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Applications of in situ spectroscopy in zeolite catalysis

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Abstract

Further progress in the field of zeolite science and heterogeneous catalysis depends on our knowledge of the coordination and chemical nature of surface sites and the mechanisms of chemical reactions catalyzed by these sites. Analytical tools for the investigation of heterogeneous reaction systems should allow the study of calcined and working catalysts under in situ conditions. In the laboratory scale, FTIR, UV–Vis, ESR, and NMR spectroscopy are suitable methods for in situ investigations of zeolites and reactions catalyzed by these materials. During the past decade, an increasing number of research groups were dealing with the development and application of new techniques allowing in situ studies under batch and continuous-flow conditions. In this contribution, a review on the most important experimental approaches of in situ FTIR, UV–Vis, ESR, and NMR spectroscopy in zeolite science is given. In addition, some characteristic applications of these methods such as for the investigation of the coordination change of iron during the calcination of microporous aluminophosphates, the mechanism of the methanol-to-olefin conversion process, and the coke formation during the synthesis of cumene and the conversion of olefins on acidic zeolites are described.
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Keywords: In situ spectroscopy; Heterogeneous catalysis; Zeolites; Reaction mechanisms; Surface sites

1. Introduction

The elucidation of reaction mechanisms in heterogeneous catalysis is a process that involves the identification and characterization of the active centers, the intermediate species, the activation processes of reactants, the surface reactions, and the study of the catalyst deactivation. In addition to kinetic investigations, increasing use is being made of modern in situ spectroscopic methods for the elucidation of heterogeneous reaction systems. In this contribution an overview of the state-of-the-art of in situ FTIR, UV–Vis, ESR, and NMR spectroscopy is presented, i.e., of laboratory scale methods, which can be applied without use of equipments accessible in large research centers only, such as synchrotrons and neutron sources. FTIR and NMR spectroscopy are universally used methods for the investigation of catalytically active sites in solid catalysts and the reactants interacting with these sites. ESR spectroscopy is a very sensitive method for the investigation of paramagnetic sites and their local structure. UV–Vis spectroscopy is particularly suitable for the observation of chemically excited states of hydrocarbons, i.e., of carbenium ions, but also of hydrocarbons with conjugated double bonds, such as aromatic compounds. An important advantage of all four methods is the possibility to investigate working catalysts in contact with reactants under near-practice conditions, i.e., under reasonably high partial pressures of these reactants. In the present contribution, special attention has been devoted to the application of the above-mentioned methods in zeolite science, not only due to their ideal crystalline structures, but also in view of their widespread use in numerous processes of industrial chemistry.

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Much of the spectroscopic work on heterogeneously catalyzed reactions was performed under batch conditions, i.e., after a single loading of the activated catalyst with reactants in a sealed sample or a spectroscopic cell. In industrial chemistry, however, processes are frequently operated under flow conditions, that is, with a continuous feed stream of reactants and removal of products. For this reason, work on the development and application of new in situ techniques for spectroscopic investigations under flow conditions is being performed by a growing number of research groups, and the present contribution focuses mainly on these techniques. They allow the study of the catalyst formation and deactivation as well as of the formation of surface complexes and intermediates in the steady state of a heterogeneously catalyzed reaction. Because of the extensive nature of this topic, no claim of completeness is made. An introduction to the basic principles and classical uses of spectroscopic methods in heterogeneous catalysis may be found in the literature [1–4].

2. Infrared spectroscopy

2.1. Methodical introduction

Nowadays, an FTIR spectrometer usually works in a non-dispersive manner, i.e., the total spectrum is analyzed by an interference process and transformed into the frequency or wave number range by means of a Fourier transform (FTIR spectroscopy). In recent years, diffuse reflectance spectroscopy (DRS) in the region of infrared radiation has been used increasingly for the characterization of solid catalysts with low transmittance. For the study of zeolites, however, transmission cells are the dominating equipments. The high sensitivity of FTIR spectroscopy is of considerable advantage for in situ investigations in the field of zeolite science and heterogeneous catalysis.

Fig. 1 shows the scheme of an IR flow cell developed by Karge and Nießen for transmission operation which is characterized by a particularly short optical path and the in situ calcination of the sample material pressed to a thin self-supporting wafer ($\rho_{surface} \approx 10$ mg cm^{-2}) in the upper part of the cell [5]. After calcination in the furnace, the wafer is moved into the optical path where it is measured in a vacuum or under the influence of adsorbates or reactants. Also the lower part of the cell is equipped with a heating system allowing the study of heterogeneous reaction systems at temperatures of up to 923 K and at a pressure of 1 bar.

The IR cell shown in Fig. 2, developed by Lercher and co-workers [6], is suitable for experiments at pressures of up to 5 bar. The self-supporting wafer is heated by the sample holder. This design allows an operation in a temperature range of 300 to 870 K. Commercial high-temperature IR cells are offered, e.g., by In situ Research Instruments, USA, and reach a temperature of 673 K and a pressure of up to 15 bar.

2.2. Study of heterogeneously catalyzed reactions by in situ FTIR spectroscopy

Cumene, an important intermediate in the synthesis of phenol, acetone and α-methylstyrene is formed in acidic media via alkylation of benzene with propene. In traditional processes, solid phosphoric acid (SPA) and, to a smaller extent, $AlCl_3$ are being used as catalysts. Due to different reasons, these catalysts are not up-to-date and are replaced step by step by acidic zeolites [7,8]. Catalysts interesting for the development of new processes are zeolites H-Beta, H-MCM-22 and dealuminated H-mordenite [8]. A strong limitation for an application of these catalysts is the deactivation due to coke deposits. Recently, a detailed investigation of the deactivation of acidic zeolite catalysts applied in the synthesis of cumene was performed using in situ FTIR spectroscopy under continuous-flow conditions [9]. The

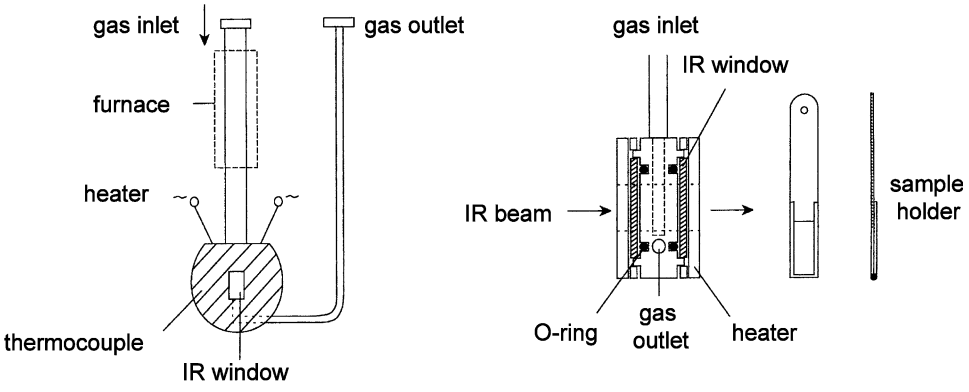


Fig. 1. Scheme of a variable-temperature IR cell for in situ experiments under flow conditions. The heating of the sample is performed via heaters in the housing [5].

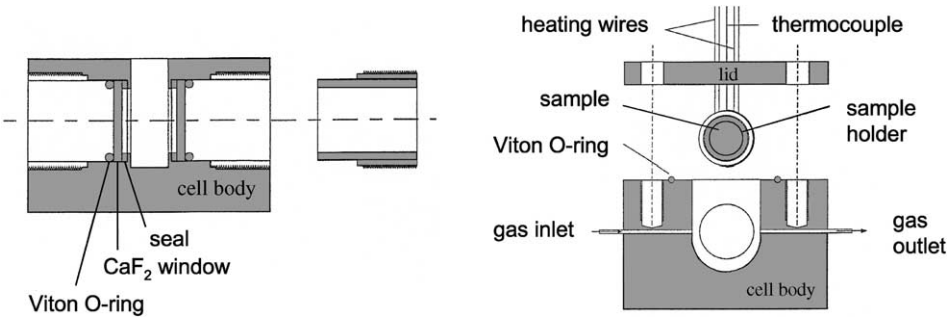


Fig. 2. Scheme of a high-temperature IR cell for in situ experiments under flow conditions. The heating of the sample is performed via the sample holder [6].

catalysts investigated were zeolites H-Beta (three-dimensional 12-ring-pore system), H-NU-87, H-EU-1, and H-MCM-22. The latter three zeolites are characterized by pore systems which are accessible by 10-ring-pores only, but exhibit side-pockets or cages inside.

As an example, Fig. 3 shows the in situ FTIR spectra of zeolite H-EU-1 (n_{Si}/n_{Al} = 17) recorded during the synthesis of cumene at different times-on-stream at a reaction temperature of 448 K. The catalytic conversion of benzene (Bz) and propene (Pr) was carried out with a weight hourly space velocity of $WHSV_{Pr} = 0.25\ h^{-1}$ and an $\dot{n}_{Bz}/\dot{n}_{Pr}$ ratio of 9. Before starting the reaction, the catalyst was loaded with benzene, which is an important prerequisite to avoid a rapid catalyst deactivation by propene oligomerization. The propene flow was started after a complete loading of the catalyst with benzene, i.e., after the benzene vibration at 1479 cm^{-1} reached a stationary behavior. The addition of propene led to a rapid decrease of the benzene vibration and to the occurrence of ring vibration of cumene at 1492 cm^{-1} and symmetric CH_3 deformation vibrations of cumene and diisopropyl benzene at 1386 and 1366 cm^{-1}, respectively. As shown in Fig. 3, there is no significant variation of the vibrations caused by reactants after a period of approximately 20 min. Only the vibration at 1600 cm^{-1}, which is caused by coke deposits, shows a further increase with time-on-stream. In Fig. 4, the conversions of propene on zeolites H-EU-1 and H-NU-87 with different n_{Si}/n_{Al} ratios are plotted as a function of the integral absorption of the vibration at 1600 cm^{-1}. With increasing n_{Si}/n_{Al} ratio, i.e., with a decreasing number of catalytically active Brønsted acid sites, a diminution of the propene conversion occurs for all zeolites under study. Zeolite catalysts with low aluminum contents show a stronger decrease of the propene conversion with increasing coke formation in comparison with the catalysts having high aluminum contents (Fig. 4). This finding indicates that deactivation of zeolite catalysts is caused by a direct blocking of catalytically active Brønsted acid sites.

The side-chain alkylation of toluene with methanol on basic zeolites catalysts is an interesting process for the production of styrene and ethylbenzene. This process has been claimed to be economically attractive due to lower raw material cost compared with the traditional way. Often applied zeolite catalysts for the side-chain alkylation of toluene are alkali-exchanged zeolites X and Y. According to Yashima et al. [10], the zeolite catalyst has two functions: (i) conversion of the reactant methanol to the alkylating agent formaldehyde on base

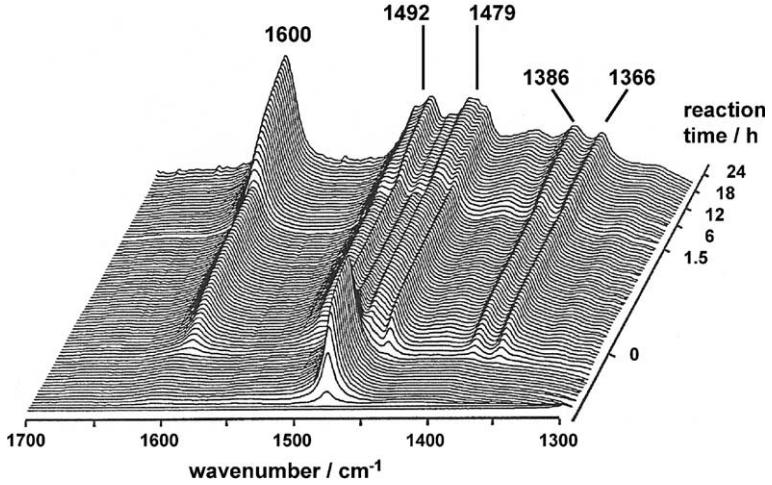


Fig. 3. FTIR spectra recorded during the synthesis of cumene by benzene and propene on zeolite H-EU-1 at 448 K [9].

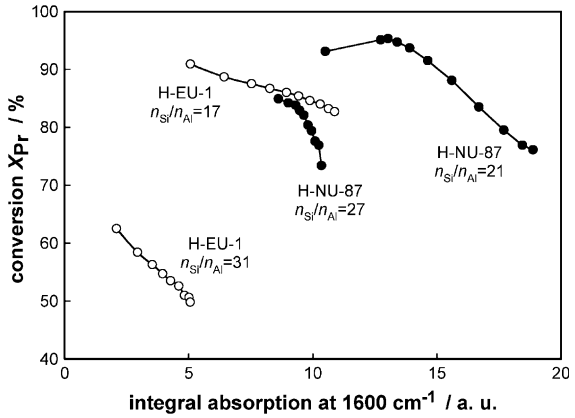


Fig. 4. Dependence of the conversion of propene (X_{Pr}) during the synthesis of cumene on various acidic zeolites H-EU-1 and H-NU-87 at 448 K on the integral intensity of the "coke band" at 1600 cm^{-1} as measured by in situ FTIR spectroscopy [9].

sites and (ii) activation of the reactant toluene by the adsorbent. Step (i), i.e., the formation of formaldehyde, can be accompanied by a formation of surface species such as formates and carbonates [11].

The FTIR spectra shown in Fig. 5 were recorded after coadsorption of toluene and methanol at 308 K [11]. A ratio of toluene to methanol of 1:1 and a reactant pressure of 5×10^{-3} mbar were applied. The characteristic bands of adsorbed toluene and methanol are indicated by solid and dashed lines, respectively. The bands due to adsorbed methanol (OH stretching vibrations at 3250–3350 cm^{-1} and CH stretching vibrations at 2820–2840 cm^{-1}) were the most important ones in the case of adsorption on zeolite Na–X. On the other hand, the bands characteristic for adsorbed toluene (C–C vibrations at 1495 to 1598 cm^{-1}) were the main spectral features in the case of adsorption on zeolites

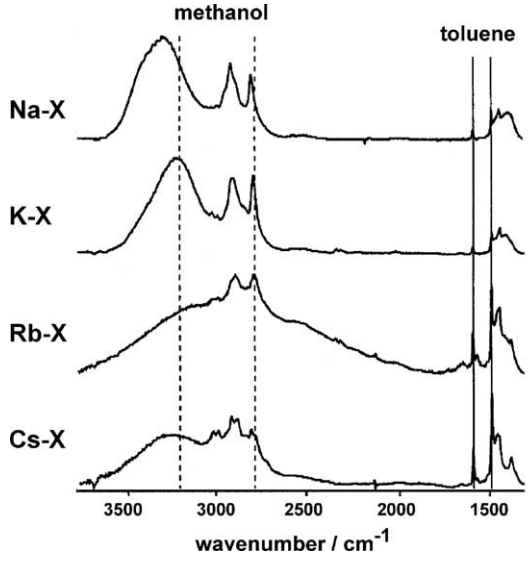


Fig. 5. FTIR spectra recorded during the coadsorption of toluene and methanol on various alkali-exchanged zeolites X [11].

Cs–X and Rb–X. According to these experiments, the ratio of toluene to methanol on the surface of zeolite Cs–X of 2:1 is the highest for all catalysts under study (1:4 for Na–X, 4:3 for Rb–X). This finding indicates a strong coordination of the toluene on cesium cations in zeolite Cs–X, which may be responsible for the activation of adsorbed toluene molecules (step (ii)).

Fig. 6 shows in situ FTIR spectra recorded during the temperature-programmed reaction of toluene and methanol on zeolite Cs–X [12]. The reaction was performed with a toluene to methanol ratio of 3:1, a reactant pressure of 60 mbar and a modified residence time of $W/F = 1.8 \times 10^4$ g s/mol. At low temperatures, the main bands are characteristic for adsorbed toluene (ring deformation and C–C vibrations at 1465, 1495, and 1598 cm^{-1}). With increasing temperature, a new band occurs at 1661 cm^{-1}, which has its maximum intensity at approximately 433 K and disappears completely at 523 K. At this temperature, dimethyl ether is formed by conversion of methanol as detected by on-line gas chromatography. At temperatures of 473–573 K, an additional band (shoulder) was observed at 1610 cm^{-1}. This band is overlapped by the band of adsorbed toluene at 1598 cm^{-1}. By exposing zeolite Cs–X only to methanol, the band at 1610 cm^{-1} could be assigned to surface formate species [12]. A further increase of the reaction temperature to 673 K led to a disappearance of the band of surface formate species at 1600 cm^{-1}. Hence, these species are not accumulated during the reaction on the surface of zeolite Cs–X and do not lead to a catalyst deactivation.

3. UV–Vis spectroscopy

3.1. Methodical introduction

UV–Vis spectroscopy allows the investigation of electron transfers between orbitals or bands of atoms, ions, and molecules in the gas phase as well as adsorbed on solid catalysts. The spectral region of 250–500 nm is of special interest for an in situ UV–Vis spectroscopic detection of hydrocarbons with conjugated double bonds and unsaturated carbenium ions [13]. Additional applications of UV–Vis spectroscopy in heterogeneous catalysis are in situ investigations of the synthesis of solid catalysts, support interactions, and for the modification of solid catalysts during calcination and poisoning. Corresponding applications of UV–Vis spectroscopy have been summarized in Ref. [14]. Fig. 7 shows the scheme of a UV–Vis cell connected with an integration sphere [15]. This setup allows simultaneous in situ UV–Vis and NIR investigations under flow conditions. The distance between the reactor cell and the integrating sphere is bridged by a quartz light conductor (Suprasil 300, Heraeus), which leads the light to the

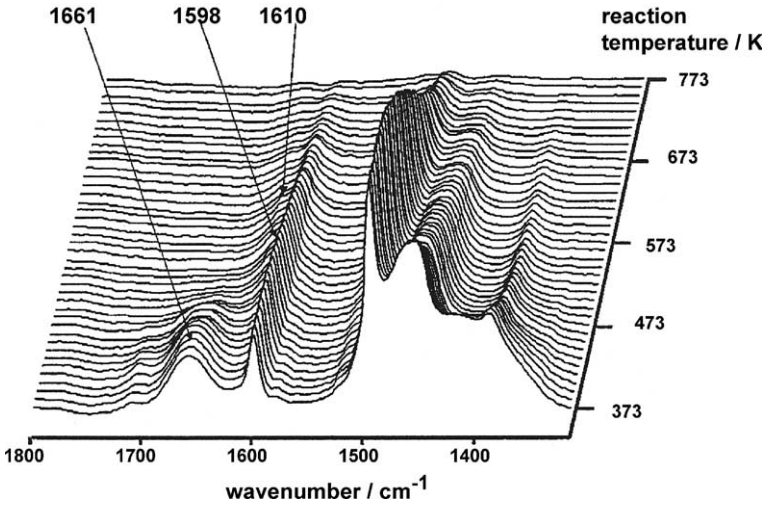


Fig. 6. FTIR spectra recorded during the side-chain alkylation of toluene with methanol on zeolite Cs–X under flow conditions at reaction temperatures of 373–773 K [12].

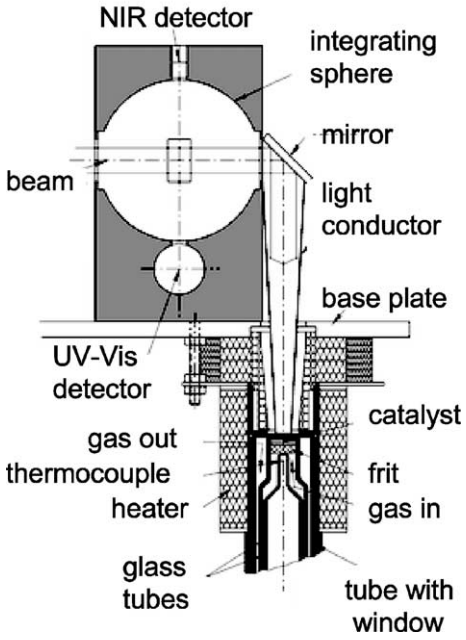


Fig. 7. Scheme of an UV–Vis/NIR setup suitable for in situ investigations of heterogeneously catalyzed reactions at temperatures of up to 723 K [15].

sphere by total reflection. The quartz glass reactor is situated in the center of an oven ensuring a small temperature gradient even at high reaction temperatures. The sample material lies on a glass frit being in a horizontal position. The setup shown in Fig. 7 was applied for in situ experiments at temperatures of up to 723 K [15].

3.2. Study of heterogeneous reaction systems by in situ UV–Vis spectroscopy

The first UV–Vis investigations of the conversion of methanol on zeolite H-ZSM-5 were performed by Derouane and co-workers [16,17]. Bands between 300 and 400 nm, which occur even at 473 K indicate the presence of carbenium ions. The reaction of ethene on H-ZSM-5 zeolite was first investigated by Laniecki and Karge [18]. These authors observed a band at 300 nm which they explained by allyl cations. The bands occurring at 280 to 330 nm, 360 to 380 nm, and 430 to 470 nm during the adsorption of olefins on acidic zeolites were attributed to unsaturated mono-, di- and trienyl carbenium ions, respectively [13]. Flego et al. [19] investigated the alkylation of isobutane with 1-butene on zeolites LaH–Y under f1ow conditions. Directly after adsorption of 1-butene and an isobutane/1-butene mixture, these authors observed UV–Vis bands of monoenyl carbenium ions (315 nm) and dienyl carbenium ions (370 nm). Since the intensity of these bands depended on the activation temperature of the catalyst (Fig. 8), Lewis acid sites were discussed to be responsible for the formation of the carbenium ions [13,19]. It was found that the formation of unsaturated carbenium ions was favored by reaction temperatures of up to 523 K, long contact times, and a high concentration of Lewis acid sites.

In Section 5.3, the application of in situ UV–Vis spectroscopy is described in combination with in situ NMR spectroscopy for the investigation of the methanol-to-olefin conversion process on acidic zeolite catalysts.

4. ESR spectroscopy

4.1. Methodical introduction

An important feature of electron spin resonance (ESR) spectroscopy is its high sensitivity, which allows the study of active sites and intermediates of chemical reactions with very low abundance in the framework or on the surface of catalysts. In the zeolite framework,

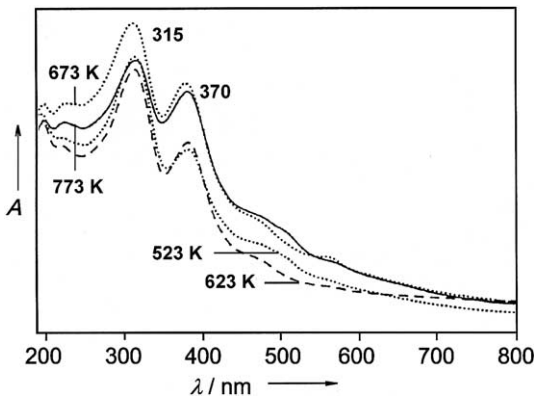


Fig. 8. UV–Vis spectra recorded during the conversion of isobutane and 1-butene (9:1) on zeolite LaH–Y at reaction temperatures of 523–773 K [13,19].

unpaired electrons, necessary for a detection by ESR spectroscopy, are formed by defects or by a substitution of framework atoms. Molecules amenable to ESR spectroscopy must exist as radicals on the surface of the catalyst, formed, e.g., by a spontaneous oxidation at a Lewis acid site or via irradiation of the sample with γ-quanta (radiolysis/ESR) [20,21]. Short relaxation times of electron spins and exchange processes lead to a broadening of the ESR signals. The use of ESR spectroscopy is, therefore, often limited in its maximum measurement temperature [14]. Frequently, ESR measurements are carried out at temperatures of 77 K or below after stopping the reaction under study. In situ cells differ in their construction according to whether they are used for investigations under batch conditions or under flow conditions [22–25]. The ESR cell for studies of heterogeneous reaction systems under flow conditions, shown in Fig. 9, was designed for the X-band, i.e., for an electron spin resonance frequency of $\nu_0 = 95$ GHz or a wavelength of $\lambda = 3$ cm. It consists of a reactor tube with an internal diameter of 3 mm to which a heating wire is attached. At the top of the reactor, a glass fiber optics is inserted allowing simultaneous in situ UV–Vis and ESR spectroscopic investigations [25].

4.2. Coordination change of iron atoms in microporous aluminophosphates studied by in situ ESR spectroscopy

Typical applications of ESR spectroscopy in zeolite science are investigations on the preparation and formation of zeolites, the characterization of adsorbed species, and investigations of heterogeneously catalyzed reactions [14,26–28]. This includes the spectroscopic characterization of framework building blocks, which act as active sites, and adsorbate molecules and reactants.

ESR spectra of Fe^{3+} ions in zeolites often consist of two signals at $g = 2.0$ and 4.2 and allow a differentiation of the nature of the iron species as a function of the treatment (see Refs. [29–31] and references therein).

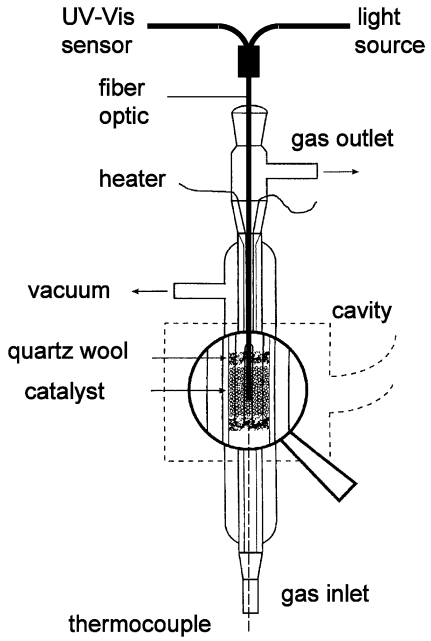


Fig. 9. Scheme of an X-band ESR/UV–Vis cell suitable for in situ investigations of catalysts and heterogeneously catalyzed reactions at temperatures of up to 760 K [25].

Hexaaqua Fe^{3+} complexes in a Na–Y zeolite exchanged with iron lead to a strong signal at $g \approx 2.0$. After calcination of a zeolite Fe-ZSM-5 prepared by sublimation of $FeCl_3$, the signal of the Fe^{3+} ions at $g \approx 2.0$ disappears and signals at $g = 4.3$, 5.6, and 6.5 appear, which Kucherov et al. [31] assigned to tetrahedrally coordinated or distorted tetrahedrally coordinated extra-framework Fe^{3+} species. If this catalyst is exposed to a mixture of NO, C_3H_6, and O_2, a significant reduction of the extra-framework Fe^{3+} species at $g = 4.3$ occurs.

Recently, Brueckner et al. [32] showed that the iron in aluminophosphates and silicoaluminophosphates also causes ESR signals with g-factors of 2.0 and 4.3. These signals were explained by octahedrally coordinated Fe^{3+} ions on framework positions and by Fe^{3+} ions on defect sites, respectively. The ESR spectra illustrated in Fig. 10 were taken in steps of 20 K during the calcination of an iron-modified aluminophosphate Fe/$AlPO_4$-5 in an air stream after synthesis (as-synthesized) [32]. The signal of Fe^{3+} ions on defect sites at $g = 4.3$ is strongly decreased in the temperature range of 373 K to 573 K, whereas at the same time a considerable broadening of the signal of the Fe^{3+} on framework positions at $g = 2.0$ can be observed. A narrow signal occurring at $g = 2.0$ in the temperature range of 453 to 613 K is caused by the thermal decomposition of the template and the formation of paramagnetic coke species. After complete decomposition of the template residues, spectra of Fe^{3+} ions are obtained which consist of three signal components. The analysis of the ESR spectrum taken after calcination at 773 K gives a fraction of Fe^{3+} ions on framework positions of 45% [32].

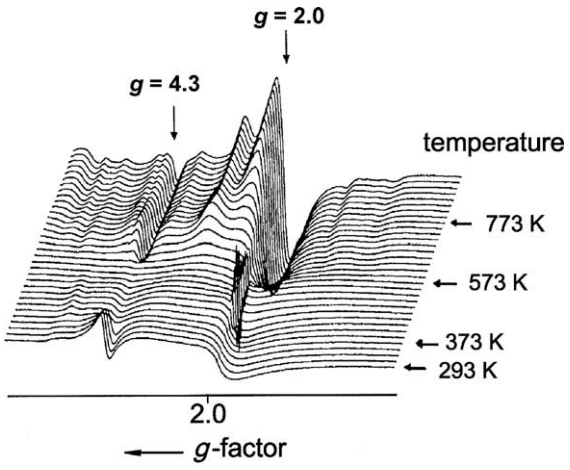


Fig. 10. X-band ESR spectra of Fe/$AlPO_4$-5 recorded during calcination in a stream of dry nitrogen at temperatures between 293 and 773 K [32].

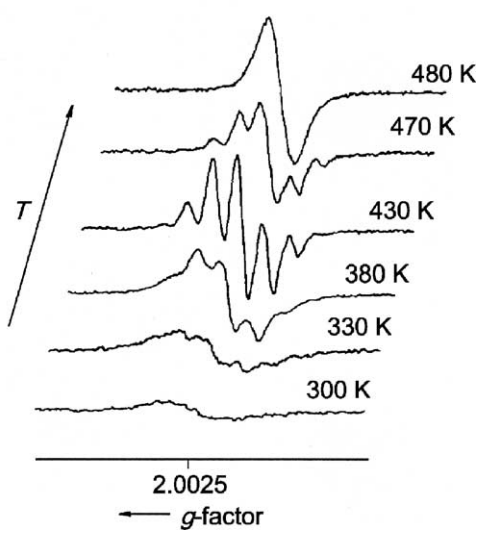


Fig. 11. X-band ESR spectra of radical cations recorded during the formation of coke during the conversion of ethene on H-mordenite at temperatures of 300–480 K [23].

4.3. Formation of coke by conversion of olefins on acidic zeolites studied by in situ ESR spectroscopy

In a number of studies, zeolites have been used as matrix for the stabilization of radical cations formed by a spontaneous oxidation. Crockett and Roduner [33,34] investigated the dimerization and transannular reactions of cycloalkenes and the oxidation of terpenes on H-mordenite. After loading a calcined H-mordenite with different terpenes, ESR signals of the radical cations were found in each case. With a deuterated mordenite (D-mordenite), the deuterons of which were not incorporated into the product molecule, it was possible to establish that the above-mentioned reactions are catalyzed by Lewis acid sites. In contrast, Rhodes [35] and Rhodes and Standing [36] explained the formation of the radical cation of 1,2,3,4,5,6,7,8-octahydronaphthaline on H-mordenite after loading with cyclopentene and different acyclic dienes by a Brønsted acid catalyzed conversion of the reactants prior to the formation of radical cations.

Karge and co-workers investigated the formation of hydrocarbon deposits (coke) during the reaction of olefins on H-mordenites under flow conditions [22,23]. In the temperature range of 380–470 K, signals with a hyperfine splitting of $a = 1.6$ mT and a g-factor of $g = 2.0025$ were observed (Fig. 11) [23]. After a further increase of the reaction temperature to 480 K, this hyperfine splitting disappeared and a signal typical of high-temperature coke appeared. Olefinic and allylic hydrocarbons were suggested as major constituents of the low-temperature coke ($T < 500$ K). The high-temperature coke formed at temperatures of $T \geqslant 480$ K, probably caused by polyaromatic radical cations, gave a narrow ESR spectrum [23]. With radiolysis/ESR, Piocos et al. [37] established that the ESR signals occurring during the oligomiserization of olefins on dealuminated H-mordenite and zeolite H-ZSM-5 arose from radical cations of 2,3-dimethybutene and larger branched olefins. Pradhan el al. [38] investigated the formation of coke during the disproportionation of ethylbenzene on zeolite H-ZSM-5. In contrast to the work of Karge and co-workers [22,23], Pradhan et al. [38] were unable to find any hyperfine splitting of the ESR signals. This was explained by the polycyclic and aromatic nature of the low-temperature coke formed from ethylbenzene.

5. NMR spectroscopy

5.1. Methodical introduction

The strong line broadening due to solid-state interactions in heterogeneous reaction systems requires the application of the technique of rapid sample rotation around an axis in the magic angle (MAS), whereby the anisotropic solid-state interactions can be averaged out or at least reduced. Air-beared turbines with sample rotation frequencies of up to 40 kHz are used almost exclusively for rapid sample rotation. The application of the MAS technique causes significantly higher demands on the preparation of samples and the procedures of in situ experiments than in the case of FTIR, UV–Vis, and ESR spectroscopy. For in situ measurements under batch conditions, catalyst samples can be fused in symmetrical glass ampoules which fit in MAS rotors (see Refs. [39–41]). Another possibility is the application of special loading apparatus such as the CAVERN equipment (cryogenic adsorption vessel enabling rotor nestling), which allows a direct preparation of samples in gas-tight MAS rotors [42].

Generally, 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 located inside a high-temperature MAS NMR probe.

The ''pulse-quench'' technique of Haw et al. [43,44] utilizes an external microreactor for a pulsed introduction of 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 and the reaction products strongly adsorbed on the catalyst surface are investigated by NMR spectroscopy at ambient or sub-ambient temperatures.

In 1995, the first technique for in situ MAS NMR investigations of heterogeneously catalyzed reactions under continuous-flow conditions was introduced (approach (ii)). This technique is based on the continuous injection of carrier gas loaded with vapors of the reactants into the spinning MAS NMR rotor via an injection tube (Fig. 12) [45,46]. 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. 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 and an internal gas standard leaving the spinning MAS NMR rotor reactor were sucked up and led to the sampling loop of an on-line gas chromatograph [47]. Recently, this experimental technique was combined with a fiber optics, which allows a simultaneous investigation of heterogeneous reaction systems by in situ MAS NMR and UV–Vis spectroscopy (Fig. 13) [48]. The rotor of a 7 mm MAS NMR probe was equipped at the bottom with a quartz glass window. Via this quartz glass window and using a glass fiber, the catalyst sample inside the rotor can be investigated by a fiber optic UV–Vis spectrometer.

5.2. Study of the MTO process by in situ MAS NMR spectroscopy under steady-state conditions

The conversion of methanol to hydrocarbons on acidic zeolites is, since the first report in 1976 [49], 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 [50]. Recently, various NMR spectroscopic techniques were applied to investigate the conversion of methanol on acidic zeolites to dimethyl ether (DME) in the low-temperature range ($T \leqslant 523$ K) and to olefins and gasoline in the high-temperature range ($T \geqslant 523$ K). Successfully applied techniques are the in situ stop-and-go method under batch conditions [51,52], the pulse-quench method [53], and flow techniques [54–58].

For the conversion of methanol to hydrocarbons on acidic zeolites, various reaction mechanisms were proposed [50]. Haag [59], Hoelderich et al. [60], Dessau [61], and Kolboe [62] and Dahl and Kolboe [63] ex-

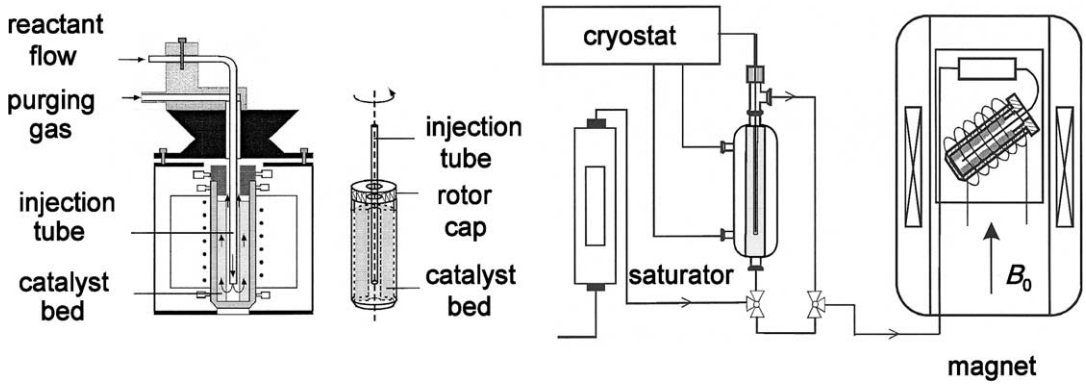


Fig. 12. Scheme of an MAS NMR setup for in situ experiments under continuous-flow (CF) conditions [45,46].

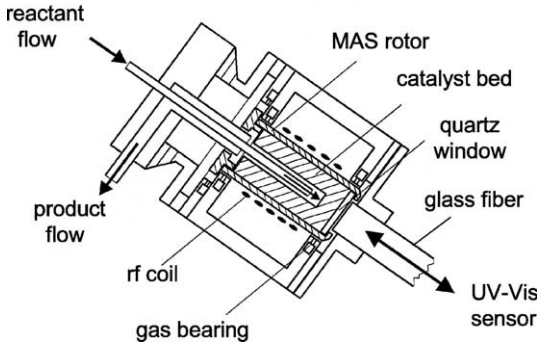


Fig. 13. Scheme of a probe for simultaneous CF MAS NMR and UV–Vis investigations under in situ conditions [48].

plained the formation of light olefins by a hydrocarbon 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 reactants and split off reaction products. The hydrocarbon pool was proposed to represent adsorbates with many characteristics of ordinary coke described by $(CH_x)_n$ with $0 < x < 2$ [50]. More recently, Mikkelsen et al. [64] and Haw and co-workers [65] proposed polymethylbenzenes to contribute to the hydrocarbon pool and to play a key role in the conversion of methanol on acidic zeolites.

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 [55,58,66]. 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 [58]. A comparison of the results achieved in the fixed-bed reactor and in the spinning MAS NMR rotor reactor showed a reasonably good agreement [58]. 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 calcined zeolites H-ZSM-5, H-SAPO-18 or H-SAPO-34 [55,58]. As an example, Fig. 14 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 523–573 K [55]. The signal occurring at δ_{13C} = 61 ppm in the in situ ^{13}C CF MAS NMR spectra of zeolite H-ZSM-5 recorded at 523 K indicates the conversion of methanol (δ_{13C} = 51 ppm) to DME. This finding agrees with the

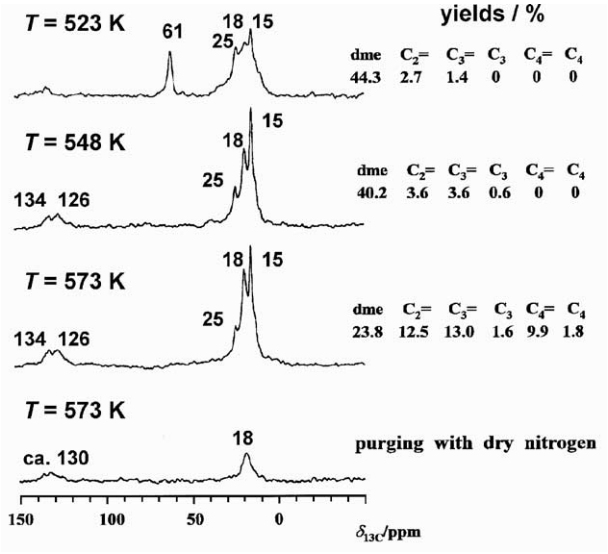


Fig. 14. ^{13}C CF MAS NMR spectra recorded during the conversion of ^{13}C-enriched methanol (W/F = 25 g h/mol) on zeolite H-ZSM-5 at reaction temperatures of 523 to 573 K. The bottom spectrum was recorded after purging the used catalyst with dry nitrogen gas at 573 K. On the right-hand side, the yields 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 [55].

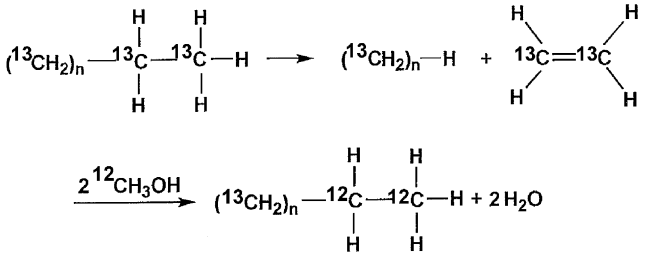
high yields of DME (Y_{dme} = 44.3%) obtained at this temperature by on-line gas chromatography (Fig. 14, right). The signals occurring at 15–25 ppm are caused by alkyl groups of hydrocarbons formed on the catalyst. After increasing the reaction temperature to 548 K and higher, additional ^{13}C MAS NMR signals occur in the olefinic and aromatic region at δ_{13C} = 126–13 ppm. 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. 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 (Fig. 14, bottom). The spectrum obtained after purging consists of weak signals at δ_{13C} = 18 and approximately 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 a commercial software (see Ref. [58]). 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 hydrocarbon pool containing a mixture of olefins and diolefins, such as *n*-hexene-3 (δ_{13C} = 14, 25, and 131 ppm), *n*-hexadiene-2,4 (δ_{13C} = 18, 127, and 132 ppm), and alkylated octadienes (δ_{13C} = 15, 23, 25, and 133–135 ppm). In addition, the formation of cyclic compounds, such as cyclopentene (δ_{13C} = 23, 33, and 131–133 ppm), and alkylated cyclopentenes, such as diethylcyclopentene (δ_{13C} = 14–

33 ppm and 133–135 ppm) and *para*-xylene (δ_{13C} = 21, 129, and 134 ppm), has been claimed [55]. Recently, Song et al. [65] proposed polymethylaromatics to be the most active carbonaceous compounds catalyzing the methanol-to-hydrocarbons conversion on acidic zeolites. These polymethylaromatic compounds may cause the signals occurring at δ_{13C} = 18 and approximately 130 ppm after purging the catalyst material with dry nitrogen at 573 K.

To support the catalytic role of the hydrocarbon 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 changing other reaction parameters. If the alkyl groups of the hydrocarbon pool were 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 $^{12}CH_3OH$ (see Scheme 1).

Fig. 15 shows in situ ^{13}C and ^{1}H CF MAS NMR spectra recorded during the conversion of methanol on zeolite H-ZSM-5 at a reaction temperature of 573 K [66]. The parameters of these experiments were the same as used to record the spectra shown in Fig. 14. To quantify the ^{13}C-isotope abundance of the alkyl groups contributing to the hydrocarbon pool, the spectral region of δ_{13C} = 0–40 ppm was integrated using spectra Fourier-transformed via the absolute intensity mode. This integral was set to 100% for the spectrum recorded during the conversion of $^{13}CH_3OH$ (Fig. 15, top). 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 hydrocarbon pool by approximately 40% was found (Fig. 15, bottom). The simultaneously recorded ^{1}H CF MAS NMR spectra on the right–hand side of Fig. 15 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 hydrocarbon pool by alkyl groups with a natural ^{13}C-isotope abundance indicates that the olefinic and aromatic compounds of this pool are involved in the conversion of methanol. This finding strongly supports the hydrocarbon pool mechanism for the conversion of methanol to olefins on acidic zeolites.



Scheme 1.

5.3. Reactivity of surface methoxy groups investigated by in situ stopped-flow (SF) MAS NMR spectroscopy

The in situ NMR experiments discussed in Section 5.2 evidenced that the hydrocarbon pool plays a catalytically active role in the MTO process on acidic zeolites. Further investigations focused on the formation of the first carbon–carbon bonds. Impurities in the methanol feed could be the initial compounds responsible for the formation of the hydrocarbon pool on zeolite catalysts [67]. On the other hand, recent in situ MAS NMR investigations indicated that methoxy groups may contribute to the formation of DME [68] and hydrocarbons [69]. The investigations on the reactivity of surface methoxy groups were performed by stopped-flow experiments as shown in Fig. 16. The stopped-flow experiment consists of the following steps: (i) recording of the in situ CF MAS NMR spectra at reaction temperature under steady-state conditions during a continuous injection

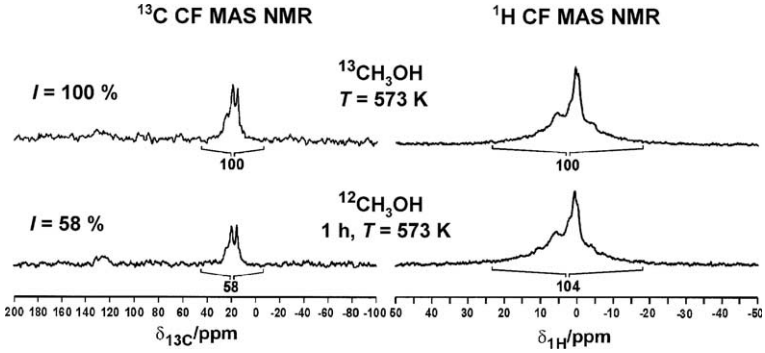


Fig. 15. ^{13}C and ^{1}H CF MAS NMR spectra recorded during the conversion of methanol (W/F = 25 g h/mol) on zeolite H-ZSM-5 at a reaction temperature of 573 K. The bottom spectra were recorded 1 h after switching the methanol feed from $^{13}CH_3OH$ to $^{12}CH_3OH$. The relative intensities given 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 [66].

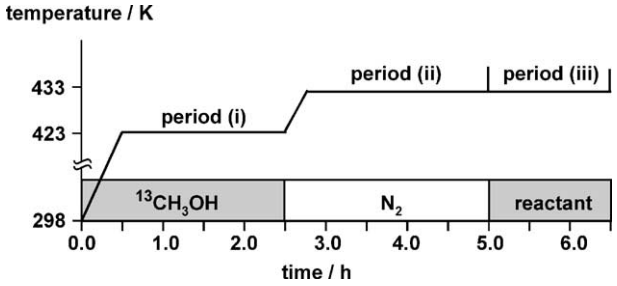


Fig. 16. Protocol of a stopped-flow (SF) MAS NMR experiment [68].

of ^{13}C-enriched methanol into the MAS rotor reactor, (ii) recording of MAS NMR spectra after stopping the reactant flow and purging the catalyst with dry nitrogen after raising the temperature, and (iii) recording of MAS NMR spectra at reaction temperature after starting the flow of a second reactant such as non-enriched methanol, alkanes or aromatic compounds. Since the in situ SF MAS NMR technique allows a direct investigation of the further conversion of adsorbate complexes formed on the catalyst during period (i), this approach can provide detailed information on reaction mechanisms.

The above-mentioned stopped-flow protocol made it possible to prepare *pure* surface methoxy species on solid acid catalysts. In this way, the reactivity of surface methoxy species can be further studied by using different reactants. The ^{13}C MAS NMR spectra shown in Fig. 17 are an experimental evidence for the reaction of surface methoxy species with cyclohexane (natural abundance of ^{13}C-isotopes) on methylated zeolite Y (CH_3–Y) at elevated temperatures [69]. After surface methoxy species were prepared in situ, the methylated catalyst was loaded with cyclohexane. Fig. 17 shows the ^{13}C MAS NMR spectrum directly recorded after adsorption of cyclohexane at temperatures of 298 to 523 K (period (iii)). At 298 K, the spectrum is dominated by the methoxy species at 56.2 ppm with spinning sidebands and a weak signal at 27.2 ppm due to cyclohexane. The reaction starts at 493 to 503 K, which is indicated by the decrease of the intensity of methoxy species and the occurrence of a signal at 23.7 ppm due to the ^{13}C-enriched methyl groups of methylcyclohexane. The signals in the aliphatic range (10–40 ppm) are highlighted (see insets) for all spectra recorded at elevated temperatures. Up to a reaction temperature of 523 K, almost all surface methoxy groups and cyclohexane are consumed and the spectrum is dominated by a signal at 23.7 ppm (Fig. 17, bottom).

As a control experiment, the possible cracking of cyclohexane on zeolite H–Y was investigated, which did not start until 623 K. Therefore, the methylation of cyclohexane on methylated zeolite Y occurs only by the reaction of cyclohexane with surface methoxy species. At reaction temperatures of $T \geqslant 493$ K, these surface methoxy species most probably act as precursors of carbene or ylide intermediates.

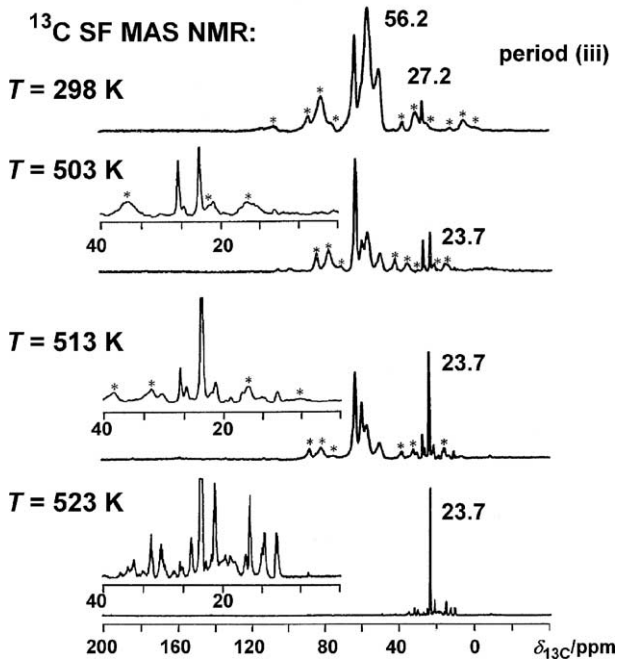


Fig. 17. ^{13}C MAS NMR spectra of methylated zeolite Y (CH_3–Y) recorded after loading with cyclohexane (natural abundance of ^{13}C-isotopes) and thermal treatments at 503–523 K. The signals appearing at 0 to 40 ppm are highlighted in the insets. Asterisks denote spinning sidebands [69].

In a further in situ MAS NMR experiment, the reactivity of surface methoxy groups on zeolite CH_3–Y without addition of another reactant 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. [68]. The ^{13}C CF MAS NMR spectrum in Fig. 18, top, shows the signal of the methoxy groups on zeolite H–Y occurring at 56.2 ppm [69]. This spectrum was recorded at the end of period (ii), i.e., after purging of all volatile species. Upon increasing the temperature to 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 approximately 128 to 142 ppm [69]. It is interesting to note, that 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. [58]). The ^{13}C MAS NMR signals in the spectrum recorded at 523 K can be explained by olefins and dienes, such as propene

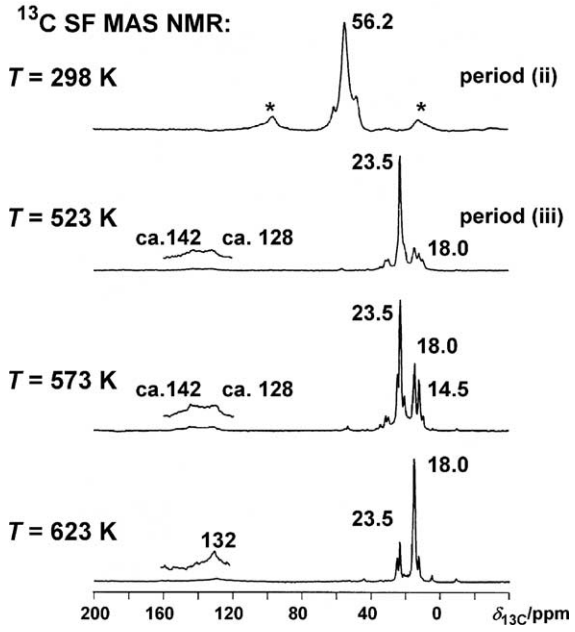


Fig. 18. ^{13}C MAS NMR spectra of methylated zeolite Y (CH_3–Y) recorded after thermal treatments at 523 to 623 K. Asterisks denote spinning sidebands [69].

(δ_{13C} = 16.1 and 16.3 ppm), isobutene (δ_{13C} = 23.7, 119.5, and 141.4 ppm), and dimethylbutadiene (δ_{13C} = 20.1, 111.3, and 142.1 ppm), and by aromatic compounds such as benzene (δ_{13C} = 128.6 ppm) and hexamethylbenzene (δ_{13C} = 17.4 and 132.1 ppm). After increasing the temperature to 623 K, the spectrum is dominated by the signals of hexamethylbenzene (Fig. 18, bottom). This finding indicates a possible formation of the first hydrocarbons during the kinetic induction period of the MTO process via the conversion of pure surface methoxy species. After the first hydrocarbons are formed, or in the presence of a small amount of organic impurities, surface methoxy groups contribute to a further methylation of these organic compounds leading to the formation of a reactive hydrocarbon pool which plays an active role in the steady state of the MTO process at reaction temperatures of $T \geqslant 573$ K.

5.4. Formation of cyclic compounds and carbenium ions on zeolite catalysts studied by in situ CF MAS NMR/UV–Vis spectroscopy

Very recently, it could be shown that on Brønsted acidic zeolites H–Y, H-ZSM-5, and H-SAPO-34, surface methoxy groups contribute to the formation of the hydrocarbons in the induction period of the methanol conversion at 433–523 K (see Section 5.2). On the other hand, UV–Vis investigations of the methanol conversion on dealuminated zeolites H-ZSM-5 indicated that cyclohexenylic, polyenylic, and diphenylic carbenium ions as well as condensed aromatics are formed already at 400 K [70]. Therefore, a novel in situ CF MAS NMR/UV–Vis technique was applied to study the formation of hydrocarbons by the conversion of methanol on a weakly dealuminated zeolite H-ZSM-5 at low reaction temperatures. A commercial variable-temperature 7 mm MAS NMR probe of Bruker BioSpin was modified with an injection system as described in Section 5.1. In addition, a glass fiber optics was fixed at the bottom of the stator as shown in Fig. 13.

The weakly dealuminated zeolite H-ZSM-5 (n_{Si}/n_{Al} = 22) was dehydrated at 673 K in vacuum for 12 h before it was filled into the MAS NMR rotor under dry nitrogen inside a glove box. The methanol ($^{13}CH_3OH$) flow (W/F = 25 g h/mol) was started after reaching the temperature of 413 K. The ^{13}C MAS NMR spectrum recorded at 413 K during the continuous conversion of methanol (Fig. 19, top, left) shows signals at 51 and 61 ppm due to methanol and DME, respectively, and a very weak signal at approximately 23 ppm, probably caused by alkanes or alkylated cyclic compounds [48]. The occurrence of the signals at 23 and 61 ppm indicates that the conversion of methanol on weakly dealuminated zeolites H-ZSM-5 starts already at 413 K. The simultaneously recorded UV–Vis spectrum (Fig. 19, top, right) consists of bands at approximately 275, 315, and 375 nm. The narrow peaks at approximately 500 nm are due to the equipment. According to the literature, the band at 275 nm indicates the formation of neutral aromatic compounds [13,71], while the bands at 315 and 375 nm may be due to mono- and dienylic carbenium ions [13], respectively. Bjørgen et al. [71] found that adsorption of hexamethylbenzene on zeolite H-Beta leads to the formation of hexamethylbenzenium ions causing a band at 390 nm. It is important to note, that the UV–Vis spectrum of the non-dealuminated zeolite H-ZSM-5, i.e., of the parent zeolite H-ZSM-5, recorded under the same reaction conditions, consists only of a very weak band at approximately 300 nm. This indicates that the formation of first hydrocarbons and carbenium ions, already at 413 K, is influenced by the presence of extra-framework aluminum species acting as Lewis acid sites.

As the first reaction product of the methanol to olefin conversion on acidic zeolites, often the formation of ethene is discussed [50]. In the present case, therefore, the organic compounds responsible for the ^{13}C MAS NMR signals at 23 ppm and the UV–Vis bands at 275, 315, and 375 nm may be formed also by ethene. To verify this assumption, the weakly dealuminated zeolite H-ZSM-5, used to convert methanol, was subsequently applied to study the conversion of ethene (Fig. 19, middle). ^{13}C MAS NMR signals appearing at 14, 23, and 32 ppm, during conversion of ethene at 413 K for 1 h, are due to alkyl groups of small amounts of alkylated cyclic compounds, such as cyclopentene, cyclohexene, cyclohexadiene, and benzene. The simultaneously recorded UV–Vis spectrum shows bands at 300 and

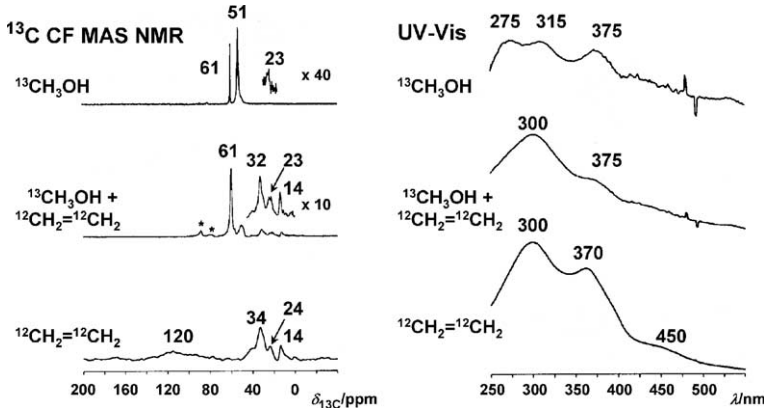


Fig. 19. ^{13}C CF MAS NMR (left) and UV–Vis (right) spectra of a dealuminated zeolite H-ZSM-5 recorded during conversion of $^{13}CH_3OH$ at 413 K for 2 h (top), during the subsequent conversion of $^{12}CH_2{=}^{12}CH_2$ at 413 K for 1 h (middle), and during the conversion of $^{12}CH_2{=}^{12}CH_2$ at 413 K on a non-used catalyst for 2 h (bottom). Asterisks denote spinning sidebands [48].

375 nm. Again, these bands are a hint for the formation of neutral cyclic compounds and dienylic carbenium ions, respectively [13].

The conversion of ethene on a non-used dealuminated zeolite H-ZSM-5 led to the spectra shown in Fig. 19, bottom. The ^{13}C MAS NMR spectrum consists of signals at 14, 24, and 34 ppm caused by alkyl groups of cyclic compounds. In addition, a broad signal in the chemical shift range of olefinic and aromatic compounds occurred at approximately 120 ppm. The UV–Vis spectrum consists of bands similar to those in the former experiment and an additional weak band at approximately 450 nm, which may be due to condensed aromatics or trienylic carbenium ions [13,16]. A weak shoulder at approximately 400 nm could be an indication for the formation of hexamethylbenzenium ions [71].

In conclusion, the simultaneous investigation of methanol conversion on weakly dealuminated zeolite H-ZSM-5 by in situ ^{13}C CF MAS NMR and UV–Vis spectroscopy shows that first cyclic compounds and carbenium ions are formed already at 413 K. Probably, extra-framework aluminum species acting as Lewis acid sites are responsible for the formation of hydrocarbons and carbenium ions at this low reaction temperature. While NMR spectroscopy allows an identification of the signals of the main reactants in more detail, UV–Vis spectroscopy gives hints to the formation of low amounts of cyclic compounds and carbenium ions.

6. Outlook: in situ spectroscopy in zeolite science

By means of examples this contribution has demonstrated that in situ FTIR, UV–Vis, ESR, and NMR spectroscopy are able to provide important information on the mechanisms of heterogeneously catalyzed reactions. Over the coming decade it is expected that our knowledge of zeolites and heterogeneous catalysis will be improved significantly by the systematic application of these and other in situ techniques. A significant

Table 1
Advantages and disadvantages of FTIR, UV–Vis, ESR, and NMR spectroscopy for studies of heterogeneous reaction systems under in situ conditions

Method	Advantages	Disadvantages
FTIR	• Low costs • Commercially available • Large temperature range	• Broad and overlapping bands • No direct quantitative evaluation • Problematic assignment of bands
UV–Vis	• Low costs • Very high sensitivity • Large temperature range	• Limited application (hydrocarbons with conjugated double bonds, unsaturated carbenium ions) • Broad and overlapping bands • Problematic assignment of bands
ESR	• High sensitivity • Sensitive for the local structure of adsorbates and surface sites	• Limited application (paramagnetic sites) • Strong line broadening at high-temperatures • Limited temperature range
NMR	• Large number of NMR sensitive nuclei • Good separation of signals • Sensitive for the local structure of adsorbates and surface sites	• High costs • Low sensitivity • Limited temperature range

advantage of the in situ methods described in this contribution is that they can be operated under conditions of real catalysis, that is, there is no ''pressure gap'' (or the in situ methods operate at least close to the pressures of industrial catalysis), and that they can be applied in a laboratory scale. A more general comparison of the advantages and disadvantages of these spectroscopic methods is given in Table 1.

In the near future, further improvements of the experimental techniques of in situ spectroscopy can be expected. Important aims are (i) an enhancement of their sensitivity and selectivity, e.g., by an application of higher magnetic fields, a selective enhancement of the nuclear polarization utilizing Laser-polarized xenon in NMR spectroscopy or by two-dimensional experiments in FTIR spectroscopy, and (ii) a further increase of the temperature and pressure ranges accessible for the study of heterogeneously catalyzed reactions. Furthermore, the development of new cells and novel techniques for the preparation of activated solid catalysts used for in situ studies of heterogeneous reaction systems can be expected.

Acknowledgments

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