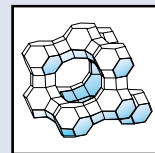


H/D Exchange of Acetone-d₆ Adsorbed on Zeolite H-ZSM-5

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Summary

H-D exchange was observed between acidic ZSM-5 zeolite and adsorbed acetone molecules at room temperature. A proposed concerted function of Brønsted acid site (bridging hydroxyl group) and neighboring Lewis base site (framework oxygen) facilitated the formation of acetone enol and subsequent H-D exchange.

Introduction

- Recently, much effort was devoted to the study of adsorption of acetone on zeolite with an aim to understand the property of Brønsted acid sites and conversions of acetone on zeolites.
- Aldol condensation and secondary reaction of acetone on zeolites have been extensively studied by ¹³C MAS NMR spectroscopy [1,2].
- As demonstrated by FT IR spectroscopy, loading of H-ZSM-5 with acetone led to an adsorption on Brønsted acid sites via a hydrogen bonding [3,4].
- Theoretical calculation showed an increase of the O-H bond length of the bridging hydroxyls group and a decrease of Si-O-Al angle after addition of an acetone molecule to a cluster model of zeolite H-ZSM-5 [5].

Results

1) ¹H{²⁷Al}TRAPDOR NMR experiments

- In the ¹H MAS NMR spectrum (Fig. 1a), the resonances at 4.0 and 1.8 ppm are due to the bridging hydroxyl protons and silanol groups at defect sites.
- After adsorption of acetone, a signal at 16.4 ppm was observed, which is ascribed in the literature to hydrogen-bonded bridging hydroxyl groups [7] suggesting a strong interaction with the adsorbed acetone molecules. The strong signal at 2.4 ppm is caused by protons of methyl group of the adsorbed acetone molecules.
- The ¹H{²⁷Al}TRAPDOR NMR experiment [8,9] showed the signal at 16.4 ppm is due to protons in the neighborhood of aluminum species. This result further supported the assignment of the signal at 16.4 ppm to the bridging hydroxyl protons disturbed by the adsorbed acetone molecules.

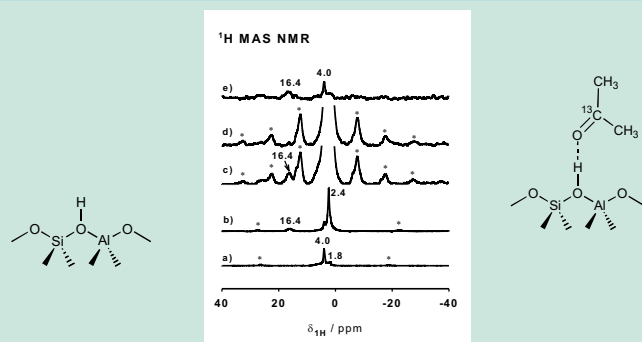


Fig. 1 ¹H MAS NMR spectra of H-ZSM-5 (a), H-ZSM-5 loaded with 0.25 mmol C-2-acetone molecules per acid site (b). In the ¹H{²⁷Al}TRAPDOR NMR experiment of H-ZSM-5 loaded with 0.51 mmol C-2-acetone molecules per acid site. A spinning frequency of 4 KHz was applied. The ¹H spin-echo was performed with a $\pi/2$ - τ - π pulse sequence, a spin-echo delay τ of 250 μ s, and a pulse delay of 10 s (e). An aluminum irradiation (32 KHz) was applied in the first delay (d). The difference spectrum (e) was obtained by a subtraction of (c) and (d). Spinning sidebands are indicated by *

2) H-D exchange between acetone and H-ZSM-5

- In Fig. 2b, the signal at 16.4 ppm is due to hydrogen-bonded protons, the signal at 4.0 ppm is caused by the undisturbed bridging hydroxyl protons in H-ZSM-5.
- In addition, a sharp signal occurred at 2.4 ppm due to protons of methyl groups in adsorbed acetone molecules indicating an occurrence of the H-D exchange.
- In the case of adsorption of ¹³C-2-acetone on D-ZSM-5, the signal at 16.4 ppm further confirmed the H-D exchange between acetone and acidic ZSM-5 (Fig. 2d).
- The ¹³C MAS NMR spectrum (Fig. 2e) consists of the carbonyl resonance at 223 ppm and the methyl resonance at 29 ppm. No conversion has been observed.

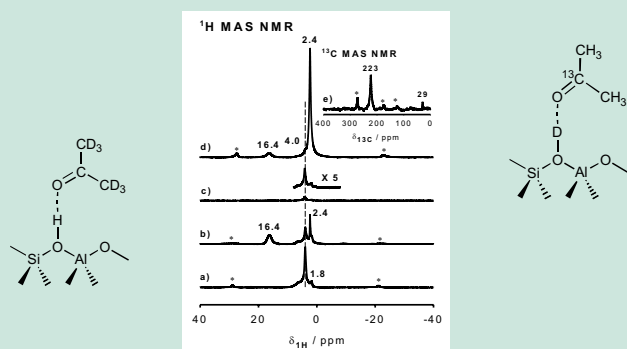


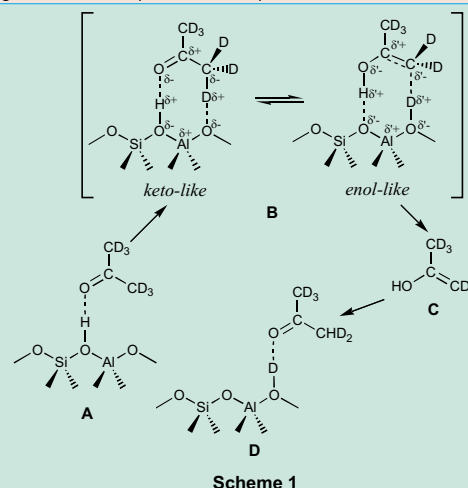
Fig. 2 The ¹H MAS NMR spectra of H-ZSM-5 (a), H-ZSM-5 loaded with 0.27 mmol acetone-d₆ per gram (b), D-H-ZSM-5 (c) and D-H-ZSM-5 loaded with 0.25 mmol ¹³C-2-acetone per gram (d) were recorded with a rotation frequency of 10 KHz and a pulse delay of 10 s. The insert is the ¹³C MAS NMR spectrum of the same sample in Fig. 2d. Quantitative data were obtained by a comparison of the signal intensity with a standard 35H₂Na-Y. Spinning sidebands are indicated by **.

Experimental section

- Zeolite ZSM-5 was synthesized as described in reference [6]. H-ZSM-5 ($n_s/n_{Al} = 21.5$) was dehydrated at 673 K for 12 h in vacuum, then sealed in a glass tube and cooled to room temperature. Quantitative amounts of acetone were introduced into H-ZSM-5 samples having a thickness below 0.25 cm.
- D-H-ZSM-5 was prepared by exposing for 9 times the dehydrated H-ZSM-5 sample to a D₂O vapor at ca. 10 mbar for 30 min at 503 K and dehydrated again.

Concerted function of Brønsted acid site and Lewis base site

- Generally, the H-D exchange of a ketone can be utilized to clarify the formation and presence of an enol or enolate [10].
- Because of the low number of acetone molecules adsorbed on zeolite H-ZSM-5 in the present study (< 0.5 molecule per acid site), an H-D exchange evolving more than one acetone molecule at one bridging hydroxyl proton can be excluded. Therefore, a single molecule mechanism must be assumed.
- The incorporation of aluminium atoms at T positions into a zeolite framework induces negative charges, which are balanced by extra-framework cations or bridging hydroxyl protons (SiOHAl). Depending on the charge compensating species, zeolites show an acidic or a basic character while both the acid sites (SiOHAl groups) and the base sites (framework oxygen) are present [11].
- Van Santen and Kramer pointed out the importance of Lewis base sites (framework oxygen) in the reactivity theory of zeolitic Brønsted acid sites [12].
- If base sites and acid sites are close in space, a concerted catalytic function of these sites is possible. Based on this point, a mechanism is suggested to interpret the experimentally observed H-D exchange between acetone-d₆ molecules adsorbed on zeolite H-ZSM-5 and bridging hydroxyl protons occurring in this material (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 some change of the local structure, which makes the framework oxygen more basic [4]. Hence, the protons of methyl group near framework oxygen can be bonded by the oxygen to form a certain carbanion-like transition state B in Scheme 1.
- A subsequent loss of the hydrogen-bonded hydroxyl proton produces the acetone enol C. The acetone enol is converted to an acetone molecule D.
- This mechanism for the H-D exchange 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, facilitating difficult enolization of carboxylate groups [13].

Conclusion

A H-D exchange between acetone and acidic ZSM-5 was observed, which could be facilitated by a concerted function of Brønsted acid site and Lewis base site. The assumed keto-like and enol-like transition states led to a formation of acetone enol.

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