Journal of Catalysis **202,** 421–426 (2001)
doi:10.1006/jcat.2001.3302, available online at http://www.idealibrary.com on IDEAL®

# $^{1}H$ MAS NMR Studies of Molecules Adsorbed on Activated Zeolites

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Received April 17, 2001; revised May 31, 2001; accepted May 31, 2001

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**The aim of this paper is to study the interaction of organic molecules with zeolites of different pores sizes (NaY, dealuminated ZSM-5, and H-ZSM-5) pretreated under conditions which led to various catalytically active sites. The behavior of the adsorbed molecules is investigated by means of high-resolution $^{1}H$ MAS NMR spectroscopy. The measurements demonstrate that complex adsorption interactions occur between adsorbed 2-butene or acetone molecules and the OH groups in the zeolites which also have a strong influence on the activity of the catalytic sites. During the adsorption of the molecules on differently activated zeolites the $^{1}H$ MAS NMR spectra show changes which can be attributed to catalytic conversions, where Brønsted and Lewis acidic sites of the zeolite catalysts are involved. A proton transfer from the bridging AlOHSi groups of the zeolite framework to the adsorbed 2-butene molecules can be clearly detected. The results for the system acetone/dealuminated ZSM-5 and acetone/H-ZSM-5 point, in particular, to the role of Lewis acid centers which may be formed in the zeolites during the applied pretreatment procedure.**

*Key Words:* **zeolites; catalysis; $^{1}H$ MAS NMR spectroscopy; acidic centers.**

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## INTRODUCTION

Zeolite materials play an important role as catalysts in many chemical processes. Therefore, there exists a considerable interest in studying the properties of Brønsted (1–5) and Lewis (6, 7) acid sites in zeolite catalysts and the interaction of adsorbed molecules with them. In a recent paper (8) it was shown that spontaneously organic radical cations are formed upon adsorption of electron-rich organic materials on zeolites. Furthermore, various spectroscopic and theoretical investigations (9–11) alternatively suggest that charged species act as intermediates in zeolite-catalyzed reactions. In many papers (4, 12) pyridine is used as probe molecule to estimate acid strengths by means of infrared spectroscopy, temperature-programmed desorption, or thermogravimetric analysis. Different NMR techniques such as *in situ* $^{13}C$ and $^{15}N$ NMR measurements (13, 14) and $^{15}N$–$^{27}Al$ double resonance studies (15) were applied to monitor the behavior of adsorbed molecules to characterize the Brønsted and Lewis acidity of the inner surface of the zeolites.

In previous studies (16, 17) we applied the $^{1}H$ MAS NMR technique to study molecules sorbed in zeolites with respect to their dynamic behavior. The present paper concentrates on $^{1}H$ MAS NMR measurements of molecules sorbed in activated zeolites (H-ZSM-5, dealuminated ZSM-5, and NaY) to investigate hydrogen transfer processes. In these studies well-defined conditions are achieved by using samples pretreated in that way that allows not only a dehydration to occur but also an activation process. Only those changes in the spectra which occur during the first phase after the adsorption of organic molecules on the activated zeolites are of interest. This can be realized if the samples are kept in vacuum and in liquid nitrogen until the samples are placed in the spectrometer.

To characterize the properties of the activated zeolites two kinds of organic molecules were used. Acetone is known as a typical C–H acidic species which undergoes addition reactions in the presence of basic centers or Lewis acid sites, whereas 2-butene molecules possess the typical properties of unsaturated hydrocarbon molecules which are able to polymerize if acidic centers are present.

## EXPERIMENTAL

*Sample characterization.* Two commercial zeolites were applied in the studies. The faujasite-type zeolite NaY with a Si/Al ratio of 2.5 was provided by UOP-UC Corp (Lot/5237-35). The dealuminated ZSM-5 zeolite was obtained from a Na-ZSM-5 material supplied by the Chemiewerk Bad Köstritz GmbH with a Si/Al ratio of 15. The dealumination of the material was done using a mixture of 25 ml hexafluorosilicic acid (Aldrich), 175 ml water, and 20 g zeolite which was intensively stirred at room temperature for 30 min. After this procedure the zeolite was washed, filtrated, and dried. The dealuminated Na-ZSM-5 specimen thus obtained was ion-exchanged three times with 0.5 M ammonium nitrate solution (Fluka) at 363 K to yield $NH_4$-ZSM-5. The latter was dried overnight at 373 K and then converted into its hydrogen form by calcination at 673 K for 24 h.

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The H-ZSM-5 zeolite was synthesized according to the following procedure: A solution of 5.11 g tetrapropylammonium bromide (Aldrich) in 9.92 g distilled water was added to 10.62 g of colloidal $SiO_2$ (Ludox-AS 40, DuPont) and stirred for 15 min at room temperature. As an aluminum source, 0.16 g aluminum triisopropylate (Aldrich) was dissolved in 24.75 ml of an aqueous solution of ammonia (25 wt%) and then added to the gel, which was vigorously stirred for 5 min. The fluid gel was heated at 453 K in a Teflon-lined stainless-steel autoclave for 7 days under autogenous pressure. After this procedure the reaction product was washed, filtrated, and dried at 373 K. To remove the organic template the zeolite was calcined at 873 K for 12 h. The H-ZSM-5 obtained has a Si/Al ratio of about 90.

*Sample preparation.* The zeolites were filled in a glass tube of 4.2 mm inner diameter (filling height of 8 mm) and then dehydrated at 673 K under permanent vacuum for 48 h. Then the samples were treated in an oxygen stream at 823 K for 2 h to remove residues of those organic molecules which were used as template in the synthesis procedure. After this procedure another vacuum treatment (at 823 K for 2 h) followed to remove traces of oxygen and other gases and to activate the samples. The samples thus obtained were loaded in vacuum with a defined amount of organic molecules (statistically about 2 molecules per supercage) and rapidly sealed while cooling in liquid nitrogen.

*NMR measurements.* The $^1$H MAS NMR spectra were recorded at a $^1$H Larmor frequency of 300.13 MHz. A rotation frequency of 4.5 kHz was used for each measurement. Typical experimental conditions were a 90° pulse width of 4.9 $\mu$s, a repetition time of 10 s, and the accumulation of 16 scans to obtain, on one hand, a sufficiently good signal-to-noise ratio in the spectra and to ensure, on the other hand, a fast measurement.

## RESULTS

To understand the changes in the $^1$H MAS NMR spectra upon adsorption at first the spectra of the activated and unloaded zeolites are characterized as shown in Figs. 1a, 2a, and 3a in comparison to the same samples obtained after the desorption of the organic compounds used for the study of the surface interactions. The latter changes in the spectra (Figs. 1b,c, 2b,c, and 3b,c) will be discussed in the following context.

It is well known (18–25) that various types of OH groups having typical ranges of chemical shifts can be detected. The $^1$H NMR spectrum of the activated zeolite NaY (Fig. 1a) consists of signals at 1.4 ppm due to the terminal silanol groups, a signal of lower intensity at 2.1 ppm due to the nonframework AlOH groups, a signal at about 4.4 ppm belonging to bridging AlOHSi groups in the large cavities, and a line at 4.7 ppm assigned to bridging AlOHSi groups of the small cavities. The lines for the bridging AlOHSi groups (at 4.4 and 4.7 ppm) cannot be detected in the $^1$H MAS NMR spectrum if the zeolite NaY is only dehydrated at 673 K. In this case the spectrum shows only peaks in the region between 1.4 and 2.1 ppm, which are typical lines for the terminal silanol groups. Therefore, the existence of the peaks previously described is related to the activation procedure leading to acidic centers in the zeolites (22–25). Because of the activation procedure used it can be excluded that the peak at 4.7 ppm belongs to bulk water molecules. In

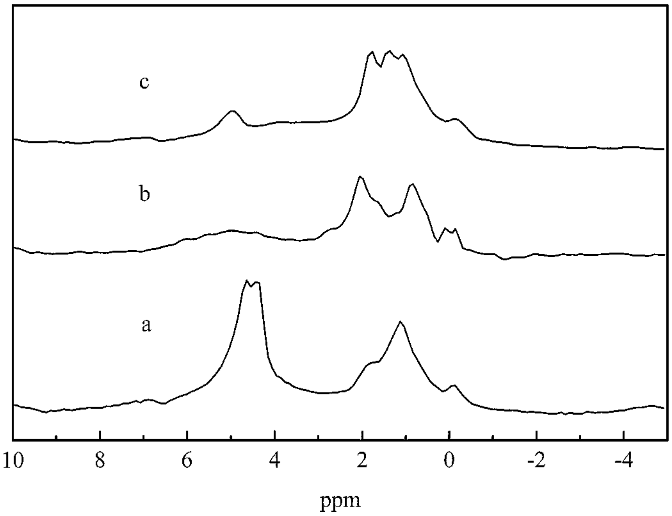

**FIG. 1.** $^1$H MAS NMR spectra of the zeolite NaY: (a) activated under vacuum at a temperature of 550°C, (b) after desorption of 2-butene, and (c) after desorption of acetone. All spectra were recorded at room temperature.

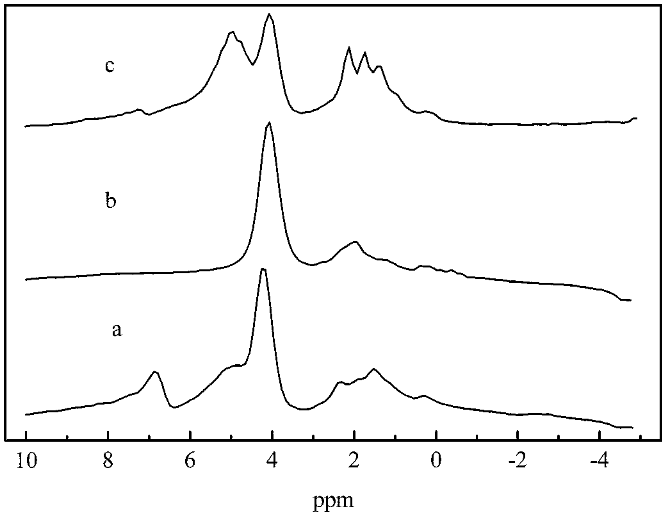

**FIG. 2.** $^1$H MAS NMR spectra of the dealuminated ZSM-5: (a) activated under vacuum at a temperature of 550°C, (b) after desorption of 2-butene, and (c) after desorption of acetone. All spectra were recorded at room temperature.

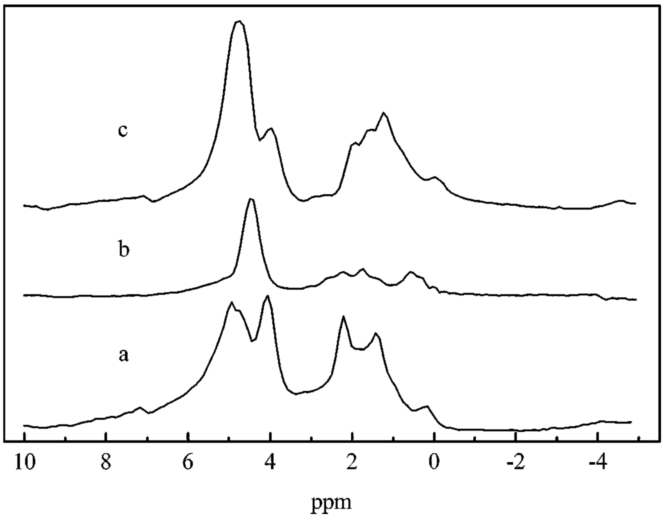

**FIG. 3.** $^1$H MAS NMR spectra of the zeolite H-ZSM-5: (a) activated under vacuum at a temperature of 550°C, (b) after desorption of 2-butene, and (c) after desorption of acetone. All spectra were recorded at room temperature.

comparison to zeolite NaY the spectra of the dealuminated ZSM-5 (Fig. 2a) and H-ZSM-5 (Fig. 3a) show peaks with higher intensity at 4.3 and 4.9 ppm caused by free-bridging AlOHSi groups in the 10-ring channel (narrow component) and perturbed bridging AlOHSi groups (broad component) (22–25). Furthermore, in these spectra weak signals can be detected at about 7.0–7.5 ppm, which are due to the residual ammonium ions $NH_4^+$ used in the zeolite synthesis or a second kind of bridging AlOHSi groups as described by Brunner (22, 24).

$^1$H MAS NMR spectra for the system 2-butene/zeolite NaY are shown in Fig. 4. During the first 20 min after removing the samples from the liquid nitrogen a drastic change occurs in the line intensities of the various types of OH groups. The typical resonance lines for physically adsorbed 2-butene, i.e., especially the intense lines for the methyl protons at about 1.8 ppm in the adsorbed state, cannot be detected at the beginning of the measurements. The peak at 4.9 ppm belonging to bridging AlOHSi groups broadens with increasing time and finally is no longer visible. Instead a peak at about 3.5 ppm appears now and increases slightly in intensity. After 45 min no more changes can be monitored in the spectra. If the adsorbed species are removed by treatment in vacuum at 400°C for 48 h (compare Fig. 1b), the $^1$H NMR line at 3.5 ppm disappears but other lines become visible at 2.3 ppm and 1.2 ppm which are typical for non-framework AlOH and terminal SiOH groups, respectively. In comparison with the spectra of the activated zeolites before adsorption (see Fig. 1a), however, the intensity of the terminal silanol groups is reduced while the line of the non-framework aluminium shows an increased intensity. The NMR lines for bridging AlOHSi groups are nearly absent.

If 2-butene was adsorbed on activated dealuminated ZSM-5 a similar behavior was observed as previously described for the zeolite NaY. But after the desorption of the organic species one can see that the peak at 1.4 ppm assigned to terminal silanol gruops nearly disappeared and the intensity of the peak at about 2.4 ppm assigned to non-framework AlOH groups decreased (Fig. 2b). The number of bridging AlOHSi groups (at about 4 ppm) is hardly reduced and the bridging AlOHSi groups of the small cavities (at about 5 ppm) totally disappeared.

For 2-butene on activated H-ZSM-5 (Fig. 5) again no or only weak intensities are seen in the region of the terminal silanol groups and the nonframework aluminum OH groups at the beginning of the measurements. Contrary to the zeolite NaY and the dealuminated ZSM-5 the peak at about 5 ppm assigned to perturbed bridging AlOHSi groups shows a weaker lost in intensity during the measurements. Additionally, after 30 min a broad line at about 7 ppm emerges and lines at about 3.5 ppm becomes visible. After removing the organic species (Fig. 3b) a similar spectrum is obtained where reduced intensities are seen for the terminal silanol and the nonframework aluminum hydroxyl groups. In comparison to the dealuminated ZSM-5 the free-bridging AlOHSi groups are nearly unchanged and the perturbed bridging AlOHSi groups are totally reduced.

Similar measurements were made where acetone molecules were adsorbed. In analogy to the results with 2-butene a decrease of the peak intensity at 4.9 ppm is observed during the adsorption for all used zeolites. For the zeolite NaY simultaneously the intensity of the peak at about 2 ppm increases as seen in Fig. 6. Furthermore, a line at 4.1 ppm

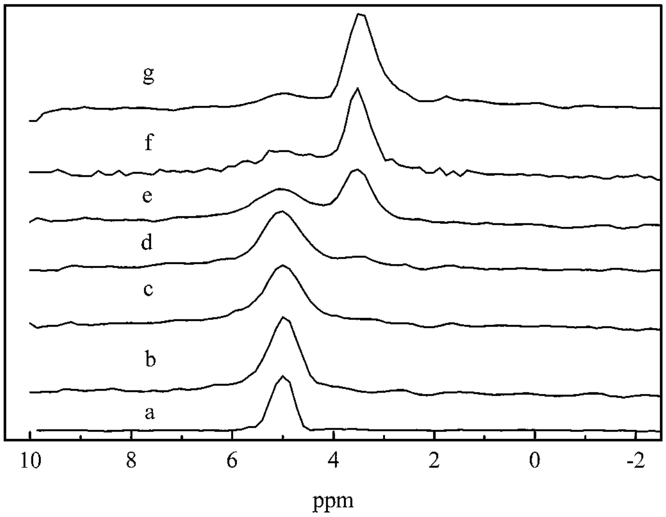

**FIG. 4.** $^1$H MAS NMR spectra of activated zeolite NaY recorded during the adsorption of 2-butene: (a) after removing from liquid nitrogen; and (b–g) after 5, 10, 15, 20, 25, and 40 min. Similar spectra were obtained when the system 2-butene/dealuminated ZSM-5 was measured.

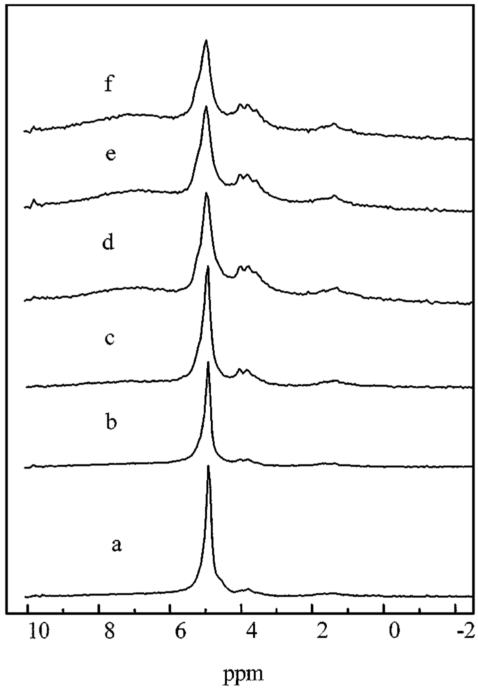

**FIG. 5.** $^1$H MAS NMR spectra of activated H-ZSM-5 zeolite recorded during the adsorption of 2-butene: (a) after removing from liquid nitrogen; and (b–f) after 5, 10, 15, 40, 50, 60, and 90 min.

can be observed after 5 min of waiting time which shows a small increase in intensity with time. After 50 min no more changes can be detected in the spectrum. First it should be noted that the intense NMR line for the system acetone/NaY at about 2 ppm has been partially attributed to the methyl groups of acetone. This can be easily demonstrated if completely deuterated acetone is adsorbed (not shown here). In this case at the beginning of the experiment the line at about 2 ppm is absent but similarly, as observed before for 2-butenes on zeolite NaY, a line of weak intensity at about 2.4 ppm appears simultaneously with the decrease of intensity at 4.9 ppm.

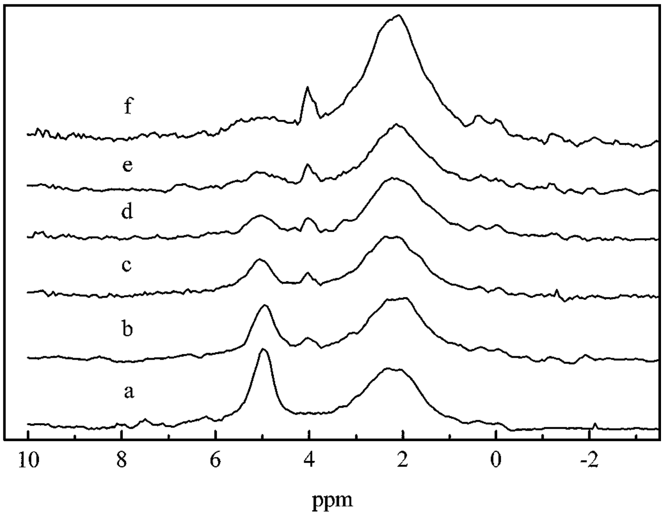

**FIG. 6.** $^1$H MAS NMR spectra of activated zeolite NaY recorded during the adsorption of acetone: (a) after removing from liquid nitrogen; and (b–f) after 5, 15, 30, 45, min and after 24 h.

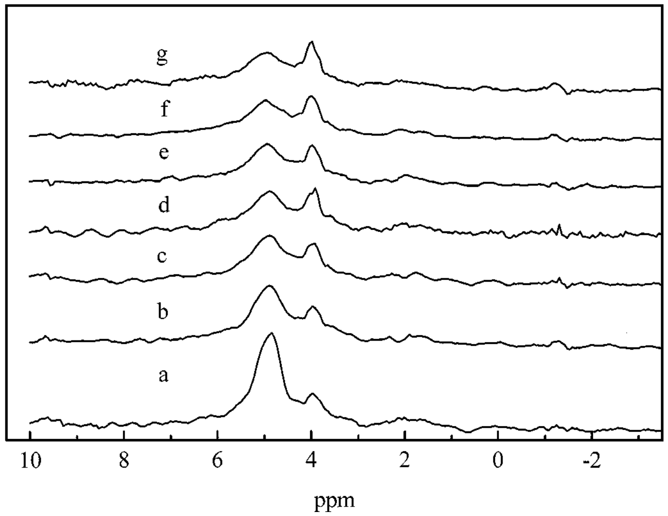

**FIG. 7.** $^1$H MAS NMR spectra of activated dealuminated ZSM-5 zeolite recorded during the adsorption of acetone: (a) after removing from liquid nitrogen; and (b–g) after 5, 15, 30, 40, 50, and 70 min.

In Fig. 7 the $^1$H MAS NMR spectra of acetone adsorbed on dealuminated ZSM-5 are shown. Again a line broadening for the peak at 4.9 ppm is seen. In contrast to the zeolite NaY no peak at 2.4 ppm appears at the beginning of the experiment, which can be attributed to adsorbed acetone. The line at 4.1 ppm is always detectable but the spectrum recorded after 70 min shows a broadening of this peak in contrast to the zeolite NaY. Compared to the results found for dealuminated ZSM-5, the spectra of acetone adsorbed on H-ZSM-5 reveal only small changes. Two effects are visible again: first, the peak at 4.1 ppm shows a loss in intensity and second the narrow line at 4.9 ppm shows a line broadening after 10 min. Furthermore, the peaks at 1.4 and 2.5 ppm possess only a weak intensity. After 40 min no more changes could be found in the $^1$H MAS NMR spectra.

The spectra obtained after removing the adsorbed acetone in a desorption process are quite different (compare Figs. 1c, 2c, and 3c). The $^1$H MAS NMR spectrum of the zeolite NaY (Fig. 1c) consists of three lines between 0.9 and 1.9 ppm which have a somewhat increased intensity compared to the unloaded zeolite and a strongly reduced peak at about 4.9 ppm. On the other hand in the spectra of the dealuminated ZSM-5 and the H-ZSM-5 (Figs. 2c and 3c) three peaks are detected between 1.2 and 2.2 ppm which possess roughly the same intensity as found for the unloaded material. A further difference to the NaY can be seen in the spectrum between 4 and 5 ppm where two peaks are detected having a reduced intensity assigned to the free

AlOHSi and an increased intensity of the perturbed bridging AlOHSi groups, respectively.

## DISCUSSION

To explain the results we concentrate at first on the behavior of 2-butene molecules in zeolite NaY and dealuminated ZSM zeolites. Again we have to point out that the resonance lines for the 2-butene are not visible from the beginning of the experiment. One reason for this situation is obviously the fast reaction of the molecules to form higher hydrocarbons. Skeletal isomerization of the butenes is not the dominant process here, because the reaction is related to the transfer of hydrogen atoms from the bridging AlOHSi groups, as reflected by the decrease of the proton peaks of bridging AlOHSi groups with the chemical shifts between 4 and 5 ppm and by the absence of these lines after desorption. Some broadening of the lines between 4 and 5 ppm was also observed during the measurements. Broadening is not excluded because it is also related to a dynamic effect (proton exchange between structural OH groups and the reacting molecules with a rate comparable with the chemical shift differences between the different proton types; see below).

The remarkable fact is that also during this interval of measurements the typical lines for the terminal silanol groups between 1.2 and 2.2 ppm are no longer visible but instead a line at about 3.5 ppm increasingly appears beginning almost at the same time when the bridging AlOHSi groups vanished. However, the lines of these silanol SiOH groups appear again with nearly the same intensity at their typical positions (1.2 and 2.2 ppm) when the molecular species were desorbed. This finding points to a reversible part of this process which seems to be related to a certain adsorption process. A precise analysis of the intensity ratios, however, is not yet possible and, hence, a quantitative control is not yet available. The line at 3.5 ppm does not appear if the reaction is still running. What can be monitored by a still decreasing intensity of the bridging AlOHSi groups? In addition to the terminal SiOH groups, nonreacted butene molecules must still be present; the absence of “sharp” $^1$H NMR lines near 3.5 ppm and adsorbed 2-butene indicates a strong interaction of the remaining nonreacted butene molecules and/or the reaction products with these terminal SiOH groups without any further chemical reaction. It cannot be excluded that these terminal SiOH groups are also involved in an exchange process with the adsorbed species and the acidic bridging AlOHSi groups between 4 and 5 ppm leading to a line broadening. This process, however, is superimposed on the transfer of those bridging AlOHSi protons to the reaction products. The situation for the system 2-butene/H-ZSM-5 shows some similarities to this behavior. Again, the reversible behavior of the terminal SiOH groups is visible, i.e., a peak appears at about 3.5 ppm in the case of adsorption and after desorption of the adsorbed butene molecules and the reaction products of the terminal SiOH group lines between 1.2 and 2.2 ppm are detectable. However, it is interesting that the intensity of the bridging AlOHSi groups in the region between 4 to 5 ppm remains about the same in that time interval when the line at 3.5 ppm is not yet present. This can be explained by the fact that the reaction of the molecules is not related to a proton transfer to the reaction products. A typical feature in this case is a strong adsorption interaction of the molecules with the terminal SiOH groups and/or a proton exchange among OH groups of the zeolite, the protons in the adsorbed butenes, and the reaction products. These experimental findings probably indicate the action of Lewis acid sites in contrast to the previously described results for NaY and dealuminated ZSM-5 zeolites.

The results obtained for the different zeolite/acetone systems show a higher complexity of interactions. For the acetone/NaY zeolite system the experimental observations are similar to those found for the 2-butenes. The permanent decrease of the bridging AlOHSi peak at 4.9 ppm is typical for the incorporation of these protons in the reaction products. The behavior of this signal on the adsorption of acetone suggests that these protons are acidic. The absence of the line for the terminal silanol groups at the beginning of the reaction and the appearance of the peak at 2.4 ppm indicates analogous interactions and/or exchange processes during the reaction as already previously discussed. However, in contrast to the situation found for the system 2-butene/NaY, the interaction of the reaction products with the terminal SiOH groups does not give rise to a strong chemical shift of the latter ones. The experiments suggest that the extent of proton transfer from the silanol groups to the adsorbed ketone is important in establishing the probability that it will condense with a second ketone molecule. It is well known (26) that Brønsted acid sites are responsible for this reaction.

Obviously other processes take place if dealuminated ZSM-5 and the H-ZSM-5 zeolites are used. As previously described only weak intensities are detected in the region of terminal SiOH and nonframework AlOH groups, respectively, apart from small changes in their relative intensities, which point to (reversible) exchange processes of the protons between these species. Acetone is known as a typical C–H-acidic compound that can undergo chemical reactions in the presence of Lewis acid sites where the increased carbonyl activity makes it possible to get enol products. The fact that most of the changes in the $^1$H MAS NMR spectra between 1.6 and 3.5 ppm belonging to nonframework AlOH and between 3.6 and 4.5 ppm belonging to the bridging AlOHSi groups can be detected seems to support the role of Lewis acid sites during the activation procedure. The centers thus formed contribute to further reactions with the adsorbed molecules. The influence of the pretreatment procedure is even stronger in the case of the dealuminated ZSM-5.

The results reveal that two kinds of the catalytically active centers of the zeolite may be of importance, depending on the properties of the adsorbed molecules. It is suggested (27, 28) that the formation of Lewis acid sites occurs in a dehydroxylation process at temperatures above 675 K, leading to $[AlO]^+$ species in the anionic zeolite lattice. However, the temperature for the formation of the so-called true Lewis sites depends on the structure of the zeolites. Another hint for the formation of Lewis centers is available from electron spin resonance measurements (29, 30) where NO molecules, which are known to undergo strong interactions with Lewis acid centers, were used as probe molecules.

## CONCLUSIONS

During the adsorption of 2-butene and acetone molecules on differently activated zeolites the $^1$H MAS NMR spectra show changes which can be attributed both to strong adsorption interactions and to catalytic conversions, where Brønsted and Lewis acidic sites of the zeolite catalysts are involved. It is clearly seen that complex adsorption interactions occur between the adsorbed organic molecules and the OH groups in the zeolites, which also have a strong influence on the activity of the catalytic sites. The results for the acetone/dealuminated ZSM-5 and acetone/H-ZSM-5 systems allow the indirect detection of the influence of Lewis acid centers which are formed in the zeolites during the pretreatment procedure.

## ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 294. The authors thank Dr. B. Staudte and J. Roland for helpful discussions.

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