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In situ NMR spectroscopy in heterogeneous catalysis

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Abstract

New experimental techniques of in situ MAS NMR spectroscopy introduced in the past decade made this analytical method to a useful tool for the study of heterogeneously catalyzed reactions. Batch and flow techniques were applied to study reactions catalyzed by basic and acidic solids. The present review introduces into in situ MAS NMR investigations of transition states, e.g., via the H/D exchange between acidic surface OH groups and reactants, the alkylation of aromatic compounds (toluene, aniline), and the formation of light olefins by conversion of methanol (MTO) on acidic zeolites. The studies of the MTO process clearly demonstrate the advantages of modern continuous-flow (CF) and stopped-flow (SF) approaches of in situ MAS NMR spectroscopy in heterogeneous catalysis.

Keywords: Heterogeneous catalysis; In situ NMR spectroscopy; Zeolites; Alkylation of aromatics; Methanol-to-olefin conversion

1. Introduction

A number of atoms in the framework and in surface sites of solid catalysts and in adsorbate complexes formed on these materials possess isotopes with a nuclear spin, which renders these isotopes NMR-active. In all these cases, NMR spectroscopy is a suitable tool for in situ studies in the wide field of heterogeneous catalysis. ^{1}H, ^{13}C, ^{15}N and ^{31}P are suitable isotopes allowing the study of a wide variety of reactants. Due to their nuclear spin of $I = 1/2$, sufficient line narrowing is reached by the conventional magic-angle spinning (MAS) NMR technique. Similar conditions exist for isotopes such as ^{1}H, ^{29}Si and ^{31}P in the framework and in surface sites of solid catalysts. Isotopes with a nuclear spin of $I > 1/2$ are characterized by an electric quadrupole moment. These nuclei are involved in quadrupolar interactions requiring the application of sophisticated solid-state NMR techniques, such as double-oriented rotation (DOR) or multiple-quantum MAS NMR (MQMAS) making their investigation more complicated.

In view of the broadness of in situ NMR spectroscopy in heterogeneous catalysis, no attempt will be undertaken to cover the field comprehensively, rather a few selected reactions will be treated. In a number of reviews, more detailed overviews on in situ NMR spectroscopy of heterogeneously catalyzed reactions are given [1–7]. In the majority of the applications of in situ NMR spectroscopy, zeolite catalysts were used, partly due to their ideal crystalline structures, partly in view of their widespread use in industrial catalysis.

2. Experimental techniques of NMR spectroscopy under in situ conditions

In 1989, Anderson and Klinowski [8] performed first MAS NMR investigations of a heterogeneously catalyzed reaction using samples of calcined solid catalysts fused in glass inserts. These glass inserts are fabricated with an outer diameter fitting exactly the inner diameter of the MAS NMR rotors applied. The glass inserts are filled with the catalyst material under study and, subsequently, connected with a vacuum line. The catalyst material is calcined under vacuum in an external oven and loaded with probe molecules or reactants using a vacuum line.

Another approach is based on the preparation of the solid catalyst directly inside an MAS NMR rotor. After calcination of the catalyst under vacuum and loading of the probe molecules or reactants, the MAS NMR rotor is sealed with a gas-tight rotor cap inside a special equipment. Haw et al. [9] introduced the so-called CAVERN (cryogenic adsorp-

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tion vessel enabling rotor nestling) equipment allowing the cooling of the catalyst material during the adsorption of adsorbate molecules and during the sealing of the rotor with a gas-tight cap.

Most large-scale industrial processes are working under flow conditions. Therefore, various groups are dealing with the development and application of experimental techniques allowing NMR investigations of surface sites and heterogeneously catalyzed reactions under comparable conditions. Nowadays, two experimental approaches of continuous-flow (CF) MAS NMR spectroscopy can be distinguished: (i) ex situ approaches with the catalytic reaction performed in an external fixed-bed reactor and a subsequent transfer of the catalyst into an MAS NMR rotor after quenching the reaction and (ii) in situ approaches utilizing the MAS NMR rotor directly as a fixed-bed reactor inside a high-temperature MAS NMR probe.

The “pulse-quench” technique of Haw et al. [6,10] utilizes an external microreactor for a continuous and/or pulsed introduction of the reactants and an analysis of the reaction products by on-line gas chromatography (approach (i)). The most significant feature of the “pulse-quench” reactor is the possibility to quickly switch the gas stream over the catalyst bed to cooled nitrogen, whereby the temperature of the catalyst can be lowered very rapidly. Upon quenching the reaction, the catalyst loaded with the reaction products is transferred into an MAS NMR rotor under dry nitrogen at ambient temperature using a glove box. Subsequently, the reaction products strongly adsorbed on the catalyst surface are investigated by NMR spectroscopy at ambient or sub-ambient temperatures. Zhang et al. [11] introduced an equipment, which is suitable to perform heterogeneous catalysis under continuous-flow conditions with the solid catalyst located inside a horizontal tube inside an external heater (Fig. 1). After stopping the reaction, the catalyst loaded with reaction products is filled without any contact to air (in situ) into a gas-tight MAS NMR rotor and measured at ambient temperature (approach (i)).

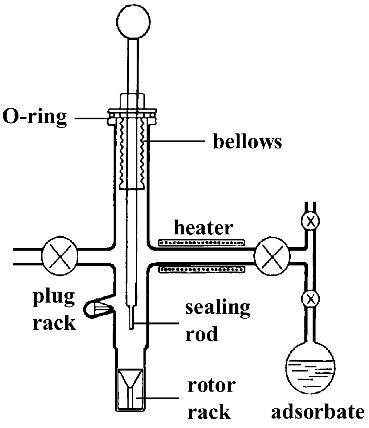

Fig. 1. Scheme of an equipment for the activation, loading, and sealing of solid catalyst samples in a gas-tight MAS NMR rotor [11].

In 1995, the first technique for in situ MAS NMR investigations of heterogeneously catalyzed reactions under continuous-flow conditions was introduced [12,13]. This technique is based on a continuous injection of carrier gas loaded with vapors of reactants into the spinning MAS NMR rotor via an injection tube (approach (ii)). For this purpose, a glass tube is inserted into the sample volume of an MAS NMR rotor via an axially placed hole in the rotor cap (Fig. 2). Using a special tool, the solid catalyst is pressed to a hollow cylinder. The feed is injected into the inner space of this hollow cylinder and flows from the bottom to the top of the MAS NMR rotor reactor. The product stream leaves the sample volume continuously via an annular gap in the rotor cap. In some applications, the reaction products leaving the spinning MAS NMR rotor reactor were sucked up and led to the sampling loop of an on-line gas chromatograph [14] (Fig. 3). Recently, this experimental approach was adopted with slight modifications by a number of groups [15–18].

3. Study of transition states of acid-catalyzed reactions

It is generally accepted that reactive carbenium ions contributing to acid-catalyzed reactions occur as transition states rather than as intermediates [18]. Consequently, these species cannot be directly observed by NMR spectroscopy. However, several experimental attempts were undertaken in an endeavor to enable indirect NMR studies of the transitions states of organic compounds in heterogeneous catalysis on solid acids.

An indirect NMR spectroscopic evidence for the presence of carbenium ions on acidic catalysts could be ob-

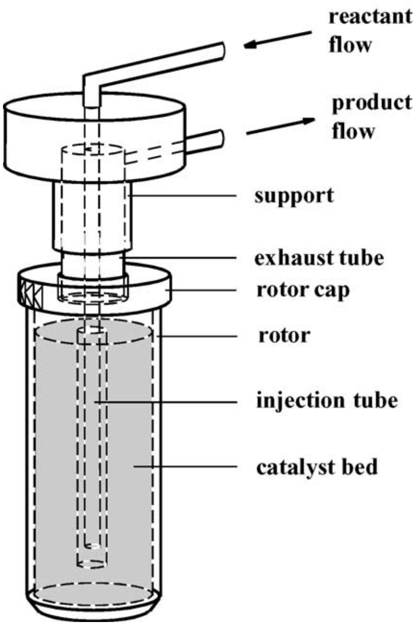

Fig. 2. Scheme of an MAS NMR rotor reactor with an injection equipment applied for in situ MAS NMR investigations under flow conditions [14].

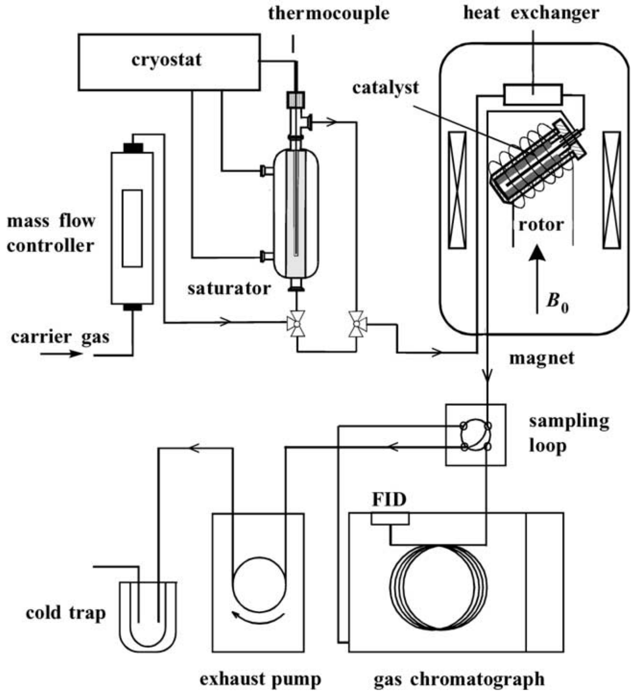

Fig. 3. Scheme of a CF MAS NMR probe coupled with an on-line gas chromatograph for simultaneous in situ MAS NMR studies under continuous-flow conditions and an analysis of reaction products leaving the MAS NMR rotor reactor [14].

tained by a trapping of these species by carbon monoxide. Stepanov et al. [19] studied carbenium ions formed on zeolite H-ZSM-5 upon adsorption of ethylene. The authors adsorbed water to quench the oxocarbenium ions formed by the reaction of carbenium ions with ^{13}C-enriched carbon monoxide. The final product of this reaction was a carboxylic acid causing a ^{13}C MAS NMR signal at $\delta_{13\mathrm{C}} = 189$ ppm due to ^{13}C-enriched carboxyl groups (Fig. 4a). The signal at 189 ppm points to a trapping of oligomeric carbenium ions by carbon monoxide and water (Fig. 4b). In addition, this experiment furnished experimental evidence for carbenium ions being in equilibrium with oligomeric alkoxy species, since the trapping of carbenium ions is accompanied by the disappearance of a weak signal at $\delta_{13\mathrm{C}} = 89$ ppm, which is indicative of oligomeric alkoxides. This experiment shows that the alkoxides are transformed into carboxylic acids via the interaction of the equilibrated carbenium ions with carbon monoxide and water. Hence, alkoxy species formed on acidic catalysts give an indirect NMR spectroscopic evidence for the presence of equilibrated carbenium ions existing as transition states.

^{1}H MAS NMR spectroscopy offers the possibility to investigate transitions states of proton transfer reactions via the H/D exchange between acidic surface OH groups and adsorbate molecules [20–24]. Stepanov et al. [21] investigated the H/D exchange between deuterated propane and acidic bridging OH groups of zeolite H-ZSM-5 by ^{1}H MAS NMR spectroscopy in a temperature range of 457–543 K. These authors determined activation energies of ca. 110 kJ/mol for an exchange of acidic bridging hydroxyl protons with hydrogen atoms of methyl and methylene groups in propane. This experimentally determined activation energy agrees well with the value theoretically obtained for the hydrogen exchange with methane ($E_\mathrm{A} = 122$ kJ/mol [22]) and ethane ($E_\mathrm{A} = 118$ kJ/mol [23]). The quantum-chemical calculations were based on a pentacoordinated transition state of the carbon atoms. An additional argument against the assumption of propyl cations as transition state was given by the non-regiospecific H/D exchange between acidic bridging hydroxyl protons and methyl and methylene groups in propane [21]. In contrast, Sommer et al. [24] observed a regiospecific H/D exchange between acidic bridging OH groups of zeolite H-ZSM-5 and deuterated isobutane with an activation energy of $E_\mathrm{A} = 50$ kJ/mol. These authors explained the difference between the activation energies derived for the H/D exchange of pentane and isobutane with zeolite H-ZSM-5 by differences in the reactivities of linear and branched alkanes. The regioselectivity experimentally observed in the latter case is an additional evidence for the formation of *tert*-butyl cations as intermediates in this reaction [24].

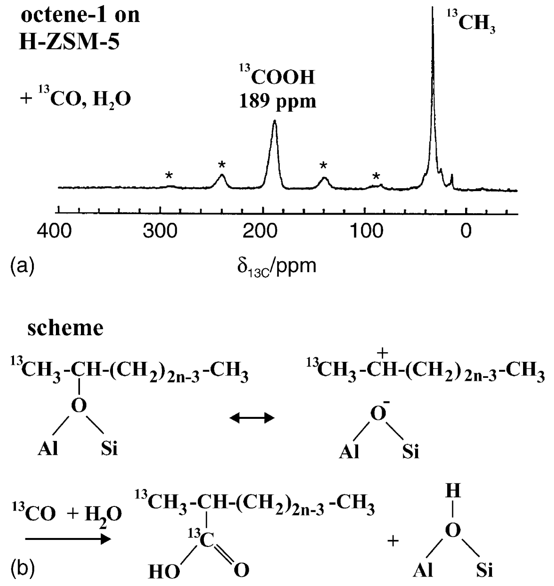

Fig. 4. ^{13}C CP/MAS NMR spectrum (a) of oligomerization products of ethylene adsorbed on calcined zeolite H-ZSM-5 together with ^{13}C-labeled CO and H_2O. Asterisks denote spinning sidebands. In (b), the mechanism explaining the trapping of carbenium ions with CO is shown [19].

4. Alkylation of aromatic compounds

The side-chain alkylation of toluene and the alkylation of aniline with methanol are both reactions of considerable industrial importance [25–27]. A more detailed understanding of the mechanisms of these reactions could contribute to a tailored design of new solid catalysts with required properties. Mechanistic information can be acquired by the recently developed techniques of in situ MAS NMR spectroscopy.

On the basis of catalytic investigations of the side-chain alkylation of toluene on basic zeolites, such as on zeolites Cs,Na-X and Cs,Na-Y, Yashima et al. [28] proposed that the catalyst has two functions: (i) A strong adsorption of toluene at cesium cations which enhances the polarization of the methyl group and (ii) the dehydrogenation of methanol to formaldehyde. Formaldehyde was suggested to be the true alkylating agent reacting with toluene to styrene, which is hydrogenated to ethylbenzene. According to the literature [29], impregnation of zeolites Cs,Na-X and Cs,Na-Y with cesium hydroxide or acetate and subsequent calcination lead to the formation of strong base sites, which are well dispersed in the zeolite pores. ^{133}Cs MAS NMR spectroscopy is a suitable technique for studying cesium cations located on extra-framework positions and guest compounds dispersed in the pores of calcined zeolites X and Y. The ^{133}Cs MAS NMR spectrum of a calcined zeolite CsOH/Cs,Na-X consists of signals at $\delta_{^{133}\text{Cs}} = -130$ and -90 ppm due to cesium cations located on SI′ and SIII positions, respectively, of the faujasite structure [30,31]. Via a line separation, additional signals were found at $\delta_{^{133}\text{Cs}} = -103$ and -57 ppm which are caused by cesium cations located on SII′ and SII positions, respectively [30,31]. Guest compounds introduced by impregnation with cesium hydroxide are responsible for broad low-field signals at $\delta_{^{133}\text{Cs}} = -10$ to 30 ppm [30,31]. Adsorption of the reactants methanol and toluene causes a significant change of the center of gravity of the ^{133}Cs MAS NMR signals due to their interaction with cesium cations located in the large cages, i.e., on SII and SIII positions [31,32]. No effect of adsorbate molecules occurred for cesium cations located on SI′ ($\delta_{^{133}\text{Cs}} = -130$ ppm) and SII′ ($\delta_{^{133}\text{Cs}} = -103$ ppm) positions [31,32]. The large low-field shift of the ^{133}Cs MAS NMR signals of cesium cations on SIII and SII positions ($\Delta\delta_{^{133}\text{Cs}}$ ca. 100 ppm) observed after adsorption of toluene provides experimental evidence for a strong adsorption of toluene molecules at accessible cesium cations. The strong sideband pattern of the low-field shifted ^{133}Cs MAS NMR signal indicates a large shielding anisotropy ($\Delta\sigma = -450$ ppm), which can be explained by a one-side docking of the toluene at the cesium cations [31,32]. This finding supports the first function (i) of cesium-exchanged zeolites as catalysts in the side-chain alkylation of toluene, i.e., the strong adsorption of toluene at cesium cations. In contrast, the weaker low-field shift of the ^{133}Cs MAS NMR signals of the cesium cations located on SIII and SII positions ($\Delta\delta_{^{133}\text{Cs}}$ ca. 50 ppm) upon loading of methanol and the absence of spinning sidebands indicates only a weak physisorption of methanol molecules on cesium cations.

In the first step, ^{13}C MAS NMR investigations of methanol and toluene adsorbed on basic zeolite CsOH/Cs,Na-X were carried out using samples fused in glass inserts [31–33]. The ^{13}C MAS NMR spectrum of calcined zeolite CsOH/Cs,Na-X loaded with a mixture of ^{13}C-enriched methanol and selectively ^{13}C-enriched toluene in a molar ratio of 3:1 and recorded at $T = 295$ K consists of signals at $\delta_{^{13}\text{C}} = 49$ ppm (methanol) and $\delta_{^{13}\text{C}} = 21$ ppm (methyl groups of toluene). After heating the catalyst at $T = 573$ K, the absence of the signal at $\delta_{^{13}\text{C}} = 49$ ppm and the appearance of a new signal at $\delta_{^{13}\text{C}} = 166$ ppm indicate a complete conversion of methanol to formate species bound at the basic framework oxygen atoms. Formaldehyde ($\delta_{^{13}\text{C}} = 197$ ppm [34]), which is formed by a dehydrogenation of methanol, was not detected. After heating the catalyst at $T = 723$ K, the signal of formate species at $\delta_{^{13}\text{C}} = 166$ ppm decreased and an additional line appeared at $\delta_{^{13}\text{C}} = 171$ ppm which is due to surface carbonates. It is important to note that the reaction product ethylbenzene ($\delta_{^{13}\text{C}} = 15$ and 29 ppm) is formed first after heating the catalyst at 723 K, i.e., *after* the methanol was fully converted to formate species. This indicates that formate species formed from methanol may act as reactive surface species contributing to the side-chain alkylation of toluene on zeolite CsOH/Cs,Na-Y.

In the second step, the in situ ^{13}C MAS NMR investigations of the side-chain alkylation of toluene were performed under continuous-flow (CF) conditions at a reaction temperature of 723 K and by injecting different reactant flows into the spinning MAS NMR rotor reactor filled with the calcined catalyst [31,33]. The spectra shown in Fig. 5 are reduced to the spectral range of surface formate ($\delta_{^{13}\text{C}} = 166$ ppm) and carbonate species ($\delta_{^{13}\text{C}} = 171$ ppm). The aim of these experiments was to study the response of the formate signal occurring at $\delta_{^{13}\text{C}} = 166$ ppm on changes of the reactant flow. The ^{13}C CF MAS NMR spectrum recorded during the conversion of pure ^{13}C-enriched methanol on zeolite CsOH/Cs,Na-X is dominated by the signal of formate

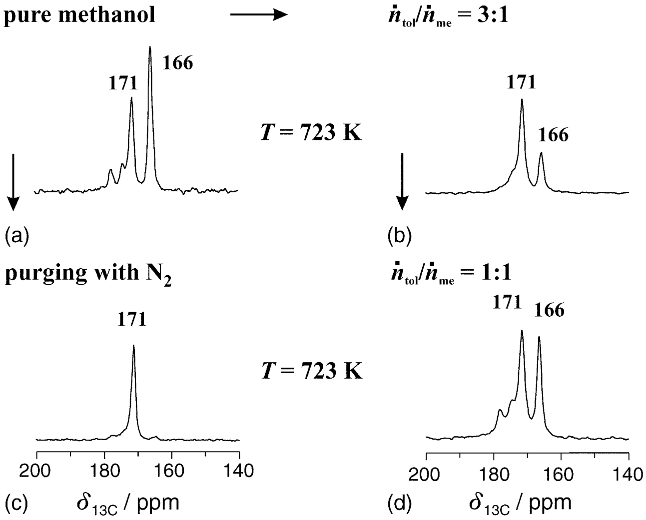

Fig. 5. ^{13}C CF MAS NMR spectra recorded at 723 K during the conversion of pure ^{13}C-enriched methanol on zeolite CsOH/Cs,Na-X (a), after purging with dry nitrogen (b) and during the conversion of mixtures of toluene and ^{13}C-enriched methanol with molar ratios of 3:1 (c) and 1:1 (d) [31].

species at $\delta_{^{13}C} = 166$ ppm accompanied by signals of carbonate species at $\delta_{^{13}C} = 171$–175 ppm (Fig. 5a). After purging the used catalyst for 1 h with dry nitrogen, only the signal of carbonate species occurred in the spectrum, which indicates that these species remain on the catalyst surface, while the formate species are chemically unstable (Fig. 5b). After switching the reactant flow from pure $^{13}CH_3OH$ to a toluene/$^{13}CH_3OH$ mixture with a molar ratio of 3:1, a strong decrease of the formate signal ($\delta_{^{13}C} = 166$ ppm) was found in the spectrum in Fig. 5c in comparison with the spectrum in Fig. 5a. This finding indicates that the formate species are consumed by the reactant toluene. To corroborate this assumption, the toluene content in the reactant mixture was decreased to a molar ratio of 1:1 leading to an increase of the signal of formate species (Fig. 5d). The lower toluene content in the reactant flow decreases the consumption of the surface formate species. This observation is a clear experimental evidence for the reactivity of the surface formate species in the side-chain alkylation of toluene on zeolite CsOH/Cs,Na-X.

To study the alkylation of aniline on zeolite catalysts, the in situ CF MAS NMR technique was combined with stopped-flow (SF) experiments [35,36]. In the first period, these protocols allow the observation of adsorbate complexes formed on solid catalysts under steady-state conditions. In subsequent periods, an identification of adsorbates acting as intermediates in the further reaction steps can be performed. Very recently, this stopped-flow technique was utilized to investigate the reaction mechanism of the alkylation of aniline with methanol on acidic zeolite H–Y [36]. From the results obtained by in situ MAS NMR spectroscopy under continuous-flow conditions it is difficult to decide the role of *N*,*N*,*N*-trimethylanilinium cations in the overall reaction leading to the formation of *N*-methylaniline, *N*,*N*-dimethylaniline and ring-alkylated products on zeolite H–Y. Therefore, the in situ stopped-flow (SF) technique was applied to investigate the reaction pathway in more detail [36].

After the *N*,*N*,*N*-trimethylanilinium cations ($\delta_{^{13}C} = 5858$ ppm) were formed on zeolite H–Y under steady state conditions (Fig. 6a), the reactant flow was stopped and an in situ MAS NMR investigation of the progressive transformation of these surface compounds was performed at different reaction temperatures. In the spectrum recorded at ambient temperature after purging the catalyst with dry nitrogen, only the signal of *N*,*N*,*N*-trimethylanilinium cations ($\delta_{^{13}C} = 58$ ppm) occurs (Fig. 6b) [36]. After raising the reaction temperature to 498 K without starting the flow of reactants again, a strong intensity increase of the signals due to *N*,*N*-dimethylanilinium cations ($\delta_{^{13}C} = 48$ ppm) and *N*-methylanilinium cations ($\delta_{^{13}C} = 39$ ppm) accompanied by a decrease of the signal at $\delta_{^{13}C} = 58$ ppm was observed (Fig. 6c). This indicates a decomposition of *N*,*N*,*N*-trimethylanilinium cations to *N*,*N*-dimethylanilinium and *N*-methylanilinium cations. At the reaction temperature of 523 K, additional signals appear at $\delta_{^{13}C} = 16$ and 21 ppm due to ring-alkylated reaction products with methyl groups in *ortho*- and *para*-positions, respectively (Fig. 6d). The ^{13}C-labeled methyl groups, which are abstracted during these decomposition processes, are suggested to react with adsorbed aniline molecules giving *N*-methylaniline and *N*,*N*-dimethylaniline and/or contribute to the ring alkylation leading to reaction products with methyl groups in *para*- and *ortho*-positions.

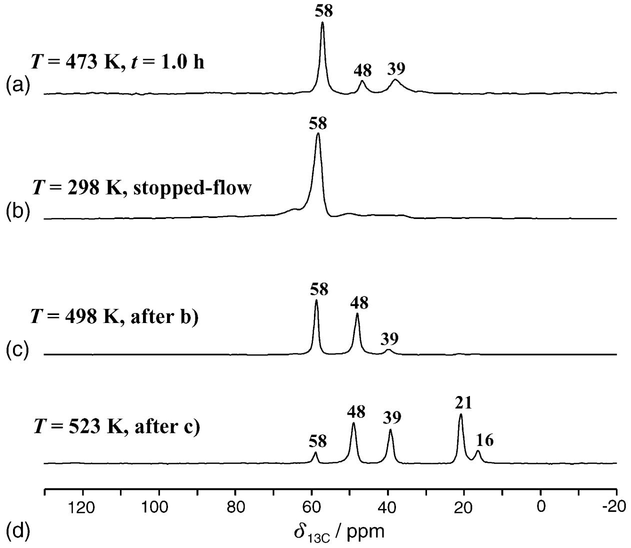

Fig. 6. ^{13}C MAS NMR spectra recorded during alkylation of aniline on zeolite H–Y under continuous-flow conditions ($W/F = 40$ g h/mol, aniline/$^{13}CH_3OH$ ratio of 1:4) at a reaction temperature of 473 K (a) for 1 h, at 298 K (b) after stopping the reactant flow and purging the catalyst with dry nitrogen, and, subsequently, at reaction temperatures of 498 K (c) and 523 K (d) without purging the catalyst [36].

Based on the above-mentioned in situ CF and SF ^{13}C MAS NMR investigations, the following reaction mechanism of aniline methylation on the acidic zeolite H–Y has been proposed [36]: The alkylation of aniline leads to a consecutive and reversible formation of *N*-methylanilinium, *N*,*N*-dimethylanilinium and *N*,*N*,*N*-trimethylanilinium cations attached to the zeolite surface and being in a chemical equilibrium. The reaction products occurring in the gas phase, i.e. *N*-methylaniline and *N*,*N*-dimethylaniline, are formed via a deprotonation of the corresponding *N*-methylanilinium and *N*,*N*-dimethylanilinium cations. Therefore, the product distribution in the gas phase is determined to a large extent by the chemical equilibrium between the different methylanilinium cations, which is in turn affected by the reaction conditions such as temperature and molar aniline to methanol ratio. C-alkylated products are formed via a transformation of methylanilinium cations at reaction temperatures higher than 523 K.

5. Conversion of methanol to hydrocarbons

The conversion of methanol to hydrocarbons on acidic zeolites is, since the first reports in 1976 [37], one of the most widely investigated reactions in heterogeneous catalysis. Nowadays, the concept of this reaction has been expanded since light olefins, i.e., ethylene and propylene, which can be produced as well via this route (MTO: methanol-to-olefins), are the most important starting materials for the petrochemical industry, and the demand for both olefins is steadily increasing [38]. Recently, various NMR spectroscopic techniques were applied to investigate the conversion of methanol on acidic zeolites in the low-temperature range ($T \leq 523\,K$) leading to dimethyl ether (DME) and in the high-temperature range ($T \geq 523\,K$) leading to the formation of olefins and gasoline. Successfully applied techniques are the in situ stop-and-go method under batch conditions [39,40], the pulse-quench method [41], and flow techniques [42–46].

For the conversion of methanol to hydrocarbons on acidic zeolites, various reaction mechanisms were proposed [38]. Haag [47], Hoelderich et al. [48], Dessau [49], and Kolboe and Dahl [50,51] explained the formation of light olefins by a carbon-pool mechanism. According to this mechanism, large carbonaceous species are formed in an initial reaction step. In the steady state of the reaction, these species add reactant molecules and split off reaction products. The carbon-pool was proposed to represent adsorbates with many characteristics of ordinary coke described by $(CH_x)_n$ with $0 < x < 2$ [38]. More recently, Mikkelsen et al. [52] and Haw and co-workers [53–55] proposed polymethylbenzenes to contribute to the carbon-pool and to play a key role in the conversion of methanol on acidic zeolites.

Recently, in situ MAS NMR spectroscopy under continuous-flow conditions was applied to shed more light on the mechanism of methanol conversion on zeolites H-ZSM-5, H-SAPO-34, and H-SAPO-18 under steady-state conditions [43,46,56]. To ensure that meaningful catalytic results were obtained using a spinning MAS NMR rotor reactor, the catalytic experiments were performed under the same conditions using a conventional fixed-bed reactor with analysis of the reaction products via on-line gas chromatography [46]. A comparison of the results achieved in the fixed-bed reactor and in the spinning MAS NMR rotor reactor showed a reasonable good agreement [46]. In particular, methanol conversion takes place in the same temperature range, and the same qualitative shapes of the conversion and yield curves were obtained. To investigate the methanol conversion under steady-state conditions by in situ CF MAS NMR spectroscopy, a flow of ^{13}C-enriched methanol ($W/F = 25\,g\,h/mol$) was injected into a spinning 7 mm MAS NMR rotor reactor filled with 100 mg of the calcined zeolites H-ZSM-5, H-SAPO-18 or H-SAPO-34 [43,46]. As an example, Fig. 7 shows the in situ ^{13}C CF MAS NMR spectra obtained during the conversion of $^{13}CH_3OH$ on zeolite H-ZSM-5 at reaction temperatures of 373–673 K [43].

The signal occurring at $\delta_{^{13}C} = 61$ ppm in the in situ ^{13}C CF MAS NMR spectra of zeolite H-ZSM-5 recorded

(a) $T = 473$ K

DME	C_2=	C_3=	C_3	C_4=	C_4
32.3	0	0	0	0	0

(b) $T = 523$ K

DME	C_2=	C_3=	C_3	C_4=	C_4
44.3	2.7	1.4	0	0	0

(c) $T = 548$ K

DME	C_2=	C_3=	C_3	C_4=	C_4
40.3	3.6	3.6	0.6	0	0

(d) $T = 573$ K

DME	C_2=	C_3=	C_3	C_4=	C_4
23.8	12.5	13.0	1.6	9.9	1.8

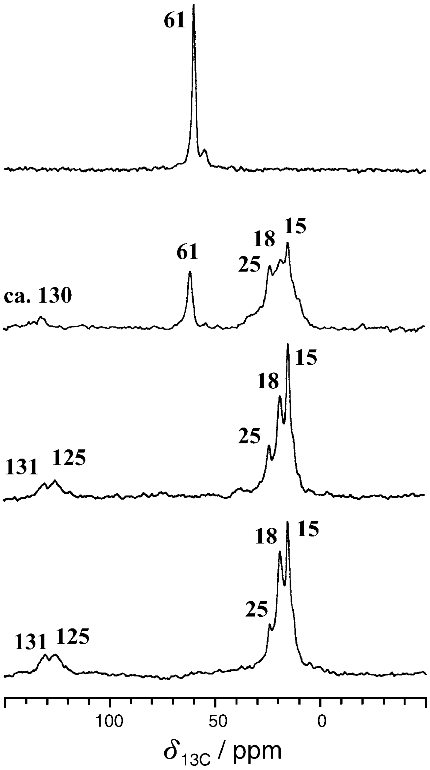

Fig. 7. ^{13}C CF MAS NMR spectra recorded during the conversion of ^{13}C-enriched methanol ($W/F = 25\,g\,h/mol$) on zeolite H-ZSM-5 at reaction temperatures of 473 K (a) to 573 K (d). On the left-hand side, the yields of dimethyl ether (DME), ethylene (C_2=), propylene (C_3=), butenes (C_4=) and butanes (C_4) simultaneously determined by on-line gas chromatography are given [43].

at 473 and 523 K during conversion of $^{13}CH_3OH$ (Fig. 7a and b, right) indicates the conversion of methanol ($\delta_{^{13}C} = 50$ ppm) to dimethyl ether (DME). This finding agrees with the high yields of DME ($Y_{DME} = 32.2$–44.3%) obtained at these temperatures by on-line gas chromatography (Fig. 7a and b, left). At this reaction temperature, the spectrum is dominated by the signal at $\delta_{^{13}C} = 61$ ppm due to DME and signals at 15–25 ppm caused by alkyl groups of hydrocarbons formed on the catalyst. After increasing the reaction temperature to $T = 548$ K and higher, additional ^{13}C MAS NMR signals occur in the olefinic and aromatic region at $\delta_{^{13}C} = 125$–131 ppm (Fig. 7c and d, right). Simultaneously, a strong increase of the yields of light olefins, such as of C_2= and C_3=, could be observed by on-line gas chromatography (Fig. 7c and d, left). To study the carbonaceous compounds which are chemically stable and occluded in the pore system of zeolite H-ZSM-5, the used catalyst was purged with dry carrier gas (30 ml/min) at 573 K after methanol conversion at the same reaction temperature (not shown). The spectrum obtained after purging consisted of weak signals at $\delta_{^{13}C} = 18$ and ca. 130 ppm which can be explained by polymethylaromatics.

For a detailed analysis of the ^{13}C MAS NMR signals, a line separation has been performed using commercial softwares, such as BRUKER WINNMR, WINFIT or X-WINNMR (see, e.g., Ref. [46]). The assignment of the signals was based on a comparison of the chemical shift values determined by line separation with those given in databases (see, e.g., Refs. [34,57,58]) or obtained by adsorption of the corresponding compounds on the catalysts under study. In this way, the ^{13}C CF MAS NMR signals observed during methanol conversion on zeolite H-ZSM-5 at reaction temperatures of 523–623 K were attributed to a carbon-pool containing a mixture of olefins, such as n-hexene-3 ($\delta_{^{13}C} =$ 14, 25, and 131 ppm), *n*-hexadiane-2,4 ($\delta_{^{13}C} =$ 18, 127, and 132 ppm), and alkylated octadienes ($\delta_{^{13}C} =$ 15, 23, 25, and 133–135 ppm). In addition, the formation of cyclic compounds, such as cyclopentene ($\delta_{^{13}C} =$ 23, 33, and 131–133 ppm), and alkylated cyclopentenes, such as diethylcyclopentene ($\delta_{^{13}C} =$ 14–33 and 133–135 ppm) and *para*-xylene ($\delta_{^{13}C} =$ 21, 129, and 134 ppm), has been claimed [43]. At high reaction temperatures, polymethylaromatics were found to be the dominating compounds of the carbon-pool observed under steady state conditions [46]. Recently, Song et al. [53–55] proposed polymethylaromatics to be the most active carbonaceous compounds catalyzing the methanol to hydrocarbon conversion on acidic zeolites.

To clarify the role of the carbon-pool in the MTO process, the methanol conversion on acidic zeolites was studied by in situ ^{13}C CF MAS NMR spectroscopy before and after changing the abundance of the ^{13}C-isotopes in the methanol feed. After a conversion of ^{13}C-enriched methanol under continuous-flow conditions, the reactant flow was switched to $^{12}CH_3OH$ without to change other reaction parameters. If the alkyl groups of the carbon-pool compounds are involved in the conversion of methanol to olefins by adding reactant molecules and splitting off product molecules, the ^{13}C-isotope abundance of these groups should decrease after switching from $^{13}CH_3OH$ to $^{12}CH_3OH$.

Fig. 8 shows the in situ ^{13}C and ^1H CF MAS NMR spectra recorded during the conversion of methanol on zeolite H-ZSM-5 at reaction temperatures of 548 and 573 K [56]. The parameters of these experiments were the same as used in Ref. [43]. The characteristic features of the spectra agree with those of the spectra in Fig. 7. To quantify the ^{13}C-isotope abundance of the alkyl groups contributing to the carbon-pool, the spectral region of $\delta_{^{13}C} = 0$–40 ppm was integrated using spectra Fourier-transformed via the absolute intensity mode. These integrals were set to 100% for the spectra recorded during the conversion of $^{13}CH_3OH$ (Fig. 8a and c, left). After switching the reactant flow from $^{13}CH_3OH$ to $^{12}CH_3OH$, a decrease of the ^{13}C-isotope abundance of the alkyl groups contributing to the carbon-pool by ca. 40% was found (Fig. 8b and d, left). The simultaneously recorded ^1H CF MAS NMR spectra on the right–hand side of Fig. 8 show no change of the total intensities of hydrocarbons within the experimental accuracy of ±5%. The replacement of ^{13}C-enriched alkyl groups of the carbon-pool by alkyl groups with a natural ^{13}C-isotope abundance indicates that the carbon-pool is involved in the conversion of methanol. This finding strongly supports the carbon-pool mechanism for the conversion of methanol to olefins on acidic zeolites.

The above-mentioned in situ NMR experiment evidenced that the carbon-pool plays a catalytically active role in the MTO process on acidic zeolites. A further question was the initial steps of the formation of the first hydrocarbons. Impurities in the methanol feed could be a possible explanation for the occurrence of initial compounds leading to the formation of a carbon-pool on zeolite catalysts [59]. On the other hand, recent in situ MAS NMR investigations indicated that catalytically active methoxy groups might contribute to the formation of DME and first hydrocarbons [60,61].

Since the ^{13}C MAS NMR signal of methoxy groups formed on zeolite H-ZSM-5 ($\delta_{^{13}C} = 59$ ppm) overlaps with the signal of DME ($\delta_{^{13}C} = 60$ ppm) [61], investigations of the reactivity of methoxy groups on acidic zeolites were performed using zeolite H–Y as acidic catalyst. The ^{13}C MAS NMR signal of methoxy groups on zeolite H–Y occurring at $\delta_{^{13}C} = 56.2$ ppm allows a good separation of this signal from that of DME. First in situ ^{13}C CF MAS NMR and ^{13}C CF CP/MAS NMR studies of the formation of methoxy groups on zeolite H–Y were performed via a continuous injection of a flow of ^{13}C-enriched methanol with a modified residence time of $W/F = 100$ g h/mol into a spinning MAS NMR rotor reactor [60]. Simultaneously, the yields of DME, Y_{DME}, were determined by on-line gas chromatography. With an increasing yield of DME, such as at a reaction temperature of 473 K ($Y_{DME} = 0.23$), an increase of the signal of surface methoxy groups ($\delta_{^{13}C} = 56.2$ ppm) was observed by ^{13}C CF CP/MAS NMR spectroscopy [61]. Since the temperatures, at which the formation of surface methoxy groups and DME starts, are very close together,

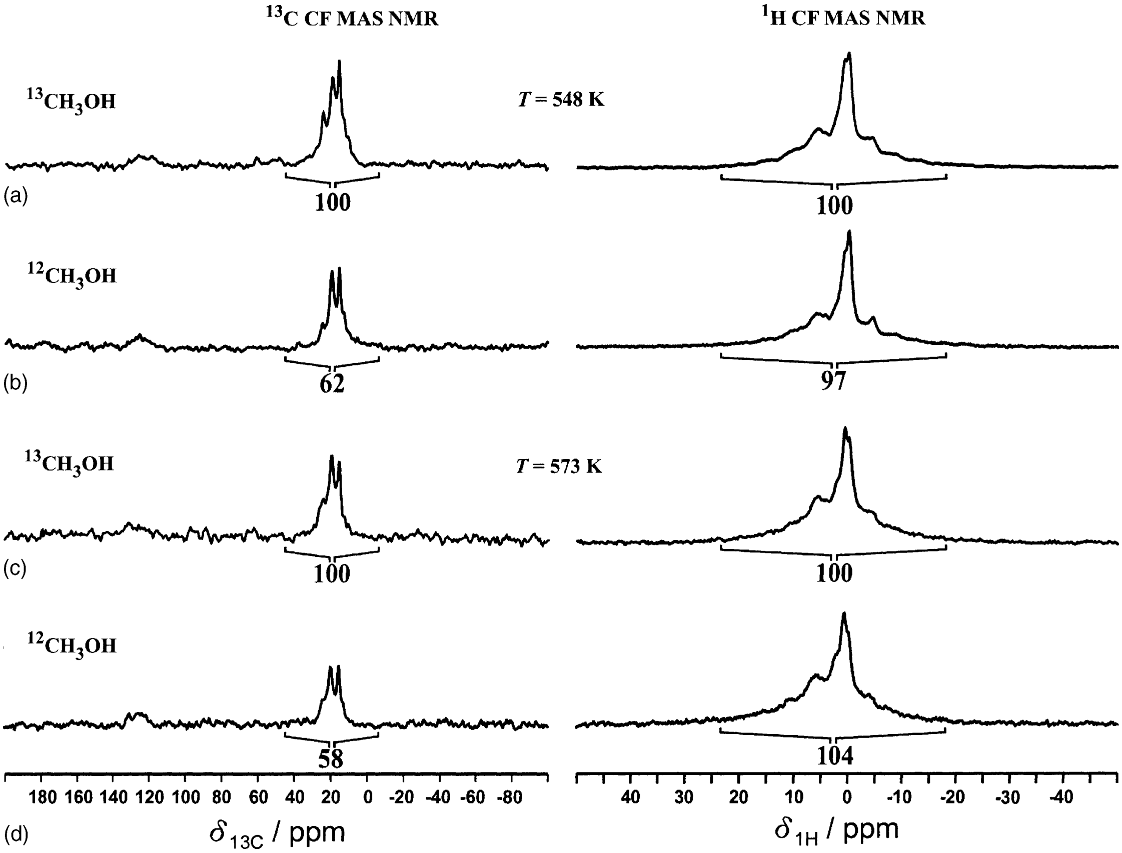

Fig. 8. ^{13}C and ^{1}H CF MAS NMR spectra recorded during the conversion of methanol ($W/F = 25$ g h/mol) on zeolite H-ZSM-5 at reaction temperatures of 548 K (a and b) and 573 K (c and d). The spectra in (b) and (d) were recorded 1 h after switching the methanol feed from $^{13}CH_3OH$ (a and b) to $^{12}CH_3OH$. The relative intensities given under the spectra were determined by an integration of the corresponding spectral region using the spectra obtained during the conversion of $^{13}CH_3OH$ as intensity standard [56].

namely at 393–433 K, it is hard to decide whether the methoxy groups react further to DME or DME is formed directly from methanol. An experiment, which sheds light on this question, was performed using a catalyst covered by methoxy species. An experimental approach allowing the preparation of pure surface methoxy species on acidic catalysts is the stopped-flow (SF) technique. The protocol of this experiment consists of: period (i) to record spectra at reaction temperature during the conversion of ^{13}C-enriched methanol, period (ii) to record spectra during purging of the catalyst with dry carrier gas, and period (iii) to record spectra at reaction temperature during the conversion of methanol molecules with natural abundance of ^{13}C-isotopes ($^{12}CH_3OH$) [61].

After the preparation of pure ^{13}C-enriched surface methoxy species on zeolite H–Y, a flow of $^{12}CH_3OH$ was injected at 433 K for 10 min into the spinning MAS NMR rotor reactor. In the ^{13}C CP/MAS NMR spectrum, weak signals occurred at $\delta_{^{13}C} = 60.5$ and 63.5 ppm hinting to a formation of DME accompanied by a decrease of the signal of surface methoxy groups at $\delta_{^{13}C} = 56.2$ ppm. This finding indicates a reaction of ^{13}C-enriched surface methoxy groups with $^{12}CH_3OH$ leading to $^{13}CH_3O^{12}CH_3$ [60]. After an injection of $^{12}CH_3OH$ at 433 K for 1.0 h into the MAS NMR rotor reactor, all signals disappeared except the ^{13}C CP/MAS NMR signal of DME at $\delta_{^{13}C} = 63.5$ ppm. In a parallel investigation carried out with zeolite H–Y methylated with $^{12}CH_3OH$, no signal of DME was observed under the same reaction conditions. This in situ NMR experiment evidenced that surface methoxy groups prepared on zeolite H–Y are very reactive and contribute to the formation of DME.

In a further in situ MAS NMR experiment, the reactivity of surface methoxy groups on zeolite H–Y without addition of other reactants was investigated. For this approach, a protocol similar to that used in the former experiment was applied. The only difference was, that in period (iii) no reactants were injected into the MAS NMR rotor reactor, while the temperature was increased in steps of 50 K. The preparation of the methoxy groups on zeolite H–Y and the in situ MAS NMR experiments were performed as described in Ref. [61]. The ^{13}C CF MAS NMR spectrum in Fig. 9a shows the signal of the methoxy groups at 56.2 ppm, recorded at the end of period (ii), i.e. after purging of all volatile species. Upon heating at 523 K, the signal of methoxy groups disappeared, and strong signals of alkyl groups occurred at 15.2–23.5 ppm accompanied by weak signals of olefinic and aromatic compounds at 128–142 ppm, respectively (Fig. 9b)

[60]. The formation of these hydrocarbons via a conversion of surface methoxy groups is observed at a temperature, which is characteristic for the detection of first olefins in the product flow by on-line gas chromatography (see, e.g., Ref. [46]). The ^{13}C MAS NMR signals in the spectrum recorded at 523 K can be explained by olefins, such as propene ($\delta_{^{13}C}$ = 16.1 and 16.3 ppm), isobutene ($\delta_{^{13}C}$ = 23.7, 119.5, and 141.4 ppm), and diemthylbutadiene ($\delta_{^{13}C}$ = 20.1, 111.3, and 142.1 ppm), and by aromatic compounds such as benzene ($\delta_{^{13}C}$ = 128.6 ppm) and hexamethylbenzene ($\delta_{^{13}C}$ = 17.4 and 132.1 ppm). After increasing the temperature to 623 K, the spectrum is dominated by the signals of hexamethylbenzene (Fig. 9d) [61]. It is interesting to note, that in the presence of aromatics or alkanes, the conversion of surface methoxy groups starts already at 433 and 498 K, respectively [60]. This finding indicates that no organic impurities are responsible for the reaction of surface methoxy groups to hydrocarbon on methylated zeolite Y, which was observed to start in the above-mentioned experiment at 523 K.

The ^{13}C MAS NMR spectra shown in Fig. 9 evidence that methoxy groups formed on acidic zeolite catalysts by a dehydration of methanol on Brønsted acid sites are reactive enough to form hydrocarbons. The formation of hydrocarbons by a conversion of methoxy groups was found at a reaction temperature, at which the first olefins are detected in the product flow. Therefore, an active role of methoxy groups can be assumed in the initial step of the methanol-to-olefin conversion on acidic zeolites via the carbon-pool mechanism. In an industrial process, the formation of first hydrocarbons by surface methoxy groups may be accelerated by the presence of organic impurities in the methanol feed.

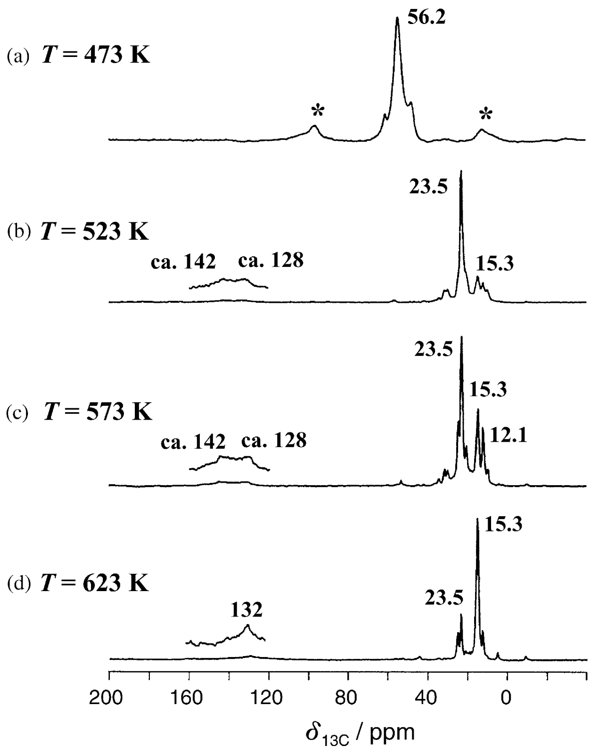

Fig. 9. ^{13}C SF MAS NMR spectra recorded after stopping the conversion of $^{13}CH_3OH$ on zeolite H–Y at 423 K (W/F = 40 g h/mol) and purging the catalyst with dry carrier gas at 298 K (a) and after heating at 523 K (b), 573 K (c), and 623 K (d) [60].

6. Conclusions

In the past decade, in situ solid-state NMR spectroscopy provided important and novel information on the nature and properties of surface sites on solid catalysts and the mechanisms of heterogeneously catalyzed reactions. To operate close to the conditions of industrial catalysis is a significant advantage of this modern spectroscopic method. A number of new techniques were introduced and applied which allow in situ solid-state NMR investigations of heterogeneously catalyzed reactions under batch and continuous-flow conditions. Depending on the scientific problems to be solved, both of these experimental techniques are useful approaches for the study of calcined solid catalysts and of surface compounds formed on these materials under reaction conditions. Problems with the time-scale of NMR spectroscopy in comparison with the time-scale of the reactions under study can be overcome by sophisticated experimental approaches such as the study of the H/D exchange dynamics and the application of stopped-flow experiments. A further development of the experimental techniques of in situ solid-state NMR spectroscopy can be expected. Important aims are (i) the enhancement of the sensitivity of in situ solid-state NMR spectroscopy, e.g., by a selective enhancement of the nuclear polarization utilizing Laser-polarized xenon, and (ii) the increase of the temperature range accessible for the study of heterogeneously catalyzed reactions. Furthermore, modern techniques of solid-state NMR spectroscopy will be applied for in situ investigations improving the resolution of the spectra obtained.

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