$^1$H MAS NMR monitoring of the $^{13}$C-labeled carbon scrambling for propane in zeolite H-ZSM-5

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Abstract

It has been demonstrated that $^1$H MAS NMR spectroscopy can be used as a tool for in situ monitoring the reaction kinetics of $^{13}$C-labeled carbon scrambling in alkane molecules adsorbed on zeolite catalysts at the reaction temperature of 540–570 K. The accuracy of the results and the time resolution are improved compared to $^{13}$C MAS NMR spectroscopy.

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1. Introduction

Solid state NMR spectroscopy has been established for the study of hydrocarbon conversion on solid acid catalysts [1–6]. Valuable information on the reaction mechanisms could be obtained by in situ monitoring the kinetics of the selective $^{13}$C-labeled carbon scrambling among the reactants and the products of the reaction [7,8]. However, $^{13}$C MAS NMR experiments are time consuming due to the low sensitivity of $^{13}$C nuclei and the long $T_1$ relaxation times. This limits the time resolution in kinetic studies. $^1$H NMR experiments exceed significantly the sensitivity and time resolution of kinetic $^{13}$C NMR measurements, but it is difficult to detect the scrambling of the $^{13}$C-label by $^1$H NMR. In principle, the J-splitting of the $^1$H NMR signal of the $^1$H nuclei connected to the $^{13}$C-labeled carbon atom can be utilized.

In this Letter, we demonstrate that mechanistic studies of alkane activation and transformation can be performed in situ by $^1$H MAS NMR observation of the $^{13}$C-labeled carbon transfer in alkane adsorbed on solid acid catalyst.

The novel technique is applied for the first time to the $^{13}$C-labeled carbon transfer in propane adsorbed on zeolite H-ZSM-5.

2. Experimental

Zeolite H-ZSM-5 was kindly provided by Tricat Zeolites. Its silicon-to-aluminum ratio was equal to 13 [7]. Propane-$^2$-$^{13}$C ($99\%$ $^{13}$C) purchased from ICON Inc. was used without further purification. The samples for the NMR measurements were prepared by heating 60 mg of the zeolite sample in the glass tubes of 5.5 mm outer diameter. The temperature was increased under vacuum at the rate of 10 K h$^{-1}$. The samples were maintained at 673 K for 24 h under vacuum (less than 10$^{-2}$ Pa). The loading of the zeolite with propane was performed at room temperature with 4 propane molecules per unit cell (ca 600 $\mu$mol g$^{-1}$). Then the glass tube (12 mm length) was sealed off.

$^1$H MAS NMR measurements were performed on a Bruker Avance 400 spectrometer at a Larmor frequency of 400.13 MHz using a Bruker high temperature probe within the temperature range ca. 540–570 K. The rotation frequency of a 7-mm-rotor with the inserted sealed glass tube was 3000 Hz. Free induction decays (FID) were recorded using a Hahn-echo sequence with the $\pi/2$-pulse.
of 4.5 μs duration and 333 μs delay between the two pulses, 4 s recycle delay, and 12 scans for the signal accumulation. The sample temperature was controlled by the Bruker BVT-1000 variable-temperature unit. The calibration of the temperature inside the rotor was performed with an accuracy of ±2 K by using lead nitrate sample as a $^{207}$Pb MAS NMR chemical shift thermometer [9].

### 3. Results and discussion

Propane-2-$^{13}$C adsorbed on zeolite H-ZSM-5 exhibits in the $^1$H MAS NMR spectrum a distinct doublet, centered at 1.5 ppm and a singlet at 1.0 ppm, at the temperature above 473 K (see Fig. 1, bottom spectrum). The singlet line belongs to the methyl groups, whereas the doublet line arises from the methylene group of propane. The separation of ca. 125 Hz between the maxima in the doublet corresponds to $J_{\text{CH}}$ - coupling arising from scalar spin-spin interaction of the $^{13}$C nuclei of the methylene group with the attached protons [10].

A reaction of the $^{13}$C-labeled carbon scrambling in the adsorbed propane can be described by the scheme

$$\text{CH}_3 - ^{13}\text{CH}_2 - \text{CH}_3 \xrightarrow{k^C} ^{13}\text{CH}_3 - \text{CH}_2 - \text{CH}_3$$

The apparent rate constant $k = k_1^C + k_2^C$ for the $^{13}$C-labeled carbon scrambling from the CH$_2$ group into the CH$_3$ groups of the adsorbed propane-2-$^{13}$C was determined by the simple exponential fits

$$I_t(\text{singlet}) = I_{\infty}(\text{singlet})[1 - \exp(-kt)] \quad \text{and}$$

$$I_t(\text{doublet}) = I_0(\text{doublet})[\exp(-kt)] + I_{\infty}(\text{doublet})[1 - \exp(-kt)], \quad (1)$$

where $I_t$, $I_{\infty}$, and $I_0$ denote the integral intensities of signals from the CH$_2$ group in the $^1$H MAS NMR spectra at the observation time $t$, $t = \infty$ (equilibrium), and $t = 0$, respectively. At $t = 0$ the temperature was rapidly increased from 503 K, at which the reaction did not yet occur, to the desired temperature of the experiment.

A transfer of $^{13}$C-labeled carbon from the methylene group into the methyl groups in the course of the reaction should result in decrease of the intensity of the doublet line at 1.5 ppm and appearance and increase of the intensity of the singlet in between of a doublet line. This singlet should correspond to the methylene group with the non-magnetic isotope $^{12}$C, which substitutes the $^{13}$C-labeled methylene groups and provides no $J_{\text{CH}}$ - splitting with the neighboring protons. So, monitoring of an increase of the intensity of a singlet line at 1.5 ppm and a decrease of the intensity of a doublet line with the same chemical shift as a function of the reaction time provides the kinetics of $^{13}$C-labeled carbon transfer in the adsorbed propane.

Fig. 1 shows the time dependent variation of the $^1$H MAS NMR spectrum of propane-2-$^{13}$C adsorbed on H-ZSM-5 at the temperature of 563 K. An increase of the singlet line and a decrease of the doublet at 1.5 ppm with time can be clearly seen. This allows an estimation of the kinetic parameters of $^{13}$C-labeled carbon scrambling. The decomposition of the signal at 1.5 ppm as a sum of the singlet line and the doublet line with $J$-splitting of 125 Hz gives the integral intensities of the corresponding signals. Variation of the intensities of the singlet and the doublet with the reaction time for the four studied temperatures is shown in Fig. 2.

Simulations of the kinetic curves yield the apparent rate constants $k = k_1^C + k_2^C$ for the $^{13}$C-labeled carbon scrambling from the CH$_2$ group into the CH$_3$ groups. The Arrhenius plot offers further the activation energy for the $^{13}$C-labeled carbon scrambling of 153 ± 5 kJ mol$^{-1}$ (see Fig. 3). The value $k_1^C$ was presented in Fig. 3 for a comparison with Fig. 6 in Ref. [7]. The comparison of the obtained data for the rate constants $k$ and the activation energy of 153 ± 5 kJ mol$^{-1}$ or the $^{13}$C-labeled carbon scrambling with similar parameters, e.g. 159 ± 13 kJ mol$^{-1}$, which were obtained earlier by $^{13}$C MAS NMR [7], shows a good agreement. The drastically increased signal-to-noise ratio of the $^1$H MAS NMR spectra compared to the $^{13}$C MAS NMR spectra yield more accurate $k$ and $k_1^C$ values (cf. Figs. 2 and 3 in this study and Figs. 5 and 6 in Ref. [7]).

Perhaps the most important advantage of the novel technique has not yet entirely demonstrated in this study. Indeed, with a 4-s-recycle delay and 12 scans for the signal accumulation, we could measure one spectrum per minute and observe much faster kinetics compared to that we have observed in the present study. Unfortunately the used probe limits our experiments to a maximum temperature of 573 K, at which the rate of the considered reaction is still quite slow.

![Fig. 1. Stack plot of the $^1$H MAS NMR spectra of propane-2-$^{13}$C adsorbed on H-ZSM-5 obtained at 563 K. The plot shows the signals of the methyl (1.0 ppm) and the methylene (1.5 ppm) groups. The first spectrum (bottom) was recorded 3 min after the temperature was raised to 563 K. The time between subsequent spectra recording was 14 min.](image-url)
4. Conclusions

$^1$H MAS NMR spectroscopy can be reliably used as a tool for in situ monitoring the reaction kinetics of $^{13}$C-labeled carbon scrambling in alkane molecules adsorbed on zeolite catalyst at the reaction temperature of 545–573 K. Kinetic parameters for propane adsorbed on zeolite H-ZSM-5 which have been obtained by $^1$H MAS NMR are in good accordance with those obtained earlier by $^{13}$C MAS NMR [7]. The accuracy of the kinetic parameters and the time resolution are improved compared to those obtained earlier by $^{13}$C MAS NMR spectroscopy.

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