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Methane Interaction with Zn^{2+} -Exchanged Zeolite H-ZSM-5: Study of Adsorption and Mobility by One- and Two-Dimensional Variable-Temperature ^1H Solid-State NMR

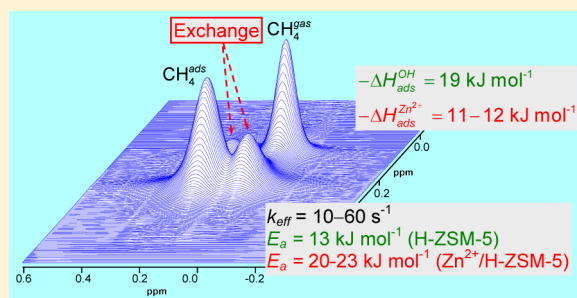
Mikhail V. Luzgin,^{†,‡} Dieter Freude,[§] Jürgen Haase,[§] and Alexander G. Stepanov^{*,†,‡}

[†]Boriskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia

[‡]Faculty of Natural Sciences, Department of Physical Chemistry, Novosibirsk State University, Pirogova Street 2, Novosibirsk 630090, Russia

[§]Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstrasse 5, 04103 Leipzig, Germany

ABSTRACT: Acidic zeolites in which protons are substituted (completely or in part) by metal cations demonstrate higher activity in catalytic reaction of light alkanes conversion in comparison with parent zeolites. The study of alkane adsorption on metal cationic species as the first stage of alkane interaction with the active sites of zeolites is crucial for understanding the mechanism of light alkane activation on metal-containing zeolites. By using variable-temperature ^1H magic-angle spinning nuclear magnetic resonance (^1H MAS NMR), the adsorption of methane on Zn^{2+} -exchanged H-ZSM-5 zeolites (Zn^{2+} /H-ZSM-5) with different Zn^{2+} content, as well as on source H-ZSM-5, has been studied at 333–463 K. The enthalpy of adsorption (ΔH_{ads}) on different centers, acid-bridged OH groups and Zn^{2+} cations, has been determined to be -18.6 ± 0.4 kJ mol $^{-1}$ for OH groups and from -10.9 to -11.7 kJ mol $^{-1}$ for Zn^{2+} cations of both Zn^{2+} /H-ZSM-5 zeolite samples studied. Two-dimensional ^1H MAS exchange NMR experiments revealed the chemical exchange between the adsorbed and gas-phase methane molecules at 353–463 K with the effective rate constant of 10–60 s $^{-1}$. The increase of Zn^{2+} content leads to a decrease of the exchange rate, whereas the apparent activation energy (E_a) of the exchange increases from 13 kJ mol $^{-1}$ for H-ZSM-5 zeolite to 20 and 23 kJ mol $^{-1}$ for the samples, in which 50% and 85% of acid protons, respectively, were substituted by Zn^{2+} cations. Variation of E_a for samples with and without Zn^{2+} cations was interpreted in terms of internal transport barriers that can exist at the intersections between the elementary building blocks of the crystals and/or between the crystal intergrowths in crystals of our zeolite samples. Additional transport barriers can arise from the bulky Zn^{2+} cations, located at the entrances of the zeolite pore system on the crystal surface.



1. INTRODUCTION

H-ZSM-5 zeolites modified with Zn are known as active catalysts for conversion of light alkanes, including dehydrogenation and aromatization reactions^{1–3} and even ethane and methane activation and conversion.^{4–9}

The initial stages of C_1 – C_2 alkanes activation by Zn-modified zeolites have been studied in detail. Theoretical studies predicted the light alkane activation to occur via heterolytic dissociation of the C–H bond over $\text{Zn}^{\delta+}$ – $\text{O}^{\delta-}$ pairs.^{10–15} Later on, these theoretical results were confirmed experimentally by IR and NMR spectroscopic methods.^{4–6,8,9,16,17}

With regard to the molecular adsorption of methane on Zn-modified zeolites, which precedes the alkane dissociation, only theoretical studies are presented in the literature.^{11,14} Physisorption of methane has been considered using different active sites possible for zinc cation, the appropriate values of the energies of methane adsorption having been calculated.^{11,14} The experimental confirmation of theoretical results would be

of great importance to achieve a more complete understanding of all stages of the methane activation and conversion on acidic zeolites modified with Zn.

In the present paper, the study of the interaction of methane with H-ZSM-5 zeolite modified with Zn^{2+} cation has been performed using solid-state NMR. The enthalpy of methane physisorption on Zn^{2+} species has been determined by means of variable-temperature ^1H MAS NMR. Two-dimensional (2D) exchange ^1H MAS NMR spectroscopy has been used for monitoring the exchange between the adsorbed and the gas-phase methane molecules.

2. EXPERIMENTAL SECTION

2.1. Materials Characterization and Sample Preparation. The template-free synthesized NH_4 -ZSM-5 (Si/Al = 13)

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zeolite was provided by Tricat Zeolites. Methane ($\geq 99.0\%$ purity) was purchased from Aldrich Chemical Co. Inc. and was used without further purification.

The hydrogen form of the zeolite (H-ZSM-5) was prepared from the parent ammonium form by calcination at 773 K for 5 h. A silicon-to-aluminum ratio of 13 was estimated for H-ZSM-5 zeolite based on ^{29}Si MAS NMR analysis¹⁸ and confirmed by chemical analysis data. No extraframework aluminum atoms were observed in the ^{27}Al MAS NMR spectrum of the hydrated H-ZSM-5 zeolite.¹⁹

The Zn-modified zeolite ($\text{Zn}^{2+}/\text{H-ZSM-5}$) was prepared by the high-temperature treatment of dehydrated H-ZSM-5 material with Zn vapor according to the procedure described earlier.^{4,7,20,21} The H-ZSM-5 zeolite was placed into a glass tube equipped with an appendix containing Zn powder. The zeolite was activated at 673 K first in air for 2 h and then in vacuum for 8 h with a residual pressure less than 10^{-2} Pa. The appendix with Zn was maintained at room temperature during the zeolite calcination. The glass tube with the appendix was sealed off from the vacuum system, and the powder of metallic zinc from the appendix was mixed with dehydrated H-ZSM-5 under vacuum conditions. The mixture was calcined at 773 K for 1 h. The glass system was opened, and the sample material was transferred under argon atmosphere into an NMR cell, which was connected to a vacuum line. Further evacuation of the sample again at 773 K for 1 h was carried out to remove argon, unreacted metallic zinc, and hydrogen that formed. Two samples of $\text{Zn}^{2+}/\text{H-ZSM-5}$ zeolite were prepared. For the first one, the metallic zinc was added in a proportion of $\text{Zn}/\text{Al} \approx 0.5$. For the second sample a 10-fold excess of zinc was used ($\text{Zn}/\text{Al} \approx 10$).

The sample of the parent H-ZSM-5 zeolite was activated by a procedure that was similar to that preceding the process of zeolite modification with Zn.

The adsorption of methane (ca. $350 \mu\text{mol g}^{-1}$) on the zeolite samples under study was performed at the temperature of liquid nitrogen. The glass tube with methane adsorbed on zeolite was then sealed off from the vacuum system, and the tube was kept at the temperature of liquid nitrogen while it was sealed off with a torch flame. The finally sealed glass tube of 3.0 mm o.d. and 10 mm length represents the NMR cell. This cell can be tightly inserted into the 4 mm NMR zirconia rotor to perform the analysis of the state of methane adsorbed on zeolite.

^1H MAS NMR spectra revealed that the treatment of H-ZSM-5 sample with Zn vapor caused the decrease of the concentration of bridged acidic Si–OH–Al groups, and the amount of silanol Si–OH groups remained unchanged (Figure 1). Using methane as an internal standard, the concentration of Si–OH–Al and Si–OH groups was estimated by ^1H MAS NMR for H-ZSM-5 and $\text{Zn}^{2+}/\text{H-ZSM-5}$ samples. This allows the determination of the degree of exchange of surface protons with zinc cations (Table 1). The concentration of bridged Si–OH–Al groups in the parent H-ZSM-5 sample correlated well with the Si/Al ratio, from which the atomic concentration of Al of $1200 \mu\text{mol g}^{-1}$ should be expected (Table 1).

For the Zn-modified zeolites produced from the initial reagents mixture with $\text{Zn}/\text{Al} \approx 0.5$, about 50% of protons of bridged Si–OH–Al groups were substituted by Zn^{2+} cations. In the case of excess zinc ($\text{Zn}/\text{Al} \approx 10$), 85% of protons were substituted. In Table 1 and below, these samples are denoted as $\text{Zn}^{2+}/\text{H-ZSM-5}(50)$ and $\text{Zn}^{2+}/\text{H-ZSM-5}(85)$, respectively.

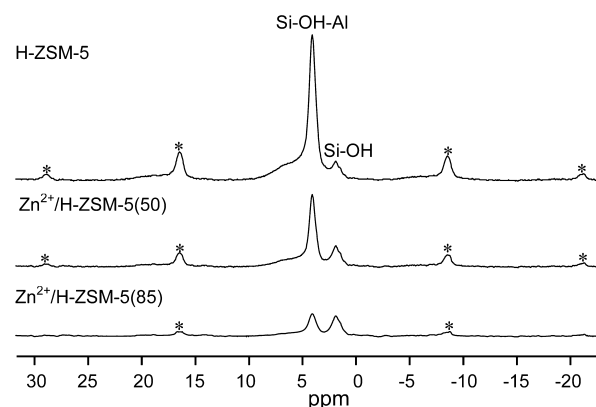


Figure 1. ^1H MAS NMR spectra of H-ZSM-5, $\text{Zn}^{2+}/\text{H-ZSM-5}(50)$ and $\text{Zn}^{2+}/\text{H-ZSM-5}(85)$ zeolites. Asterisks (*) denote spinning sidebands.

Table 1. Concentration of OH Groups for H-ZSM-5 and $\text{Zn}^{2+}/\text{H-ZSM-5}$ Zeolite Samples

zeolite sample	concn of OH groups ($\mu\text{mol g}^{-1}$)		degree of exchange by Zn^{2+} (%)
	Si–OH	Si–OH–Al	
H-ZSM-5	70	1200	
$\text{Zn}^{2+}/\text{H-ZSM-5}(50)$	70	600	50
$\text{Zn}^{2+}/\text{H-ZSM-5}(85)$	70	250	85

2.2. NMR Experiments. ^1H MAS NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (Larmor frequency of 400.117 MHz) in the temperature range of 296–473 K using a 4.0 mm MAS probe.

One-dimensional (1D) ^1H MAS NMR spectra were measured by the Hahn-echo pulse sequence with a pulse distance equal to the one period of rotor spinning, 200 μs . This echo pulse sequence was used to suppress a broad signal from the NMR probe. The relative intensities of the signals under study are equal for echo and FID measurements, as could be shown by a control experiment with the single-pulse excitation.

Two-dimensional (2D) exchange ^1H MAS NMR spectra were recorded using a NOESY pulse sequence ($90^\circ-t_1-90^\circ-\tau_{\text{mix}}-90^\circ$ -acquisition),²² where t_1 is the incremented delay and τ_{mix} is the mixing time, which was varied between 10 and 100 ms.

The following conditions were used for recording the ^1H MAS NMR spectra: the length of the 90° ^1H pulse was 5.0 μs ; the delay time between scans was 50 s for the 1D experiment, which satisfied the $10 \times T_1$ condition for all resonances, and was 1 s for the 2D experiment ($10 \times T_1$ condition for methane signals). For each 1D ^1H MAS NMR spectrum, 64 scans were collected. For the 2D experiment, 128 t_1 increments with 16–128 scans each were collected.

The spinning rate was 5 kHz. ^1H chemical shifts were referenced with respect to TMS with an accuracy of ± 0.5 ppm. The precision in the determination of the relative signal position was 0.1–0.15 ppm. The temperature of the samples was controlled by a Bruker BVT-3000 variable-temperature unit. The calibration of the temperature inside the rotor was performed with an accuracy of ± 2 K by using lead nitrate as a ^{207}Pb MAS NMR chemical shift thermometer.²³

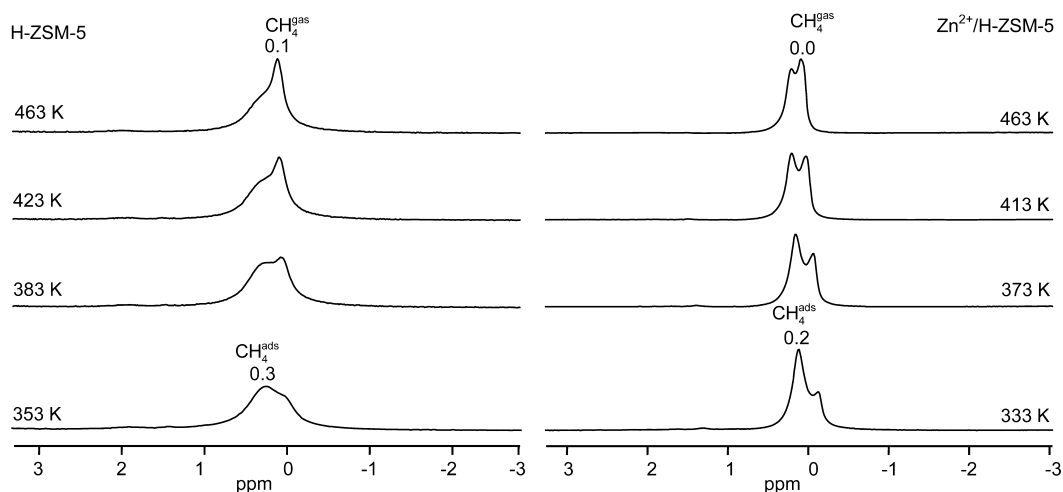


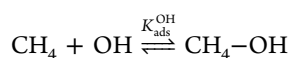
Figure 2. ^1H MAS NMR spectra recorded at 333–463 K for methane on H-ZSM-5 (left) and $\text{Zn}^{2+}/\text{H-ZSM-5(50)}$ (right) zeolites.

3. RESULTS AND DISCUSSION

3.1. ^1H MAS NMR Study of Methane on H-ZSM-5 and $\text{Zn}^{2+}/\text{H-ZSM-5}$ Zeolites. Enthalpy of Methane Adsorption. Figure 2 shows the evolution with temperature of ^1H MAS NMR spectrum of methane on H-ZSM-5 (left spectra) and on $\text{Zn}^{2+}/\text{H-ZSM-5(50)}$ zeolites (right spectra). Similar patterns are observed for both samples [as well as for $\text{Zn}^{2+}/\text{H-ZSM-5(85)}$ sample; spectra are not shown]. Two signals from methane can be distinguished at 0.3 and 0.1 ppm for H-ZSM-5 and at 0.2 and 0.0 ppm for $\text{Zn}^{2+}/\text{H-ZSM-5(50)}$ zeolites. An increase of temperature causes an increase of the intensity of high-field signals at 0.1 and 0.0 for both zeolite samples (Figure 2). We expect that the equilibrium between methane in the adsorbed state and the gas phase shifts to the gas phase with an increase of the temperature. Therefore, we conclude that the signals at 0.1 and 0.0 ppm belong to gaseous methane, whereas those at 0.3 (H-ZSM-5) and 0.2 ppm [$\text{Zn}^{2+}/\text{H-ZSM-5(50)}$] can be attributed to methane molecules adsorbed in the zeolite pores.

The methane adsorption on H-ZSM-5 zeolite occurred mainly by the formation of hydrogen-bonded complexes with the bridged hydroxyl (Si-OH-Al) groups.^{24,25} So, the signal at 0.3 ppm belongs to methane adsorbed on such bridged Si-OH-Al groups in H-ZSM-5 zeolite. Indeed, methane adsorbed on pure silica ZSM-5 (silicalite-1), which contains only nonacidic SiOH groups as the adsorption sites, shows the signal at 0.1 ppm. Its position coincides with that of resonance from gaseous methane on our H-ZSM-5 sample. So, the methane adsorption on silicalite-1 results in an upfield shift of the adsorbed methane signal with regard to the position of the signal in H-ZSM-5.

The resonance at 0.2 ppm in $\text{Zn}^{2+}/\text{H-ZSM-5}$ zeolites can be explained by methane molecules adsorbed on both zinc cationic centers and Si-OH-Al groups. The ratios between the signals from the gaseous and the adsorbed methane differ for Zn-containing and unmodified zeolites. This can be rationalized in terms of different values of equilibrium constant for adsorption, K_{ads} , on different adsorption centers. The methane adsorption on bridged hydroxyl groups can be described by the equilibrium equation



In this case, the equilibrium constant, $K_{\text{ads}}^{\text{OH}}$, can be written in terms of different species concentrations ($\mu\text{mol g}^{-1}$) as follows

$$K_{\text{ads}}^{\text{OH}} = \frac{[\text{CH}_4\text{-OH}]}{[\text{CH}_4^{\text{gas}}][\text{OH}]} \quad (1)$$

where $[\text{CH}_4^{\text{gas}}]$ and $[\text{CH}_4\text{-OH}]$ are the equilibrium concentrations of the gaseous and the adsorbed methane and $[\text{OH}]$ is the equilibrium concentration of the bridged OH groups, free of adsorbed methane. $[\text{CH}_4^{\text{gas}}]$ and $[\text{CH}_4\text{-OH}]$ are determined from the initial total concentration of methane ($350 \mu\text{mol g}^{-1}$) and the ratio $[\text{CH}_4^{\text{gas}}]/[\text{CH}_4\text{-OH}]$ obtained from the relative intensities of the signals of the adsorbed and the gaseous methane in ^1H MAS NMR spectra. $[\text{OH}]$ is equal to the difference between the known initial concentration of the Si-OH-Al groups ($1200 \mu\text{mol g}^{-1}$) and $[\text{CH}_4\text{-OH}]$. The values of $K_{\text{ads}}^{\text{OH}}$, calculated for different temperatures, are presented in Table 2.

The temperature dependence of $K_{\text{ads}}^{\text{OH}}$ allows one to estimate the enthalpy of methane adsorption on bridged OH groups of H-ZSM-5 zeolite ($\Delta H_{\text{ads}}^{\text{OH}}$), which proved to be $-18.6 \pm 0.3 \text{ kJ mol}^{-1}$. This value is close to the results of methane adsorption on silicalite-1, high-silica H-ZSM-5 ($\text{Si/Al} = 300$), and Na-ZSM-5 zeolites (from -19.0 to $-20.9 \text{ kJ mol}^{-1}$) obtained by

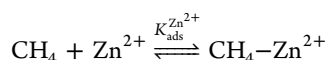
Table 2. Equilibrium Constants for Adsorption of Methane on Si-OH-Al and Zn^{2+} Centers of H-ZSM-5 and $\text{Zn}^{2+}/\text{H-ZSM-5}$ Zeolites

T (K)	$K_{\text{ads}}^{\text{OH}} \times 10^3$ ($\text{g } \mu\text{mol}^{-1}$): H-ZSM-5	$K_{\text{ads}}^{\text{Zn}^{2+}} \times 10^3$ ($\text{g } \mu\text{mol}^{-1}$)	
		$\text{Zn}^{2+}/\text{H-ZSM-5(50)}$	$\text{Zn}^{2+}/\text{H-ZSM-5(85)}$
353	3.9	10.1	8.5
363	3.3	9.0	7.4
373	2.9	8.2	6.9
383	2.6	7.5	6.2
393	2.1	6.0	5.5
403	1.9	6.3	5.0
413	1.6	5.8	4.6
423	1.4	5.3	4.4
433	1.2	4.9	4.2
443	1.1	4.5	3.9
453	1.0	4.2	3.7
463	0.85	3.9	3.5

traditional methods of adsorption isotherms, calorimetry, gravimetry, gas chromatography, and ATR-FTIR.^{26–31} Note that the acidic bridged Si–OH–Al groups are practically absent on these materials. Thus, the nature of oxygen atoms in the walls of the zeolite framework (in bridged OH, silanol OH, or –O– fragment), interacting with adsorbate (methane) molecule, has no significant effect on the adsorption heat. The dimensions of the zeolite pores seem to be the key factor determining the heats of adsorption of light alkanes on zeolite catalysts.²⁹

Very interesting for confirmation and/or refinement of results of theoretical studies^{11,14} is the evaluation of parameters of methane adsorption on Zn²⁺ cationic species in Zn²⁺/H-ZSM-5 zeolite.

For the process of methane adsorption on Zn²⁺ cationic species



we can write the equilibrium adsorption constant as follows:

$$K_{\text{ads}}^{\text{Zn}^{2+}} = \frac{[\text{CH}_4\text{--Zn}^{2+}]}{[\text{CH}_4^{\text{gas}}][\text{Zn}^{2+}]} \quad (2)$$

We assume that the processes of methane adsorption on two different centers, bridged OH group and Zn²⁺ cation, proceed independently. In this case, $K_{\text{ads}}^{\text{OH}}$ for both Zn²⁺/H-ZSM-5 samples should coincide and be equal to the methane equilibrium constant of adsorption on zinc-free H-ZSM-5 zeolite at each temperature studied. So, using $K_{\text{ads}}^{\text{OH}}$, determined for H-ZSM-5 sample, and the known initial concentration of acidic protons in Zn²⁺/H-ZSM-5 samples, the concentration of methane adsorbed on these centers, $[\text{CH}_4\text{--OH}]$, was determined from eq 1. Further, knowing the total concentration of methane adsorbed on Zn²⁺ and proton centers from NMR spectra for Zn²⁺/H-ZSM-5 samples, we were able to evaluate the concentration of CH₄–Zn²⁺ species. Finally, the equilibrium adsorption constants for methane on zinc centers were calculated using eq 2 and the known initial concentration of Zn²⁺ cations in both samples (see Table 2). It should be noted that for both Zn²⁺-containing samples we have obtained similar values of $K_{\text{ads}}^{\text{Zn}^{2+}}$ (Table 2). This confirms our assumption that the processes of methane adsorption on two different centers, the acid-bridged OH groups and Zn²⁺ cations, can be considered as independent of each other.

The temperature dependence of $K_{\text{ads}}^{\text{Zn}^{2+}}$ (Figure 3) allows us to estimate the enthalpy of the methane adsorption on cationic zinc centers, $\Delta H_{\text{ads}}^{\text{Zn}^{2+}}$. The obtained value of the $\Delta H_{\text{ads}}^{\text{Zn}^{2+}}$ was $-11.7 \pm 0.2 \text{ kJ mol}^{-1}$ for Zn²⁺/H-ZSM-5(50) and $-10.9 \pm 0.3 \text{ kJ mol}^{-1}$ for Zn²⁺/H-ZSM-5(80).

The theoretically calculated value of the adsorption enthalpy of methane on $[\text{Zn--O--Zn}]^{2+}$ centers is $+2.1 \text{ kJ mol}^{-1}$ (endothermic adsorption), on ZnO clusters modeled under the (ZnO)₄ cubic structure is -7.7 kJ mol^{-1} (exothermic adsorption), and on Zn²⁺ cations in the zeolite framework modeled as a four-membered ring cluster (“4T ring”) is $-16.8 \text{ kJ mol}^{-1}$ (exothermic adsorption).^{11,14} Thus, as far as there are no ZnO clusters in our zeolite samples, the obtained values of $\Delta H_{\text{ads}}^{\text{Zn}^{2+}}$ indicate that Zn²⁺ cations that are located in a 4T rings¹¹ might be responsible for the methane adsorption on the Zn²⁺/H-ZSM-5 zeolites.

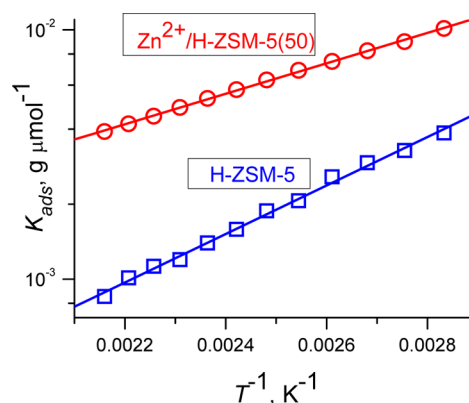


Figure 3. Temperature dependence of the equilibrium constant for the adsorption of methane on bridged OH groups of H-ZSM-5 zeolite ($K_{\text{ads}}^{\text{OH}}$, □) and on Zn²⁺ cationic centers of Zn²⁺/H-ZSM-5(50) zeolite ($K_{\text{ads}}^{\text{Zn}^{2+}}$, ○).

According to the literature data, two types of Zn²⁺ cations can exist in Zn²⁺/H-ZSM-5 zeolites, depending on Si/Al ratio. The first one is Zn²⁺ cations at the conventional exchangeable cationic positions with two neighbor aluminum atoms in the zeolite framework. The second type represents Zn²⁺ cations, the positive charge of which is compensated by the negative charges of two distantly separated $[\text{AlO}_4]^-$ tetrahedra.^{21,32} For the Si/Al ratio of 13, the Zn²⁺ cations located at two neighboring aluminum–oxygen tetrahedra³² should be the main state of zinc in the samples used in our study and responsible for the methane adsorption.

3.2. 2D ¹H MAS Exchange NMR Study of Dynamics of Methane Adsorbed on H-ZSM-5 and Zn²⁺/H-ZSM-5 Zeolites. Observation of the Exchange between the Adsorbed and the Gas-Phase CH₄. Solid-state NMR spectroscopy has been successfully employed for the characterization of the mobility of hydrocarbons adsorbed on zeolites.^{33–38} Two-dimensional exchange solid-state NMR is often used to observe and quantify dynamics of molecules.^{39,40} The 2D exchange ¹³C NMR technique was used for the study of the benzene molecular hopping between different Ca²⁺ cation adsorption sites in Ca-LSX zeolite.^{33,34} The hopping process of *n*-pentane in zeolite ZK-5 between neighboring cages³⁶ and the slow jump reorientation dynamics of benzene adsorbed on Ag–Y zeolite³⁵ have been also investigated by 2D exchange ¹³C NMR, and 2D exchange ¹²⁹Xe NMR was also applied for studying the dynamic processes and permitted a quantitative description of inter- and intracrystalline mass transfer processes.^{37,38}

However, 2D exchange ¹H NMR has not yet been applied to the studies of the dynamics of hydrocarbons adsorbed on solid catalysts. The narrow range of ¹H chemical shifts does not allow one to resolve the different signals, e.g., from the adsorbed and the gas-phase molecules, in static experiments (without MAS). In our case, the ¹H MAS NMR signals from the gaseous methane and the methane adsorbed on the zeolite proved to be resolved enough. This prompted us to study the dynamics of methane adsorbed on H-ZSM-5 and Zn²⁺/H-ZSM-5 by means of 2D exchange ¹H NMR. We have tried to observe the exchange between the adsorbed and the gas-phase methane molecules and to estimate the rate of this process.

Figure 4 shows 2D ¹H MAS NMR exchange contour plots for methane, interacting with H-ZSM-5 and Zn²⁺/H-ZSM-5 zeolites. The cross-peaks between the resonances of adsorbed

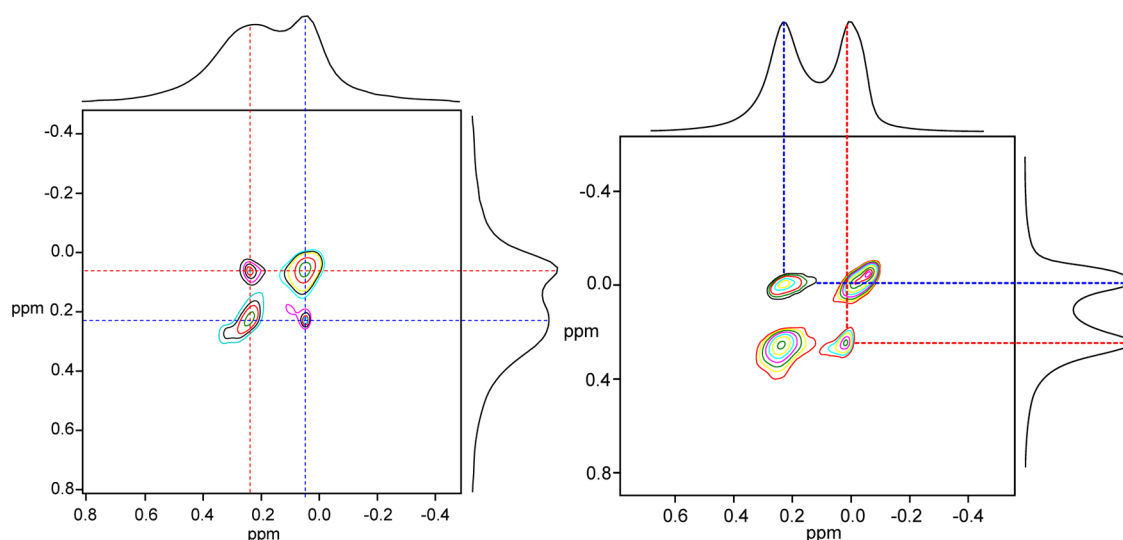


Figure 4. 2D ^1H MAS NMR exchange contour plots for methane on H-ZSM-5 at 373 K (left) and $\text{Zn}^{2+}/\text{H-ZSM-5(50)}$ at 463 K (right), recorded with mixing time $\tau_{\text{mix}} = 40$ ms. For clarity, the highest levels of 2D spectra are presented.

and gaseous methane have been observed in the temperature range of 353–403 K for H-ZSM-5 and 403–463 K for both $\text{Zn}^{2+}/\text{H-ZSM-5}$ samples. This indicates that the exchange between the gas phase and the adsorbed methane occurs for these zeolites.

The mixing time, τ_{mix} , was varied in our experiments from 1 to 100 ms. In the region of $\tau_{\text{mix}} = 10$ –40 ms, the ratio between the intensities of the cross-peaks (I_c) and diagonal ones (I_d) proved to be in good correlation with the theoretical dependence of I_c/I_d on τ_{mix} :⁴¹

$$\frac{I_c}{I_d} = \frac{1 - \exp(-k_{\text{eff}}\tau_{\text{mix}})}{1 + \exp(-k_{\text{eff}}\tau_{\text{mix}})} \quad (3)$$

The values of the effective rate constants (k_{eff}) of the exchange between gaseous and adsorbed methane are in the range of 10–60 s^{-1} (see Figure 5). This rate of exchange may

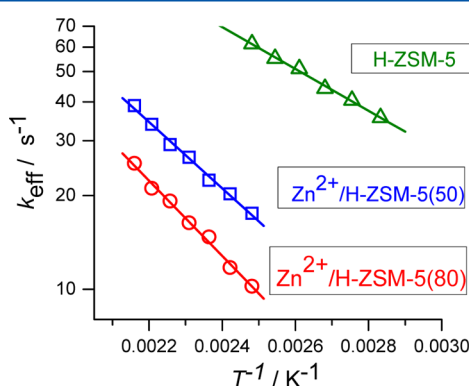


Figure 5. Arrhenius plots for the exchange rate between the adsorbed and the gas-phase methane for zeolite: H-ZSM-5 (Δ), $\text{Zn}^{2+}/\text{H-ZSM-5(50)}$ (\square), and $\text{Zn}^{2+}/\text{H-ZSM-5(85)}$ (\circ).

correspond to extremely slow diffusivity of methane on the border between zeolite crystal and gas phase. Indeed, if we accept that methane diffuses in vicinity of the crystallite for the distance of $\langle l^2 \rangle^{1/2} \sim 10$ nm to get into zeolite crystal from the gas phase, then, as could be estimated on the basis of the Einstein equation ($D = \langle l^2 \rangle / 6\tau$) for $k_{\text{eff}} \sim 50 \text{ s}^{-1}$ ($\tau \sim 0.02$ s),

the diffusion coefficient of methane to enter into the zeolite crystal should be $\sim 10^{-15} \text{ m}^2 \text{ s}^{-1}$. This value is essentially lower than the diffusion coefficient of methane in the intracrystalline void of ZSM-5 ($\sim 10^{-9}$ – $10^{-8} \text{ m}^2 \text{ s}^{-1}$)^{42–45} or methane diffusion in a gas phase ($\sim 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at the pressure of ~ 170 Torr above our samples^{46,47}). The Arrhenius plots for k_{eff} reveal a noticeable dependence of the exchange rate of temperature for all zeolite samples under study (Figure 5).

The apparent activation energy for the exchange of methane between the adsorbed and the gaseous states on unmodified H-ZSM-5 zeolite proved to be $12.9 \pm 0.5 \text{ kJ mol}^{-1}$. Pulsed field gradient NMR and quasi-elastic neutron scattering showed that the activation energy of the intracrystalline methane diffusion in ZSM-5 zeolite was 4–5 kJ mol^{-1} .^{42–45,48} However, this value was obtained at short diffusion times or in the limit of small displacements of several nanometers. The apparent activation energy of the diffusion monitored on the macroscopic length scale compared with the crystal size (several micrometers) was expected to be larger than that obtained in the limit of small displacements.⁴⁵ It was inferred that the intersections between different intergrowth components of the ZSM-5 crystals and/or between the elementary building blocks of the crystals may serve as additional activation barriers for diffusing molecules. Indeed, it was demonstrated that in the limit of large displacement, the apparent activation energy of the methane diffusion in ZSM-5 zeolite approaches the value of 13.8 kJ mol^{-1} .⁴⁵ The activation energy obtained in the present study for the exchange between the gaseous and the adsorbed methane is close to this value. So, we believe that internal transport barriers that can exist at the intersections between the elementary building blocks of the crystals and/or between the crystal intergrowths in crystals of our H-ZSM-5 zeolite provide the apparent activation energy of $\sim 13 \text{ kJ mol}^{-1}$ for the exchange of methane. On $\text{Zn}^{2+}/\text{H-ZSM-5}$ samples, the exchange (i.e., diffusion on the border between zeolite crystal and gas phase) is slower in comparison with that on H-ZSM-5 zeolite. The apparent activation energies are higher [$E_a = 20.4 \pm 0.7 \text{ kJ mol}^{-1}$ for $\text{Zn}^{2+}/\text{H-ZSM-5(50)}$ and $E_a = 23.1 \pm 0.8 \text{ kJ mol}^{-1}$ for $\text{Zn}^{2+}/\text{H-ZSM-5(85)}$ zeolites; see Figure 5]. The higher activation energies for the exchange could be rationalized by additional transport barriers that arise from

the bulky Zn^{2+} cations, strongly interacting with methane,¹⁶ located in the intracrystalline void at the place of crystal intergrowth in the crystals or at the entrances in the zeolite pore system on the crystal surface. So, it is expected that the substitution of H^+ by Zn^{2+} cations may hinder the diffusion of methane molecules through the channel system of ZSM-5, increasing the activation barrier for both the methane diffusion and the exchange of methane between the gas phase and the adsorbed state.

4. CONCLUSIONS

Using 1D and 2D ^1H solid-state NMR, the adsorption and dynamics of the interaction of methane with H-ZSM-5 and Zn^{2+} /H-ZSM-5 zeolites have been characterized.

^1H MAS NMR allowed us to distinctly identify both the gas-phase methane and methane adsorbed inside the zeolite pores. The equilibrium constants for methane adsorption on bridged hydroxyl groups and Zn^{2+} cationic centers have been determined. The temperature dependences of the equilibrium constants provided estimation of the enthalpy of the methane adsorption, which was found to be $-18.6 \text{ kJ mol}^{-1}$ for H-ZSM-5 and -10.9 and $-11.7 \text{ kJ mol}^{-1}$ for Zn^{2+} cationic centers of Zn^{2+} /H-ZSM-5 zeolites. The former value of adsorption enthalpy corresponds to methane adsorption on bridged hydroxyl groups, whereas the latter ones could be indicative of the methane adsorption on Zn^{2+} cations in the zeolite framework theoretically modeled as a four-membered ring (4T ring) cluster.¹¹

Two-dimensional exchange ^1H MAS NMR experiments have demonstrated the chemical exchange between the adsorbed and the gas-phase methane for both H-ZSM-5 and Zn^{2+} /H-ZSM-5 zeolites with the rate constants of $10\text{--}60 \text{ s}^{-1}$ at $353\text{--}463 \text{ K}$. The activation energy (E_a) for the exchange on H-ZSM-5 was found to be 13 kJ mol^{-1} , whereas this value was $20\text{--}23 \text{ kJ mol}^{-1}$ for Zn^{2+} /H-ZSM-5 zeolites. E_a of the exchange on H-ZSM-5 could be connected with internal transport barriers that can exist at the intersections between the elementary building blocks of the crystals and/or between the crystal intergrowths in crystals of our H-ZSM-5 zeolite. The higher activation energies $E_a = 20\text{--}23 \text{ kJ mol}^{-1}$ for the exchange on Zn^{2+} /H-ZSM-5 could be related to additional transport barriers that arise from the bulky Zn^{2+} cations, strongly interacting with methane¹⁶ and located in the intracrystalline void at the place of crystal intergrowth in the crystals or at the entrance in the zeolite pore system on the crystal surface.

AUTHOR INFORMATION

Corresponding Author

*Phone: +7 952 905 9559. Fax: +7 383 330 8056. E-mail: stepanov@catalysis.ru.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Mole, T.; Anderson, J. R.; Creer, G. The Reaction of Propane over ZSM-5-H and ZSM-5-Zn Zeolite Catalysts. *Appl. Catal.* **1985**, *17*, 127–141.

(2) Ono, Y. Transformation of Lower Alkanes into Aromatic Hydrocarbons over ZSM-5 Zeolites. *Catal. Rev.-Sci. Eng.* **1992**, *34*, 179–226.

(3) Hagen, A.; Roessner, F. Ethane to Aromatic Hydrocarbons: Past, Present, Future. *Catal. Rev.-Sci. Eng.* **2000**, *42*, 403–437.

(4) Kolyagin, Y. G.; Ivanova, I. I.; Ordonsky, V. V.; Gedeon, A.; Pirogov, Y. A. Methane Activation over Zn-Modified MFI Zeolite: NMR Evidence for Zn-Methyl Surface Species Formation. *J. Phys. Chem. C* **2008**, *112*, 20065–20069.

(5) Luzgin, M. V.; Rogov, V. A.; Arzumanov, S. S.; Toktarev, A. V.; Stepanov, A. G.; Parmon, V. N. Understanding Methane Aromatization on a Zn-Modified High-Silica Zeolite. *Angew. Chem., Int. Ed.* **2008**, *47*, 4559–4562.

(6) Luzgin, M. V.; Rogov, V. A.; Arzumanov, S. S.; Toktarev, A. V.; Stepanov, A. G.; Parmon, V. N. Methane Aromatization on Zn-Modified Zeolite in the Presence of a Co-Reactant Higher Alkane: How Does It Occur? *Catal. Today* **2009**, *144*, 265–272.

(7) Kolyagin, Y. G.; Ivanova, I. I.; Pirogov, Y. A. ^1H and ^{13}C MAS NMR Studies of Light Alkanes Activation over MFI Zeolite Modified by Zn Vapour. *Solid State Nucl. Magn. Reson.* **2009**, *35*, 104–112.

(8) Wu, J. F.; Wang, W. D.; Xu, J.; Deng, F.; Wang, W. Reactivity of C_1 Surface Species Formed in Methane Activation on Zn-Modified H-ZSM-5 Zeolite. *Chem.-Eur. J.* **2010**, *16*, 14016–14025.

(9) Wang, X. M.; Qi, G. D.; Xu, J.; Li, B. J.; Wang, C.; Deng, F. NMR-Spectroscopic Evidence of Intermediate-Dependent Pathways for Acetic Acid Formation from Methane and Carbon Monoxide over a ZnZSM-5 Zeolite Catalyst. *Angew. Chem., Int. Ed.* **2012**, *51*, 3850–3853.

(10) Zhanpeisov, N. U.; Zhidomirov, G. M.; Baerns, M. Cluster Quantum-Chemical Study of the Chemisorption of Methane on Zinc Oxide Surface. *J. Mol. Catal. A: Chem.* **1995**, *99*, 35–39.

(11) Barbosa, L. A. M. M.; Zhidomirov, G. M.; van Santen, R. A. Theoretical Study of Methane Adsorption on Zn(II) Zeolites. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3909–3918.

(12) Frash, M. V.; van Santen, R. A. Activation of Ethane in Zn-Exchanged Zeolites: A Theoretical Study. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1085–1089.

(13) Yakovlev, A. L.; Shubin, A. A.; Zhidomirov, G. M.; van Santen, R. A. DFT Study of Oxygen-Bridged Zn^{2+} Ion Pairs in Zn/ZSM-5 Zeolites. *Catal. Lett.* **2000**, *70*, 175–181.

(14) van Santen, R. A.; Zhidomirov, G. M.; Shubin, A. A.; Yakovlev, A. L.; Barbosa, L. A. M. M. Reactivity Theory of Zinc Cation Species in Zeolites. In *Catalysis by Unique Metal Ion Structures in Solid Matrices: From Science to Application*; NATO Science Series II; Springer: Prague-Prunice, Czech Republic, 2000; Volume 13.

(15) Barbosa, L. A. M. M.; van Santen, R. A. Study of the Activation of C–H and H–H Chemical Bonds by the $[\text{ZnOZn}]^{(2+)}$ Oxyanion: Influence of the Zeolite Framework Geometry. *J. Phys. Chem. B* **2003**, *107*, 14342–14349.

(16) Kazansky, V. B.; Serykh, A. I.; Pidko, E. A. DRIFT Study of Molecular and Dissociative Adsorption of Light Paraffins by HZSM-5 Zeolite Modified with Zinc Ions: Methane Adsorption. *J. Catal.* **2004**, *225*, 369–373.

(17) Kazansky, V. B.; Pidko, E. A. Intensities of IR Stretching Bands as a Criterion of Polarization and Initial Chemical Activation of Adsorbed Molecules in Acid Catalysis. Ethane Adsorption and Dehydrogenation by Zinc Ions in ZnZSM-5 Zeolite. *J. Phys. Chem. B* **2005**, *109*, 2103–2108.

(18) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; Wiley & Sons: Chichester, UK, 1987.

(19) Gabrienko, A. A.; Arzumanov, S. S.; Moroz, I. B.; Toktarev, A. V.; Wang, W.; Stepanov, A. G. Methane Activation and Transformation on Ag/H-ZSM-5 Zeolite Studied with Solid-State NMR. *J. Phys. Chem. C* **2013**, *117*, 7690–7702.

(20) Seidel, A.; Boddenberg, B. Introducing Zinc Cations Into Zeolite Y via the Reduction of HY with Zinc Metal Vapour. *Chem. Phys. Lett.* **1996**, *249*, 117–122.

- (21) Kazansky, V. B.; Serykh, A. I. Unusual Localization of Zinc Cations in MFI Zeolites Modified by Different Ways of Preparation. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3760–3764.
- (22) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. Investigation of Exchange Processes by Two-Dimensional NMR Spectroscopy. *J. Chem. Phys.* **1979**, *71*, 4546–4553.
- (23) Ferguson, D. B.; Haw, J. F. Transient Methods For in situ NMR of Reactions on Solid Catalysts Using Temperature Jumps. *Anal. Chem.* **1995**, *67*, 3342–3348.
- (24) Chen, L.; Lin, L.; Xu, Z.; Zhang, T.; Liang, D.; Xin, Q.; Ying, P. Interaction of Methane with Surfaces of Silica, Aluminas and HZSM-5 Zeolite. A Comparative FT-IR Study. *Catal. Lett.* **1995**, *35*, 245–258.
- (25) Chen, L.; Lin, L.; Xu, Z.; Zhang, T.; Xin, Q.; Ying, P.; Li, G.; Li, C. Fourier Transform-Infrared Investigation of Adsorption of Methane and Carbon Monoxide on HZSM-5 and Mo/HZSM-5 Zeolites at Low Temperature. *J. Catal.* **1996**, *161*, 107–114.
- (26) Hufton, J. R.; Danner, R. P. Chromatographic Study of Alkanes in Silicalite: Transport Properties. *AIChE J.* **1993**, *39*, 954–961.
- (27) Zhu, W.; van de Graaf, J. M.; van den Broeke, L. J. P.; Kapteijn, F.; Moulijn, J. A. TEOM: A Unique Technique for Measuring Adsorption Properties. Light Alkanes in Silicalite-1. *Ind. Eng. Chem. Res.* **1998**, *37*, 1934–1942.
- (28) Sun, M. S.; Shah, D. B.; Xu, H. H.; Talu, O. Adsorption Equilibria of C₁ to C₄ Alkanes, CO₂, and SF₆ on Silicalite. *J. Phys. Chem. B* **1998**, *102*, 1466–1473.
- (29) Savitz, S.; Siperstein, F.; Gorte, R. J.; Myers, A. L. Calorimetric Study of Adsorption of Alkanes in High-Silica Zeolites. *J. Phys. Chem. B* **1998**, *102*, 6865–6872.
- (30) Choudhary, V. R.; Mayadev, S. Adsorption of Methane, Ethane, Ethylene, and Carbon Dioxide on High Silica Pentasil Zeolites and Zeolite-like Materials Using Gas Chromatography Pulse Technique. *Sep. Sci. Technol.* **1993**, *28*, 2197–2209.
- (31) Ohlin, L.; Bazin, P.; Thibault-Starzyk, F.; Hedlund, J.; Grahn, M. Adsorption of CO₂, CH₄, and H₂O in Zeolite ZSM-5 Studied Using In Situ ATR-FTIR Spectroscopy. *J. Phys. Chem. C* **2013**, *117*, 16972–16982.
- (32) Kazansky, V. B.; Serykh, A. I.; Anderson, B. G.; van Santen, R. A. The Sites of Molecular and Dissociative Hydrogen Adsorption in High Silica Zeolites Modified with Zinc Ions. III DRIFT Study of H₂ Adsorption by the Zeolites with Different Zinc Content and Si/Al Ratios in the Framework. *Catal. Lett.* **2003**, *88*, 211–217.
- (33) Wilhelm, M.; Firouzi, A.; Favre, D. E.; Bull, L. M.; Schaefer, D. J.; Chmelka, B. F. Dynamics of Benzene Adsorbed on Ca-LSX Zeolite Studied by Solid-State Two-Dimensional Exchange C-13 NMR. *J. Am. Chem. Soc.* **1995**, *117*, 2923–2924.
- (34) Schaefer, D. J.; Favre, D. E.; Wilhelm, M.; Weigel, S. J.; Chmelka, B. F. Site-Hopping Dynamics of Benzene Adsorbed on Ca-LSX Zeolite Studied by Solid-State Exchange C-13 NMR. *J. Am. Chem. Soc.* **1997**, *119*, 9252–9267.
- (35) Gédéon, A.; Favre, D. E.; Reichert, D.; MacNeil, J.; Chmelka, B. F. Distributions of Site-Hopping Geometries and Rates for Benzene Adsorbed on Ag-Y Zeolite. *J. Phys. Chem. A* **1999**, *103*, 6691–6703.
- (36) Magusin, P. C. M. M.; Schuring, D.; van Oers, E. M.; de Haan, J. W.; van Santen, R. A. *n*-Pentane Hopping in Zeolite ZK-5 Studied with C-13 NMR. *Magn. Reson. Chem.* **1999**, *37*, S108–S117.
- (37) Nossow, A.; Guenneau, F.; Springuel-Huet, M.-A.; Haddad, E.; Montouillout, V.; Knott, B.; Engelke, F.; Fernandez, C.; Gédéon, A. Continuous Flow Hyperpolarized ¹²⁹Xe-MAS NMR Studies of Microporous Materials. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4479–4483.
- (38) Nader, M.; Guenneau, F.; Boissiere, C.; Grosso, D.; Sanchez, C.; Gédéon, A. Dynamics of Xenon Adsorbed in Organically Modified Silica Thin Films Using Hyperpolarized ¹²⁹Xe 2D-Exchange NMR. *Stud. Surf. Sci. Catal.* **2007**, *165*, 555–558.
- (39) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: London, 1994.
- (40) Gedeon, A.; Fernandez, C. Solid-State NMR Spectroscopy in Zeolite Science. *Stud. Surf. Sci. Catal.* **2007**, *168*, 403–434.
- (41) Suter, D.; Ernst, R. R. Spin Diffusion in Resolved Solid-State NMR Spectra. *Phys. Rev. B* **1985**, *32*, 5608–5627.
- (42) Jobic, H.; Bée, M.; Caro, M.; Bülow, M.; Kärger, J. Molecular Self-Diffusion of Methane in Zeolite ZSM-5 by Quasi-Elastic Neutron Scattering and Nuclear Magnetic Resonance Pulsed Field Gradient Technique. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 4201–4209.
- (43) Datema, K. P.; den Ouden, C. J. J.; Ylstra, W. D.; Kuipers, H. P. C. E.; Post, M. F. M.; Kärger, J. Fourier-Transform Pulsed-Field-Gradient ¹H Nuclear Magnetic Resonance Investigation of the Diffusion of Light *n*-Alkanes in Zeolite ZSM-5. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1935–1943.
- (44) Vasenkov, S.; Bohlmann, W.; Galvosas, P.; Geier, O.; Liu, H.; Kärger, J. PFG NMR Study of Diffusion in MFI-Type Zeolites: Evidence of the Existence of Intracrystalline Transport Barriers. *J. Phys. Chem. B* **2001**, *105*, S922–S927.
- (45) Vasenkov, S.; Kärger, J. Evidence for the Existence of Intracrystalline Transport Barriers in MFI-type Zeolites: A Model Consistency Check Using MC Simulations. *Microporous Mesoporous Mater.* **2002**, *55*, 139–145.
- (46) Harris, K. R. The Density Dependence of the Self-Diffusion Coefficient of Methane at –50°, 25° and 50°C. *Physica* **1978**, *94A*, 448–464.
- (47) Smith, M. E.; Stuart, S. N. A Magnetic Characterization of the Texture of Simple Porous Media. *J. Phys. D: Appl. Phys.* **1995**, *28*, 229–238.
- (48) Kärger, J.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*; Wiley-Interscience: New York, 1992.