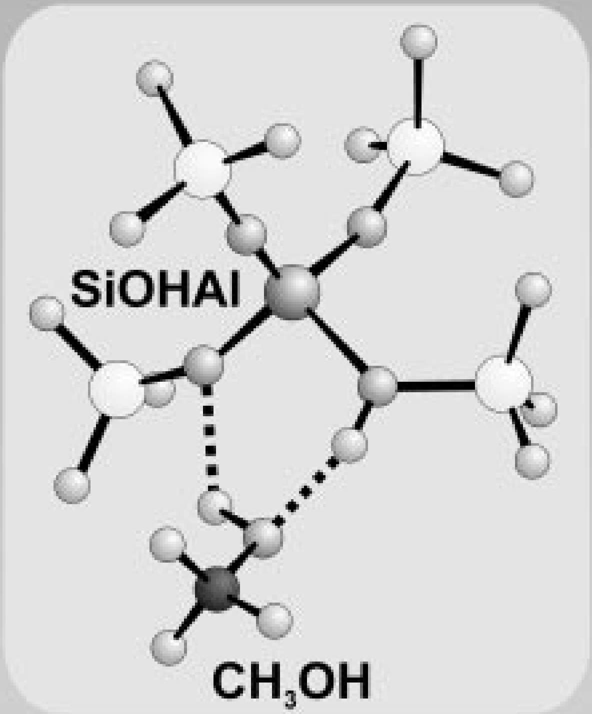
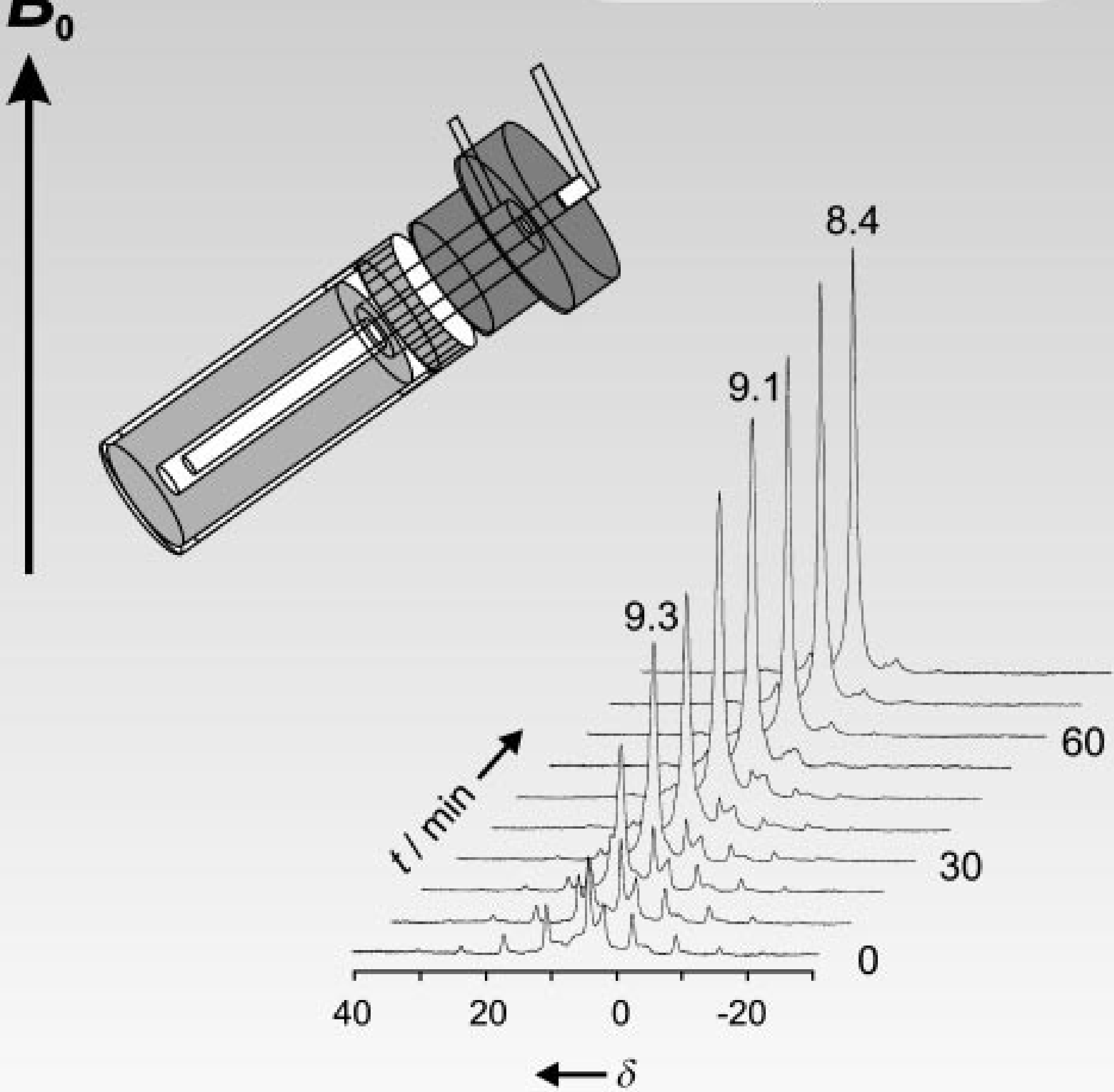
In situ Spectroscopy





ANGEWANDTE CHEMIE

In situ IR, NMR, EPR, and UV/Vis Spectroscopy: Tools for New Insight into the Mechanisms of Heterogeneous Catalysis

Michael Hunger* and Jens Weitkamp*

The development of new solid catalysts for use in industrial chemistry has hitherto been based to a large extent upon the empirical testing of a wide range of different materials. In only a few exceptional cases has success been achieved in understanding the overall, usually very complex mechanism of the chemical reaction through the elucidation of individual intermediate aspects of a heterogeneously catalyzed reaction. With the modern approach of combinatorial catalysis it is now possible to prepare and test much more rapidly a wide range of different materials within a short time and thus find suitable catalysts or optimize their chemical composition. Our understanding of the mechanisms of reactions catalyzed by these materials must be developed, however, by spectroscopic investigations on working catalysts under conditions that are as close as possible to practice (temperature, partial pressures of the reactants, space velocity). This demands the development and the application of new techniques of in situ spectroscopy. This review will show how this objective is being achieved. By the term in situ (Lat.: in the original position) is meant the investigation of the chemical reactions which are taking place as well as the changes in the working catalysts directly in the spectrometer.

Keywords: active centers · heterogeneous catalysis · in situ spectroscopy · reaction mechanisms · solid catalysts

1. Introduction

The elucidation of reaction mechanisms in heterogeneous catalysis is a process that involves the design and selection of a suitable reaction network, the determination of the stoichiometry of each individual intermediate step of this network, and the identification and characterization of the active centers, the intermediate products, the activation processes of the reactants, and the surface reactions. In addition to the methods of reaction kinetics increasing use is being made of the modern procedures of in situ spectroscopy for the elucidation of these reaction networks. In this review an overview of the state of development and the applications of the most important techniques of IR, NMR, EPR, and UV/Vis spectroscopy in heterogeneous catalysis will be presented. IR, NMR, and EPR spectroscopy are universally used methods for the investigation of catalytically active sites in solid catalysts and the reactants interacting with these sites. UV/Vis spectroscopy is particularly suitable for the observation of chemically excited states of hydrocarbons. An important advantage of all four methods lies in the possibility of being able to investigate working catalysts in contact with the reactants under near-practice conditions, that is under reasonably high partial pressures of these reactants. This requirement is also met by X-ray diffraction (XRD), X-ray absorption spectroscopy (EXAFS, XANES), and Raman spectroscopy.[1–4] These methods, not described in this work, are finding increasing application in the characterization of active sites in solid catalysts under in situ conditions. Similarly, spectroscopic methods that require the use of high vacuum, such as X-ray and UV photoemission spectroscopy (XPS and UPS), electron energy loss spectroscopy (EELS), and Auger electron spectroscopy (AES) will not be dealt with.[1–4] In these methods, which have convincingly established their strength in numerous investigations of ideal solid-state surfaces, the practical partial pressures of the reactants lie several orders of magnitude below those of industrial processes (*pressure gap*). Special attention will be devoted to zeolites, not only due to their ideal crystalline structures, but also in view of their widespread use in numerous processes of industrial chemistry. In addition, a large number of amorphous and crystalline solid catalysts of importance to industrial chemistry will be discussed.

Much of the spectroscopic work on heterogeneously catalyzed reactions was performed under batch conditions,

---

[*] Prof. Dr. M. Hunger, Prof. Dr. J. Weitkamp
Institut für Technische Chemie
Universität Stuttgart
70550 Stuttgart (Germany)
Fax: (+49) 711-685-4065
E-mail: michael.hunger@po.uni-stuttgart.de
jens.weitkamp@po.uni-stuttgart.de

that is after a single loading of the activated catalyst with reactants in a sealed sample or 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 pursued by a growing number of groups. Catalyst formation and deactivation as well as the formation of surface complexes and intermediates in the steady state of a reaction can be observed spectroscopically with these techniques. An overview of new applications of the most important of these spectroscopic techniques will also be presented. Owing to the extensive nature of this topic, no claim to completeness is made. An introduction to the basic principles and classical uses of spectroscopic methods in heterogeneous catalysis may be found in the literature.[2–4]

2. Infrared Spectroscopy

Infrared spectroscopy is based upon the interaction of electromagnetic radiation with species that possess a permanent or induced dipole moment and the excitation of different vibrational states. An IR spectrometer usually records the energy of the electromagnetic radiation which is transmitted through a sample as a function of the wavenumber or frequency. Today, nondispersive spectrometers are almost exclusively used when the total spectrum is analyzed by an interference process and transformed into the frequency or wavenumber 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. The so-called DRIFT technique (*d*iffuse *r*eflectance *i*nfrared *F*ourier *t*ransform) is used in those cases where the sample does not have adequate transparency. A quantitative evaluation of band intensities requires the knowledge of extinction coefficients which are a function of the wavenumber. In some cases the extinction coefficients can be taken from the literature, but they are often limited in their accuracy. The high sensitivity of IR spectroscopy is of considerable advantage for in situ investigations in the area of heterogeneous catalysis. With its help it is possible to carry out investigations under both batch conditions and flow conditions.

Figure 1 shows the scheme of an IR flow cell developed by Karge and Nießen for transmission operation which is

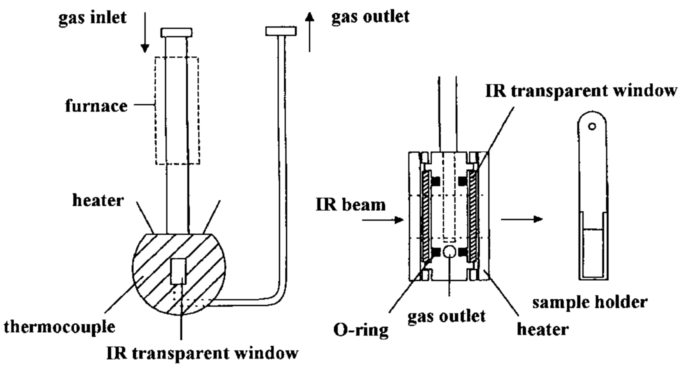


Figure 1. Schematic representation of an IR flow cell for in situ investigations of heterogeneously catalyzed reactions.[5]

Michael Hunger studied physics at the University of Leipzig and gained his doctorate in 1984 at the Department of Experimentalphysik. At that time he was engaged on the spectroscopic investigation of solid acids, in particular zeolites. In 1992, after his Habilitation and a number of periods abroad, he moved to the Institute of Chemical Technology of the University of Stuttgart. Two years later he was appointed Lecturer in Chemical Technology. In 1999 he was appointed Professor at the Faculty of Chemistry of the University of Stuttgart. In the same year he was appointed member of the management board of the DECHEMA Working Group Zeolites. His interests are centered on the development of new techniques of solid-state NMR and IR spectroscopy for the characterization of micro- and mesoporous solid catalysts and in situ spectroscopy of heterogeneous catalytic reactions.

M. Hunger

J. Weitkamp

Jens Weitkamp studied chemistry at the University of Karlsruhe and the Free University of Berlin. He obtained his doctorate and Habilitation at the Faculty of Chemical Engineering of the Universtiy of Karlsruhe. From 1986 to 1988 he held the post of C3 professor for Chemical Technology at the University of Oldenburg, and since 1988 he has been Head of the Institute of Chemical Technology of the University of Stuttgart. His main areas of research are heterogeneous catalysis, separation and purification technology by adsorption, and materials science with an emphasis on zeolites. He is currently President of the International Zeolite Association, Editor-in-Chief of the journal Microporous and Mesoporous Materials and a member of the board of directors of DECHEMA e.V., Frankfurt am Main, as well as of the Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V., Hamburg.

characterized by a particularly short optical path and thus a low gas-phase excitation.[5] The cell allows in situ calcination of a self-supporting sample, compressed to a very thin wafer ($\rho_{surface} \approx 10\,mg\,cm^{-2}$), in an oven located in the upper section. After calcination the sample is moved into the optical path with a magnet where it is measured in a vacuum or under the influence of an adsorbate or reactant. The most important areas of application of in situ spectroscopy in heterogeneous catalysis are the characterization of the framework of solid catalysts after their preparation and during the process of catalyst modification, the investigation of the species acting as adsorption centers or catalytically active sites, and the characterization of adsorbate complexes and intermediates on the surfaces of solid catalysts.[6]

2.1. IR Investigations of the Preparation of Solid Catalysts and the Interaction of Catalytically Active Sites with Reactants

Classical areas of application of IR spectroscopy in the characterization of solid catalysts are the investigation of framework vibrations of silicates and aluminosilicates and the OH stretching region of acidic solid-state catalysts.[7–12] The region of OH stretching of calcined, crystalline aluminosilicates is made up of bands of the terminal and defect SiOH groups at 3740 cm^{-1}, the high-frequency (HF) bands of the accessible bridging OH groups in zeolites at 3610 to 3650 cm^{-1}, and the low-frequency (LF) bands of bridging OH groups in the small cages of zeolites at about 3540 cm^{-1}.[10] IR spectroscopy is frequently used for the characterization of bridging OH groups which are acting as Brønsted centers in zeolites. Different probe molecules (e.g. pyridine, benzene, CO) are used for the determination of the accessibility and acid strength of these Brønsted centers,[13, 14] when the decay or displacement of the stretching bands of the OH groups are investigated. Lewis acid sites of these materials and the framework oxygen atoms acting as bases are characterized, for example, with pyridine or with chloroform and methylacetylene (see ref. [13, 14] and references therein).

An interesting technique for the investigation of the preparation and modification of solid catalysts is the ATR/FTIR spectroscopy (ATR: *a*ttenuated *t*otal *r*eflectance). This technique, developed by Moser and co-workers, is based upon a multiple reflection of the infrared radiation within a cylindrical crystal rod (CIR: *c*ylindrical *i*nternal *r*eflectance) which is led through the reaction space of the synthesis autoclave or reactor when it comes into contact with the fluid or solid-phase material under investigation.[15, 16] Calabro et al. used ATR-FTIR spectroscopy for in situ investigations of the synthesis of silicon-rich, mesoporous MCM-41 materials.[17] In the spectral window restricted by the use of ZnS as crystal rod, bands of template deformation vibrations occur at 1500 to 1350 cm^{-1} and those of internal asymmetric Si-O-Si stretch vibrations at 1250 to 1000 cm^{-1}. At room temperature, a synthesis experiment with cetyltrimethylammonium hydroxide as template showed two dominant bands at 1104 cm^{-1} and 997 cm^{-1}, an indication that this template promotes the formation of double 4-ring units (D4R), that are cubic octamers ($Si_8O_{20}^{8-}$). These D4R units disintegrate rapidly on increasing the temperature with the formation of oligomers with very different band positions. The resulting MCM-41 material shows two bands at 1045 to 1060 cm^{-1} and 1210 to 1221 cm^{-1}, the intensity and wavenumbers of which are dependent upon the texture. Holmes et al. undertook analogous investigations and made a quantitative evaluation of the intensities of these bands. They found that the rate of synthesis of the MCM-41 material is determined by the dissolution process of the silicon source.[18]

In the investigation of the reduction of V_2O_5 catalysts by NH_3 and H_2 Sullivan et al. used infrared emission spectroscopy (IRES: *i*nfra*r*ed *e*mission *s*pectroscopy).[19] Here the sample was situated on a heated sample table within the IR cell. The radiation emitted from the heated sample is collected by a parabolic mirror and deflected into the FTIR spectrometer whose IR source is switched off.[19, 20] By means of IRES, the near-surface species can be investigated preferentially. With this technique Sullivan et al. observed the stepwise reduction of V^{5+} and V^{4+} in V_2O_5 and found that the rate of reduction is limited by the solid-state diffusion of O atoms.[19]

2.2. H/D Exchange on Solid Catalysts

H/D exchange between surface OH groups and adsorbate molecules is a valuable method for the investigation of acid strength of OH groups and the mechanism of acid-catalyzed reactions. Armendariz et al. investigated the H/D exchange between deuterated benzene and the OH groups on sulfated ZrO_2 catalysts.[21] The authors observed that OH groups whose stretching bands appear at 3630 cm^{-1} form hydrogen bonds to adsorbed benzene molecules, whereas H/D exchange occurs between the OH groups at 3300 cm^{-1} and adsorbed C_6D_6 molecules. On the basis of this finding the OH groups absorbing at 3300 cm^{-1} were assigned a greater acid strength than those at 3630 cm^{-1}. Lee et al. investigated the H/D exchange between CH_4, C_2H_6, C_3H_8, and C_6H_{14} with the acidic OH groups of deuterated ferrierite.[22] By comparison of the activation energies of the H/D exchange reaction determined experimentally (130 to 143 $kJ\,mol^{-1}$) with data calculated by quantum-mechanical methods, the authors derived a reaction mechanism which passed through a neutral transition state.

Kondo et al. have investigated the mechanism of the double-bond isomerization of 1-butene on acid forms of mordenite and ZSM-5 zeolite.[23–25] With deuterated zeolites the authors were able to establish that starting from the π complex of 1-butene at the SiODAl groups, a reaction to *cis*- and *trans*-2-butene occurred even at 230 K without an H/D exchange of the acidic OD groups. H/D exchange, which causes a reduction in the intensity of the OD stretching band and an increase in the OH stretching band of the π complex, was observed only after a further increase in temperature. At temperatures below 230 K, the double-bond isomerization of 1-butene thus occurs without formation of a protonated intermediate species. On D-ZSM-5 zeolite a temperature above 250 K leads to dimerization of the 2-butenes, whereas on D-mordenite 2-butenes form paraffinic alkoxy groups even at temperatures as low as 230 K.[26]

In the reaction of acetone and ammonia on the acidic zeolites H-Y, H-Beta, H-ZSM-5, and H-mordenite, Kotrla et al. observed the formation of dimethylketimine ($(CH_3)_2C{=}NH$, DMKI).[27] A band at 1707 cm^{-1} was identified as the C=N- stretching band of the $>C{=}NH_2^+$ group of the protonated DMKIH$^+$, which forms ion-pair complexes with framework oxygen anions. This assignment was confirmed by a H/D exchange between the catalyst and the reactants, which shifts the C=N- stretching band to 1683 cm^{-1} ($>C{=}NHD^+$).

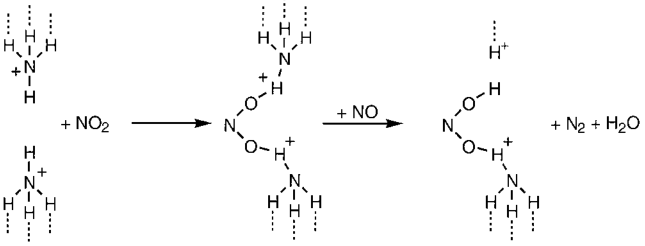
2.3. IR Investigations of the Decomposition of NO on Metal-Containing Solid Catalysts

The reactive surface species which are formed during the decomposition of NO and the selective catalytic reduction (SCR) of NO_x on zeolites exchanged with copper have already been reviewed.[9] The characteristic wavenumbers of these surface complexes can be obtained from the literature.[28–39] A frequently used catalyst for the decomposition of NO is Cu-ZSM-5 zeolite (see ref. [40, 41] and references therein). After loading this material with NO, Ganemi et al. observed bands at 1631, 1589 to 1575, and 2130 cm^{-1} which the authors ascribed to nitrate groups bridged to Cu^{2+}-O-Cu^{2+} dimers, monodentate nitrate species bonded to isolated copper ions, and NO$^+$ ions on the zeolite framework.[40] The authors postulated N_2O_3 species bound to Cu^{2+}-O-Cu^{2+} dimers as the reactive intermediates which are not detectable spectroscopically because of their short life span.

Konduru et al. used different transient species techniques to investigate the dynamic behavior of the adsorbates during the decomposition of NO on Cu-ZSM-5 zeolites.[41] With these techniques the authors were able to demonstrate that NO decomposition on Cu-ZSM-5 zeolites leads to a very rapid establishment of the equilibrium between gaseous NO and $Cu^+(NO)$ and $Cu^{2+}(NO_3)^{-1}$ species on the catalyst surface. The formation of N_2 immediately after the appearance of the band of $Cu^+(NO)$ species suggests that the NO decomposition is initiated by Cu^+ ions.

2.4. IR Investigations of the Selective Catalytic Reduction of NO_x

The mechanism of the selective catalytic reduction of NO with NH_3 on H-ZSM-5 zeolites and H-mordenite has been investigated by Eng and Bartholomew.[42] Bands for NH_3 and NO_2 species appeared in the in situ FTIR spectra of the most reactive samples. Based on their experimental data, the authors suggested a reaction mechanism in which a NO_2 species forms an active surface complex with pairwise aligned NH_3 species which reacts with NO to form N_2 (Scheme 1). Centeno et al. used the DRIFT technique for the investigation of the SCR of NO with NH_3/O_2 on an V_2O_5/Al_2O_3 catalyst.[43] They interpreted their results on the basis of an Eley–Rideal mechanism the essence of which is that an adsorbed reactant, that is here the ammonium species, reacts with other, nonadsorbed reactants, that is in this case gaseous NO. The authors rejected a coordinately bound ammonia since mainly NH_4^+ ions were observed at the reaction temperature with the highest NO turnover.



Scheme 1. Proposed mechanism for the catalytic reduction of NO with NH_3 on H-ZSM-5 zeolites and H-mordenites.

Acke et al. investigated the SCR of NO with HNCO and O_2 on a Pt/γ-Al_2O_3 catalyst at temperatures of 373 to 723 K.[44] During the reaction the authors observed the formation of isocyanate species at 2263 and 2240 cm^{-1}, surface-coordinated ammonia at 1587 and 1270 cm^{-1}, and ammonium ions at 1656, 1500, and 1477 cm^{-1} (Figure 2). The authors proposed a mechanism in which adsorbed ammonia and ammonium species are important species in the formation of N_2 and N_2O. Similarly, Captain and Amiridis investigated the SCR of NO with propene on a Pt/γ-Al_2O_3 catalyst.[45] The in situ FTIR spectra of Pt/γ-Al_2O_3 and γ-Al_2O_3 measured during the introduction of NO into the measurement cell indicated the formation of nitrate species on the γ-Al_2O_3 support and the adsorption of NO onto the platinum. After the introduction of C_3H_6, the authors observed the formation of carboxyl species and the adsorption of CO onto the platinum. In contrast, when a mixture of NO, C_3H_6, and O_2 was used, two bands of cyanide and isocyanate species appeared. The occurrence of the band of the isocyanate species under optimal reaction conditions indicates that these surface complexes are reactive intermediates of the SCR. In the reaction of NO and NO_2 on H-mordentite, Gerlach et al. observed a band which they attributed to chemisorbed nitrosyl cations (NO$^+$).[46] The authors were able to demonstrate that these nitrosyl cations are very reactive and react with C_3H_6 to form acrylonitrile. The authors suggested a reaction mechanism with 3-nitrosopropene and propenal oxime as intermediates. Zeolites exchanged with cobalt proved to be particularly active in the

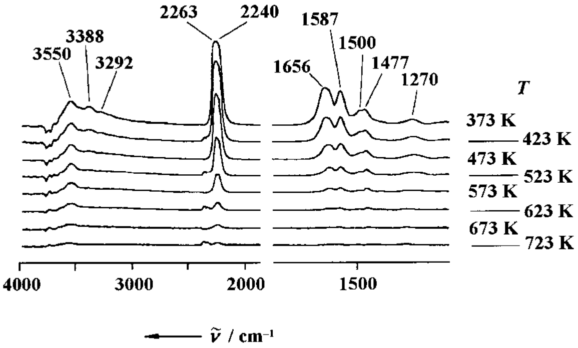


Figure 2. IR spectra of γ-Al_2O_3 recorded after the reaction of a mixture of HNCO, NO, and O_2 at temperatures in the range 373 to 723 K.[44]

SCR of NO with methane. NO is adsorbed mainly as highly stable dinitrosyl species on Co zeolites, whereas mononitrosyl species are very unstable.

2.5. The Conversion of Hydrocarbons on Metal-Containing Solid Catalysts

De La Cruz and Sheppard have investigated the dehydrogenation ethane on a Pt/SiO_2 catalyst.[47] Even at a reaction temperature of 90 K the authors observed a band at 2920 cm^{-1}, which is indicative of the formation of a monolayer of di-σ-C_2H_4 or di-σ/di-π-C_2H_4 species on platinum particles. Whereas the IR spectrum of the Pt/SiO_2 catalyst loaded with ethene contained bands of π-C_2H_4 complexes, the authors found no indications of the formation of such species after the dehydrogenation of ethane at 294 K. Weng et al. have carried out high-temperature in situ FTIR investigations (1023 to 1073 K) on the oxidative coupling of methane on LaOF and BaF_2/LaOF catalysts.[48] They established that gas-phase oxygen is activated to superoxide (O_2^-) on the catalyst surface. This O_2^- species reacts with CH_4 with the formation of C_2H_4 and CO_2.

The synthesis of methanol from H_2/CO_2 and H_2/CO on Cu/SiO_2 and $Cu/ZrO_2/SiO_2$ catalysts has been investigated by Fisher and Bell.[49, 50] $Cu/ZrO_2/SiO_2$ proved to be the more effective catalyst on which both CO_2 and CO interact preferentially with ZrO_2 leading to the formation of monodentate and bidentate carbonate and bidentate bicarbonate. During the course of the surface reaction, these species are finally hydrogenated to solely bidentate formate species and methoxy species, where the presence of copper has an accelerating effect. Copper also promotes the reductive elimination of the methoxy species as methanol. A further increase in the activity of Cu/SiO_2 was observed by modification of the catalyst with a mixture of TiO_2 and ZrO_2.[51] Wokaun and co-workers used the DRIFT technique for the investigation of the synthesis of methanol on Cu/ZrO_2.[52] In a multistep experiment, paraformaldehyde and formic acid (^{13}C labeled and in the natural abundance) were adsorbed and then hydrogenated. The authors established that methanol is synthesized solely via η^2-H_2CO (η^2-$H_2{}^{13}CO$: 1130 cm^{-1}) as intermediate, not via formate species, whose asymmetric and symmetric $^{13}C-O$ stretching vibrations appear at 1525 and 1335 cm^{-1}, respectively.

Voskoboinikov et al. used the DRIFT technique for the investigation of the Diels–Alder cyclodimerization of 1,3-butadiene to vinylcyclohexene on H-Y, Cu-Y, Cu-Beta, and Cu-EMT zeolites.[53] During the conversion of butadiene on H-Y zeolites, the authors observed broad bands of alkenyl cations, which are formed by the cationic oligomerization of the reactant. In contrast, the formation of polycyclic naphthenes with a low ratio of CH_3 to CH_2 groups occurred on zeolites exchanged with copper.

2.6 Acid-Catalyzed Reactions of Hydrocarbons

Dardas et al. and Süer et al. have used a CIR cell (see Section 2.1) in their investigation of the cleavage of heptane on H-Y zeolite under subcritical and supercritical conditions.[54, 55] At a pressure of 4 MPa the authors observed an increased concentration of heptane in the pores of the cracking catalyst and a change in the stretching vibrations of the C–H bonds as a result of increased generation of intermolecular hydrogen bonds. Supercritical conditions led to a partial regeneration of the catalysts deactivated in the subcritical range.

In their work Bordiga et al. turned their attention to the polymerization of acetylene, methylacetylene, and ethylacetylene on H-ZSM-5 catalysts.[56] The authors identified as catalytically active sites bridging OH groups whose OH stretching bands appear at 3610 cm^{-1}. The bands at 3260 and 1950 cm^{-1} occurring immediately after the adsorption of acetylene were explained by OH and C=C stretching vibrations of the adsorbed complexes bonded through hydrogen bonds. In contrast, ethylacetylene does not form hydrogen-bonded complexes. These molecules were protonated immediately after adsorption. After an increase in the reaction temperature to 420 K, the start and progress of the polymerization of the acetylene could be monitored by the appearance of bands at 1702, 1640, 1580, and about 1500 cm^{-1}. These bands correspond to C=C stretching vibrations of monomeric $C_2H_3^+$, dimeric $C_4H_5^+$, trimeric $C_6H_7^+$, and polymeric $C_{2n}H_{2n+1}^+$ species, respectively. Geobaldo et al. investigated the reaction of propene and the formation of oligomers on H-mordenite at 100 to 300 K (Figure 3).[57] The weakening of the bands of the bridging OH groups at 3609 cm^{-1} observed with increasing temperature is caused by hydrogen bond formation of these hydroxy protons with propene molecules, which at the same time leads to a shift of the OH band to 3100 cm^{-1} and the appearance of a C=C stretching band of the adsorbate molecule at 1632 cm^{-1}. A band at 1380 to 1366 cm^{-1} is an indication of the existence of $CH(CH_3)_2$ groups in protonated species. The protonation of the adsorbed propene molecules and their oligomerization commenced at temperatures above 180 K and led to characteristic stretching vibration bands of the CH_3 and CH_2 groups in oligomers.

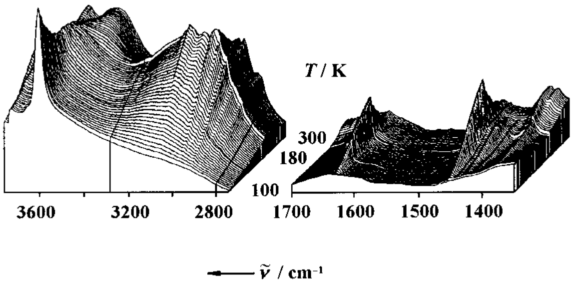


Figure 3. FTIR spectra of H-mordenite recorded during the reaction of propene in a temperature range of 100 to 300 K.[57]

Trombetta et al. investigated the skeletal isomerization of *n*-butene to isobutene on γ-Al_2O_3 and H-ZSM-5 zeolite and the interaction of 1-butene, *cis*-2-butene, *trans*-2-butene, *sec*-butanol, and *tert*-butyl alcohol on these catalysts.[58, 59] γ-Al_2O_3 proved to be the more suitable catalyst for the isomerization of *n*-butene to isobutene at 753 K. At 733 K the H-ZSM-5 zeolite exhibited a higher turnover of *n*-butene but with a low selectivity for isobutene. At 250 K the reaction of *n*-butene on H-ZSM-5 zeolite led to the formation of *tert*-butoxy species which are considered to be intermediates in the polymerization of isobutene.[59] In contrast, no IR bands of *tert*-butoxy species were detected on γ-Al_2O_3. In the opinion of the authors at the temperatures which are necessary to generate alkoxy species on γ-Al_2O_3 (>473K) the decomposition of these surface species occurs faster than their generation.[58] The adsorption and reaction of isobutene on deuterated D-mordenite has been investigated by Ishikawa et al.[60] Below 160 K the authors observed the formation of adsorbate complexes with strong π bonding character to the acidic OD groups of the D-mordenite. The increase in the band intensity of the interaction-free SiODAl groups occurring at 170 K was explained by a dimerization of the π complexes of the isobutene molecules. By adsorption of 2,4,4-trimethyl-1-pentanol on ZrO_2 and comparison of the spectra it was possible to show that isobutene dimerization on the D-mordenite leads to the formation of 2,4,4-trimethyl-1-pentoxy species. During investigations on the skeletal isomerization of *n*-butene to isobutene on H-ferrierite, Wichterlova et al. found a relationship between the isobutene yield and the concentration of bridging OH groups in the 10-ring channels.[61] According to the authors, Lewis acid sites in the neighborhood of bridging OH groups promote the dimerization and oligomerization of the butene and the subsequent cleavage of the reaction products into C_3, C_4, and C_5 alkanes.

Flego et al. investigated the hydrocarbon deposition arising during the alkylation of isobutane with 1-butene on a LaH-Y zeolite (coke).[62] They observed a decrease in oligomerization of 1-butene with an increase in the fraction of isobutane in the reaction mixture. Attempts at desorption of the coke deposition at temperatures above 523 K led to the formation of a band attributable to aromatic compounds at 3050 cm^{-1}.

The disproportionation of ethylbenzene on H-Y zeolite has been investigated by Karge and co-workers under flow conditions.[63] The authors found that from the start of the reaction to the establishment of the steady state the composition of the sorbates on the catalyst changes continuously, with a constant decrease in the ethylbenzene concentration. After an induction period of about one hour the steady state was reached simultaneously on the adsorbent and in the gas phase. This experimental finding was used to suggest that the induction period in the disproportionation of ethylbenzene is caused by a delayed establishment of the equilibrium between the gas phase and the adsorbate phase consisting of benzene, ethylbenzene, and the different diethylbenzenes.

Veefkind and Lercher studied the amination of methanol on H-mordenite.[64] For this purpose methoxy groups were prepared on the catalyst and their reaction with ammonia was observed. The authors found that the reaction rate of the methylammonium ions formed from methoxy groups was comparable to the reaction rate of the direct alkylation of ammonium ions. In view of the low number of free Brønsted sites which are available for the formation of methoxy groups under the reaction conditions, the amination of alkoxy species as a reaction pathway should be, however, of low significance.[64]

2.7 Base-Catalyzed Reactions of Hydrocarbons

In recent years increased efforts have been devoted to the development of solid catalysts for base-catalyzed reactions. FTIR spectroscopy has proved a valuable method for the characterization of the base strength of these materials (see ref. [13] and references therein). One reaction investigated by a number of groups is the alkylation of toluene with methanol which is directed towards side chain alkylation by basic solid catalysis. An important intermediate step, which was investigated with the help of IR spectroscopy, was the conversion of methanol on the solid base.[65, 66] King and Garces investigated the side chain alkylation of toluene with methanol on Cs-X, Rb-X, K-X, Na-X, and Li-X zeolites.[67] In the reaction of methanol on Cs-X, Rb-X, and K-X zeolites, bands of monodentate and bidentate surface formate species were observed. IR spectroscopic experiments suggest that only the monodentate surface formate species contribute to the side chain alkylation of toluene. In their investigations on the side chain alkylation of toluene on hydrotalcite, MgO and Cs-X, Rb-X, K-X, and Na-X zeolites, Lercher and co-workers found a preferred adsorption of toluene on strongly basic zeolites, whereas less basic zeolites adsorbed methanol preferentially.[68, 69] Based on these spectroscopic investigations three criteria for an active catalyst for side chain alkylation of toluene with methanol could be formulated: 1) adequate base strength for the dehydrogenation of methanol to formaldehyde, 2) sites for the stabilization of toluene and for polarization of the methyl group of this molecule, and 3) establishment of a suitable sorption equilibrium of the reactants toluene and methanol.

3. NMR Spectroscopy

Modern NMR spectrometers (NMR: *n*uclear *m*agnetic *r*esonance) record the decay of the magnetic induction of nuclear spin produced by irradiation with a radio frequency pulse which after a Fourier transform produces the spectrum of resonance signals of nuclear spins as a function of frequency. The most important parameter of solid-state NMR spectroscopy is the chemical shift, δ, which is caused by the shielding effect of the electron shell and which gives information on the chemical nature of the atoms under study. Information on the near structure of the atoms can be obtained with help of the dipole–dipole interaction between spatially neighboring nuclear spins and the quadrupolar interaction between the electrical nuclear quadrupole moment (in nuclei with spin $I \geq 1$) and the electrical field gradient at the site of the nucleus. The dipolar interaction gives data on distances between nuclei, whereas the quadrupole interaction reflects the charge distribution in the environment of the nucleus and thus the atom coordination. The broad solid-state NMR signals produced by solid-state interactions require the use of the technique of rapid sample rotation around an axis in the magic angle (MAS: *m*agic *a*ngle *s*pinning) with whose help the anisotropic solid-state interactions can be averaged out or at least reduced. Air-beared turbines with sample rotation frequencies of up to 30 kHz are used almost exclusively for rapid sample rotation. The use of the MAS technique causes significantly higher demands on the preparation of samples and the procedures of in situ experiments than is the case for IR and EPR spectroscopy. For in situ measurements under batch conditions, catalyst samples can be fused in symmetrical glass ampoules which fit in MAS rotors (see ref. [70–72]). Another possibility exists in the use of special loading apparatus such as, for example, CAVERN equipment (CAVERN: *c*ryogenic *a*dsorption *v*essel *e*nabling *r*otor *n*estling), which allows the preparation of samples in gas-tight MAS rotors (Figure 4).[73]

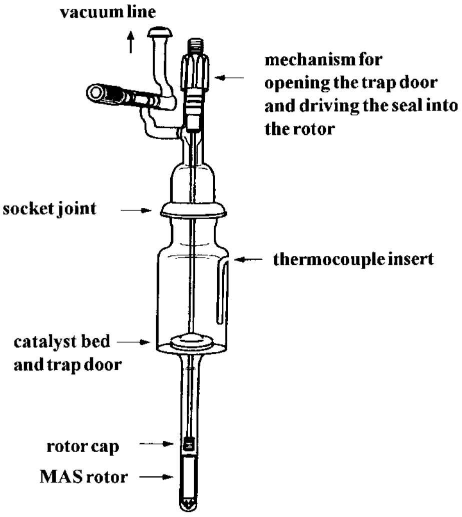


Figure 4. Schematic representation of a CAVERN apparatus for the preparation of catalyst samples for in situ MAS NMR spectroscopy.[73]

With the CAVERN equipment connected to a vacuum line catalyst samples can be calcined and repeatedly loaded with reactants before the MAS rotor is sealed with a gas-tight cap. In a technique used by many groups for in situ MAS NMR investigations of heterogeneously catalyzed reactions under flow conditions, MAS turbines with an axially arranged injection tube are used through which a continuous flow of reactants is led into the MAS NMR rotor during the NMR experiment.[74] After the conversion of the reactants in the catalyst bed shaped as a hollow cylinder the reaction products leave the MAS NMR rotor through an annular gap in the rotor cap or are instead bled off at this point through a pump. In the latter case it is possible to couple the in situ MAS NMR probe directly with an on-line gas chromatograph (Figure 5).[75–77] In another in situ NMR/GC technique, the heterogeneously catalyzed reaction is carried out in a micropulse reactor and stopped within a few hundred milliseconds by cooling with liquid nitrogen (pulse-quench reactor). The catalyst loaded with reactants is then transferred to a MAS NMR rotor at low temperatures and measured.[78] Investigations on reaction kinetics are carried out with MAS NMR probes with Laser pulse heating.[79–81] In this technique the course of a reaction as a function of time is monitored by the use of short heating pulses. Further methods for in situ MAS NMR spectroscopy may be found in the literature[82–85]

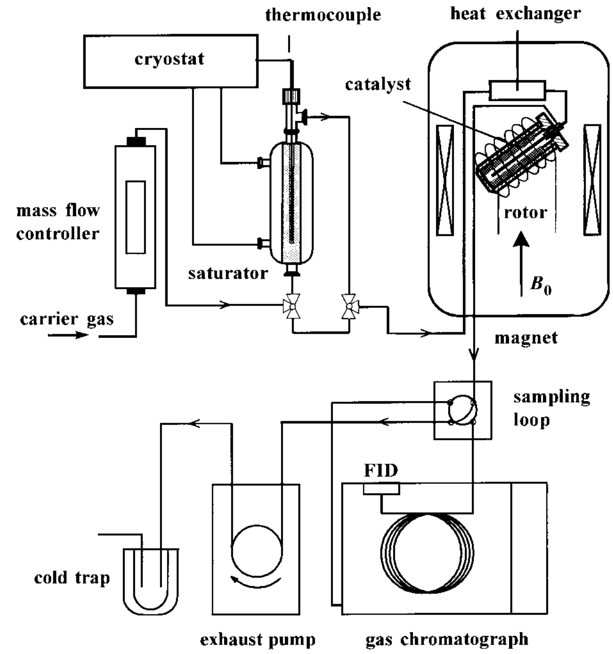


Figure 5. Schematic representation of the equipment applied for in situ MAS NMR experiments under flow conditions coupled with on-line gas chromatography.[77]

The wide range of the chemical shifts of the reactants and their characteristic resonance positions are an advantage for the use of ^{13}C MAS NMR spectroscopy in in situ investigations of heterogeneously catalyzed reactions. With direct excitation of the ^{13}C nuclei, the intensities of the NMR signal appearing in the spectra can be correlated directly with the concentration of the spins. Disadvantages for NMR spectroscopy are its low sensitivity in comparison to IR and EPR spectroscopy and the observation times of up to a few milliseconds, which impedes the investigation of short-lived intermediates. Currently, a number of groups is working on the development of a technique to improve the sensitivity of NMR spectroscopy by the injection of Laser-polarized xenon in the sample volume. With this technique, the polarization of the spin system necessary for the NMR experiment is amplified by contact of the resonant nuclei with optically excited xenon.[86–88] This is linked with the possibility of a selective excitation of the nuclei of atoms and molecules on the outer surface of a solid catalyst.[89] Although many of the atoms which serve as building blocks for the catalyst framework are accessible to NMR spectroscopy by means of isotopes with a nuclear spin, further discussion will be concentrated on investigations of surface OH groups and the reactants of heterogeneously catalyzed reactions

3.1. The Characterization of Acid Sites and Their Interaction with Probe Molecules and Reactants

Calcined solid catalysts provide ^{1}H MAS NMR signals of metal OH groups at chemical shifts of $\delta = -0.5$ to $+0.5$, SiOH groups at $\delta = 1.2$ to 2.2, and bridging OH groups in zeolites at $\delta = 3.6$ to 4.3.[6, 72] Hydrogen bonds of these OH groups to neighboring oxygen atoms or probe molecules shift these resonance positions to greater values by 20 ppm. A considerable advantage of ^{1}H MAS NMR spectroscopy compared to IR spectroscopy lies in the quantitative assessment of the signal intensities, which permits a direct determination of the OH concentrations. Different probe molecules are used for characterization of the acid strength of solid-state OH groups. Pyridine forms a hydrogen bond with weakly acidic hydroxy protons (low field shift by ca. 8 ppm) and is protonated by strongly acidic bridging OH groups (signals at $\delta = 15$ to 20).[6, 72] A likewise frequently used probe molecule is trimethylphosphane (TMP), which gives a ^{31}P MAS NMR signal at $\delta \approx -3$ through interaction with Brønsted acid centers, whereas in an interaction with Lewis acid centers a ^{31}P MAS NMR signal is produced at $\delta = -32$ to -58.[90, 91]

A more precise differentiation of the acid strength of strongly acidic OH groups is possible with the aid of the ^{13}C NMR shift of the carbonyl atoms of adsorbed acetone molecules. The resonance shift relative to the resonance position of the carbonyl carbon in pure acetone arising from adsorption onto acidic OH groups of zeolites lies between 10.1 ppm for H-SAPO-5 and 18.7 ppm for H-ZSM-22.[92] Haw et al. have reported a scale of ^{13}C NMR shifts of the carbonyl atoms of acetone adsorbed on different acidic catalysts and they compare these values with the resonance positions of the molecules in H_2SO_4 solutions of different concentration.[73] According to Haw et al., the acid strength of the bridging OH groups in the zeolite H-ZSM corresponds to an 80 vol% H_2SO_4 solution.

3.2. H/D Exchange on Acidic Catalysts

In analogy to IR spectroscopy, ^{1}H MAS NMR spectroscopy also offers the possibility to investigate H/D exchange between surface OH groups and adsorbed molecules over a large temperature range. With this technique Beck et al. calculated activation energies of 107, 85, and 60 kJ mol^{-1}, respectively, for H/D exchange between deuterated benzene and acidic HNa-Y, USY, and H-ZSM-5 zeolites.[93] Freude and co-workers were able to confirm these values applying a Laser MAS NMR probe.[94, 95] They calculated activation energies of 102 and 93 kJ mol^{-1} for H-Y zeolites which were exchanged by 85 and 92%, respectively. According to Beck et al. the activation energies for benzene complexes determined by quantum mechanical probability density calculations, in which the benzene is attached to the acidic bridging OH groups of the zeolites by van der Waals bonds agreed well with the experimental values.[93] The authors concluded from this that H/D exchange between tho OH groups and benzene does not take place through the formation of a carbocation intermediate of protonated benzene. This assumption was confirmed by ^{13}C MAS NMR investigations of benzene adsorbed on H-Y zeolite. No signal for a carbocation appeared, only a signal for adsorbed benzene.

Stepanov et al. investigated the H/D exchange between deuterated propane and the acidic OH groups of H-ZSM-5 zeolite by ^{1}H MAS NMR spectroscopy over a temperature range of 457 to 543 K.[96] The authors determined activation energies of 108 kJ mol^{-1} for an exchange of the propane methyl groups, and 117 kJ mol^{-1} for an exchange of the propane methylene group. These values correspond to the activation energies which were calculated by quantum-chemical methods for a hydrogen exchange of methane (122 kJ mol^{-1})[97] and ethane (118 kJ mol^{-1}).[98] The calculations were based upon a pentacoordinate transition state of the carbon atoms for the hydrogen exchange. A further argument against the assumption of a propyl cation as transition state was that the exchange was not regiospecific.[96] In contrast, Sommer et al. observed a regiospecific exchange for the H/D exchange between deuterated isobutane and the acidic OH groups of H-ZSM-5 zeolite, with an activation energy of 50 kJ mol^{-1}.[99] The authors explained the differences between the activation energies for H/D exchange derived experimentally and those mentioned previously by differences in the reactivities of linear and branched alkanes. The regioselectivity, on the other hand, is an indication of the formation of *tert*-butyl cations as intermediates in the reaction.[99]

3.3 The Reaction of Hydrocarbons on Acidic Catalysts

In recent years a number of reviews on in situ ^{13}C MAS NMR spectroscopy of adsorbed complexes on solid catalysts and the investigation of heterogeneously catalyzed reactions has been published.[70, 71, 73, 100–103] After the adsorption of olefines and alcohols onto acidic H-ZSM-5 and H-Y zeolites, various groups have observed the formation of alkoxy species with the ^{13}C MAS NMR shifts given in parenthesis for the carbon atoms attached to oxygen: methoxy groups ($\delta = 58$),[104] ethoxy groups ($\delta = 68$),[98] isopropoxy groups, ($\delta = 87$),[105] and *tert*-butoxy groups ($\delta = 77$ to 86).[106–108] Because of the low activation energy for the transition of the alkoxy species into the alkylcarbenium ion state, Aronson et al. called these species surface complexes with carbenium-like properties.[106] During investigations of the synthesis of methyl *tert*-butyl ether (MTBE) from isobutene and methanol on a H-Beta zeolite under flow conditions, ^{13}C MAS NMR signals of secondary and tertiary carbon atoms in alkoxy species were observed at chemical shifts of $\delta = 77$ to 90.[109] A simultaneous analysis of the products leaving the MAS NMR rotor reactor by on-line gas chromatography showed that the intensities of the signals correlate with the yields of MTBE.[77] With different zeolite catalysts weaker signals for the alkoxy species were found at $\delta = 77$ to 90 for the less active materials (H-Y, H-ZSM-5).[110] These observations suggest that alkoxy species can act as reactive components and have an influence upon the course of the reaction.

Today it is assumed that reactive carbenium ions on acidic solids only exist as transition states.[111] Consequently these species cannot be observed directly by NMR spectroscopy. An indirect proof of carbenium ions adsorbed on acidic catalysts is possible, however, with reactions whose mechanisms are based upon the trapping of these species by other reactants. Stepanov and Luzgin have investigated the reaction of acetonitrile with 1-octene and *tert*-butyl alcohol on acid H-ZSM-5 zeolite at 296 K under batch conditions, and observed a ^{13}C MAS NMR signal at $\delta = 108$ which they attributed to *N*-alkylnitrilium cations.[112] The authors explained the formation of these alkylnitrilium cations by the "trapping" of chemically unstable alkylcarbenium ions which themselves are formed by adsorption of 1-octene on the acidic OH groups of the H-ZSM-5 zeolite. This experiment was confirmed by Barich et al. with a pulse–quench reactor (see Section 3).[113] Parameters of the ^{13}C shielding of the alkylnitrilium cation calculated by probability density calculations agree very well with the values determined experimentally.

Carbenium ions present on the surface of acidic catalysts which are detectable directly by NMR spectroscopy usually possess an alkyl-substituted, cyclic structure and are formed, for example by the reaction of the respective olefine or diene with the acidic zeolite. For a H-Y zeolite which was loaded with ^{13}C-enriched propene, Haw et al. observed ^{13}C MAS NMR signals at $\delta = 249$, 145, and 47 which they assigned to alkyl-substituted cyclopentadienyl cations.[114] A signal of the trivalent carbon atom of the carbenium ion of propene, the propyl-2 cation, which occurred in superacid solutions at $\delta \approx 320$ was not observed.[114] The formation of alkyl-substituted cyclopentadienyl cations was also observed in the reaction of methanol and acetone on H-ZSM-5 zeolite with a pulse–quench reactor.[78, 115, 116] It was assumed, however, that these very stable carbenium ions are the final step of a number of reactions and at the best play only a secondary role in the course of the reaction. Reviews on carbenium ions in acidic zeolites observed with in situ ^{13}C MAS NMR spectroscopy are found in the literature.[73, 100]

With isotopically labeled reactants under controlled conditions in fused glass ampoules it is possible to use ^{13}C MAS NMR spectroscopy for the clarification of reaction pathways. With this technique, Derouane et al. and Ivanova et al. have investigated the isopropylation of benzene on H-ZSM-11 zeolite,[117] the transformation of *n*-hexane on aluminum/magnesium oxides and K-L zeolites modified with Pt and Pd ,[118, 119] the dehydrogenating cyclodimerization of propane and the alkylation of benzene with propane on gallium-modified H-ZSM-5 zeolites,[120, 121] and the activation of propane on H-ZSM-5 zeolite.[122] The mechanism of the formation of *n*-propylbenzene from cumene in the presence of benzene as side reaction of cumol synthesis on H-ZSM-11 zeolite has been investigated by Ivanova et al. by the reaction of two different benzene/cumene mixtures under identical reaction conditions.[117] In reaction 1 the carbon atoms in the aromatic ring of cumenes were enriched with ^{13}C, in experiment 2 those of benzene. The ^{13}C-enriched aromatic carbon atom of cumene to which the isopropyl group is bonded has a chemical shift of $\delta = 149$. The disappearance of this signal in experiment 1 and its appearance in experiment 2 is caused by the transfer of propyl groups from the ^{13}C-enriched cumene molecules to the nonenriched benzene molecule and vice versa. Thus this experiment provides the evidence for an intermolecular reaction mechanism for the formation of *n*-propylbenzene on acid zeolites.

A large number of ^{13}C MAS NMR investigations is concerned with the conversion of methanol into hydrocarbons (MTG: *m*ethanol *t*o *g*asoline, MTO: *m*ethanol *t*o *o*lefins) on acid zeolites under batch conditions, that is in sealed glass ampoules. The zeolites H-ZSM-5,[123–129] H-SAPO-5,[127, 130] H-SAPO-11, [130] H-SAPO-34,[128, 131–133] H-Y,[127] H-EMT,[127] H-ZSM-12,[134] H-ZSM-23,[130] H-erionite,[135] H-mordenite,[127] and H-offretite,[135, 136] as well as montemorillonite,[137] and saponite[137] have been used as catalysts. Even at reaction temperatures of 373 to 423 K, dehydration of methanol ($\delta = 50$) adsorbed on acidic OH groups to dimethyl ether ($\delta = 61$) occurs. This intermediate is converted into C_2 hydrocarbons such as ethene ($\delta = 123$) after a further increase in temperature. In a series of the work described above methoxy groups, whose signal appears at $\delta \approx 58$, have been debated as reactive species. In in situ ^{13}C MAS NMR experiments on the conversion of methanol on a H-ZSM-5 zeolite under flow conditions signals occurring at chemical shifts of $\delta = 12$ to 25 and 125 to 131 were explained by the formation of a hydrocarbon pool consisting of C_4 to C_6 olefins (Figure 6).[138]

Simultaneous with the measurement of the ^{13}C MAS NMR spectra, the reaction products leaving the MAS NMR rotor reactor were analyzed by gas chromatography with the technique illustrated in Figure 5 (numerical values on the left side of Figure 6). The presence of C_4 to C_6 olefins on a

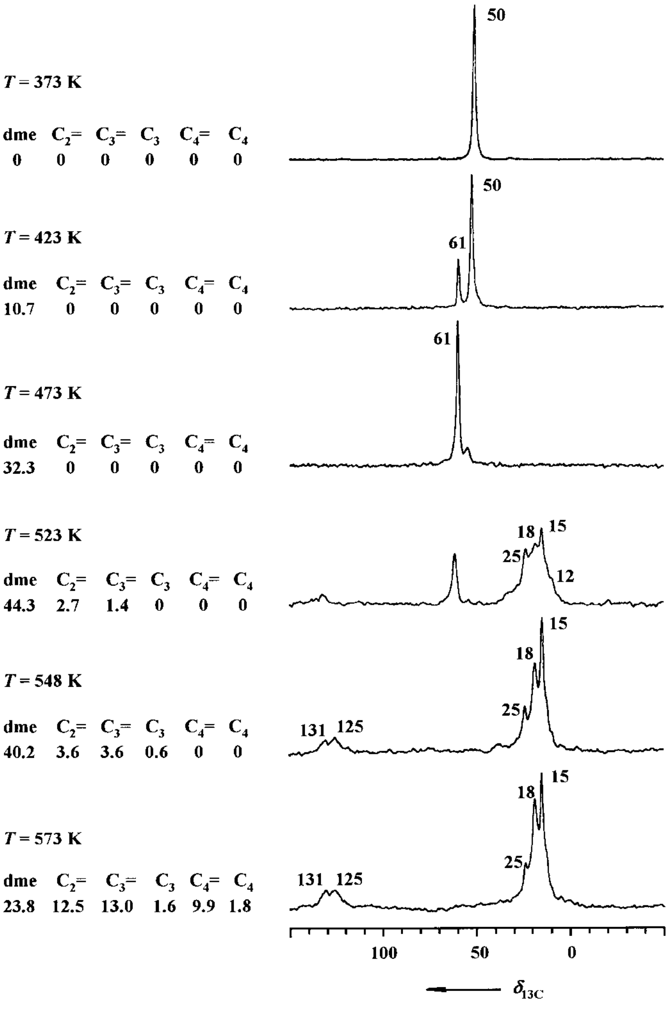


Figure 6. ^{13}C MAS NMR spectra recorded during the reaction of $^{13}CH_3OH$ on H-ZSM-5 zeolite under flow conditions with a modified residence time of $W/F = 25$ g h mol^{-1} and at reaction temperatures of 373 to 573 K. On the left side the yields (%) of dimethyl ether (dme), ethene (C_2=), propene (C_3=), propane (C_3), butenes (C_4=), and butanes (C_4) measured simultaneously by on-line gas chromatography are given.[138]

working zeolite catalyst during the conversion of methanol provides experimental confirmation of the hydrocarbon pool mechanism previously suggested by von Haag in 1984.[139] According to this mechanism, a pool of higher hydrocarbons, predominantly olefins, to which on the one hand methanol and/or dimethyl ether couple and which otherwise undergo cationic β-cleavage, is present in the pores of acid zeolites during the conversion of methanol.

3.4. The Base-Catalyzed Conversion of Hydrocarbons

Unlike the Brønsted acid sites of solid catalysts, which are directly accessible to FTIR and ^{1}H MAS NMR spectroscopy, the characterization of oxygen atoms of the catalyst framework acting as base sites requires the use of molecular probes. Because of the necessary isotopical enrichment and the strong quadrupolar interactions of these nuclei (spin $I = 5/2$), the use of ^{17}O MAS NMR spectroscopy has hitherto been of limited use.[140–143] Bosacek has suggested the use of the ^{13}C NMR shift of methoxy groups which are bound to the Si-O-Al bridges of the zeolite framework for the determination of the base strength of these materials.[144, 145] After the preparation of these methoxy groups by loading the catalysts with methyl iodide, Bosacek found a correlation between the chemical shifts of the methoxy groups and the mean Sanderson electronegativity, S^m,[146] of the zeolite framework. According to this correlation, a low ^{13}C NMR shift of the methoxy groups ($\delta = 54$ for CsNa-X zeolite)[145] corresponds to a low mean electronegativity or a high base strength of the zeolite framework and vice versa. Methoxy groups on highly basic guest components, for example clusters of alkali metal acetates and oxides on Y and X zeolites, give signals in the range $\delta = 48.7$ to 50.0.[147–149].

^{13}C MAS NMR investigations on the side chain alkylation of toluene with methanol on X and Y zeolites exchanged with alkali metal cations have been carried out under both batch and flow conditions.[148, 150, 151] In agreement with Lazo et al. and Murray et al., signals observed at $\delta = 166$ to 168 were attributed to formate species which arise from the conversion of methanol on the basic zeolite framework (see also Section 2.7).[152, 153] Formaldehyde, which would be formed by the dehydration of methanol, could not be detected. It was observed, however, that during the side chain alkylation of toluene on an impregnated X zeolite exchanged and impregnated with cesium ions, the formation of ethylbenzene was first initiated at temperatures at which methanol was already fully converted into formate species.[151] The formate species formed from methanol could thus act as reactive surface species. This assumption was supported by in situ experiments under flow conditions where an increase in the toluene content in the reactant flow caused a reduction in the ^{13}C MAS NMR signal of the formate species at $\delta = 166$.[151]

4. EPR Spectroscopy

Electron paramagnetic spectroscopy (EPR), also called electron spin resonance (ESR), is suitable for the characterization of paramagnetic species with one or more unpaired electrons. The magnetic moment of the electrons responsible for the resonance transitions in a magnetic field is a function of the electron spin operator, the Bohr magneton, and the g-factor. If the nucleus of the atom at which the unpaired electron is localized possesses a nuclear spin an interaction of the magnetic moment of the electrons with the magnetic moment of the atom nucleus and thus a splitting of the EPR signal occur. This interaction is called hyperfine interaction (hf). Its parameter is the hyperfine coupling constant (a tensor). If there is also an interaction of the unpaired electron with the nuclear spin of atoms in the local structure a superhyperfine coupling (shf) occurs which causes a further splitting of the EPR signal. By determination and analysis of the g tensor, the a tensor, and the shf splitting, EPR spectroscopy can provide important information on paramagnetic species and their near structure.

A special feature of EPR spectroscopy is its high sensitivity, which allows active sites and intermediates of chemical reactions with very low abundance in the framework or on the surface of catalysts under investigation. In the catalyst framework the unpaired electrons necessary for detection by EPR spectroscopy are formed by defects or by a substitution of the framework atoms. The molecules accessible to EPR spectroscopy must exist as radicals on the surface of the catalyst, formed, for example by a spontaneous oxidation at a Lewis acid sites or through irradiation of the sample with γ-quanta.[154–158] Short relaxation times of electron spin and exchange processes lead to a broadening of the EPR signals. The use of EPR spectroscopy is therefore often limited in its maximum measurement temperature.[159] Frequently, EPR measurements are carried out at temperatures of 77 K or below after stopping the reaction. In situ cells differ in their construction according to whether they are used for investigations under batch conditions or under flow conditions.[160–162] The EPR measurement cell for reactions under flow conditions illustrated in Figure 7 was designed for the X-band, that is a resonance frequency of $\nu_0 = 9.5$ GHz or a wave length of $\lambda = 3$ cm, and consists of a reactor tube with an internal diameter of 3 mm to which is attached a heating wire. It is charged with 200 to 400 mg catalyst powder through which reactants are passed in a vertical direction. Typical applications of EPR spectroscopy in heterogeneous catalysis are investigations on the preparation and formation of catalysts, the characterization of adsorbed species, and investigations of heterogeneously catalyzed reactions.[159, 163–165] To the first two points count both the spectroscopic characterization of the framework building blocks which act as active sites, and the adsorbate molecules and reactants.

4.1. EPR Investigations of Metal Ions in Solid Catalysts and Their Interactions with Reactants

Isolated Cu^{2+} ions in zeolites exchanged with copper produce spectra with characteristic anisotropies of the g tensors and the hf splitting which are dependent upon the cation site which the Cu^{2+} ions occupy. Table 1 shows a list of these parameters for Cu^{2+} ions in A, X, and Y zeolites as well as chabasite and mordenite.[166] After in situ calcination of

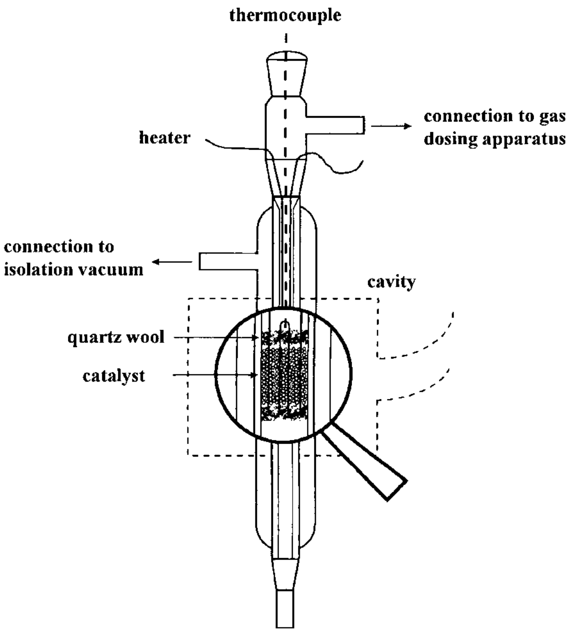


Figure 7. Schematic representation of an EPR resonator for in situ investigations of heterogenously catalyzed reactions under flow conditions.[162]

Table 1. EPR parameters of Cu^{2+} ions at different cation positions in various zeolites and Cu^{2+} in H-mordenite and H-ZSM-5 zeolite mixed physically with different copper compounds and calcined in situ at 823 K, 973 K, and 1073 K.[166, 167]

Catalyst	Cation site	$g_\parallel$	$g_\perp$	$a_\parallel$ [mT]	$a_\perp$ [mT]
zeolite A	I	2.397	2.065	12.6	0.22
zeolites X and Y	II	2.387	2.073	12.4	1.34
zeolite X	III	2.354	2.068	14.0	1.60
zeolite Y	I′	2.332	2.067	15.7	1.86
chabasite	I′	2.340	2.073	16.0	2.00
mordenite	I	2.327	2.062	15.4	1.49
mordenite	VI	2.277	2.057	16.8	1.19
H-mordenite/CuO/823 K		2.325	2.055	14.4	1.9
HNa-ZSM-5/CuO/823 K		2.33	2.07	14.2	1.75
H-ZSM-5/CuO/1073 K		2.29	2.05	15.6	2.3
H-ZSM-5/CuF_2/973 K		2.31		15.3	
H-ZSM-5/$Cu_3(PO_4)_2$/973 K		2.29		15.6	

mixtures of H-mordenite (H-M), HNa-ZSM-5 zeolite, and H-ZSM-5 zeolite with CuO, CuF_2, and $Cu_3(PO_4)_2$ at temperatures between 823 K and 1073 K (e.g. H-M/CuO/823 K), EPR signals were observed which correspond to Cu^{2+} at cation sites (see Table 1 below).[167] This observation shows that a thermal treatment of physical mixtures of copper compounds with zeolites in their H form leads to a migration of the copper atoms into the zeolite pores and to a cation exchange. In the use of Cu-ZSM-5 zeolite as catalyst for the selective reduction of NO_x, the change in the oxidation state of copper in the interaction of reactants and trace gases (He, CH_4, C_3H_6, C_2H_5OH, CO, NO, NO_2, H_2O, O_2) is important.[168] Thus in a stream of CH_4 an extensive reduction in the intensity of the EPR signal of the Cu^{2+} cations ($g_\parallel = 2.28$ and $a_\parallel = 17$ mT) was observed which is again totally reversed by changing to an O_2 or NO stream.[168] In a stream of He mixed with C_3H_6, NO, and O_2 the reduction of some of the Cu^{2+} ions of the CuH-ZSM-5 zeolite occurs even at room temperature.[169]

Paramagnetic Pt species are formed by the exchange of Na-Y zeolite in an aqueous solution of $[Pt(NH_3)_4]Cl_2$ and subsequent reduction with H_2.[170] Ghosh and Kevan investigated Na-X and Ca-X zeolites exchanged with palladium as catalysts for the dimerization of ethene.[171] Paramagnetic species with anisotropic g-tensors were found. These species were attributed to Pd^+ ions which act as catalytically active sites and coordinate ethene before it is converted into butene. A contribution of Pd^{3+} ions to the EPR spectrum was excluded.

A number of groups has investigated the incorporation of Ni, Co, and Mn into the framework of micro- and mesoporous aluminophosphates and the accessibility of these metal ions for probe molecules.[172–175] After reduction of NiH-SAPO-5 and Ni-SAPO-5 with H_2, different Ni^+ ions with symmetric g tensors are present.[175] Electron spin echo experiments with ^{31}P modulation made it possible to detect different localizations of these nickel species in SAPO-5. In NiH-SAPO-5, the Ni^+ ions are located in the centers of hexagonal prisms (SI position), whereas the nickel atoms in Ni-SAPO-5 are preferentially tetrahedrically coordinated into the framework. Experiments on the adsorption of ethene showed that nickel incorporated into the framework forms adsorbed complexes consisting of two ethene molecules, whilst Ni^+ ions on SI positions coordinate only one ethene molecule.[175]

EPR spectra of Fe^{3+} ions in zeolites often consist of two signals at $g = 2.0$ and $g = 4.2$ and allow a differentiation of the nature of the iron species present (see ref. [176–179] and references therein). Hexaaqua Fe^{3+} complexes in a Na-Y zeolite exchanged with iron lead to an strong signal at $g = 2.0$. After calcination of an Fe-ZSM-5 zeolite prepared by sublimation of $FeCl_3$ the signal of the Fe^{3+} ions at $g \approx 2.0$ disappears and signals at $g = 4.27$, $g = 5.6$ and 6.5 appear which Kucherov et al. assigned to tetrahedrally coordinated or distorted tetrahedrally coordinated extra-framework Fe^{3+} species.[179] If this SCR 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 $g = 4.27$ occurs. Recent work has been concerned with the characterization of iron in aluminophosphates and silicoaluminophosphates. Fe^{3+} ions in aluminophosphate $AlPO_4$-5 (Fe/$AlPO_4$-5) also produce EPR signals with g-factors of 2.0 and 4.3 which are explained by octahedrally coordinated Fe^{3+} ions on framework positions and by Fe^{3+} ions on defect sites, respectively.[180] The EPR spectra illustrated in Figure 8 were taken in steps of 20 K during the calcination of Fe/$AlPO_4$-5 in an air stream after synthesis (as-synthesized). The signal of Fe^{3+} ions on defect sites at $g = 4.3$ falls 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 $g = 2.0$ may 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 calcination of the template residues, spectra of Fe^{3+} ions are obtained which consist of three signal components. The analysis of the EPR

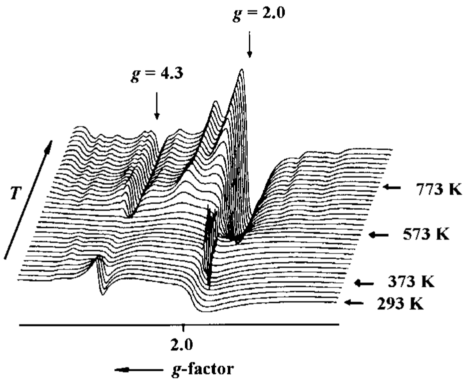


Figure 8. X-band EPR spectra ($0 < B_0 < 600$ mT) of Fe/AlPO$_4$-5 recorded during calcination ($293\,K < T < 773\,K$) in a stream of dry air. The measurement temperature was increased in stages of 20 K.[180]

spectrum taken after calcination at 773 K gives a fraction of Fe^{3+} ions on framework positions of 45%.

Other materials which have been investigated for their suitability as SCR catalysts are H-ZSM-5 zeolites modified with chromium and rhodium (Cr/H-ZSM-5, Rh/H-ZSM-5),[181–184] and γ-Al$_2$O$_3$ modified with rhodium.[183, 184] After calcination of the Cr/H-ZSM-5 zeolite at 773 K in O$_2$ and He a symmetrical signal of Cr^{5+} ions with an hf splitting of $a = 4.5$ mT and an shf splitting of 0.74 mT is formed.[181] The shf splitting is an indication that the Cr^{5+} ions are isolated and incorporated into the neighborhood of framework aluminum atoms. During adsorption of propene onto the Cr/H-ZSM-5 zeolite under flow conditions an irreversible reduction of the Cr^{5+} signal occurs which indicates a reduction of the Cr^{5+} ions by propene.

Vanadium–phosphorus oxides (VPO) are materials which are used inter alia for the selective oxidation and oxidative amination of hydrocarbons. VO^{2+} ions which show an hf splitting of $a_\parallel = 20.2$ mT and $a_\perp = 7.2$ mT have been debated as the catalytically active sites of these VPO catalysts.[185] If neighboring VO^{2+} ions are present spin–spin exchange and averaging of the hf splitting occurs. In investigations of the oxidative amination of toluene and the selective oxidation of *n*-butane on VPO catalysts under flow conditions, the spin–spin exchange behavior between VO^{2+} ions on the catalysts surface was determined by a signal shape analysis.[162, 185, 186] The authors found a correlation between the catalytic activity of the VPO catalysts in the oxidative amination of toluene and the strength of the spin–spin exchange.[185] It could thus be confirmed that isolated VO^{2+} sites, between which no spin–spin exchange occurs, do not participate in the catalytic process. The proposed reaction mechanism is based on vanadyl dimers with an oxidation state of the neighboring vanadium atoms changing between +4 and +3 during the oxidative amination of toluene and the concurrent reduction and reoxidation steps at the vanadium centers.

4.2. EPR Investigations of Adsorbate Molecules on Solid Catalysts

The time scale of EPR spectroscopy, which is of the order of nanoseconds, allows the determination of the mobility of molecules in the pores of solid catalysts. By means of temperature-dependent EPR spectroscopy, Biglino et al. found a translation movement or a rotary diffusion for NO$_2$ on mordenite, ferrierite, and ZSM-5, Beta, L, X, and Y zeolites, dependent upon the respective structure.[187] Roduner et al. investigated the mobility of organic radical cations in zeolites by a quantitative analysis of the anisotropy of the hf splitting and the *g* tensors.[188] They established that the radical cation formed through spontaneous oxidation of 2,3-dimethylbut-2-ene in H-ZSM-5 zeolite at room temperature rotates about an axis vertically to the molecular plane, whereas the radical cation of 2,5-dimethylhexa-1,5-diene in H-mordenite undergoes rotational movement in the time scale of about 50 ns.

An important problem investigated by EPR spectroscopy of radical cations formed by spontaneous oxidation of organic molecules is that of the nature of the oxidizing sites. Harvey et al. carried out investigations on dealuminated H-mordenites which had been loaded with a number of different alkenes.[189] The EPR signals of the radical cations formed on the dealuminated H-mordenites correlated well in their intensity with the quantity of extra-framework aluminum in the pores of the zeolites. This is a hint to the oxidative action of the Lewis acid sites associated with the extra-framework aluminum species. Since the calcination of the zeolites can also lead to dealumination and hence to a formation of Lewis acid sites precise control and definition of the calcination conditions is an important requirement for the implementation of reproducible experiments.

4.3. EPR Investigations of Heterogeneously Catalyzed Surface Reactions

There have been numerous EPR spectroscopic investigations of heterogeneous catalytic reactions.[159, 164, 165, 190, 191] In a number of these works, zeolites have been used as matrix for the stabilization of radical cations formed by spontaneous oxidation. Crockett and Roduner have investigated the dimerization and transannular reactions of cycloalkenes and the oxidation of terpenes on H-mordenite.[192, 193] After loading the H-mordenite with different terpenes (α-pinene, *trans*-isolimonene, α-terpinene) the EPR spectrum of the radical cation of α-terpinene was found in each case.[193] With deuterated D-mordenite, whose deuterons were not incorporated into the product molecule, it was possible to establish that the above-mentioned reactions are not catalyzed by Brønsted acid centers but by Lewis acid sites. In contrast, Rhodes and Rhodes and Standing 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 an acid catalyzed conversion of the reactants prior to formation of the radical cations.[194, 195] Similarly, the formation of the radical cation of 2,5-dimethyl-2,4-hexadiene after adsorption of 2,3-dimethyl-1-butene and 2-methylpropene on H-mordenite has been observed.[196] On H-mordenite, the radical cations of 1,2,3,4,5,6,7,8-octahydronaphthalene undergo electron transfer reactions with other adsorbate molecules which act as electron acceptors.[197] Similar electron transfer reactions also occur with radical cations which are formed by adsorption of benzene and tetracyanoethene on H-mordenite.[197]

A possible extension of the scope of EPR spectroscopy for the clarification of heterogeneously catalyzed reactions arises in the preparation of paramagnetic species through irradiation of the samples with γ-quanta, usually with ^{60}Co as γ-source. In this case, a one-electron oxidation takes place with formation of a radical cation or H addition with the formation of a neutral H adduct radical. In this way this technique is not dependent upon the spontaneous oxidation of reactants at Lewis acid sites which often only takes place at temperatures at which the paramagnetic species is very rapidly degraded again. Paramagnetic species can be produced at very low temperatures by the γ-radiation. This is of great importance because of the high reactivity of this species. With the radiation technique (radiolysis/EPR), reactions which are catalyzed at Brønsted sites are also accessible to EPR spectroscopy. However, in view of the reactivity of paramagnetic species investigations need to be performed during the use of radiolysis/EPR spectroscopy to establish whether or not the paramagnetic species themselves participate as reactive intermediates in the reaction under investigation. One suitable way is available through parallel investigations of the respective reaction on an inactive and an active catalyst (e.g. Na-ZSM-5 and H-ZSM-5 zeolite).[198]

Radiolysis/EPR spectroscopy has been used for investigations of the isomerization of different olefins on H-ZSM-5 zeolite.[199] In contrast to earlier work (see ref. [194–196]), no radical cations produced by the spontaneous oxidation of the reactants on the calcinated zeolites were observed in the radiolysis/EPR experiments, only radical cations formed by irradiation.[199] Werst et al. explained these differences in radical formation by the different calcination of the zeolites in air and in vacuum.[199] The formation of neutral radicals was found after radiation of cycloheptatriene and cyclohexane which had been adsorbed on Na-AZM-5 and H-ZSM-5 zeolites.[200] Based on the observed relationship between the yield of neutral radicals and the aluminum content of the zeolite framework, a proton transfer from the adsorbed radical cations onto the zeolite framework was assumed as mechanism of the radical formation. Piocos et al. used the radiolysis/EPR technique for the investigation of the dimerization and isomerization of isobutene and other acyclic monoolefines on zeolites.[198, 201] The authors established that the dimerization and isomerization of isobutene on H-ZSM-5 zeolite took place as low as 77 K, and cleavage reactions occured even at below room temperature. In the reaction of different cyclic olefins on H-ZSM-5 zeolite the formation of radical cations of 1,2-dimethylcyclopentene was observed in each case.[202] The formation of radical cations of differently alkylated bicyclododecenes occurred on H-mordenite under the same reaction conditions. This different catalytic behavior of the solid catalysts used was explained by the shape-selective action of the 10-ring pores of H-ZSM-5 zeolite.

A very interesting experimental approach to investigate the mechanism of heterogeneously catalyzed reactions is the MIESR technique (MIESR: *m*atrix *i*solation *e*lectron *s*pin *r*esonance). In this technique, developed by Lunsford and co-workers, the reactants flow through the catalyst bed arranged in a tubular flow reactor, and after their desorption from the catalyst surface they are trapped as radical cations in a solid argon matrix on a sapphire rod at a temperature of 16 K.[203] For detection of the trapped radical cations, the sapphire rod is placed in a microwave resonator. This technique has already been used for the investigation of the oxidation of propene on Bi_2O_3, MoO_3, and bismuth molybdate catalysts,[203] the oxidative coupling of methane on MgO,[204] and the formation of methyl radical cations on La_2O_3, CeO_2, Nd_2O_3, Sm_2O_3, Eu_2O_3, and Yb_2O_3.[205]

Karge and co-workers have investigated the formation of hydrocarbon deposits (coke) during the reaction of olefins on H-mordenites under batch and flow conditions.[160, 161] In the temperature range of 380 to 470 K, spectra with an hf splitting of $a = 1.6$ mT and a g-factor of $g = 2.0025$ were observed under both static and flow conditions (Figure 9) With a further increase in temperature to 480 K, this hf splitting disappeared and a signal typical of high-temperature coke appeared. Olefinic and allylic hydrocarbons were suggested for the nature of the low-temperature coke ($T < 500$ K). The high-temperature coke formed at temperatures of $\geqslant 480$ K, probably formed of polyaromatic radical cations, gave a narrow and structureless EPR spectrum.[161] With radiolysis/EPR, Piocos et al. established that the EPR spectra produced in the oligomiserization of olefins on dealuminated H-mordenite and H-ZSM-5 zeolite arose from radical cations of 2,3-dimethybutene and larger branched olefins.[198] Pradhan et al. investigated the formation of coke in the disproportion of ethylbenzene on H-ZSM-5 zeolite.[206] In contrast to the work of Karge and co-workers,[160, 161] Pradhan et al.[198] were unable to find any hf splitting of the EPR signals. This was explained by the polycyclic and aromatic nature of the low-temperature coke formed from ethylbenzene.

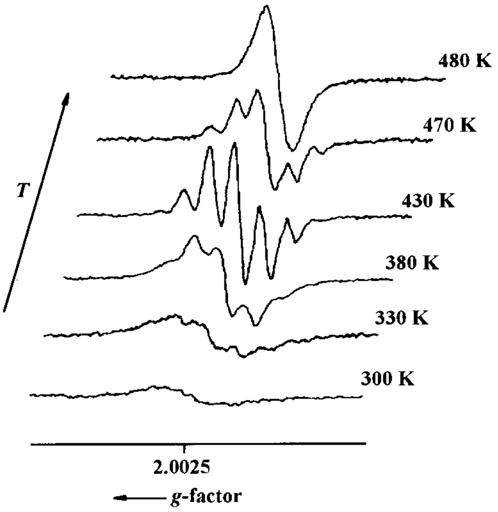


Figure 9. X-band EPR spectra of radical cations recorded during the formation of coke in the reaction of ethene on H-mordenite.[161]

5. UV/Vis spectroscopy

With UV/Vis spectroscopy it is possible to investigate electron transfers between orbitals or bands of atoms, ions, and molecules in the gas phase as well as in liquids and solids. The spectral region of 250 to 500 nm is of special interest for in situ UV/Vis spectroscopy. Investigations of solutions and crystals usually take place in transmission, whereas powder samples are often measured in diffuse reflections (DRS: *d*iffuse *r*eflectance *s*pectroscopy). A significant advantage of UV/Vis spectroscopy lies in the individual detection of electron transfers without superimposition by neighboring vibrational bands. Unlike IR spectroscopy, where the use of Fourier transform techniques predominates, dispersive spectrometers are almost exclusively applied for UV/Vis spectroscopy because of the large band widths. Important 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 reference [159]. The $\pi-\pi^*$ transitions observed in the investigation of surface reactions are an indication of the existence of unsaturated carbenium anions. The detection of these transitions under in situ conditions provides important information on the mechanism of the chemical reactions catalyzed by active sites.

Initial UV/Vis investigations on the reaction of methanol on H-ZSM-5 zeolite took place at the beginning of the 1980s.[207, 208] 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.[209] 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.[210] Flego et al. investigated the alkylation of isobutane with 1-butene on LaH-Y zeolites under flow conditions.[62] Directly after adsorption of 1-butene and an isobutane/1-butene mixture, the authors were able to detect UV/Vis bands of monoenyl carbenium ions (315 nm) and dienyl carbenium ions (370 nm). Since the intensity of these bands depended upon the activation temperature of the catalyst (Figure 10), the Lewis acid sites were held responsible for the formation of the carbenium ions. It was found that the formation of unsaturated carbenium ions was favored by reaction temperatures of up to 523 K, long contact times, and high concentration of Lewis sites.

Sulfated ZrO_2 is an interesting catalyst for skeletal isomerization of *n*-butane to isobutane at room temperature. Hitherto unexplained was the origin of the rapid rise and the subsequent slow decay in the activity of these solid catalysts during the initial phase of skeletal isomerization. To explain this effect, Knözinger investigated the formation of hydrocarbon depositions during the isomerization of *n*-butane on sulfated ZrO_2 under flow conditions.[211] UV/Vis bands appearing at 366 and 400 nm suggested that immediately after the start of the reaction alkenyl and cycloalkenyl cations were formed. These carbocations are an initial step in the formation of arenes, which in their turn cause the later deactivation of the catalyst.

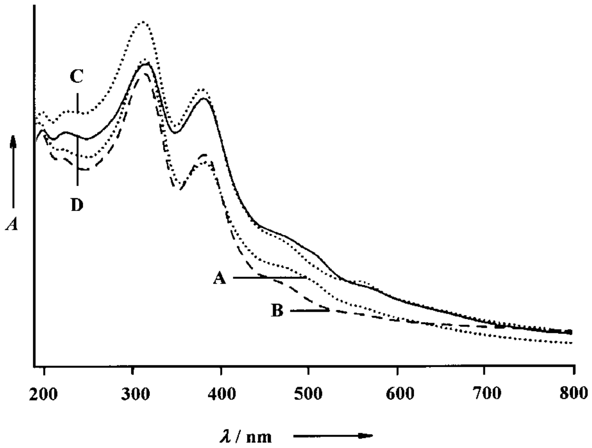


Figure 10. UV/Vis spectra of a LaH-Y zeolite recorded during the reaction of an isobutane/1-butene mixture (9:1) with LSHV = 4.07 h^{-1} at a reaction temperature of 353 K and a pressure of 30 bar. Prior to the reaction the zeolite was activated at temperatures of 523 K (A), 623 K (B), 673 K (C), and 773 K (D).[62]

6. Outlook: The Role of In Situ Spectroscopy in Modern Catalyst Research

By means of examples this contribution has demonstrated that in situ IR, NMR, EPR, and UV/Vis spectroscopy are able to provide important novel information on the mechanisms of heterogeneously catalyzed reactions. Over the coming decade it is to be expected that our knowledge of heterogeneous catalysis will be improved significantly by the systematic application of the these and other in situ techniques. A significant 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 in many cases can be used at temperatures of up to 800 K.

In situ spectroscopy and the modern approaches of combinatorial catalysis research can thus complement each other in an ideal way (Figure 11): whereas the latter has as objective the empirical testing of new catalysts with high efficiency, in situ spectroscopy has the complementary, at least equally important and intellectually demanding role of providing the factual basis for an understanding of the processes on the surface of solid catalysts and for mechanistic models of heterogeneous catalysis. Only in this way will rational and scientifically sound catalyst design be generally possible. The cycle of combinatorial catalysis research and in situ spectroscopy will in many cases have to be run through many times before the catalyst necessary for industrial application is available.

Whereas combinatorial catalyst research and in situ spectroscopy will significantly contribute to an increase in efficiency, they will not be able to replace the traditional

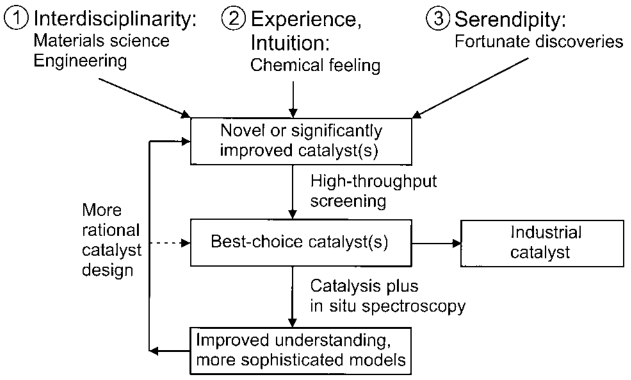


Figure 11. Elements of research in heterogeneous catalysis from innovation to the industrially used catalyst.

sources of materials innovation: 1) Fundamental research in the area of materials science and solid-state chemistry will provide novel materials with a potential for catalysis. It is imperative that these are put into practical applications in catalysis more rapidly and more professionally than hitherto. 2) Experience, intuition, and know-how will still play an important role in the search for novel catalyst for the reactions described. 3) Purely chance discoveries in catalysis which have led repeatedly to new industrial processes in the 20th century will become rarer. However, that in the future innovation in catalyst research will succeed through pure chance cannot be excluded.

Received: July 2000 [A 422]

---

[1] R. Schlögl, *Angew. Chem.* **1993**, *105*, 402; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 381.
[2] B. Imelik, J. C. Vedrine, *Catalyst Characterization*, Plenum, New York, **1994**, pp. 11–607.
[3] J. W. Niemantsverdriet, *Spectroscopy in Catalysis*, VCH, Weinheim, **1995**, pp. 1–284.
[4] G. Ertl, H. Knözinger, J. Weitkamp, *Handbook of Heterogeneous Catalysis, Vol. 2*, Wiley-VCH, Weinheim, **1997**, pp. 427–770.
[5] H. G. Karge, W. Nießen, *Catal. Today* **1991**, *8*, 451.
[6] H. G. Karge, M. Hunger, H. Beyer in *Catalysis and Zeolites* (Eds.: J. Weitkamp, L. Puppe), Springer, Berlin, **1999**, p. 198–326.
[7] W. B. White, R. Roy, *Am. Mineral.* **1964**, *49*, 1670.
[8] H. Dutz, *Ber. Dtsch. Keram. Ges.* **1969**, *46*, 75.
[9] V. A. Matyshak, A. N. Il'ichev, A. A. Ukharsky, V. N. Korchak, *J. Catal.* **1997**, *171*, 245.
[10] P. A. Jacobs, J. B. Uytterhoeven, *J. Chem. Soc. Faraday Trans. I* **1973**, *69*, 359.
[11] E. M. Flanigen in *Zeolite Chemistry and Catalysis* (Ed.: J. A. Rabo), American Chemical Society, Washington, DC, **1976**, pp. 80–117.
[12] J. R. Sohn, P. J. DeCanio, J. H. Lunsford, D. J. O. Donnell, *Zeolites* **1986**, *6*, 225.
[13] H. Knözinger, S. Huber, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2047.
[14] J. A. Lercher, C. Gründling, G. Eder-Mirth, *Catal. Today* **1996**, *27*, 353.
[15] W. R. Moser, J. E. Cnossen, A. W. Wang, P. A. Knouse, *J. Catal.* **1985**, *19*, 21.
[16] W. R. Moser, J. C. Chaing, J. E. Cnossen, *J. Mater. Sci. Res.* **1985**, *19*, 315.
[17] D. C. Calabro, E. W. Valyocsik, F. X. Ryan, *Microporous Mater.* **1996**, *7*, 243.
[18] S. M. Holmes, V. L. Zholobenko, A. Thursfield, R. J. Plaisted, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2025.
[19] D. H. Sullivan, M. P. Harold, W. C. Conner, Jr., *J. Catal.* **1998**, *178*, 108.
[20] D. H. Sullivan, W. C. Conner, M. P. Harold, *Appl. Spectrosc.* **1992**, *46*, 811.
[21] H. Armendariz, C. Sanchez Sierra, F. Figuears, B. Coq, C. Mirodatos, F. Lefebvre, D. Tichit, *J. Catal.* **1997**, *171*, 85.
[22] B. Lee, J. N. Kondo, F. Wakabayashi, K. Domen, *Catal. Lett.* **1999**, *59*, 51.
[23] J. N. Kondo, L. Shao, F. Wakabayashi, K. Domen, *J. Phys. Chem. B* **1997**, *101*, 9314.
[24] J. N. Kondo, S. Liquin, F. Wakabayashi, K. Domen, *Catal. Lett.* **1997**, *47*, 129.
[25] J. N. Kondo, K. Domen, F. Wakabayashi, *Microporous Mesoporous Mater.* **1998**, *21*, 429.
[26] J. N. Kondo, F. Wakabayashi, K. Domen, *Catal. Lett.* **1998**, *53*, 215.
[27] J. Kotrla, D. Nachtigallova, V. Bosacek, J. Novakova, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2613.
[28] M. Iwamoto, H. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa, S. Kagawa, *J. Phys. Chem.* **1992**, *96*, 9360.
[29] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura, M. Anpo, *J. Catal.* **1992**, *136*, 510.
[30] J. Valyon, W. K. Hall, *J. Phys. Chem.* **1993**, *97*, 7054.
[31] G. Spoto, S. Zecchina, S. Bordiga, G. Ricchiardi, G. Marta, G. Leofanti, G. Petrini, *Appl. Catal.* **1994**, *3*, 151.
[32] A. W. Aylor, P. C. Larsen, J. A. Reimer, A. T. Bell, *J. Catal.* **1995**, *157*, 592.
[33] G. D. Lei, B. J. Adelman, J. Sarkany, W. M. H. Sachtler, *Appl. Catal.* **1995**, *5*, 245.
[34] T. B. Hoost, K. A. Laframboise, K. Otto, *Catal. Lett.* **1995**, *33*, 105.
[35] K. Hadjiivanov, D. Klissurski, G. Ramis, G. Busca, *Appl. Catal. B* **1996**, *7*, 251.
[36] T. Cheung, P. K. Bhargava, M. Hobday, K. Foger, *J. Catal.* **1996**, *158*, 301.
[37] H. Y. Chen, L. Chen, J. Lin, K. Tan, J. Li, *Inorg. Chem.* **1997**, *36*, 1417.
[38] K. Hadjiivanov, J. Saussey, J. L. Freysz, J. C. Lavalley, *Catal. Lett.* **1998**, *52*, 103.
[39] J. Szanyi, M. T. Paffett, *J. Catal.* **1996**, *164*, 232.
[40] B. Ganemi, E. Björnbom, J. Paul, *Appl. Catal. B* **1998**, *17*, 293.
[41] M. V. Konduru, S. S. C. Chuang, *J. Phys. Chem. B* **1999**, *103*, 5802.
[42] J. Eng, C. H. Bartholomew, *J. Catal.* **1997**, *171*, 27.
[43] M. A. Centeno, I. Carrizosa, J. A. Odriozola, *Appl. Catal. B* **1998**, *19*, 67.
[44] F. Acke, B. Westerberg, M. Skoglundh, *J. Catal.* **1998**, *179*, 528.
[45] D. K. Captain, M. D. Amiridis, *J. Catal.* **1999**, *184*, 377.
[46] T. Gerlach, F.-W. Schütze, M. Baerns, *J. Catal.* **1999**, *185*, 131.
[47] C. De La Cruz, N. Sheppard, *Phys. Chem. Chem. Phys.* **1999**, *1*, 329.
[48] W. Weng, M. Chen, H. Wan, Y. Liao, *Catal. Lett.* **1998**, *53*, 43.
[49] I. A. Fisher, A. T. Bell, *J. Catal.* **1997**, *172*, 222.
[50] I. A. Fisher, A. T. Bell, *J. Catal.* **1998**, *178*, 153.
[51] T. C. Schilke, I. A. Fisher, A. T. Bell, *J. Catal.* **1999**, *184*, 144.
[52] E. E. Ortelli, J. M. Weigel, A. Wokaun, *Catal. Lett.* **1998**, *54*, 41.
[53] T. V. Voskoboinikov, B. Coq, F. Fajula, R. Brown, G. McDougall, J. L. Couturier, *Microporous Mesoporous Mater.* **1998**, *24*, 89.
[54] Z. Dardas, M. G. Süer, Y. H. Ma, W. R. Moser, *J. Catal.* **1996**, *159*, 204.
[55] M. G. Süer, Z. Dardas, Y. H. Ma, W. R. Moser, *J. Catal.* **1996**, *162*, 320.
[56] S. Bordiga, G. Ricchiardi, G. Spoto, D. Scarano, L. Carnelli, A. Zecchina, C. O. Arean, *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 1843.
[57] F. Geobaldo, G. Spoto, S. Bordiga, C. Lamberti, A. Zecchina, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 1243.
[58] M. Trombetta, G. Busca, S. A. Rossini, V. Piccoli, U. Cornaro, *J. Catal.* **1997**, *168*, 334.
[59] M. Trombetta, G. Busca, S. A. Rossini, V. Piccoli, U. Cornaro, *J. Catal.* **1997**, *168*, 349.
[60] H. Ishikawa, E. Yoda, J. N. Kondo, F. Wakabayashi, K. Domen, *J. Phys. Chem. B* **1999**, *103*, 5681.
[61] B. Wichterlova, N. Zilkova, E. Uvarova, J. Cejka, P. Sarv, C. Paganini, J. A. Lercher, *Appl. Catal. A* **1999**, *182*, 297.
[62] C. Flego, I. Kiricsi, W. O. Parker, Jr., M. G. Clerici, *Appl. Catal. A* **1995**, *124*, 107.
[63] N. Arsenova, H. Bludau, W. O. Haag, H. G. Karge, *Microporous Mesoporous Mater.* **1998**, *23*, 1.
[64] V. A. Veefkind, J. A. Lercher, *Appl. Catal. A* **1999**, *181*, 245.

[65] M. L. Unland, *J. Phys. Chem.* **1978**, *82*, 580.

[66] M. Ziolek, J. Czyzniewska, J. Lamotte, J. C. Lavalley, *Catal. Lett.* **1996**, *37*, 223.

[67] S. T. King, J. M. Garces, *J. Catal.* **1987**, *104*, 59.

[68] A. E. Palomares, G. Eder-Mirth, J. A. Lercher, *J. Catal.* **1997**, *168*, 442.

[69] A. E. Palomares, G. Eder-Mirth, J. A. Lercher, *J. Catal.* **1998**, *180*, 56.

[70] I. I. Ivanova, E. G. Derouane, *Stud. Surf. Sci. Catal.* **1994**, *85*, 357.

[71] M. W. Anderson, *Top. Catal.* **1996**, *3*, 195.

[72] M. Hunger, *Catal. Rev. Sci. Eng.* **1997**, *39*, 345.

[73] J. F. Haw, J. B. Nicholas, T. Xu, L. W. Beck, D. B. Ferguson, *Acc. Chem. Res.* **1996**, *29*, 259.

[74] M. Hunger, T. Horvath, *J. Chem. Soc. Chem. Commun.* **1995**, 1423.

[75] M. Hunger, M. Seiler, T. Horvath, *Catal. Lett.* **1999**, *57*, 199.

[76] M. Hunger, T. Horvath, *J. Catal.* **1997**, *167*, 187.

[77] M. Hunger, M. Seiler, T. Horvath, *Catal. Lett.* **1999**, *57*, 199.

[78] J. F. Haw, P. W. Goguen, T. Xu, T. W. Skloss, W. Song, Z. Wang, *Angew. Chem.* **1998**, *110*, 993; *Angew. Chem. Int. Ed.* **1998**, *37*, 948.

[79] H. Ernst, D. Freude, T. Mildner, I. Wolf, *Stud. Surf. Sci. Catal.* **1995**, *94*, 413.

[80] H. Ernst, D. Freude, T. Mildner, I. Wolf, *Solid State Nucl. Magn. Reson.* **1996**, *6*, 147.

[81] T. Mildner, H. Ernst, D. Freude, W. F. Hölderich, *J. Am. Chem. Soc.* **1997**, *119*, 4258.

[82] T. Xu, J. F. Haw, *Top. Catal.* **1997**, *4*, 109.

[83] E. MacNamara, D. Raftery, *J. Catal.* **1998**, *175*, 137.

[84] P. K. Isbester, A. Zalusky, D. H. Lewis, M. C. Douskey, M. J. Pomije, K. R. Mann, E. J. Munson, *Catal. Today* **1999**, *49*, 363.

[85] C. Keeler, J. Xiong, H. Lock, S. Dec, T. Tao, G. E. Maciel, *Catal. Today* **1999**, *49*, 377.

[86] M. Haake, A. Pines, J. A. Reimer, R. Seydoux, *J. Am. Chem. Soc.* **1997**, *119*, 11712.

[87] D. Raftery, E. MacNamara, G. Fisher, C. V. Rice, J. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 8746.

[88] R. Seydoux, A. Pines, M. Haake, J. A. Reimer, *J. Phys. Chem. B* **1999**, *103*, 4629.

[89] E. MacNamara, G. Fisher, J. Smith, C. V. Rice, S.-J. Hwang, D. Raftery, *J. Phys. Chem. B* **1999**, *103*, 1158.

[90] J. H. Lunsford, W. P. Rothwell, W. Shen, *J. Am. Chem. Soc.* **1985**, *107*, 1540.

[91] J. H. Lunsford, P. N. Tutunjian, P.-J. Chu, E. B. Yeh, D. J. Zalewski, *J. Phys. Chem.* **1989**, *93*, 2590.

[92] A. I. Biaglow, R. J. Gorte, G. T. Kokotailo, D. White, *J. Catal.* **1994**, *148*, 779.

[93] L. W. Beck, T. Xu, J. B. Nicholas, J. F. Haw, *J. Am. Chem. Soc.* **1995**, *117*, 11594.

[94] H. Ernst, D. Freude, T. Mildner, H. Pfeifer in *Proc. 12th Int. Zeolite Conf.* (Eds.: M. M. J. Treacy, B. K. Marcus, M. E. Bisher, J. B. Higgins), Materials Research Society, Warrendale, PA, **1999**, pp. 2955–2962.

[95] T. Mildner, D. Freude, *J. Catal.* **1998**, *178*, 309.

[96] A. Stepanov, H. Ernst, D. Freude, *Catal. Lett.* **1998**, *54*, 1.

[97] G. J. Kramer, R. A. van Santen, C. A. Emeis, A. K. Nowak, *Nature* **1993**, *363*, 529.

[98] G. J. Kramer, R. A. van Santen, *J. Am. Chem. Soc.* **1995**, *117*, 1766.

[99] J. Sommer, D. Habemacher, R. Jost, A. Sassi, A. G. Stepanov, M. V. Luzgin, D. Freude, H. Ernst, J. Martens, *J. Catal.* **1999**, *181*, 265.

[100] J. F. Haw in *NMR Techniques in Catalysis* (Eds.: A. T. Bell, A. Pines), Marcel Dekker, New York, **1994**, pp. 139–194.

[101] J. F. Haw, T. Xu, *Adv. Catal.* **1998**, *42*, 115.

[102] E. G. Derouane, H. He, S. B. Derouane-Abd Hamid, I. I. Ivanova, *Catal. Lett.* **1999**, *58*, 1.

[103] J. F. Haw, *Top. Catal.* **1999**, *8*, 81.

[104] D. K. Murray, J.-W. Chang, J. F. Haw, *J. Am. Chem. Soc.* **1993**, *115*, 4732.

[105] J. F. Haw, B. R. Richardson, J. S. Oshiro, N. D. Lazo, J. A. Speed, *J. Am. Chem. Soc.* **1989**, *111*, 2052.

[106] M. T. Aronson, R. J Gorte, W. E. Farneth, D. White, *J. Am. Chem. Soc.* **1989**, *111*, 840.

[107] N. D. Lazo, B. R. Richardson, P. D. Schettler, J. L. White, E. J. Munson, J. F. Haw, *J. Phys. Chem.* **1991**, *95*, 9420.

[108] A. G. Stepanov, *Catal. Today* **1995**, *24*, 341.

[109] M. Hunger, T. Horvath, J. Weitkamp, *Microporous Mesoporous Mater.* **1998**, *22*, 357.

[110] T. Horvath, M. Seiler, M. Hunger, *Appl. Catal. A* **1999**, *193*, 227.

[111] V. B. Kazansky, *Catal. Today* **1999**, *51*, 419.

[112] A. G. Stepanov, M. V. Luzgin, *Chem. Eur. J.* **1997**, *3*, 47.

[113] D. H. Barich, T. Xu, W. Song, Z. Wang, F. Deng, J. F. Haw, *J. Phys. Chem. B* **1998**, *102*, 7163.

[114] J. Haw, B. R. Richardson, I. S. Oshiro, N. D. Lazo, J. A. Speed, *J. Am. Chem. Soc.* **1989**, *111*, 2052.

[115] P. W. Goguen, T. Xu, D. H. Barich, T. W. Skloss, W. Song, Z. Wang, J. B. Nicholas, J. F. Haw, *J. Am. Chem. Soc.* **1998**, *120*, 2650.

[116] J. F. Haw, J. B. Nicholas, W. Song, F. Deng, Z. Wang, T. Xu, C. S. Heneghan, *J. Am. Chem. Soc.* **2000**, *122*, 4763.

[117] I. I. Ivanova, D. Brunel, J. B. Nagy, E. G. Derouane, *J. Mol. Catal. A* **1995**, *95*, 243.

[118] I. I. Ivanova, A. Pasau-Claerbout, M. Seirvert, N. Blom, E. G. Derouane, *J. Catal.* **1996**, *158*, 521.

[119] I. I. Ivanova, M. Seirvert, A. Pasau-Claerbout, N. Blom, E. G. Derouane, *J. Catal.* **1996**, *164*, 347.

[120] E. G. Derouane, S. B. Abdul Hamid, I. I. Ivanova, N. Blom, P.-E. Højlund-Nielsen, *J. Mol. Catal.* **1994**, *86*, 371.

[121] I. I. Ivanova, N. Blom, E. G. Derouane, *J. Mol. Catal. A* **1996**, *109*, 157.

[122] I. I. Ivanova, E. B. Pomakhina, A. I. Rebrov, E. G. Derouane, *Top. Catal.* **1998**, *6*, 49.

[123] M. W. Anderson, J. Klinowski, *Nature* **1989**, *339*, 200.

[124] M. W. Anderson, J. Klinowski, *J. Am. Chem. Soc.* **1990**, *112*, 10.

[125] C. Tsiao, D. R. Corbin, C. Dybowski, *J. Am. Chem. Soc.* **1990**, *112*, 7140.

[126] M. Hunger, T. Horvath, *J. Am. Chem. Soc.* **1996**, *118*, 12302.

[127] A. Thursfield, M. W. Anderson, *J. Phys. Chem.* **1996**, *100*, 6698.

[128] F. Salehirad, M. W. Anderson, *J. Catal.* **1998**, *177*, 189.

[129] G. Mirth,. J. A. Lercher, M. W. Anderson, J. Klinowski, *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 3039.

[130] F. Salehirad, M. W. Anderson, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2857.

[131] M. W. Anderson, B. Sulikowski, P. J. Barrie, J. Klinowski, *J. Phys. Chem.* **1990**, *94*, 2730.

[132] F. Salehirad, M. W. Anderson, *J. Catal.* **1996**, *164*, 301.

[133] A. Philippou, F. Salehirad, D.-P. Luigi, M. W. Anderson, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2851.

[134] F. Salehirad, M. W. Anderson, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 1911.

[135] M. W. Anderson, M. L. Occelli, J. Klinowski, *J. Phys. Chem.* **1992**, *96*, 388.

[136] M. D. Alba, A. A. Romero, M. L. Occelli, J. Klinowski, *J. Phys. Chem. B* **1997**, *101*, 5166.

[137] H. He, L. Zhang, J. Klinowski, M. L. Occelli, *J. Phys. Chem.* **1995**, *99*, 6980.

[138] M. Seiler, U. Schenk, M. Hunger, *Catal. Lett.* **1999**, *62*, 139.

[139] W. O. Haag in *Proc. 6th Int. Zeolite Conf.* (Eds.: D. Olson, A. Bisio), Butterworths, Surrey, UK, **1984**, pp. 466–478.

[140] L. M. Bull, A. K. Cheetham, T. Anuld, A. Reinhold, A. Samoson, J. Sauer, B. Bussemer, Y. Lee, S. Gann, J. Shore, A. Pines, R. Dupree, *J. Am. Chem. Soc.* **1998**, *120*, 3510.

[141] J.-P. Amoureux, F. Bauer, H. Ernst, C. Fernandez, D. Freude, D. Michel, U.-T. Pingel, *Chem. Phys. Lett.* **1998**, *285*, 10.

[142] U.-T. Pingel, J.-P. Amoureux, T. Anupold, F. Bauer, H. Ernst, C. Fernandez, D. Freude, A. Samoson, *Chem. Phys. Lett.* **1998**, *294*, 345.

[143] A. V. Chadwick, I. J. F. Poplett, D. T. S. Maitland, M. E. Smith, *Chem. Mater.* **1998**, *10*, 864.

[144] V. Bosacek, *J. Phys. Chem.* **1993**, *97*, 10732.

[145] V. Bosacek, *Z. Phys. Chem.* **1995**, *189*, 241.

[146] R. T. Sanderson, *J. Am. Chem. Soc.* **1983**, *105*, 2259.

[147] M. Hunger, U. Schenk, B. Burger, J. Weitkamp, *Angew. Chem.* **1997**, *109*, 2613; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2504.

[148] M. Hunger, U. Schenk, J. Weitkamp, *J. Mol. Catal. A* **1998**, *134*, 97.

[149] U. Schenk, M. Hunger, J. Weitkamp, *Magn. Reson. Chem.* **1999**, *37*, 75.

[150] A. Philippou, M. W. Anderson, *J. Am. Chem. Soc.* **1994**, *116*, 5774.

[151] M. Hunger, U. Schenk, M. Seiler, J. Weitkamp, *J. Mol. Catal. A* **2000**, *156*, 153.

[152] N. D. Lazo, D. K. Murray, M. L. Kieke, J. F. Haw, *J. Am. Chem. Soc.* **1992**, *114*, 8552.

[153] D. K. Murray, J. W. Chang, J. F. Haw, *J. Am. Chem. Soc.* **1993**, *115*, 4732.

[154] X.-Z. Quin, A. D. Trifunac, *J. Phys. Chem.* **1990**, *94*, 4751.

[155] M. V. Barnabas, D. W. Werst, A. D. Trifunac, *Chem. Phys. Lett.* **1993**, *204*, 435; M. V. Barnabas, D. W. Werst, A. D. Trifunac, *Chem. Phys. Lett.* **1993**, *206*, 21.

[156] D. W. Werst, E. E. Tartakovsky, E. A. Piocos, A. D. Trifunac, *J. Phys. Chem.* **1994**, *98*, 10249.

[157] D. W. Werst, P. Han, *Catal. Lett.* **1997**, *45*, 253.

[158] X.-Z. Qin, A. D. Trifunac, *J. Phys. Chem.* **1990**, *94*, 4751.

[159] M. Che, F. Bozon-Verduraz in *Handbook of Heterogeneous Catalysis, Vol. 2* (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH, Weinheim, **1997**, pp. 641 – 664.

[160] J.-P. Lange, A. Gutsze, H. G. Karge, *J. Catal.* **1988**, *114*, 136.

[161] H. G. Karge, J.-P. Lange, A. Gutsze, M. Laniecki, *J. Catal.* **1988**, *114*, 144.

[162] A. Brückner, B. Kubias, B. Lücke, *Catal. Today* **1996**, *32*, 215.

[163] M. Che, E. Giamello in *Catalyst Characterization: Physical Techniques for Solid Materials* (Eds.: B. Imelik, J. C. Vedrine), Plenum, New York, **1994**, chapter 5.

[164] Z. Sojka, *Catal. Rev. Sci. Eng.* **1995**, *37*, 461.

[165] K. Dyrek, M. Che, *Chem. Rev.* **1997**, *97*, 305.

[166] R. A. Schoonheydt, *Catal. Rev. Sci. Eng.* **1993**, *35*, 129.

[167] A. V. Kucherov, A. A. Slinkin, *J. Mol. Catal.* **1994**, *90*, 323.

[168] A. V. Kucherov, J. L. Gerlock, H.-W. Jen, M. Shelef, *Zeolites* **1995**, *15*, 15.

[169] A. V. Kucherov, J. L. Gerlock, H.-W. Jen, M. Shelef, *J. Catal.* **1995**, *152*, 63.

[170] T. Schmauke, E. Möller, E. Roduner, *Chem. Commun.* **1998**, 2589.

[171] A. K. Ghosh, L. Kevan, *J. Phys. Chem.* **1988**, *92*, 4439.

[172] A. M. Prakash, M. Hartmann, L. Kevan, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 1233.

[173] A. M. Prakash, M. Hartmann, L. Kevan, *J. Phys. Chem. B* **1997**, *101*, 6819.

[174] D. Zhao, Z. Luan, L. Kevan, *J. Phys. Chem. B* **1997**, *101*, 6943.

[175] M. Hartmann, N. Azuma, L. Kevan, *J. Phys. Chem.* **1995**, *99*, 10988.

[176] E. Wloch, B. Sulikowski, R. Dula, E. M. Serwicka, *Colloids Surf. A* **1996**, *115*, 257.

[177] B. Wichterlova, P. Jiru, *React. Kinet. Catal. Lett.* **1980**, *13*, 197.

[178] D. Goldfarb, M. Bernardo, K. G. Strohmaier, D. E. W. Vaughan, H. Thomann, *J. Am. Chem. Soc.* **1994**, *116*, 6344.

[179] A. V. Kucherov, C. N. Montreuil, T. N. Kucherov, M. Shelef, *Catal. Lett.* **1998**, *56*, 173.

[180] A. Brückner, U. Lohse, H. Mehner, *Microporous Mesoporous Mater.* **1998**, *20*, 207.

[181] A. V. Kucherov, C. P. Hubbard, M. Shelef, *Catal. Lett.* **1995**, *33*, 91.

[182] A. V. Kucherov, S. G. Lakeev, M. Shelef, *Appl. Catal. B* **1998**, *16*, 245.

[183] S. G. Lakeev, A. V. Kucherov, M. Shelef, *Stud. Surf. Sci. Catal.* **1998**, *116*, 441.

[184] A. V. Kucherov, P. G. Lakeev, M. Shelef, *Microporous Mesoporous Mater.* **1998**, *20*, 355.

[185] A. Brückner, A. Martin, B. Kubias, B. Lücke, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2221.

[186] A. Brückner, A. Martin, N. Steinfeldt, G.-U. Wolf, B. Lücke, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 4257.

[187] D. Biglino, H. Li, R. Erickson, A. Lund, H. Yahiro, M. Shiotani, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2887.

[188] E. Roduner, R. Crockett, L.-M. Wu, *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 2101.

[189] G. Harvey, R. Prins, R. Crockett, E. Roduner, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2027.

[190] J. H. Lunsford, *Stud. Surf. Sci. Catal.* **1993**, *75*, 103.

[191] C. J. Rhodes, C. S. Hinds in *Radicals on Surfaces. Topics in Molecular Organization and Engineering, vol. 13* (Eds.: A. Lund, C. J. Rhodes), Kluwer, Dordrecht, **1995**, pp. 119 – 132.

[192] R. Crockett, E. Roduner, *J. Chem. Soc. Perkin Trans. 2* **1993**, 1503.

[193] R. Crockett, E. Roduner, *J. Chem. Soc. Perkin Trans. 2* **1994**, 347.

[194] C. J. Rhodes, *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 3179.

[195] C. J. Rhodes, M. Standing, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1455.

[196] E. Roduner, L.-M. Wu, R. Crockett, C. J. Rhodes, *Catal. Lett.* **1992**, *14*, 373.

[197] R. Crockett, E. Roduner, *Stud. Surf. Sci. Catal.* **1994**, *84*, 527.

[198] E. A. Piocos, P. Han, D. W. Werst, *J. Phys. Chem.* **1996**, *100*, 7191.

[199] D. W. Werst, E. E. Tartakovsky, E. A. Piocos, A. D. Trifunac, *J. Phys. Chem.* **1994**, *98*, 10249.

[200] D. W. Werst, E. A. Piocos, E. E. Tartakovsky, A. D. Trifunac, *Chem. Phys. Lett.* **1994**, *229*, 421.

[201] E. A. Piocos, P. Han, D. W. Werst, *J. Phys. Chem.* **1996**, *100*, 7191.

[202] D. W. Werst, P. Han, *Catal. Lett.* **1997**, *45*, 253.

[203] D. J. Driscoll, K. D. Campell, J. H. Lunsford, *Adv. Catal.* **1987**, *35*, 139.

[204] J. H. Lunsford, *Catal. Today* **1989**, *6*, 235.

[205] Y. Tong, M. P.Rosynek, J. H. Lunsford, *J. Phys. Chem.* **1989**, *93*, 2896.

[206] A. R. Pradhan, T.-S. Lin, W.-H. Chen, S.-J. Jong, J.-F. Wu, K.-J. Chao, S.-B. Liu, *J. Catal.* **1999**, *184*, 29.

[207] J. C. Vedrine, P. Dejaifve, E. D. Garbowski, E. G. Derouane, *Stud. Surf. Sci. Catal.* **1980**, *5*, 29.

[208] P. Dejaifve, J. C. Vedrine, V. Bolis, E. G. Derouane, *J. Catal.* **1980**, *63*, 331.

[209] M. Laniecki, H. G. Karge in *Proc. 6th Int. Symp. Heterogeneous Catal., Vol. 2* (Ed.: D. Sopov), Bulgarian Academy of Science, Sofia, **1987**, p. 129.

[210] I. Kiricsi, H. Förster, G. Tasi, J. B. Nagy, *Chem. Rev.* **1999**, *99*, 2085.

[211] H. Knözinger, *Top. Catal.* **1998**, *6*, 107.