules from the Ag^+ cationic sites. Further, ethene becomes involved in the reaction with Brønsted acid sites, which offers first ethene oligomers and finally the aromatic products. Capability of methane to compete with ethene suggests that methane could form some adsorption complexes with Ag^+ cations. Apparently, these complexes precede methoxy species, which was found to be the first intermediate in aromatization of pure methane without the presence of coadsorbed ethene.

Internal architecture of zeolite pores and localization of the active sites inside the pores should significantly influence the intramolecular dynamics and the diffusivity of adsorbed reactant hydrocarbons. The diffusivity in turn could strongly affect the reactivity of hydrocarbon molecules. In this respect,

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Table 1. Concentration of Different OH Groups and Composition of the Zeolite Unit Cell for the Ag/H-ZSM-5 Zeolite Sample

zeolite sample	concentration of OH groups ($\mu\text{mol}\cdot\text{g}^{-1}$)			zeolite unit cell
	SiOH, 1.8 ppm	AlOH, 2.4 ppm	SiOHAl, 4.0–6.0 ppm	
Ag/H-ZSM-5	100	200	500	$\text{Al}^{\text{Oct}}_{0.1} \text{Ag}_{1.1} \text{H}_{3.1} \text{Ag}^+_{3.7} \text{Al}^{\text{tet}}_{6.8} \text{Si}_{89.1} \text{O}_{192}$

for the reaction of methane and ethene on Ag/H-ZSM-5 and the found evident influence of methane on ethene reactivity,¹³ it could be of interest to have some knowledge on the diffusivity of methane in the presence of ethene on this silver-modified zeolite H-ZSM-5. This would give us some insight on the methane activation pathway and the mechanism of methane influence on ethene reactivity on Ag/H-ZSM-5 zeolite.

In this article, we have performed an analysis of the diffusivity of methane on Ag/H-ZSM-5 with PFG ^1H MAS NMR in the presence and the absence of ethene. This allows us to conclude both on the existence of methane interaction with Ag^+ cations and the influence of the zeolite active sites, Ag^+ cations, and coadsorbed ethene on the diffusion of methane in this zeolite.

2. EXPERIMENTAL SECTION

2.1. Material Characterization and Sample Preparation. The template free synthesized NH_4 -ZSM-5 (Si/Al = 13) zeolite was kindly provided by Tricat Zeolites. The parent ammonium form of the zeolite was transformed into the hydrogen form (H-ZSM-5) by calcination at 773 K for 5 h. The silicon-to-aluminum ratio of 13 was estimated for the H-ZSM-5 zeolite based on ^{29}Si MAS NMR analysis¹⁸ and confirmed by the chemical analysis data. No extra framework aluminum atoms were observed in the ^{27}Al MAS NMR spectrum of the hydrated H-ZSM-5 zeolite. The Ag-modified zeolite (Ag/H-ZSM-5) was prepared by ion-exchange of 2.5 g of H-ZSM-5 with 25 mL of 0.15 M AgNO_3 aqueous solution overnight at 25 $^\circ\text{C}$ in the dark with subsequent filtration,¹⁹ washing with distilled water, drying at 393 K for 14 h, and further calcination at 673 K for 4 h in a flow of air. The silver-to-aluminum ratio 0.7 (8.2 wt % Ag) in the final sample of Ag/H-ZSM-5 zeolite was obtained by chemical analysis. Concentrations of bridged SiOHAl, silanol SiOH, and extra framework AlOH groups were estimated by ^1H MAS NMR with adsorbed methane as internal standard. The detailed composition of the unit cell for the used zeolite sample has been established in terms of Si/Al, Ag/Al ratios, and SiOHAl group concentrations (Table 1).

Scanning electron microscopy (SEM) analysis showed that the dimensions of zeolite crystallites were in a range of 0.2–0.5 μm .

Silver mainly exists as an exchanged ion (Ag^+) in Ag-ZSM-5 zeolite.^{10,20–22} The silver cations are considered to be symmetrically bidentated to two oxygen atoms of zeolite $[\text{AlO}_4]^-$ tetrahedron, and the interaction is of ionic character.^{10,21} We have supposed that unexchanged silver exists as metallic species formed by thermal decomposition of AgNO_3 during calcination.²³ Indeed, according to Miao et al.,^{10,22} the silver atoms (Ag^0) or the metallic clusters (Ag_n^0) are formed in Ag/H-ZSM-5 zeolite samples with high silver loading (10–15 wt %). So, we believe that in our Ag/H-ZSM-5 zeolite sample silver exists in a form of the exchanged ion (Ag^+) and the metallic species (Ag), the former being the prevailing species (Table 1).

Methane ($\geq 99.0\%$ purity) and ethene ($\geq 99.0\%$ purity) were purchased from Aldrich Chemical Co. Inc. (ACC inc.) and were used without further purification. The sample of Ag/H-ZSM-5 (20 mg) in a glass tube (0.05 cm^3 volume) was

activated at 673 K for 24 h under vacuum with the residual pressure less than 10^{-3} Pa. Then, 600 $\mu\text{mol}\cdot\text{g}^{-1}$ (~ 4 mol/u.c.) of ethene was adsorbed on the sample under vacuum at room temperature for 10 min. Further, 300 $\mu\text{mol}\cdot\text{g}^{-1}$ (~ 2 mol/u.c.) of methane was coadsorbed on the sample at the temperature of liquid nitrogen for a few minutes. Then the sample was sealed by a torch flame keeping the sample material in the lower part of the glass tube in liquid nitrogen to prevent its heating by the flame. The zeolite sample with coadsorbed ethene and methane located in an axially high symmetrical sealed glass tube of 3 mm outer diameter and 10 mm length could be tightly inserted into a NMR zirconia rotor (4 mm outer diameter) for PFG ^1H MAS NMR analysis of methane diffusivity.

2.2. NMR Measurements. NMR spectra were recorded at 9.4 T on a Bruker Avance 400 spectrometer equipped with a broad-band double-resonance-MAS probe. Zirconia rotors with the inserted sealed glass tube were spun at 5–15 kHz by dried compressed air. ^1H MAS NMR spectra were recorded by the Hahn-echo pulse sequence ($\pi/2-\tau-\pi-\tau$ -acquisition), where τ equals to one rotor period (100 μs). The excitation pulse length was 5.0 μs ($\pi/2$), and typically 8–32 scans were accumulated with a 4–60 s delay. Registration of ^{27}Al and ^{29}Si MAS NMR spectra for the zeolite structure characterization was performed similar to the procedure described earlier in ref 13.

The sample temperature was controlled by a Bruker BVT-2000 variable-temperature unit. The calibration of the temperature (296–373 K) inside the rotor was performed (accuracy of ± 1 K) by using lead nitrate, located inside the rotor, as a ^{207}Pb MAS NMR chemical shift thermometer.²⁴

2.3. ^1H MAS PFG NMR Diffusion Measurements. Pulse field gradient (PFG) NMR diffusion measurements were performed on a Bruker AVANCE 750 spectrometer with a wide-bore magnet (17.6 T). The MAS frequency was $\nu_{\text{rot}} = 10$ kHz. The 10-kHz rotation of a 4 mm rotor increases the temperature within the rotor by 10 K with respect to the detected temperature of the air flow outside the rotor.²⁵ The temperature of measurements given below is the sample temperature within the rotor. The external magnetic field was calibrated by means of the ^1H MAS NMR signal of highly viscous polydimethylsiloxane (PDMS) with a chemical shift of 0.07 ppm in a spinning rotor (external standard).

A 4 mm MAS probe with pulsed field gradient capabilities (maximum gradient strength 0.54 $\text{T}\cdot\text{m}^{-1}$) and a maximum radio frequency (RF) power of $\nu_{\text{RF}} = 100$ kHz was used for diffusion measurements. A stimulated-echo sequence with bipolar sine-gradient pulses and eddy current delay^{26,27} was applied (see Figure 1). The sequence for alternating sine shaped gradient pulses and longitudinal eddy current delay (LED) (Figure 1) consists of seven RF pulses, four magnetic field gradient pulses of duration δ and intensity g , and two eddy current quench pulses. We used a gradient pulse duration of $\delta = 0.5$ ms and a π -pulse length $p_\pi = 5$ μs , an observation time of $\Delta = 10$ ms, a delay between gradient and RF pulses $\tau = 0.5$ ms, and an eddy current delay $\tau_{\text{ecd}} = 4.5$ ms. The repetition delay was 5 s and much longer than the longitudinal relaxation time T_1 , which has a length of about 0.1 s. The gradient pulse

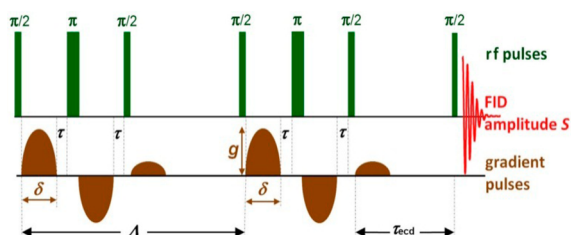


Figure 1. Stimulated-echo sequence with bipolar sine-gradient pulses and eddy current delay before detection.

strength was varied between 0.02 and 0.15 T m⁻¹. The duration of observation time, gradient pulse duration, and the spacing between gradient pulses were multiples of the rotation period of 100 μs.

The self-diffusion coefficient, D , of molecules was obtained from the analysis of signal attenuation $\psi = S/S_0$ depending on the field gradient intensity, g ,²⁷

$$\psi = \frac{S}{S_0} = \exp \left[-D \left(\frac{4\delta g \gamma}{\pi} \right)^2 \left(\Delta - \frac{\tau}{2} - \frac{2\delta}{3} - p_\pi \right) \right]$$

where γ denotes the gyromagnetic ratio, and other values were explained above.

3. RESULTS AND DISCUSSION

Methane adsorbed on Ag/H-ZSM-5 zeolite exhibits a signal at 0.93 ppm, whereas in the presence of coadsorbed ethene, methane shows two signals at 0.23 and 0.73 ppm in the ¹H MAS NMR spectrum (Figure 2). The observed signal from methane should represent some averaged signal of methane in the adsorbed state in the zeolite crystallites and methane in the gas phase of the intercrystallite void. According to the adsorption isotherm of methane on H-ZSM-5 at 296 K,²⁸ methane loading of 300 μmol g⁻¹ implies that ca. 94% of

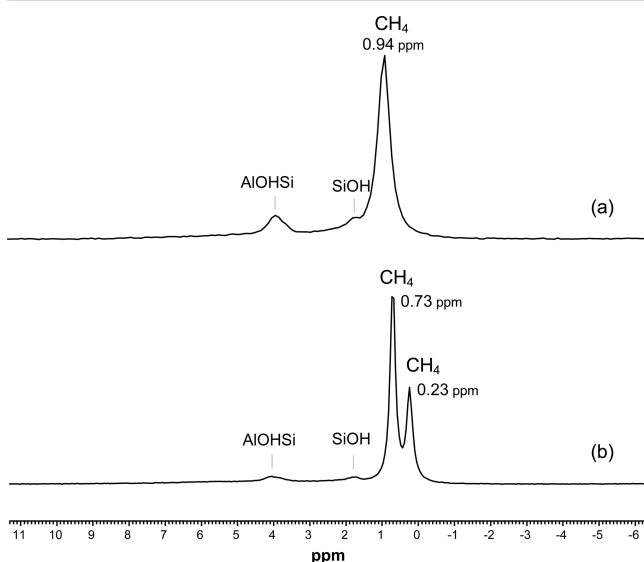


Figure 2. ¹H MAS NMR spectra at 296 K of methane adsorbed on Ag/H-ZSM-5 zeolite. In the absence (a) and presence of coadsorbed ethene (b). Three hundred micromole per gram methane and 600 μmol g⁻¹ ethene were coadsorbed. The signal from coadsorbed ethene (expected at ca. 5.5 ppm) in b is not observed due to the extremely large line width.

methane is located inside the crystallites, while ca. 6% of methane should be in a gas phase with the equilibrium pressure of about 150 Torr above the zeolite crystallites. No gaseous methane with the expected chemical shift of about 0.1 ppm²⁹ is observed in our spectra at 296 K (see Figures 2 and 3). The

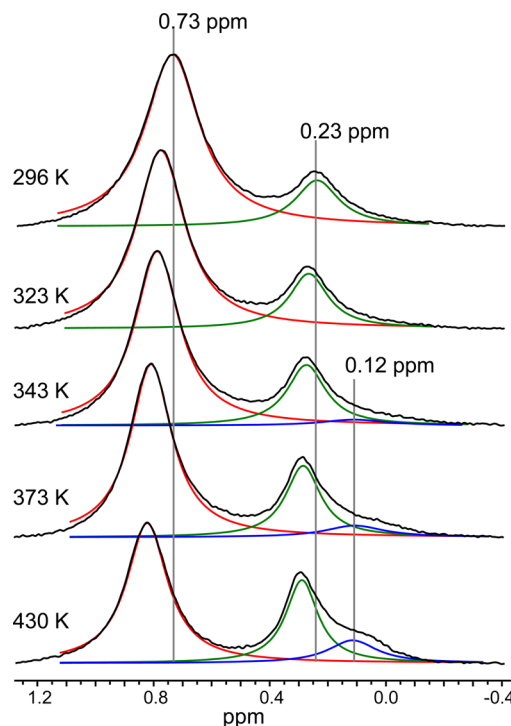


Figure 3. Evolution with temperature of the ¹H MAS NMR spectrum of methane adsorbed on Ag/H-ZSM-5 zeolite in the presence of coadsorbed ethene. The signal of gas phase methane at 0.12 ppm becomes clearly detectable above 343 K.

signal from the gas phase methane becomes clearly visible at 0.12 ppm in our system only at a temperature above 343 K (Figure 3). Thus, all of the observed resonances of methane in Figure 2 should be considered as the signals averaged by methane exchange over all possible adsorption sites in the zeolite framework.

Two signals from methane on Ag/H-ZSM-5 zeolite in the presence of coadsorbed ethene (Figure 2b) implies two ensembles of adsorbed methane in the intracrystalline void. The exchange between two ensembles is rather slow. The rate of this exchange could be estimated to be less than the distance between two methane signals (0.73 and 0.23 ppm), i.e., $1/\tau_{\text{exch}} \ll 200 \text{ s}^{-1}$.

PFG ¹H MAS NMR analysis of methane diffusivity in Ag/H-ZSM-5 at 306–373 K has shown that the diffusion coefficients for methane are in the range of $(16\text{--}109) \times 10^{-8} \text{ m}^2/\text{s}$. Diffusivity of methane in the presence of coadsorbed ethene is higher. Two ensembles of adsorbed methane, exhibiting different signals, show the diffusion coefficients in the range of $(90\text{--}120) \times 10^{-8} \text{ m}^2/\text{s}$ and $(190\text{--}300) \times 10^{-8} \text{ m}^2/\text{s}$ at 306–373 K for the signals 0.73 and 0.23 ppm, respectively.

The averaged squared diffusion pathway, $\langle l^2 \rangle$, can be estimated by the Einstein equation, $D = \langle l^2 \rangle / 6\Delta$, for diffusion of the molecule during the observation time ($\Delta = 10 \text{ ms}$). We obtain the distance $\langle l^2 \rangle^{1/2} = 100\text{--}250 \text{ μm}$. This is much larger than the size of the crystallites of Ag/H-ZSM-5 zeolite (0.2–0.5 μm) used in our experiments. Therefore, the measured

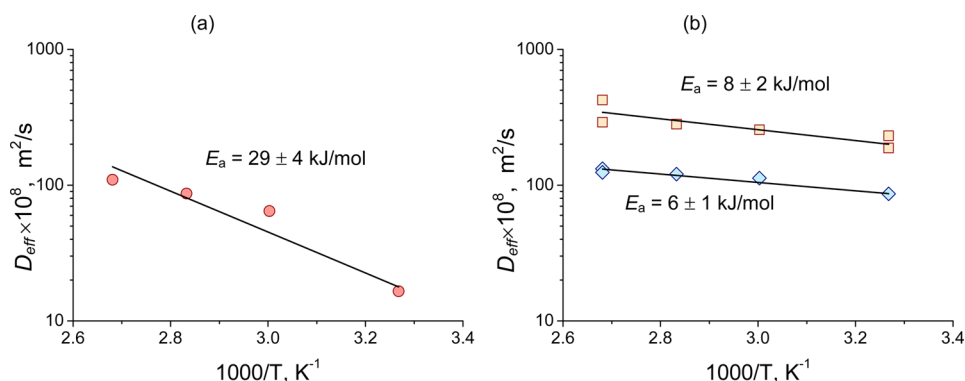


Figure 4. Arrhenius plots for the diffusivity of methane adsorbed on Ag/H-ZSM-5 zeolite in the absence (a) and presence of coadsorbed ethene (b). In b: \square corresponds to methane with the signal at 0.23 ppm; \diamond corresponds to methane with the signal at 0.73 ppm.

diffusion coefficients represent the so-called effective self-diffusion coefficient, D_{eff} of methane diffusivity inside the crystallites, D_{intra} , and in the intercrystalline gas phase, which we denote as D_{gas} :³⁰

$$D_{\text{eff}} = p_{\text{intra}} D_{\text{intra}} + p_{\text{gas}} D_{\text{gas}} \quad (1)$$

where p_{intra} and $p_{\text{gas}} = 1 - p_{\text{intra}}$ are the relative equilibrium molar fractions of the molecules to be found inside the crystallites and in the gas phase, respectively.

Molar fractions p_{intra} and p_{gas} can be estimated from the adsorption isotherm for methane on H-ZSM-5. Taking into account the temperature effect on the adsorption isotherm specified by isosteric heat of methane adsorption (23 kJ/mol),²⁸ one could observe for our sample packed into a sealed ampule that p_{gas} varies in the range from 0.07 to 0.20 corresponding to the studied temperatures (306–373 K). Consequently, the equilibrium pressure in the gas phase, estimated on the basis of the known ampule volume, is 200–750 Torr. The diffusion coefficients, D_{gas} , which correspond to the equilibrium pressure should be $\sim 9 \times 10^{-5} - 3 \times 10^{-5} \text{ m}^2/\text{s}$.³¹ If we assume that D_{intra} is of the order of the diffusion coefficients measured for pure acidic zeolite H-ZSM-5, i.e., $D_{\text{intra}} \sim 10^{-8} \text{ m}^2/\text{s}$,^{32–34} then the effective diffusivity D_{eff} can be calculated from eq 1.

The calculated D_{eff} does not agree with experimentally measured diffusion coefficients for methane on Ag/H-ZSM-5. D_{eff} was several times higher than the experimental one. The possible reason for such a discrepancy might be a significant difference between D_{intra} on H-ZSM-5 and on Ag/H-ZSM-5. Also, it could be of importance that an effective lowering of D_{gas} due to diffusion is observed in the void between crystallites with the distance among them comparable with the mean free flight path of methane molecules in gas phase at the given pressures and the temperature.

Despite the fact that a quantitative analysis on the basis of eq 1 turned out to be unachievable, our data allows qualitative information concerning the diffusivity of methane in the absence and presence of ethene on Ag/H-ZSM-5. Indeed, assuming that the adsorption equilibrium remained constant, the diffusivity D_{gas} should be identical for both studied samples. Hence, the observed difference in D_{eff} for two samples and for two signals of methane in the presence of coadsorbed ethene should be totally related to the difference in the intracrystalline diffusivity D_{intra} in the two studied samples.

The Arrhenius plot for methane diffusivity in Ag/H-ZSM-5 gives the activation energy $E_a = 29 \pm 4 \text{ kJ mol}^{-1}$ (Figure 4).

The value of E_a for methane diffusivity is rather high compared to the earlier measured $E_a = 4\text{--}5 \text{ kJ mol}^{-1}$ for methane in H-ZSM-5.^{32–34}

The high value of the energy barrier for methane diffusion compared to that for nonmodified zeolite H-ZSM-5 could be rationalized in terms of the strong interaction of methane with Ag^+ cations. This interaction is higher compared to weaker van der Waals interactions of methane with the walls of the zeolite channels and intrachannel acid OH groups. The strong interaction of methane with Ag^+ cations in Ag/H-ZSM-5 displayed as high activation energy barriers for methane diffusion in this zeolite accounts for the earlier observed influence of methane on the reactivity of ethene in this zeolite.¹³ Indeed, it has been found that in the presence of methane, the temperature of ethene involvement in the chemical reaction on Ag/H-ZSM-5 zeolite essentially decreases.¹³ It is clear now that methane can compete with ethene for adsorption centers, Ag^+ cations.

The appearance of two ensembles of adsorbed methane, which are different by diffusivity at ethene coadsorption on the zeolite, could be rationalized as follows. At adsorption of ethene on Ag/H-ZSM-5, it forms strong π -complexes with Ag^+ cations. Therefore, the diffusion of ethene in the intracrystalline void of the zeolite is suppressed completely with respect to methane diffusion. One can suggest that there are two pathways for methane diffusion over the system of the zeolite channels. On the one hand, inside the intracrystalline void methane can diffuse through the zeolite channel system containing ethene adsorbed on Ag^+ cations, located at channel intersection sites, and the acid OH groups. On the other hand, methane may diffuse through the channels and channel intersection sites that do not contain Ag^+ cations with adsorbed ethene molecules, but only OH groups exist on a pathway of methane diffusion. In each of the two cases, diffusing the methane molecules perceive different interaction with the wall of channels, provided by ethene on Ag^+ cations and the zeolite acid OH groups. This offers two ensembles of methane, exhibiting different chemical shifts and different diffusivities. One can assume that methane with the signal at 0.23 ppm and higher values of $D_{\text{eff}} = (190\text{--}300) \times 10^{-8} \text{ m}^2/\text{s}$ belongs to methane diffusing over zeolite channels with OH groups. Methane exhibiting the signal at 0.73 ppm and lower values of $D_{\text{eff}} = (90\text{--}120) \times 10^{-8} \text{ m}^2/\text{s}$ could be assigned to methane diffusing through the channels and channel intersection sites containing Ag^+ cations with ethene adsorbed on them. Despite the fact that the activation energies for the diffusion of methane in these two cases are similar, 6–8 kJ mol^{-1} (Figure 4), the lower

diffusivity in the latter case can be related with more strong interaction of methane with ethene on Ag^+ centers, compared to the interaction of methane with the acid OH groups.

It should be emphasized again that two ensembles of diffusing methane exhibit two separate signals with the distance between the signals of about 0.5 ppm, i.e., the exchange rate between methane molecules diffusing by different pathways is less than 200 s^{-1} . This is unexpected for methane diffusion in the ZSM-5 zeolite framework. We believe that this phenomenon might be related to some specifics of localization of Ag^+ cations in the zeolite channel system, as well as with the presence in the zeolite void of some small quantity of Ag^0 species or the metallic clusters (Ag_n^0). Ethene adsorbed on the Ag^+ cations may block the exchange of methane between two ensembles. A special study to clarify the localization of Ag^+ cations and the reason for the absence of the exchange between differently diffusing methane ensembles is required, which is, however, beyond the scope of the present article.

4. CONCLUSIONS

PFG ^1H MAS NMR analysis of the diffusion coefficients for methane in $\text{Ag}/\text{H-ZSM-5}$ allowed us to clarify the peculiarities of methane diffusivity in the presence and absence of coadsorbed ethene. Diffusion of methane in the absence of ethene occurs more slowly than in the presence of coadsorbed ethene. In the absence of ethene, the activation energy for methane diffusion is 29 kJ mol^{-1} . This high value of activation energy for diffusion can be related with some strong interaction of methane with Ag^+ cations located in the zeolite channel system. In the presence of coadsorbed ethene, the diffusion of methane occurs faster. Two ensembles of diffusing methane become distinguishable. The activation energies of diffusion ($6\text{--}8 \text{ kJ mol}^{-1}$) become close to the activation energy of methane intracrystalline diffusion in H-ZSM-5 ($4\text{--}5 \text{ kJ mol}^{-1}$).^{32–34} Decrease of activation energy and acceleration of diffusion in the latter case might be related to the shielding effect of ethene adsorbed on Ag^+ cations to form π -complexes. An absence of direct interaction of methane with Ag^+ cations provides a significant decrease of activation energy and acceleration of methane diffusion. Two ensembles of diffusing methane may arise from the two pathways of methane diffusion through the channel system. By one pathway, methane may diffuse over π -complexes of ethene with Ag^+ cations and the zeolite acid OH groups, and the other pathway may include the methane diffusion in the zeolite channels exclusively over the zeolite OH groups.

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Notes

The authors declare no competing financial interest.

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