

Formation of acetone enol on acidic zeolite ZSM-5 evidenced by H/D exchange

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H/D exchange observed between bridging hydroxyl groups in acidic zeolite ZSM-5 and adsorbed acetone (acetone- d_6 /H-ZSM-5 and ^{13}C -2-acetone/D-ZSM-5) indicates a concerted catalytic function of Brønsted acid sites and neighbouring framework oxygen atoms acting as Lewis base sites.

Recently, increasing efforts have been devoted to investigating the adsorption of acetone on acidic zeolites with the aim of understanding the Brønsted acidic properties of zeolites and the conversion of acetone to hydrocarbons.^{1–7} Aldol condensation and secondary reactions of acetone on zeolite H-ZSM-5 were extensively studied by ^{13}C NMR spectroscopy.^{6,7} However, less knowledge is available about the chemical state of acetone adsorbed on acidic solids, which is even a matter of dispute.^{4,8,9} Here we reveal more detailed information by multi-nuclear MAS NMR and TRAPDOR NMR spectroscopy of acetone- d_6 and ^{13}C -2-acetone adsorbed on zeolites H- and D-ZSM-5 ($n_{\text{Si}}/n_{\text{Al}} = 21.5$). The observed H/D exchange between Brønsted acid sites and adsorbate molecules indicates the formation of an enol *via* a concerted action of bridging hydroxyl protons and neighbouring framework oxygen atoms in zeolite H-ZSM-5.

As found by FTIR spectroscopy, acetone is adsorbed at bridging hydroxyl groups (SiOHAl) in zeolite H-ZSM-5 *via* a hydrogen bond.^{2,10} Theoretical calculations gave an increase of the O–H bond length of the SiOHAl groups from 0.0971 to 0.1038 nm and a decrease of the Si–O–Al angle from 130.8 to 127.0° after addition of one acetone molecule to a SiOHAl cluster model.¹¹

Upon adsorption of 0.25 molecules of ^{13}C -2-acetone per SiOHAl group in zeolite H-ZSM-5,¹² a sharp ^{13}C MAS NMR signal occurs at 223 ppm due to the carbonyl atoms of adsorbed acetone molecules (not shown).⁶ A featured sideband pattern hints at the formation of rigid complexes of acetone molecules adsorbed at SiOHAl groups.^{4,7} A signal at 29 ppm is due to the methyl groups of the acetone molecules. The absence of any other resonance signal excluded conversions to other products.

Fig. 1a shows the ^1H MAS NMR spectrum of zeolite H-ZSM-5. Upon adsorption of acetone (0.25 molecules per SiOHAl group), a signal at 16.4 ppm was observed, which is ascribed to bridging hydroxyl protons involved in a strong hydrogen bond with the adsorbed acetone molecules (Fig. 1b). The observed resonance shift to 16.4 ppm is in good agreement with earlier studies¹³ and with the quantum chemically derived value of 16.1 ppm.¹⁴ The ^1H MAS NMR signal at 4.0 ppm is due to the undisturbed SiOHAl groups (Fig. 1a). The strong signal at 2.4 ppm in Fig. 1b is caused by protons of methyl groups of adsorbed acetone molecules. As shown by a simulation of the spectrum in Fig. 1b, the intensity of the signal at 16.4 ppm is about 1/6 of the methyl signal which corresponds to one hydroxyl proton interacting with the carbonyl group of one acetone molecule.

$^1\text{H}\{^{27}\text{Al}\}$ TRAPDOR NMR spectroscopy^{15,16} is a suitable technique to study the local environment of resonating nuclei in solids. ^{27}Al irradiation during a ^1H spin-echo experiment leads to a dephasing out of the transversal magnetization of hydroxyl protons coupled to aluminium species.^{16,17} As shown in Fig. 1d, ^{27}Al irradiation during the first ^1H spin-echo delay causes a

disappearance of the signal at 16.4 ppm. In the difference spectrum (Fig. 1e), two signals at 16.4 and 4.0 ppm were observed. The former signal is due to hydrogen-bonded bridging hydroxyl protons while the latter is caused by undisturbed SiOHAl groups. The results further support the assignment of the signal at 16.4 ppm to hydrogen-bonded bridging hydroxyl protons in complexes with adsorbed acetone molecules.

The chemical state of acetone adsorbed on acidic zeolite ZSM-5 was clarified by investigating the H/D exchange within adsorbate complexes. Fig. 2 shows the ^1H MAS NMR spectra of zeolite H-ZSM-5 before (a) and after (b) adsorption of acetone- d_6 at room temperature. As mentioned above, the signal at 16.4 ppm is due to hydrogen-bonded bridging hydroxyl protons, while the signal at 4.0 ppm is caused by undisturbed SiOHAl groups in H-ZSM-5 (Fig. 2a, b). In addition, a sharp signal occurs at 2.4 ppm. This signal, which is due to protons of methyl groups in adsorbed acetone molecules, hints at H/D exchange between SiOHAl groups and adsorbed acetone- d_6 molecules.

As shown in Figs. 2c and d, the H/D exchange between the methyl groups of adsorbed acetone molecules and Brønsted acid sites in zeolite H-ZSM-5 occurred also upon adsorption of ^{13}C -2-acetone on a deuterated catalyst (D,H-ZSM-5¹⁸) at room temperature. In this case, the number of hydrogen-bonded bridging hydroxyl protons occurring at 16.4 ppm (0.14 mmol g^{-1}) was found to be higher than that of non-deuterated SiOHAl groups in the unloaded zeolite D,H-ZSM-5 (0.08 mmol g^{-1}). The ^{13}C MAS NMR spectrum of ^{13}C -2-acetone adsorbed on zeolite D,H-ZSM-5 (Fig. 2e) consists of the carbonyl signal at 223 ppm with a featured sideband pattern and a methyl signal at 29 ppm. No significant conversion of acetone can be identified.

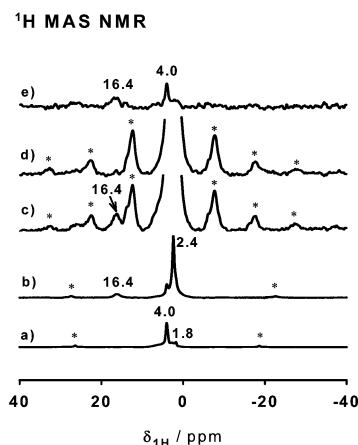


Fig. 1 ^1H MAS NMR spectra of zeolite H-ZSM-5 before (a) and after (b) adsorption of 0.25 molecules ^{13}C -2-acetone per SiOHAl group. The spectrum of H-ZSM-5 loaded with 0.50 molecules ^{13}C -2-acetone per SiOHAl group (c) was obtained with a ^1H spin-echo ($\pi/2-\tau-\pi-\tau$) sequence, a pulse delay of $\tau = 250 \mu\text{s}$ and a repetition time of 10 s. The $^1\text{H}\{^{27}\text{Al}\}$ TRAPDOR NMR experiment in (d) was performed with aluminium irradiation ($\nu_{\text{rf}} = 32 \text{ kHz}$) during the first delay. In (e), the difference spectrum of (c) and (d) is shown. Spinning sidebands are indicated by '*'.

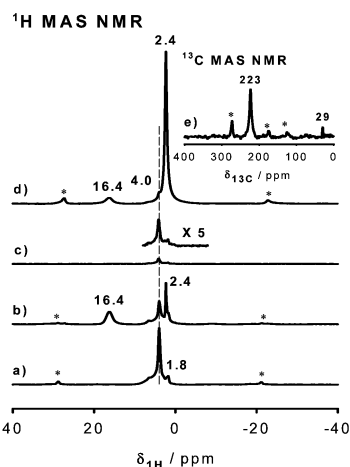
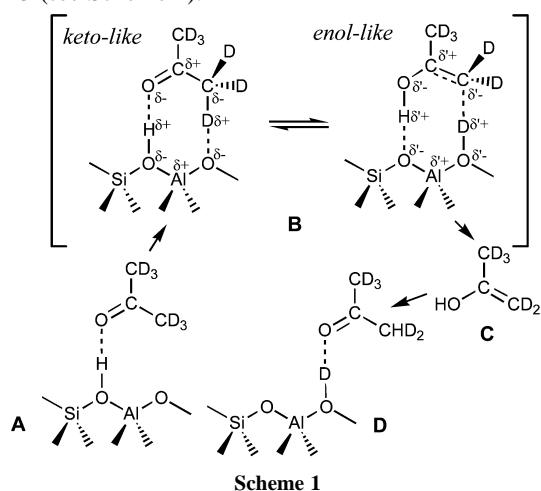


Fig. 2 ^1H MAS NMR spectra of zeolite H-ZSM-5 before (a) and after (b) adsorption of 0.33 mmol acetone- d_6 per gram of zeolite. In (c) and (d), the spectra of zeolite D,H-ZSM-5 before and after loading, respectively, with 0.34 mmol acetone- ^{13}C -2 per gram zeolite are shown. Inset (e) is the ^{13}C MAS NMR spectrum of the sample in (d). Quantitative data were obtained by comparison with an external intensity standard (zeolite 35H,Na-Y). Spinning sidebands are indicated by '*'.

Generally, the H/D exchange of a ketone can be utilized to clarify the formation and presence of enol or enolate.¹⁹ Because of the low number of acetone molecules adsorbed on zeolite H-ZSM-5 in the present study (≤ 0.50 acetone per SiOHAl), an H/D exchange involving more than one acetone molecule at one SiOHAl group can be excluded. Therefore, a monomolecular mechanism must be assumed as discussed below.

Depending on the type of the species compensating the negative framework charges,²⁰ zeolites exhibit acidic or basic character, while both acid sites (SiOHAl) and base sites (framework oxygen) are always present. Van Santen and Kramer pointed out the importance of Lewis base sites (framework oxygen) in the 'reactivity theory of zeolitic Brønsted acid sites' in zeolites.²¹ Theoretical studies of the keto-enol isomerization of acetaldehyde on H-ZSM-5 also shows the involvement of framework oxygen atoms in the vicinity of the bridging hydroxyl protons.²² Assuming that Brønsted acid sites and Lewis base sites are close together, a concerted function of these sites is expected. Such a concerted function of surface sites is suggested to cause the experimentally observed H/D exchange between adsorbed acetone molecules and bridging hydroxyl groups in zeolites H- and D-ZSM-5 (see Scheme 1).



Scheme 1

As shown in Scheme 1(A), the acetone molecule is adsorbed at a bridging hydroxyl group *via* a hydrogen bond. This hydrogen bond induces a partial charge transfer from the framework to the carbonyl group and causes some changes of the local structure¹¹ making the framework oxygen more

basic.²⁰ Hence, the protons of the methyl group near the framework oxygen can be bonded by the framework oxygen to form the carbanion-like transition state B in Scheme 1. A subsequent or simultaneous transfer of the hydrogen-bonded bridging hydroxyl proton produces the acetone enol C. Finally, the unstable acetone enol is converted to an acetone molecule D. *Via* this reaction mechanism, H/D exchange is realized without resulting in other reaction products. On the other hand, aldol reactions are a family of nucleophilic additions of enolate ions (carbanion) to carbonyl groups.^{23,24} The formation of the carbanion-like transition state B in Scheme 1 is expected to be responsible for the observed aldol condensation in this strongly acidic solid. The above-described reaction mechanism is supported by Cleland and Kreevoy, who mentioned that the formation of a low-barrier hydrogen bond can supply 10 to 20 kcal mol⁻¹ and thus facilitate difficult reactions such as enolization of carboxylate groups.²⁵

Enols and enolates have been recognized as reactive intermediates in various reactions of ketones and related compounds and all aspects of carbanion chemistry.²³ As shown in Scheme 1, a concerted function of Brønsted acid sites and Lewis base sites in zeolites may facilitate the formation of acetone enol. This suggests a strong potential of acidic zeolites in the manufacture of fine chemicals utilizing this type of reaction.

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