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Conversion of Propan-2-ol on Zeolites LaNaY and HY Investigated by Gas Chromatography and *in Situ* MAS NMR Spectroscopy under Continuous-Flow Conditions

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The conversion of propan-2-ol on zeolites HY and LaNaY has been investigated by gas chromatography (GC) and *in situ* ^{1}H and ^{13}C MAS NMR spectroscopy under continuous-flow conditions using a new MAS NMR microreactor with cylindrical catalyst bed. At reaction temperatures of $T = 373$ K and $T = 393$ K a propan-2-ol conversion of 50 and 100%, respectively, and the formation of propene, diisopropyl ether, and small amounts of acetone was determined by GC. Applying *in situ* ^{1}H and ^{13}C MAS NMR spectroscopy, the initial step of the reaction was found to be the physisorption of propan-2-ol on Brønsted acid sites. A formation of isopropoxy species could be excluded by ^{13}C MAS NMR spectroscopy. ^{1}H MAS NMR spectroscopy indicated that the Brønsted acid sites of the zeolites LaNaY and HY were hydrated by water molecules in the first part of the induction period. These water molecules were formed in result of the propan-2-ol dehydration. The strong low-field shift of the ^{1}H MAS NMR signals of the hydrated Brønsted acid sites is due to a partial protonation of adsorbed water molecules. At $T = 393$ K, a significant ^{13}C MAS NMR signal of strongly bonded acetone molecules appeared at 220 ppm in the spectra of zeolites LaNaY and HY. As demonstrated by propan-2-ol conversion on a partially dealuminated zeolite HY, this by-reaction is promoted by extra-framework aluminium species. The formation of coke precursors which caused ^{13}C MAS NMR signals at 10–50 ppm is explained by an oligomerization of propene. *In situ* ^{13}C MAS NMR experiments carried out under a continuous flow of propene showed that the above-mentioned coke precursors are also formed on partially rehydrated zeolite HY. © 1997 Academic Press

INTRODUCTION

The conversion of alcohols is a well-established reaction for the characterization of solid catalysts (1, 2). The dehydration of propan-2-ol was studied on acidic zeolites HNaX (3), HNaY (4), and dealuminated HY (5). The reaction was found to be of first order with respect to adsorbed propan-2-ol and the products were confined to propene, diisopropyl ether, and water. On basic catalysts propan-2-ol is dehydrogenated to acetone (6) (see Scheme 1).

In the present paper the conversion of propan-2-ol on acidic zeolites LaNaY and HY has been investigated. The Brønsted acidity of these zeolites is caused by acidic hydroxyl protons bonded at oxygen bridges between a fourfold coordinated framework silicon and a fourfold coordinated and negatively charged framework aluminium atom. These bridging OH groups were formed by an exchange of the sodium cations of the parent zeolite NaY with ammonium ions and subsequent thermal treatment (zeolite HY) or with multivalent cations (zeolite LaNaY). In the latter case, metal OH groups and bridging OH groups (SiOHAl) are formed by the dissociation of water molecules in the strong electric fields of the multivalent cations. By application of ^{1}H MAS NMR spectroscopy the types and concentrations of hydroxyl groups in zeolites can be determined (for a review see (7)).

The understanding of the mechanisms of hydrocarbon conversions on zeolites is a prerequisite for a progress in this field. Therefore, in a number of investigations *in situ* MAS NMR spectroscopy was applied for the study of reactions catalyzed by sites on the inner surface of zeolites (for reviews see (8, 9)). In most of these works *ex situ* prepared samples, sealed in glass ampoules or gas-tight MAS rotors, were used. However, most of the heterogeneously catalyzed reactions in the chemical industry work under flow conditions. Recently, a new experimental technique was developed which allows *in situ* MAS NMR investigations of chemical reactions under a continuous flow of reactant molecules (10, 11). In the present work the application of this new *in situ* technique is compared with gas chromatography. Both methods used the same microreactor with cylindrical catalyst bed (10, 11) which allows the comparison of the data. Gas chromatography was applied to optimize the reaction parameters and to determine the product distribution in the gas phase. The advantage of *in situ* MAS NMR spectroscopy is its ability for the detection of reactants and compounds in the zeolite pores. In this study the new *in situ* MAS NMR technique was applied to investigate the initial step of the propan-2-ol conversion, the behavior of bridging OH groups in the course of the

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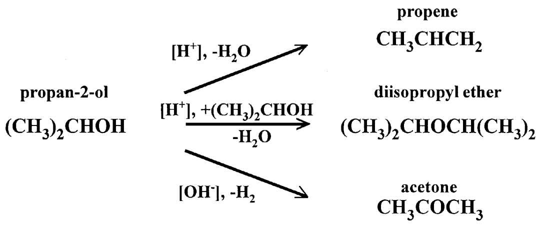


SCHEME 1

reaction, and the formation of by-products and coke precursors in the zeolite pores.

EXPERIMENTAL

Preparation of Zeolites

The parent zeolite NaY was a commercial product of Union Carbide (Tarrytown, NY) with a unit cell composition $Na_{53.3}Al_{53.3}Si_{138.7}O_{384} \cdot nH_2O$. The hydrogen form of this zeolite (HY) was prepared by fourfold ion exchange at the temperature of $T = 353$ K in a surplus of 0.1 *M* aqueous solution of NH_4NO_3 yielding an exchange degree of 88%. The lanthanum exchange of zeolite NaY was carried out at 353 K in four steps using an aqueous 0.3 *M* solution of $La(NO_3)_3$ which resulted in a sodium exchange degree of 73%. After exchange the zeolite powder was washed in demineralized water, dried at room temperature, and characterized by AES, XRD, and NMR. Before the catalytic investigations the powder material was pressed binder-free, crushed, and sieved into particles with a diameter between 0.2 and 0.3 mm. After this the zeolites LaNaY and HY were calcined for 12 h under vacuum at $T = 523$ K and $T = 673$ K, respectively. By ^{27}Al MAS NMR spectroscopy of the calcined and rehydrated zeolites LaNaY and HY ca. 5% of the aluminium atoms were found on extra-framework positions. In previous studies, the concentrations of bridging OH groups in the supercages of calcined zeolites were derived by ^{1}H MAS NMR spectroscopy (7, 11). For zeolites LaNaY and HY calcined at $T = 523$ K and $T = 673$ K, respectively, concentrations of 1.1 and 1.5 mmol accessible SiOHAl groups per gram of zeolite were determined (7, 11).

NMR Spectroscopy

The MAS NMR probe used for the *in situ* investigations under flow conditions is based on a commercial 7-mm Bruker MAS NMR probe (Fig. 1) (10, 11). A glass tube with 1.8 mm outer diameter and fixed by a support was axially placed in the center of the MAS rotor. Prior to the *in situ* MAS NMR investigations, 300 mg of dehydrated zeolite powder was filled into the MAS rotor under dry nitrogen gas in a glove box. With a special tool an axial hole of 2.5 mm diameter was pressed into the powder material resulting in a catalyst bed having the shape of a hollow cylinder. Before transferring the rotor into the MAS NMR probe, the axial hole in the cap was closed by a plug. After this plug was removed, the injection tube was carefully inserted into the rotor. During the measurements, the spinning rotor was heated via the bearing gas of the MAS NMR turbine. Using this MAS NMR microreactor it is possible to study heterogeneously catalyzed reactions under atmospheric pressure and in a temperature range which is limited by the heating system of the commercial MAS NMR probe.

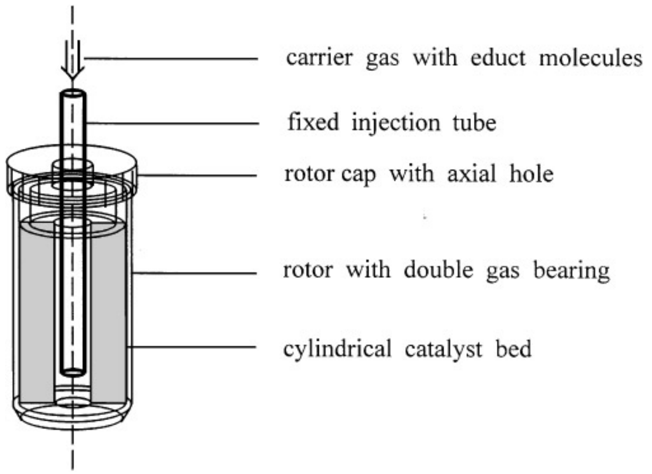


FIG. 1. Schematic drawing of the 7 mm double bearing MAS rotor modified for *in situ* MAS NMR investigations under continuous-flow conditions.

Figure 2 shows the carrier gas supply system. The flow rate of the carrier gas (nitrogen) was controlled by a needle valve and rotameter. Using a saturator the carrier gas was loaded with $^{13}C(2)$-enriched propan-2-ol (99 atom%, Isotec Inc., U.S.A.). This saturator was held at a temperature of $T = 285$ K, whereas the tube connecting the saturator to the MAS NMR probe was kept at room temperature. Hence, no condensation of educt molecules occurs in the tube. Before

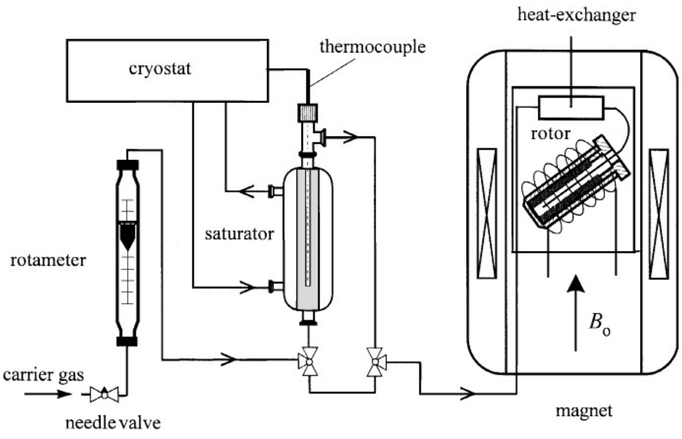


FIG. 2. Schematic drawing of the carrier gas supply system used for *in situ* MAS NMR investigations under continuous-flow conditions.

the loaded carrier gas is injected into the MAS rotor, it was preheated in a heat exchanger. This heat exchanger was placed in the upper part of the MAS NMR probe, covered by a glass bell. After the injection of the carrier gas into the MAS rotor, it flows inside the rotor from the bottom to the top and leaves the rotor via an annular gap in the rotor cap. A dewar placed on top of the glass bell led the hot carrier gas and the bearing and driving gas of the MAS NMR turbine out of the probe.

The NMR measurements were carried out on a Bruker spectrometer MSL 400 at the resonance frequencies of 400.1 MHz for ^{1}H and 100.5 MHz for ^{13}C. The temperature inside the MAS rotor was calibrated by measuring the ^{207}Pb chemical shift of $Pb(NO_3)_2$ (12). The temperature gradient, ΔT, over the whole sample, as determined by the line broadening of the ^{207}Pb MAS NMR signal, was $\Delta T \leq 5$ K at $T = 393$ K. The *in situ* MAS NMR spectra were recorded after single pulse excitation, with 25 scans and repetition times of 4 and 30 s for ^{1}H and ^{13}C MAS NMR, respectively. The ^{1}H and ^{13}C MAS NMR spectra were recorded in intervals of 15 min. In all experiments the MAS rate was adjusted to $\nu_{\text{rot}} = 2.5$ kHz and all chemical shifts were referenced to TMS.

Gas Chromatography

The gas chromatographic experiments were performed with the flow-type apparatus shown in Fig. 3. The carrier gas supply system was identical to that applied for *in situ* MAS NMR experiments. In the saturator the carrier gas (nitrogen) was loaded with propan-2-ol (Merck, No. 9634.2500). Via a combination of four- and six-way valves the loaded carrier gas was led to the reactor and the output of the reactor was connected with a cold trap or the gas chromatograph. For the GC investigations the same microreactor was applied as for *in situ* MAS NMR spectroscopy. A 20-mm glass tube contained a 7-mm MAS NMR rotor which was filled with zeolite powder arranged in a cylindrical catalyst bed. The whole reactor system was placed in a furnace. As done in the NMR spectroscopic experiments the loaded carrier gas was injected into the microreactor via a glass tube. The product analysis was carried out by on-line sampling with a capillary gas chromatograph HP 5890 equipped with a DB-WAX column (J&W Scientific) of 30 m length and 0.25 mm inner diameter and a flame ionization detector. Using this equipment the product stream was sampled and analyzed in steps of 16 min.

RESULTS AND DISCUSSION

Conversion of Propan-2-ol on Zeolites LaNaY and HY Investigated by Gas Chromatography

In the present study gas chromatography was used (a) to optimize the parameters of propan-2-ol conversion on acidic zeolites Y, i.e., the modified residence time of the educt molecules and the reaction temperature, and (b) to determine the distribution of reactants and products in the gas phase outside of the zeolite particles. Since the *in situ* MAS NMR experiments were carried out with ^{13}C(2)-enriched propan-2-ol, a small educt flow, i.e., a high modified residence time of the propan-2-ol was desirable. In Figs. 4 and 5 the conversion of propan-2-ol on zeolites LaNaY and HY, respectively, and the yields of propene,

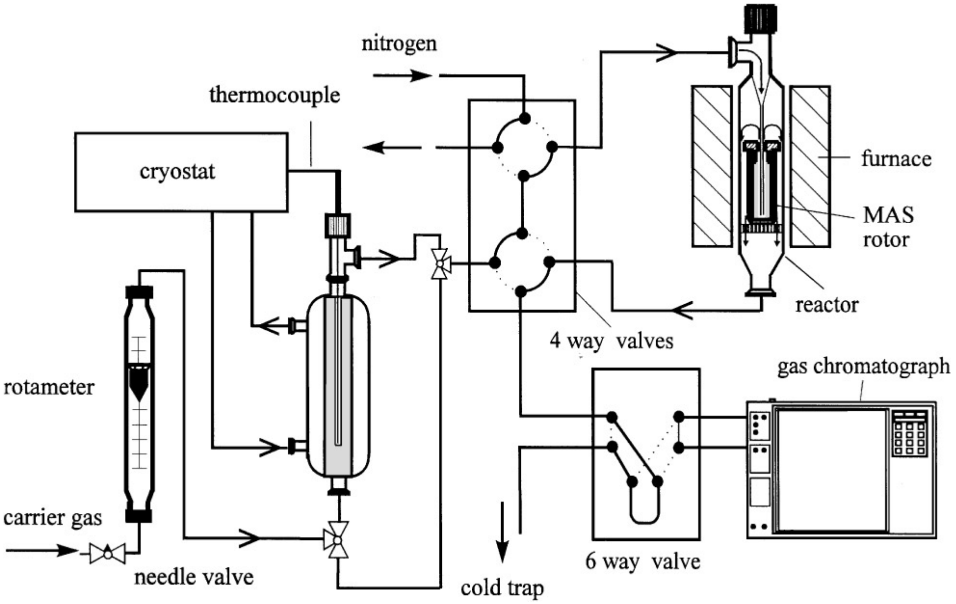


FIG. 3. Schematic drawing of the on-line gas chromatographic equipment consisting of the carrier gas supply system, the MAS NMR microreactor arranged in the reactor tube, valve systems, and the gas chromatograph.

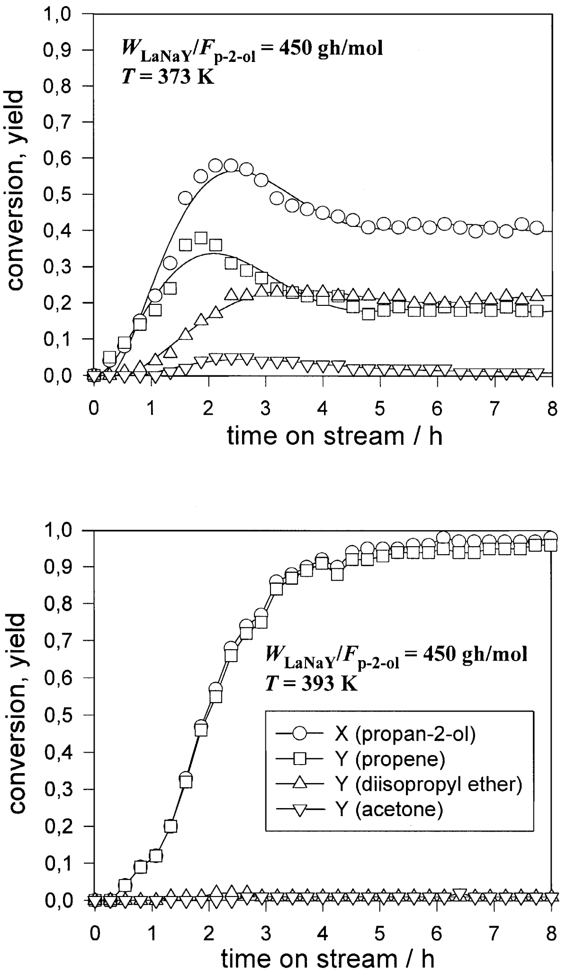


FIG. 4. Conversions of propan-2-ol on zeolite LaNaY and yields of propene, diisopropyl ether, and acetone obtained with a modified residence time of $W_{LaNaY}/F_{p\text{-}2\text{-}ol} = 450$ gh/mol and at reaction temperatures of $T = 373$ K (top) and $T = 393$ K (bottom).

diisopropyl ether, and acetone are shown. During the GC measurements the modified residence time was adjusted to $W/F_{p\text{-}2\text{-}ol} = 450$ gh/mol and the temperatures were $T = 373$ K (top) and $T = 393$ K (bottom).

At $T = 373$ K, the propan-2-ol conversion ran through an induction period of up to 7 h. In the steady state a propan-2-ol conversion of ca. 50% is reached. At this state, on both zeolites LaNaY and HY about the same amouts of propene and diisopropyl ether were formed. At $T = 393$ K, the propene was the main product with a yield of up to 100%. At this temperature, the steady state was reached after 4 h for zeolite LaNaY and after 2 h for zeolite HY. On both zeolites diisopropyl ether was formed with a yield of maximum 2%. It is interesting to note that acetone was also found on both zeolites LaNaY and HY, however, with a yield of maximum 2%.

The gas chromatographic investigations have shown that a modified residence time of $W/F_{p\text{-}2\text{-}ol} = 450$ gh/mol and reaction temperatures of $T = 373$ K and $T = 393$ K are suitable to reach propan-2-ol conversions between 50 and 100%. In addition, the variation of the reaction temperature from $T = 373$ K to $T = 393$ K led to a significant change in the product distribution. At $T = 393$ K, the main route of the propan-2-ol conversion on zeolites LaNaY and HY corresponds to the upper line of Scheme 1. Considering the above-mentioned modified residence time and concentrations of accessible bridging OH groups of 1.1 mmol/g for zeolite LaNaY and of 1.5 mmol/g for zeolite HY, the conversion of 100% observed at $T = 393$ K corresponds to site-time yields of 5.6×10^{-4} and 4.1×10^{-4} s^{-1}, respectively. Investigations carried out using a standard plug flow reactor yielded the same steady-state propan-2-ol conversions as found for conversion in the MAS NMR microreactor. However, the induction period was significantly shorter (ca. 50%) than for the curves shown in Figs. 4 and 5.

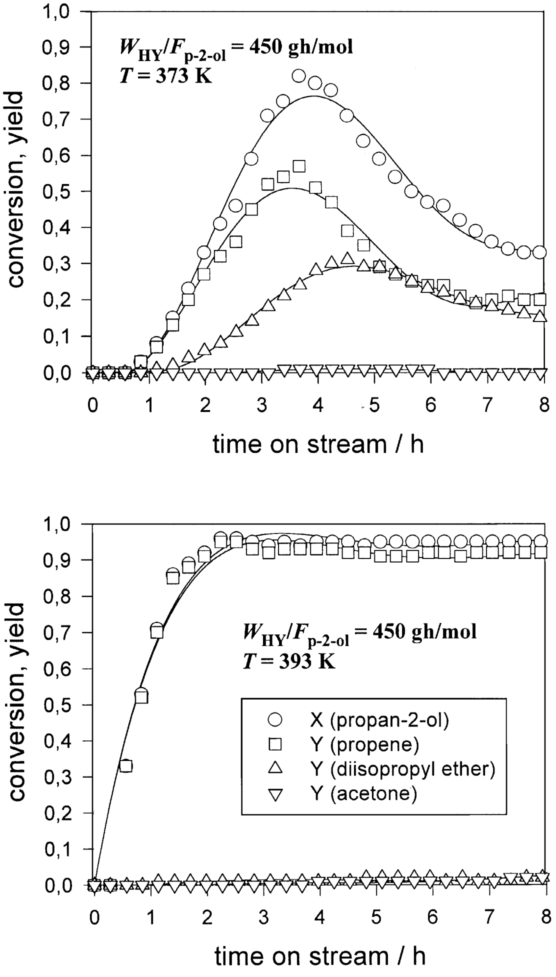


FIG. 5. Conversions of propan-2-ol on zeolite HY and yields of propene, diisopropyl ether, and acetone obtained with a modified residence time of $W_{HY}/F_{p\text{-}2\text{-}ol} = 450$ gh/mol and at reaction temperatures of $T = 373$ K (top) and $T = 393$ K (bottom).

Conversion of Propan-2-ol on Zeolites LaNaY and HY Investigated by in Situ ^{1}H MAS NMR Spectroscopy

Due to the high magnetogyric ratio of proton nuclei, the ^{1}H MAS NMR spectroscopy has the advantage of a high sensitivity. On the other hand, the ^{1}H NMR shifts cover a range of maximum 10 ppm and the homonuclear dipole–dipole interaction causes a strong broadening of signals which are due to rigid compounds (16). Therefore, the ^{1}H MAS NMR spectra recorded after adsorption or conversion of hydrocarbons on zeolites mainly consist of signals caused by mobile compounds which are involved in isotropic reorientations or by groups which rotate around a fixed axis like methyl groups. In addition, the resonance positions undergo an adsorption-induced low-field shift. In Table 1 all ^{1}H MAS NMR shifts of the reactants and products of Scheme 1 are summarized. These values were derived after *ex situ* adsorption of propan-2-ol, diisopropyl ether, and acetone on calcined zeolite HY and by measuring the sealed samples (13). The ^{1}H MAS NMR investigation of propene was carried out by *in situ* adsorption. A continuous flow of propene ($W/F_{\text{propene}} = 900$ gh/mol) was led into the MAS rotor during the ^{1}H MAS NMR measurement (13).

^{1}H MAS NMR spectra of zeolites LaNaY and HY, recorded under a continuous flow of propan-2-ol, are shown in Figs. 6 and 7. Before the loaded carrier gas was led into the MAS rotor, the calcined zeolites were heated for 2 h at temperatures of $T = 373$ K (Fig. 6) and $T = 393$ K (Fig. 7) under purging the samples with dry nitrogen gas. The ^{1}H MAS NMR spectra recorded under these conditions were used to prove the correct preparation of the *in situ* MAS NMR samples (Fig. 8, bottom). A weak rehydration of the sample would lead to a significant decrease in the MAS NMR sidebands and a low-field shift of the ^{1}H MAS NMR signals of the bridging OH groups (compare with (17)). Starting at the reaction time of 0 h, the carrier gas loaded with propan-2-ol was injected into the MAS NMR microreactor.

TABLE 1

^{1}H and ^{13}C NMR Chemical Shifts δ^1H and δ^{13}C (Referenced to TMS) of the Reactant Molecules Adsorbed on Zeolite HY (a) (13) or Measured in $CDCl_3$ (b) and in the Gas Phase (c) (14, 15)

Assignment		$\delta_{^1H}$ (ppm)	$\delta_{^{13}C}$ (ppm)
Propan-2-ol	CH_3	1.2[a]	25.1[b]
	C*H	4.3[a]	63.4[b]
	OH	7.0[a]	
Diisopropyl ether	CH_3	1.4[a]	24.3[b]
	C*H	4.5[a]	69.2[b]
Propene	CH_3	1.9[a]	19.4[c]
	CH_2	5.3[a]	115.2[c]
	C*H	6.3[a]	133.4[c]
Acetone	CH_3	2.6[a]	30.6[b]
	C*O		206.6[b]

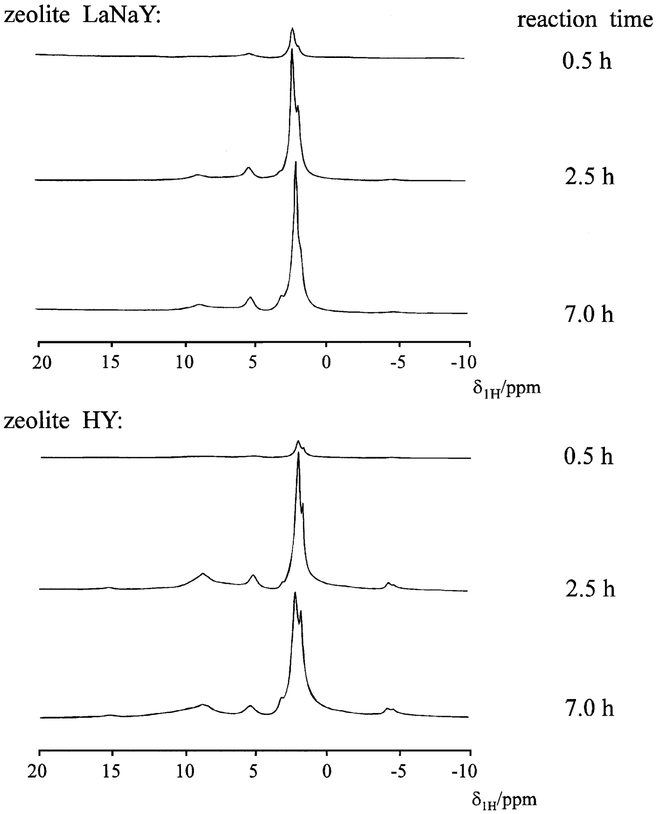


FIG. 6. *In situ* ^{1}H MAS NMR spectra of zeolites LaNaY (top) and HY (bottom) recorded at the temperature of $T = 373$ K under a continuous flow of propan- 2-ol with a modified residence time of $W/F_{\text{p-2-ol}} =$ 450 gh/mol and after reaction times between 0.5 and 7.0 h.

Figure 6 shows the ^{1}H MAS NMR spectra of zeolites LaNaY (top) and HY (bottom) recorded under a flow of propan-2-ol with a modified residence time of $W/F_{\text{p-2-ol}} =$ 450 gh/mol and at the reaction temperature of $T = 373$ K. The spectra consist of narrow signals at 1.2–3.0 ppm due to methyl groups (see Table 1) and of broad signals at about 5 and 7–9 ppm. While the resonance position of the signal at ca. 5 ppm does not depend on the reaction time, the signal at 7–9 ppm shows a low-field shift with increasing reaction times. According to Table 1, the signal at ca. 5 ppm was attributed to CH groups. A contribution of CH_2 groups due to propene could be excluded since this signal should be accompanied by the signal of CH groups at 6.3 ppm. The behavior of the broad signal at 7–9 ppm is characteristic of adsorption of water on the acidic bridging OH groups of zeolite Y (*vide infra*) (17, 18). Considering the signals of methyl groups and their line positions, summarized in Table 1, the shoulder at 1.2 ppm is caused by the CH_3 groups of propan-2-ol, the strong line at 1.6 ppm is caused by CH_3 groups of diisopropyl ether, and the weak line at ca. 3.0 ppm is due to CH_3 groups of acetone. In agreement with the results of the gas chromatographic investigations carried out at $T = 373$ K, the strong signal at 1.6 ppm indicates a

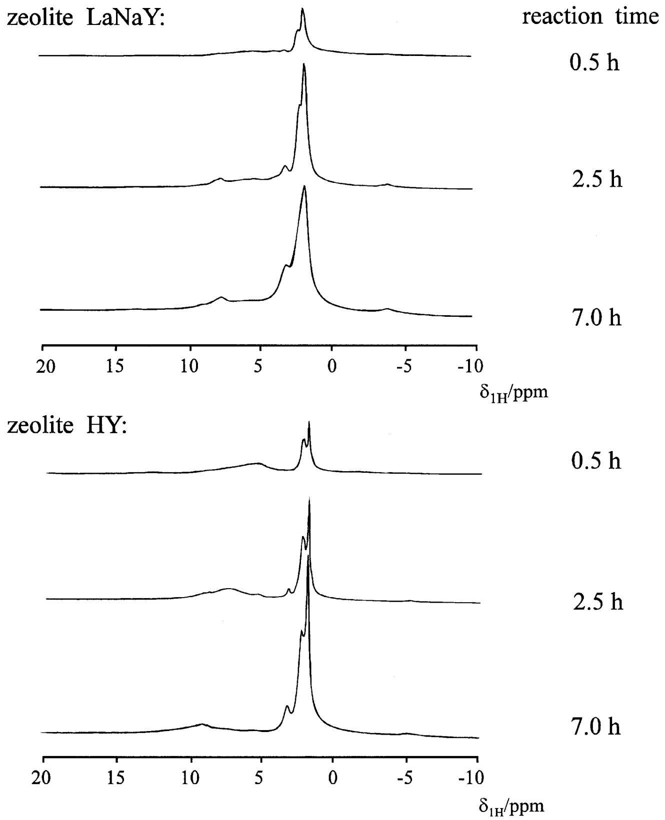


FIG. 7. *In situ* ^{1}H MAS NMR spectra of zeolites LaNaY (top) and HY (bottom) recorded at the temperature of $T = 393$ K under a continuous flow of propan-2-ol with a modified residence time of $W/F_{\text{p-2-ol}} =$ 450 gh/mol and after reaction times between 0.5 and 7.0 h.

high yield of diisopropyl ether and the signal at ca. 5 ppm corresponds to CH groups of these molecules. No signal due to methyl groups of propene was found.

In Fig. 7 the ^{1}H MAS NMR spectra of zeolites LaNaY (top) and HY (bottom) recorded under a flow of propan-2-ol with a modified residence time of $W/F_{\text{p-2-ol}} = 450$ gh/mol and at the reaction temperature of $T = 393$ K are shown. The arguments which were used to assign the ^{1}H MAS NMR signals are the same as before. Comparing the spectra recorded at $T = 373$ K and $T = 393$ K, the signal at 1.6 ppm due to CH_3 groups of diisopropyl ether is strongly decreased at the reaction temperature of $T = 393$ K. This behavior agrees with the results of GC measurements which found only small amounts of diisopropyl ether at the higher reaction temperature. In addition, a strong decrease of the signal at ca. 5 ppm due to CH groups of diisopropyl ether was observed. Again, no signals of propene (1.9, 5.3, and 6.3 ppm) were found in the spectra recorded at $T = 393$ K.

After a reaction time of 0.5 h the ^{1}H MAS NMR spectra were dominated by signals of educt and product molecules. The investigation of the behavior of Brønsted acidic sites, therefore, requires ^{1}H MAS NMR investigation carried out in the first minutes of the propan-2-ol conversion. In Fig. 8 the ^{1}H MAS NMR spectra of zeolite HY recorded at $T = 373$ K before starting the propan-2-ol conversion (bottom) and after a reaction time of 15 min (top) are shown. The spectrum of the pure zeolite HY (bottom) consists of the signal of bridging OH groups at ca. 4 ppm. This signal shows characteristic MAS NMR sidebands which are marked by asterisks. The MAS NMR sideband pattern is caused by the heteronuclear H–Al interaction of the hydroxyl protons with the neighboring framework aluminium atoms (7). MAS NMR sideband patterns occur if the thermal correlation time, τ_c, of hydroxyl protons is large in comparison with the period of the MAS, $\tau_{\text{rot}} = 1/\nu_{\text{rot}}$ (7, 16). Hence, the hydroxyl protons of the bridging OH groups of the unloaded zeolite HY, recorded at $T = 373$ K, are rigidly bonded on the zeolite framework. After the reaction time of 15 min (top) the line at ca. 4 ppm as well as the MAS NMR sideband pattern does not appear (top). The spectrum consists of two narrow signals at 1.6 and ca. 5 ppm which are due to CH_3 and CH groups of diisopropyl ether. In addition, in the low-field range a broad line appears at ca. 8 ppm.

Since the broad ^{1}H MAS NMR signal at ca. 8 ppm has no sideband pattern, it should be caused by mobile hydroxyl protons. According to previous ^{1}H MAS NMR investigations (17, 18) of partially hydrated bridging OH groups, a rapid exchange between hydroxyl protons and hydrogen-bonded water molecules adsorbed on acidic bridging OH groups leads to a low-field shift of the signal at ca. 4 ppm. For coverages of more than one water molecule per SiOHAl group also hydroxonium ions contribute to the low-field signal at 7–9 ppm (19). In the zeolites under study, water molecules are formed by the dehydration of propan-2-ol and are adsorbed on Brønsted acid sites. The spectrum shown in Fig. 8 (top), therefore, indicates a hydration of

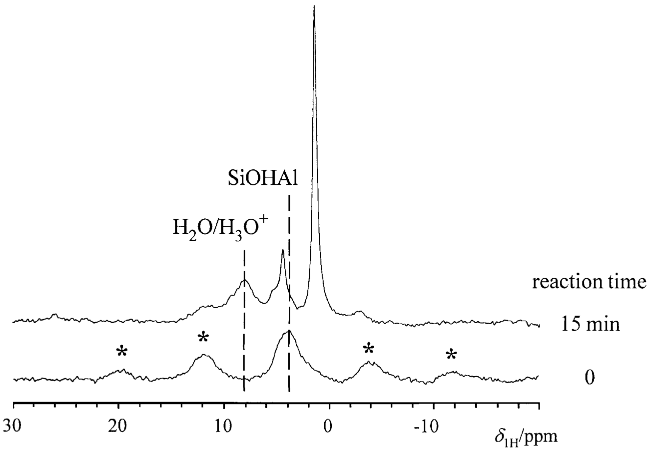


FIG. 8. *In situ* ^{1}H MAS NMR spectra of zeolite HY recorded at the temperature of $T = 373$ K under a flow of dry nitrogen gas (bottom) and after 15 min under a continuous flow of propan-2-ol with a modified residence time of $W/F_{\text{p-2-ol}} = 450$ gh/mol (top).

acidic bridging OH groups in the first part of the induction period. During this hydration process the signal of the bridging OH groups at ca. 4 ppm is strongly decreased. After reaction times of some hours the physisorption and partial protonation of water molecules leads to a broad low-field signal which is shifted to maximum 9 ppm.

Conversion of Propan-2-ol on Zeolites LaNaY and HY Investigated by in Situ ^{13}C MAS NMR Spectroscopy

Figure 9 shows the ^{13}C MAS NMR spectra recorded during propan-2-ol conversion on zeolites LaNaY and HY at a reaction temperature of $T = 373$ K and with a continuous flow of propan-2-ol according to a modified residence times of $W/F_{\text{p-2-ol}} = 450$ gh/mol. The NMR spectra recorded after a reaction time of 0.5 h (top) consist of a signal at 65–70 ppm due to isotopically enriched C(2)-atoms of physisorbed propan-2-ol and/or diisopropyl ether molecules (compare Table 1). After a reaction time of 2.5 h (middle) additional signals between 10 and 50 ppm can be observed. These signals form two groups of lines with peaks at the chemical shifts of 20 and 33 ppm. Since the methyl groups of the educt and product molecules appear at 19–24 ppm (see Table 1), only the high-field lines can be explained by a scrambling of isotopically enriched carbon atoms. The signals at 30–50 ppm indicate the formation of coke precursors. After a reaction time of 7.0 h (bottom) an additional weak signal appears at 220 ppm due to ketones. Considering the results of the gas chromatographic investigations, this weak line should be caused by acetone. Though propene is one of the main reaction products at $T = 373$ K (see results of GC measurements), no ^{13}C MAS NMR signal appears at 130 ppm.

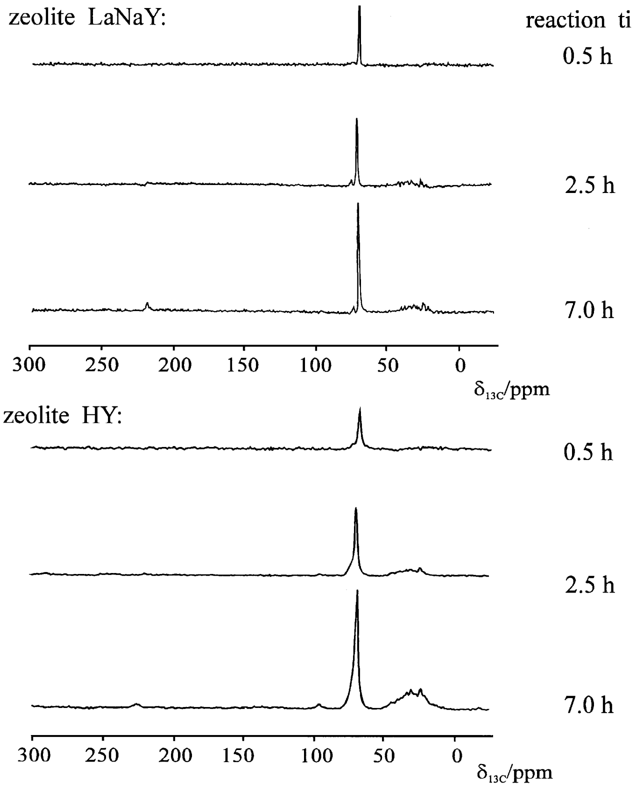


FIG. 9. *In situ* ^{13}C MAS NMR spectra of zeolites LaNaY (top) and HY (bottom) recorded at the temperature of $T = 373$ K under a continuous flow of propan-2-ol with a modified residence time of $W/F_{\text{p-2-ol}} =$ 450 gh/mol and after reaction times between 0.5 and 7.0 h.

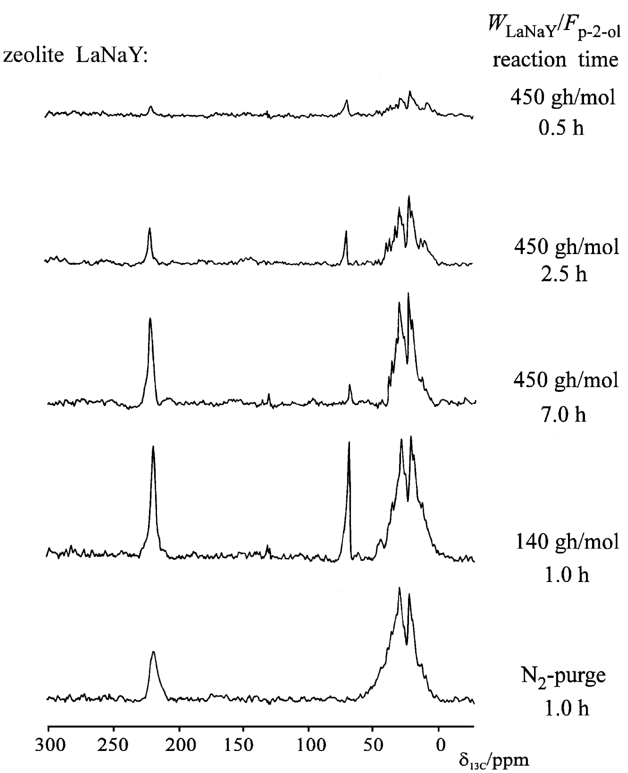


FIG. 10. *In situ* ^{13}C MAS NMR spectra of zeolite LaNaY recorded at the temperature of $T = 393$ K under a continuous flow of propan-2-ol with a modified residence time of $W/F_{\text{p-2-ol}} = 450$ gh/mol and after reaction times between 0.5 and 7.0 h (top three). The two spectra shown on bottom were recorded at $T = 393$ K under an educt flow corresponding to $W/F_{\text{p-2-ol}} =$ 140 gh/mol and after purging the sample with dry nitrogen gas for 1 h.

The ^{13}C MAS NMR spectra recorded during the conversion of propan-2-ol on zeolites LaNaY (Fig. 10) and HY (Fig. 11) at $T = 393$ K show a strong increase of the signals at 10–50 and at 220 ppm caused by coke precursors and acetone, respectively. Again, no signal of the ^{13}C(2)-enriched carbon atoms of propene was observed at 130 ppm. A variation of the modified residence time from 450 to 140 gh/mol led to a strong increase of the signal at 65–70 ppm. This behavior agrees with the above-mentioned assigment of this signal (*vide supra*) since an increase in the educt flow should result in an increase of the signal of physisorbed educt molecules. After purging the sample with dry nitrogen gas at $T = 393$ K (bottom) the signal at 65–70 ppm was completely removed. Hence, all molecules contributing to this line were purged by dry nitrogen gas which indicates

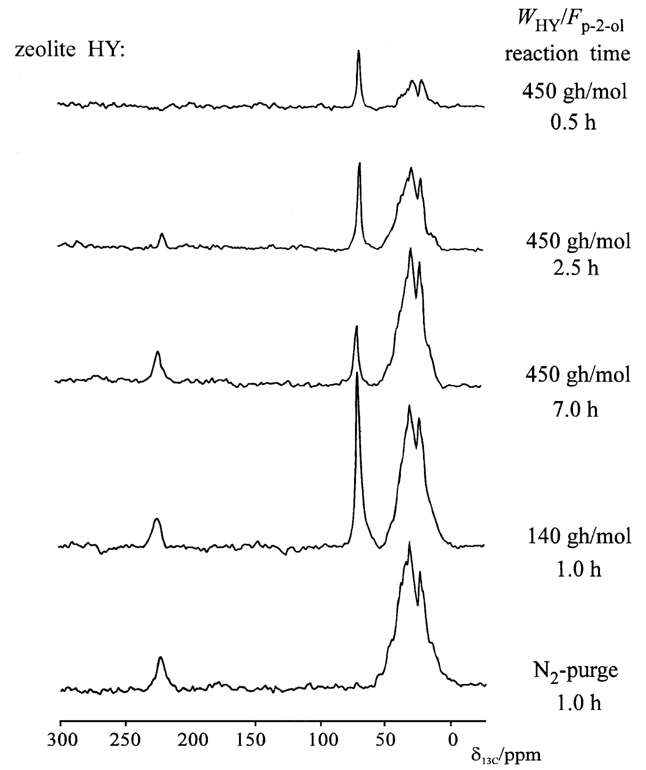


FIG. 11. *In situ* ^{13}C MAS NMR spectra of zeolite HY recorded at the temperature of $T = 393$ K under a continuous flow of propan-2-ol with a modified residence time of $W/F_{p\text{-}2\text{-}ol} = 450$ gh/mol and after reaction times between 0.5 and 7.0 h (top three). The two spectra shown on bottom were recorded at $T = 393$ K under an educt flow corresponding to $W/F_{p\text{-}2\text{-}ol} = 140$ gh/mol and after purging the sample with dry nitrogen gas for 1 h.

their weak bonding on the zeolite framework. In contrast to this behavior, the line at 220 ppm due to acetone molecules was only decreased by a factor of maximum two. This points to a strong adsorption of acetone molecules formed by dehydrogenation of propan-2-ol on zeolite LaNaY and HY which renders its detection by chromatographic methods difficult. After purging the sample with dry nitrogen gas no change in the signals of coke precursors at 10–50 ppm was observed.

Considering the above-mentioned results of the *in situ* MAS NMR investigations under flow condition questions arise concerning (a) the nature of the catalytic compound which is responsible for the formation of acetone, (b) the mechanism of the coke precursor formation, (c) the initial reaction step of the propan-2-ol conversion, and (d) the invisibility of propene. The following experiments and discussions aim on the clarification of these topics.

Nature of the Catalytic Compound Responsible for the Formation of Acetone

The curves at the top of Fig. 12 show the numbers of acetone molecules depicted as a function of the reaction time. These numbers were derived by a comparison of the ^{13}C MAS NMR intensities of the signal at 220 ppm with that of an external intensity standard recorded at the same temperature. As shown in Fig. 12, at both temperatures of $T = 373$ K and $T = 393$ K more acetone is formed on zeolite LaNaY than on zeolite HY. The largest amount of ca. 1.25 mmol acetone molecules per gram of zeolite was found on zeolite LaNaY after propan-2-ol conversion at $T = 393$ K. In zeolites exchanged with multivalent cations, OH groups are formed by dissociation of water molecules in the strong intracrystalline electric fields (mechanism of Hirschler–Plank (20, 21)). This process leads to a formation of acidic bridging OH groups as well as of nonacidic metal OH groups (7) and of different lanthanum oxides and hydroxides. Most of these lanthanum oxides and hydroxides are located in sodalite

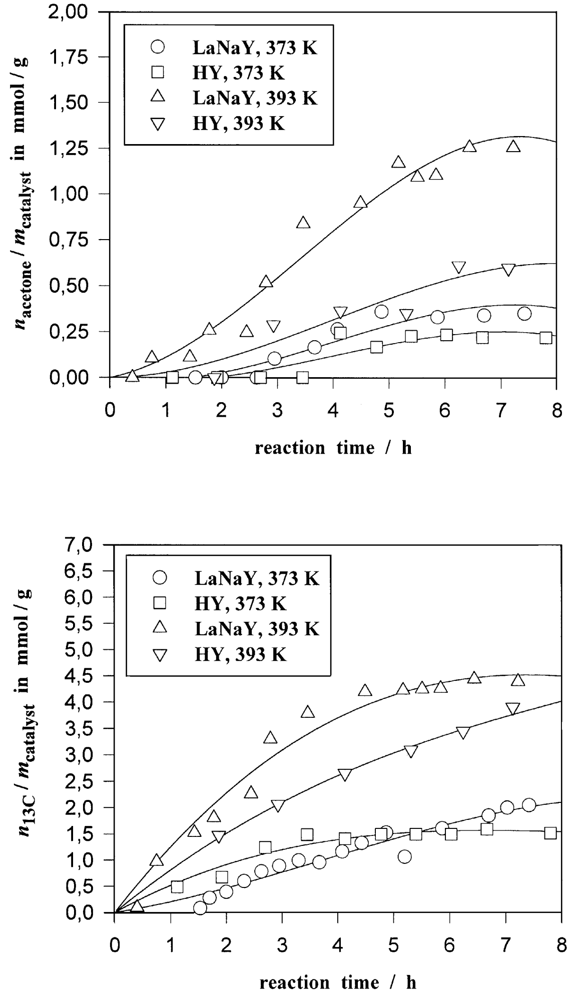


FIG. 12. Numbers of acetone molecules formed by conversion of propan-2-ol on zeolites LaNaY and HY (top) and ^{13}C-atoms of coke precursors (bottom) depicted as a function of the reaction time. These numbers were derived by a comparison of the ^{13}C MAS NMR intensities of the signals at 220 and at 10–50 ppm, respectively, with that of an external intensity standard recorded at the reaction temperature.

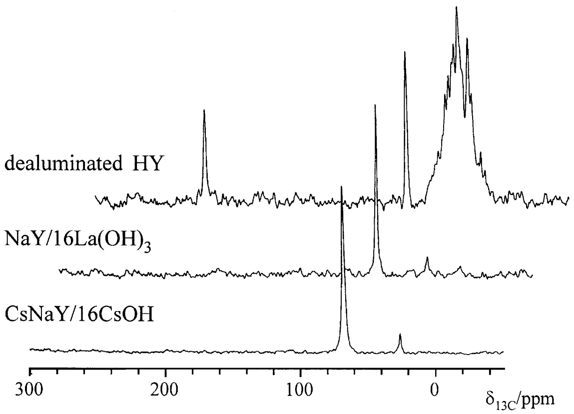


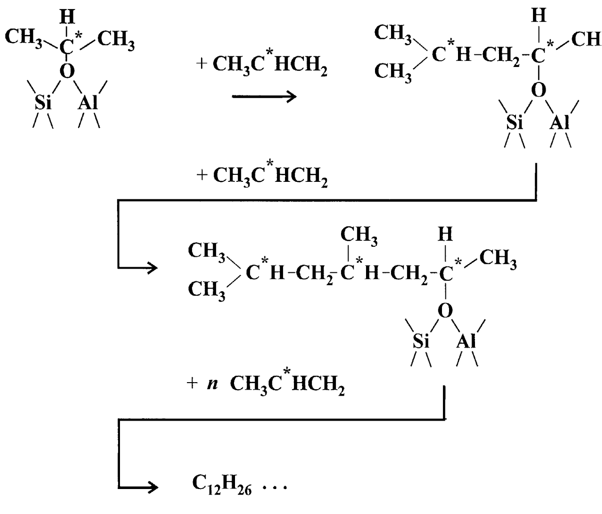
FIG. 13. *In situ* ^{13}C MAS NMR spectra of dealuminated (top) and impregnated (middle and bottom) zeolites Y, recorded at the temperature of $T = 393$ K under a continuous flow of propan-2-ol with a modified residence time of $W/F_{\text{p-2-ol}} = 450$ gh/mol and after a reaction time of 2.5 h.

cages (22, 23). Further *in situ* MAS NMR investigations of the propan-2-ol conversion on modified zeolites Y were carried out which should clarify whether metal oxides and/or hydroxides can act as basic compounds responsible the formation of acetone. One of these modified samples is a Cs-exchanged zeolite NaY (Si/Al = 2.6, cation exchange degree of 73%) impregnated with 16 CsOH per unit cell (CsNaY/16CsOH). The other sample was prepared by an impregnation of the parent zeolite NaY with 16 La(OH)$_3$ per unit cell (NaY/16La(OH)$_3$). The basicity of the zeolite CsNaY/16CsOH was proved by gas chromatographic investigations of the propan-2-ol conversion at $T = 673$ K. In these experiments a preferred formation of acetone was found (compare Scheme 1). In Fig. 13, the ^{13}C MAS NMR spectra of zeolites CsNaY/16CsOH (bottom) and NaY/16La(OH)$_3$ (middle) are shown which were recorded after 2.5 h under a continuous flow of propan-2-ol ($W/F_{\text{p-2-ol}} = 450$ gh/mol) and at the reaction temperature of $T = 393$ K. The spectra consist of a signal at 65 ppm due to the physisorbed educt molecules and/or diisopropyl ether and a weak line at ca. 25 ppm caused by methyl groups of these molecules. The absence of a signal at 220 ppm indicates that the presence of basic compounds does not lead to a formation of acetone at low temperatures. A further experiment was aimed at the influence of extra-framework aluminium species on the formation of acetone. By ^{27}Al MAS NMR spectroscopy about 5% of the aluminium atoms in the calcined and rehydrated zeolites LaNaY and HY were found at extra-framework positions (*vide supra*). In Fig. 13 the ^{13}C MAS NMR spectrum of a dealuminated zeolite HY is shown (top) which was recorded after 2.5 h under a continuous flow of propan-2-ol ($W/F_{\text{p-2-ol}} = 450$ gh/mol) and at the temperature of $T = 393$ K. This sample was prepared by a hydrothermal treatment of the zeolite HY for 2 h at 813 K. In the ^{27}Al MAS NMR spectrum of this sample about 12% of the aluminium atoms were found at extra-framework positions which corresponds to 6.4 Al$^{\text{ex}}$/uc. The ^{13}C MAS NMR spectrum of this sample shows an increase in the signal of physisorbed acetone at 220 ppm by a factor of about two in comparison with the same signal observed in the spectrum of the parent zeolite. Hence, the formation of acetone is promoted by the presence of extra-framework aluminium species.

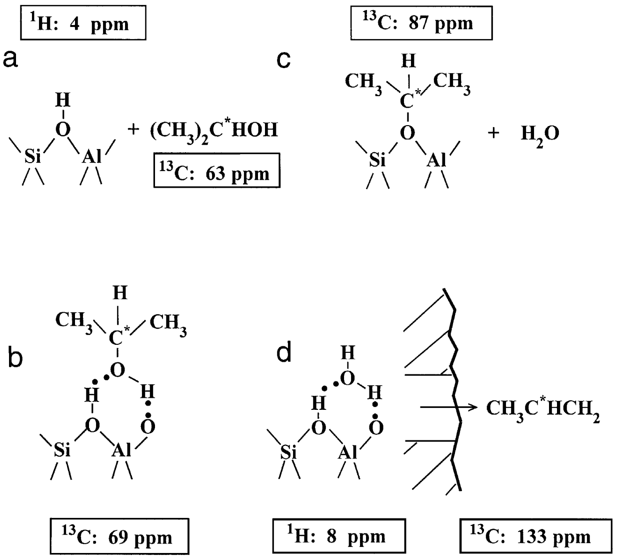
Formation of Coke Precursors

The curves on bottom of Fig. 12 give the qualitative behavior of the coke precursor formation as a function of the reaction time. These curves were derived by an evaluation of the intensities of the ^{13}C MAS NMR signals at chemical shifts between 10 and 50 ppm (CH, CH_2, and CH_3 groups). Considering these curves, the formation of coke precursors is significantly higher at the reaction temperature of $T = 393$ K than at $T = 373$ K. At $T = 393$ K, by gas chromatography (*vide supra*) a yield of propene of up to 100% was found. On acidic zeolites propene has the strong tendency to oligomerize. In a previous work, Haw *et al.* (24) studied the oligomerization of propene by *in situ* ^{13}C MAS NMR spectroscopy of zeolite HY *ex situ* loaded with propene. As a result of these ^{13}C MAS NMR investigations, Haw *et al.* (24) proposed the oligomerization mechanism according to Scheme 2. The addition of propene on alkoxy species formed on Brønsted acid sites leads to the formation of alkanes with different chain lengths (C_6H_{14}, C_9H_{20}, $C_{12}H_{26}$...).

In the present study the propene molecules responsible for the oligomerization are formed by the propan-2-ol dehydration. Since the C(2)-atoms of the propan-2-ol molecules are ^{13}C-enriched, also most of the C(2)-atoms of propene molecules are isotopically enriched (marked by asterisks). Assuming an oligomerization of these propene molecules according to Scheme 2, the strongest ^{13}C MAS



SCHEME 2



SCHEME 3

NMR signals of the coke precursors should be caused by ^{13}C-enriched carbon atoms marked by asterisks. In agreement with Scheme 2, the strong peak at ca. 33 ppm observed in the spectra shown in Figs. 10 and 11 can be explained by carbon atoms marked by asterisks which cover a range of 25 and 35 ppm (14). The second strong peak at the chemical shift of ca. 20 ppm, which is characteristic for methyl groups (see Table 1), indicates an additional scrambling of the isotopically enriched carbon atoms.

Initial Reaction Step of the Propan-2-ol Conversion

Gentry and Rudham (3) proposed a mechanism of the propan-2-ol conversion on acidic zeolites Y (see Scheme 3) which starts with the adsorption of propan-2-ol on bridging OH groups (a) and the formation of hydrogen bonded adsorbate complexes (b). As a result of dehydration of the hydrogen bonded complex (a) an isopropoxy species (c) is formed. In scheme 3 the characteristic ^{1}H and ^{13}C MAS NMR shifts of the species (a), (b), and (c) are given. The resonance position of a isopropoxy species at 87 ppm was determined by *in situ* ^{13}C MAS NMR studies of propene adsorbed on calcined zeolite HY (24). In the above-mentioned *in situ* ^{13}C MAS NMR spectra recorded under a continuous flow of ^{13}C(2)-enriched propan-2-ol (Figs. 10 and 11) no signal was observed at ca. 87 ppm which indicates that no or only a negligible amount of isopropoxy species was formed. In addition, no ^{1}H MAS NMR signal of gaseous water molecules at ca. 0.3 ppm (25) was found. On the other hand, the resonance position of the complex (b) in Scheme 3 agrees well with that of the experimentally observed signals at 65–70 ppm. Therefore, the *in situ* MAS NMR experiments support the existence of hydrogen bonded complexes (b). The *in situ* ^{1}H MAS NMR spectra shown in Figs. 6, 7, and 8 indicated that the formation of complex (b) is followed by a splitting off and desorption of the propene molecule, while the reaction water remains on the bridging OH group (see complex (d) in Scheme 3). The physisorbed reaction water causes the broad low-field line at ca. 8 ppm.

Invisibility of Propene

After desorption from the surface sites and before leaving the MAS NMR microreactor the propene molecules stay in the pore volume of ca. 130 mm^3 and the free reactor volume of ca. 30 mm^3. Considering the flow rate of the carrier gas of 6 ml/min, the mean residence time of the propene molecules in the free reactor volume amounts to maximum 300 ms. Since for a complete propan-2-ol conversion maximum 0.02 μmol propene molecules are in the free reactor volume, this concentration is too small for a detection by NMR spectroscopy. The propene molecules staying in the zeolite pores are adsorbed on free or hydrated bridging OH groups and execute jumps between these sites. Since the residence time of the propene molecules in the adsorbed state (^{13}C MAS NMR shift of 87 ppm (Scheme 3c) or 69 ppm (Scheme 3b)) is large in comparison with the time of jumps, these molecules also yield no signal at 130 ppm. The above-mentioned explanation for the absence of propene signals in the *in situ* MAS NMR experiments under flow conditions is supported by the spectra shown in Fig. 14. The *ex situ* ^{13}C MAS NMR spectra (middle and bottom) were recorded at room temperature after adsorption of propene molecules on partially rehydrated zeolites HY using a vacuum line. The ^{13}C MAS NMR signals of coke precursors at 10–50 ppm indicate that the acidity of partially rehydrated zeolites HY is sufficient to oligomerize propene. In Fig. 14 (top), the *in situ* ^{13}C MAS NMR spectrum of a partially

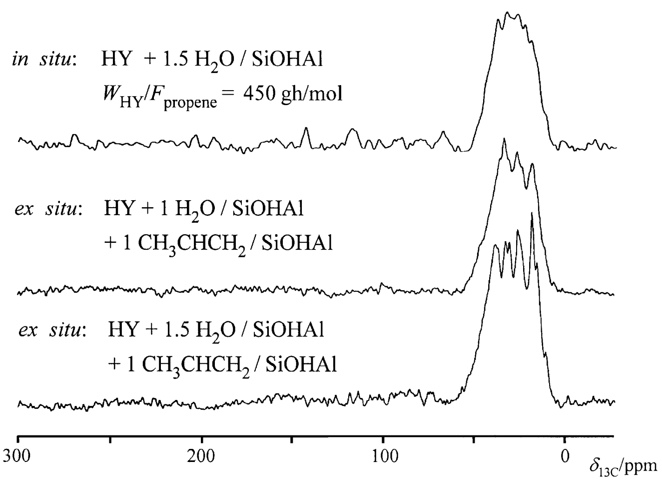


FIG. 14. ^{13}C MAS NMR spectra of partially rehydrated zeolite HY loaded with propene under *in situ* (top) and *ex situ* (middle and bottom) conditions, recorded at room temperature. During the preparation and the measurement, the samples were kept at room temperature.

rehydrated zeolite HY recorded at room temperature and under a continuous flow of propene is shown. Again, no signal of propene molecules appears at 130 ppm. However, the strong signals of coke precursors at 10–50 ppm indicate an oligomerization of propene. Hence, also if propene is directly injected into the MAS NMR microreactor, it cannot be detected by NMR spectroscopy.

CONCLUSIONS

In the present study of propan-2-ol conversion on acidic zeolites Y a new experimental technique was applied which allows *in situ* MAS NMR spectroscopy under continuous-flow conditions. Using a microreactor with a cylindrical catalyst bed, NMR spectroscopic and on-line gas chromatographic measurements under same reaction conditions were carried out. Via gas chromatography, propan-2-ol conversions between 50% and about 100% at reaction temperatures of $T = 373$ K and $T = 393$ K were observed, respectively. In these experiments the formation of propene, diisopropyl ether, and small amounts of acetone was found.

By *in situ* ^{1}H and ^{13}C MAS NMR spectroscopy the initial step of the reaction, the formation of by-products and coke precursors were studied. The initial step of the propan-2-ol conversion was found to be the physisorption of propan-2-ol on bridging OH groups. Neither in the induction period nor in the steady-state ^{13}C MAS NMR signals of isopropoxy species were observed. The results of ^{1}H MAS NMR spectroscopy indicated a hydration of the bridging OH groups in the first part of the induction period of the propan-2-ol conversion. The corresponding water molecules were formed by dehydration of the propan-2-ol. The strong low-field shift which was observed for the ^{1}H MAS NMR signal of the hydrated bridging OH groups is due to a partial protonation of adsorbed water molecules.

At the reaction temperature of $T = 393$ K, a strong ^{13}C MAS NMR signal at 220 ppm indicated the formation of acetone. Propan-2-ol conversion on a partially dealuminated zeolite HY proved that the formation of this by-product is promoted by the presence of extra-framework aluminium species. ^{13}C MAS NMR signals at chemical shifts of 10–50 ppm are due to coke precursors which were formed by an oligomerization of propene. Experiments carried out under a flow of propene proved that the oligomerization of these molecules occurs also on partially hydrated Bronsted acid sites.

The experiments described in the present paper have demonstrated that *in situ* MAS NMR spectroscopy under continuous-flow conditions is an interesting method for investigating the formation of compounds which have a long residence time on surface sites or in the pores of solid catalysts.

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