

In situ FTIR studies of extraframework aluminum bound methoxy species in H-ZSM-5 zeolites

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Abstract

In situ infrared spectra of dimethyl ether (or methanol) adsorbed on three H-ZSM-5 zeolites are reported which are different in both lattice and extraframework aluminium contents. A number of dissociatively adsorbed dimethyl ether species associated respectively with the Brønsted acid sites, the external silanol groups and extraframework aluminium species at differing temperatures are identified. In particular, dimethyl ether (or methanol) reacts with non-acidic hydroxyl species associated with extraframework aluminium to form a third type of methoxy species, i.e. an extraframework aluminum bound methoxy group.

Keywords: In situ FTIR; Dimethyl ether adsorption; Extraframework aluminium bound methoxy species

1. Introduction

The study of the interaction of dimethyl ether with H-ZSM-5 zeolite has obvious importance in the elucidation of complex chemistry associated with methanol conversion to gasoline. Dimethyl ether, which is the simple dehydration product of methanol [1], has been chosen for this adsorption study. There have been few spectroscopic studies of dimethyl ether adsorption in H-ZSM-5 under reaction conditions. Forester and Howe [2] have reported infrared evidence for the formation of protonated dimethyl ether species and corresponding methoxy species over H-ZSM-5 samples. However three types of methoxy groups associated respectively with the external silanol groups, the Brønsted acid sites and extraframework alu-

minium species have not been revealed. Kubelkova et al. [3] have reported the presence of a third type methoxy group in AlHY and AlHZSM-5 which they identified as $AlnOCH_3$ formed by the reaction of methanol with extraframework Al^{3+} cations in the zeolite channels. Meanwhile several studies have reported the importance of these extraframework aluminium species as a factor affecting the catalytic behavior of the catalysts in methanol to gasoline process [4,5]. Nevertheless in none of the previous spectroscopic studies were spectra recorded under reaction conditions for H-ZSM-5 sample containing extraframework aluminium, either synthesized, or as a result of catalyst treatment. Accordingly an in situ FTIR study of the interaction of dimethyl ether (or methanol) with three H-ZSM-5 zeolites (one (Si:Al = 12)

contains negligible extraframework aluminium; the second (Si:Al = 27) contains certain contents of the extraframework aluminium (2.1 per unit cell); the third (Si:Al = 16) contains a large proportion of extraframework aluminium (3.75 per unit cell)) was undertaken to reveal the formation of a third type of methoxy species associated with extraframework aluminium.

2. Experimental

Three ZSM-5 zeolites differing in the contents of both lattice and extraframework aluminium as given in Table 1 were used in this study. A ZSM-5 zeolite with Si:Al = 12 (named as HZ-12) was provided by Toyosada in the sodium-exchanged form and subsequently proton exchanged. The other two ZSM-5 zeolites respectively with Si:Al = 27 (named as HZ-27) and Si:Al = 16 (named as HZ-16) were purchased from Conteka in hydrogen form. These zeolites were fully characterized by X-ray diffraction, ^{27}Al MAS NMR spectroscopy and chemical analysis. Dimethyl ether cylinder (99% in purity) was purchased from Aldrich. All reagents used were spectroscopic or AR grade.

The in situ infrared experiments were carried out in an infrared cell similar to that described by Katzer et al. [6]. The samples were pressed into a self-supported wafer (ca. 10 mg/cm²) and activated in the IR cell by heating in flowing dry nitrogen (ca. 330 ml/min) at 673 K for 4 h. Dimethyl ether (1.0 ml) was injected into the cell by a syringe at various temperatures under a nitrogen flow.

Infrared spectra were recorded on a Bomem

MB-100 FTIR spectrometer operating at 2 cm⁻¹ resolution and typically 250 interferograms were averaged. Reference spectra of these freshly activated ZSM-5 samples were recorded at each reaction temperature prior to introducing dimethyl ether (or methanol). For clearly exhibiting the presence of a third methoxy species associated with extraframework aluminium, the sample HZ-16 has been chosen and a pulse of methanol (0.5 μl) instead of dimethyl ether was used.

3. Results and discussion

3.1. Characterization

X-ray diffraction patterns (not shown) confirmed these samples were highly crystalline H-ZSM-5 zeolites. As listed in Table 1, the bulk silicon-to-aluminium ratios by chemical analysis gave 12, 27 and 16 respectively, depending on different sources. On the ^{27}Al MAS NMR spectra (not shown) the peak area of tetrahedral ^{27}Al MAS NMR signal at 54 ppm was used to calculate the framework aluminium content of each sample. By subtraction of the framework aluminium content from the bulk aluminium content, the extraframework aluminium content was obtained as given in Table 1. It can be seen therein that the sample of HZ-12 contains considerably high framework aluminium (7.6 per unit cell) while the extraframework aluminium content is negligible. The sample of HZ-27 does contain 2.1 extraframework aluminium per unit cell, while the framework aluminium content is fairly low (1.4 per unit cell). The third sample

Table 1
Characterization of H-ZSM-5 samples

Sample	Bulk Si:Al	Bulk aluminium (per unit cell)	Framework aluminium (per unit cell)	Extraframework aluminium (per unit cell)	Source
HZ-12	12	7.68	7.6	~ 0	Toyosoda Japan
HZ-16	16	6.0	2.25	3.75	Conteka Swed
HZ-27	27	3.5	1.4	2.1	Conteka Swed

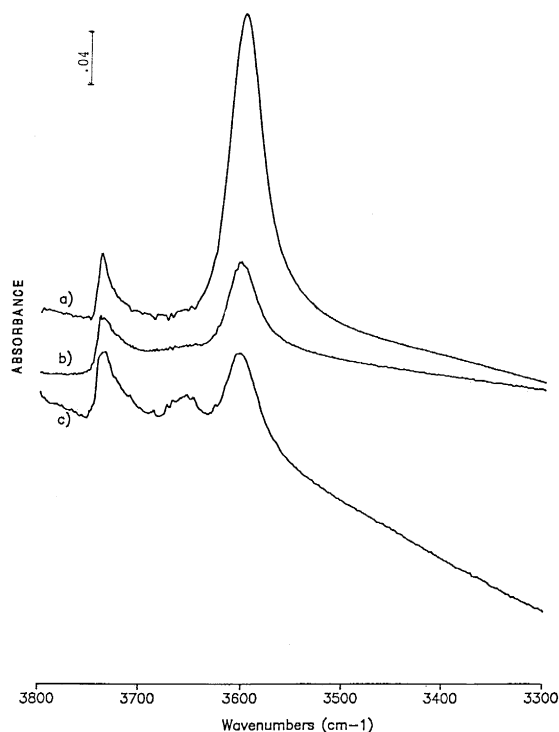


Fig. 1. Infrared absorbance spectra in the OH stretching vibration region recorded from freshly activated H-ZSM-5 samples prior to dimethyl ether (or methanol) adsorption at 523 K onto (a) HZ-12 sample (Si:Al = 12); (b) HZ-27 sample (Si:Al = 27); (c) HZ-16 sample (Si:Al = 16).

of HZ-16 contains a large proportion of extraframework aluminium (3.75 per unit cell) and certain contents of framework aluminium (2.25 per unit cell).

Fig. 1 shows the infrared spectra of three H-ZSM-5 samples in the $\nu(\text{OH})$ region recorded at 523 K after activation in flowing nitrogen. The vertical scale of each was corrected for variations in wafer thickness to allow comparison of hydroxyl group concentrations. The infrared absorption band at 3610 cm^{-1} is attributed [7–10] to Brønsted acid sites associated with framework aluminium within the zeolite channels. The 3720 cm^{-1} band has been assigned to silanol groups associated with silica impurities or to hydroxyl groups terminating the zeolite framework at the external surface [11,12], and the latter assignment was preferred [2]. Comparison of Fig. 1 with Table 1 indicates that the concentration of Brønsted acid sites is essentially proportional to the framework aluminium contents in the H-ZSM-5 samples. The broad band at ca. 3660 cm^{-1} over the sample HZ-16 was assigned to hydroxyl species associated with extraframework aluminium [3].

3.2. *In situ* infrared spectra

Exposure of HZ-12 sample to dimethyl ether at various temperatures produced the difference infrared spectra as shown in Fig. 2 in which a negative feature corresponds to species lost from the zeolite and a positive feature to species formed during reaction. As Brønsted acid sites are capable of donating protons to adsorbed

Table 2
Vibrational frequencies of species derived from dimethyl ether

Species	(cm^{-1}) ^a	Assignment	Ref.
$\text{CH}_3\text{O}^+\text{HCH}_3$ (protonated dimethyl ether)	3011	$\nu(\text{CH})$ asymm.	[2]
	2971	$\nu(\text{CH})$ asymm.	[2]
	2947	combination	[2]
	2844	$\nu(\text{CH})$ symm.	[2]
SiOCH_3Al (Brønsted acid bound methoxy)	2979	$\nu(\text{CH})$ asymm.	this work
	2868	$\nu(\text{CH})$ symm.	this work
SiOCH_3 (external silanol bound methoxy)	2959	$\nu(\text{CH})$ asymm.	[11,12]
	2855	$\nu(\text{CH})$ symm.	[11,12]
AlOCH_3 (extra framework aluminium bound methoxy)	2970	$\nu(\text{CH})$ asymm.	this work
	2864	$\nu(\text{CH})$ symm.	this work

^a In this work $\pm 2\text{ cm}^{-1}$.

dimethyl ether, Fig. 2a shows the loss of the intensity at band 3610 cm^{-1} , indicating considerably strong adsorption of dimethyl ether onto the Brønsted acid sites to form a protonated dimethyl ether species at 423 K. Four dominant $\nu(\text{CH})$ bands at 3011, 2971, 2947 and 2844 cm^{-1} are assigned to the asymmetric, combination and symmetric stretching vibration of protonated dimethyl ether species [2] as given in Table 2. At 473 K the infrared spectrum of dimethyl ether adsorbed on the freshly activated HZ-12 sample is presented in Fig. 2b in which partial dissociation of protonated dimethyl ether species and its remainder gave a complex spectrum. Upon elevating the temperature up to 523 K the dissociative adsorption of protonated dimethyl ether was almost achieved and then became dominant as shown in Fig. 2c. The assignment of the bands at 2979 and 2868 cm^{-1} in the $\nu(\text{CH})$ region has been given (Table 2) as the bridging Brønsted acid bound methoxy group, SiOCH_3Al , which is essentially identical with those produced from dissociative adsorption of methanol over Brønsted acid sites [7–9]. In Fig. 2c the infrared bands of 2959 and 2853 cm^{-1} in the $\nu(\text{CH})$ region attributed to external silanol bound methoxy group, SiOCH_3 , were consistent with previous reports [11,12].

The difference infrared spectra of dimethyl

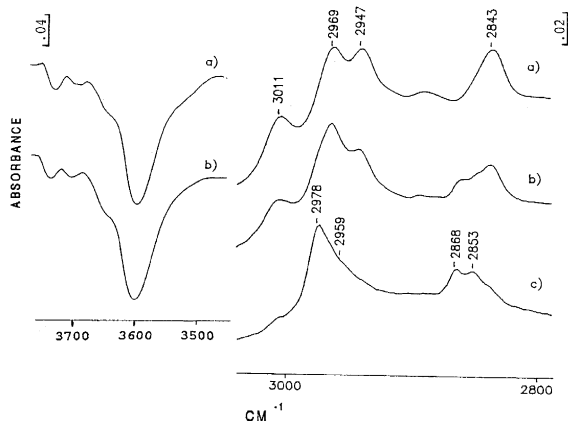


Fig. 2. Difference infrared spectra recorded after injecting a 1.0 ml pulse of dimethyl ether onto the freshly activated HZ-12 (Si:Al = 12) sample at different temperatures: (a) 423 K; (b) 473 K; (c) 523 K.

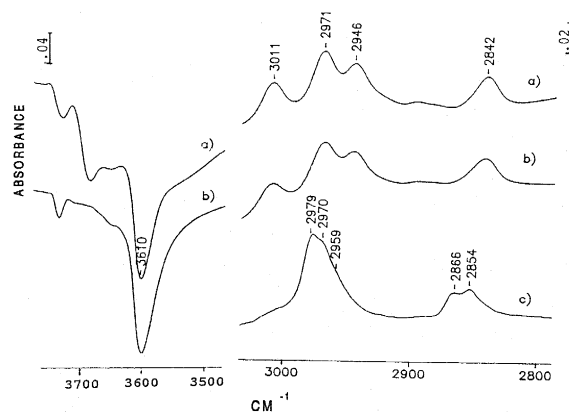


Fig. 3. Difference infrared spectra recorded after injecting a 1.0 ml pulse of dimethyl ether onto the freshly activated HZ-27 (Si:Al = 27) sample at differing temperatures: (a) 423 K; (b) 473 K; (c) 523 K.

ether adsorbed onto the freshly activated HZ-27 sample at various temperatures were shown in Fig. 3. At 423 K (Fig. 3a), in the $\nu(\text{OH})$ and $\nu(\text{CH})$ regions, the spectra were similar to that of the HZ-12 sample (Fig. 2a). The decrease in the 3610 cm^{-1} band is accompanied by the appearance of the most characteristic bands of the protonated dimethyl ether. Upon exposure of the freshly activated HZ-27 sample to dimethyl ether at the elevating temperature of 473 K, however, the spectrum in the $\nu(\text{CH})$ region (Fig. 3b) has no obvious change compared with Fig. 3a, implying that dissociative adsorption of protonated dimethyl ether has not occurred yet over the sample HZ-27 at this temperature. In this point of view HZ-27 is obviously different from HZ-12. This may be attributed to the different concentrations of Brønsted acid sites in these samples as shown in Fig. 1. The HZ-12 sample contains an about 5–6 times higher contents of Brønsted acid sites than the HZ-27 sample. At higher temperature, 523 K, the infrared spectrum recorded as dimethyl ether adsorbed on freshly activated HZ-27 sample was presented in Fig. 3c. It can be seen therein that besides the Brønsted acid bound methoxy species (viz., the bands of 2979 and 2868 cm^{-1} in the $\nu(\text{CH})$ region), the external silanol bound methoxy species (viz., the

bands 2959 and 2854 cm^{-1} in the $\nu(\text{CH})$ region) were assigned as given in Table 2; a new band at 2970 cm^{-1} which was not observed in the spectrum of the HZ-12 (Fig. 2c) appeared in Fig. 3c. According to the assignment reported by Kubelkova et al. [3], this band was characterized to the asymmetric stretching vibration of dissociatively adsorbed dimethyl ether on the extraframework aluminium. Unfortunately a band (ca. 2864 cm^{-1}) assigned to the symmetric stretching vibration of this species associated with extraframework aluminium was interfered by a band at 2868 cm^{-1} attributed to the symmetric stretching vibration of the Brønsted acid bound methoxy species.

In order to confirm the occurrence of the third type of methoxy species associated with extraframework aluminium, methanol was used instead of dimethyl ether to avoid the interference of the asymmetric stretching vibration of the third methoxy species at 2970 cm^{-1} by the formation of the protonated dimethyl ether (viz. 3011, 2971, 2947, 2844 cm^{-1}) and the symmetric stretching vibration of this methoxy species at 2864 cm^{-1} by the appearance of a Brønsted

acid bound methoxy group (viz. 2979 and 2868 cm^{-1} in the $\nu(\text{CH})$ region). Therefore the adsorption temperature of methanol should be as low as possible at 423 K to achieve the appearance of the third type of methoxy species before forming the Brønsted acid bound methoxy species. The difference infrared spectra recorded at various temperatures by adsorption of methanol onto the freshly activated HZ-16 sample which contains a considerable large portion of extraframework aluminium were presented in Fig. 4. It can be seen therein that loss of all three distinct hydroxyl groups was observed following adsorption of methanol; but where only about 25% and 50% of the silanol and Brønsted acid sites, respectively, were lost on adsorption at 423 K and less at higher temperatures, complete loss of the band at ca. 3660 cm^{-1} attributed to extraframework aluminium hydroxyl groups [3] was observed at all temperatures. This indicates that adsorption of methanol on the nonacidic extraframework aluminium hydroxyl groups is clearly very favorable. A band at ca. 2970 cm^{-1} was observed in the spectra at all temperatures over this sample and thus was

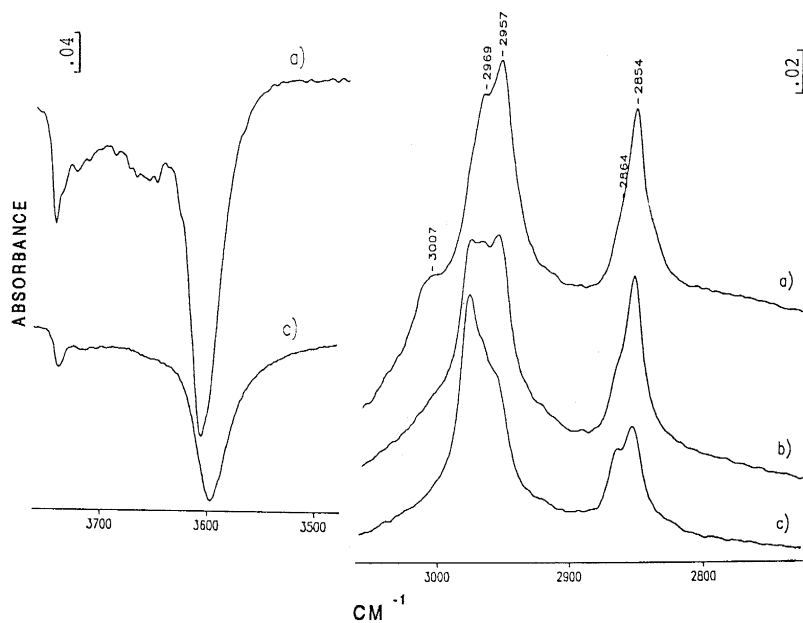


Fig. 4. Difference infrared spectra recorded after injecting a 0.5 μl pulse of methanol onto the freshly activated HZ-16 (Si:Al = 16) sample at various temperatures: (a) 423 K; (b) 473 K; (c) 523 K.

assigned to the asymmetric stretching vibration of methanol adsorbed on extraframework aluminium species. A band was observed at 2864 cm^{-1} in the spectrum (Fig. 4a) at 423 K, though a band due to the bridging Brønsted acid bound methoxy species will appear at 2868 cm^{-1} , the latter species was not formed in readily observable quantities at this temperature. Therefore the band at 2864 cm^{-1} was assigned to the symmetric stretching vibration of methanol interacting with extraframework aluminium species. A third band was not observed for this species indicating its symmetric form. In Fig. 4a the band at 3007 cm^{-1} was attributed to protonated methanol species associated with Brønsted acid sites in the zeolite lattice [7] as demonstrated by the loss at high temperatures. The bands at 2959 and 2855 cm^{-1} in the $\nu(\text{CH})$ stretching vibration region, as mentioned above, are assigned to the silanol bound methoxy species (Table 2). It has to be pointed out that there was no evidence of hydroxyl stretch or deformation vibrations associated with methanol adsorbed on extraframework aluminium species indicating that this species was again a methoxy species associated with the aluminium atoms in the extraframework aluminium. For convenience the third methoxy species, AlOCH_3 , is termed as the extraframework aluminium bound methoxy species which demonstrates a characteristic asymmetric stretching vibration band at ca. 2970 cm^{-1} and a symmetric stretching vibration band at ca. 2864 cm^{-1} in the $\nu(\text{CH})$ stretching region. Such species produced either by methanol or dimethyl ether adsorption onto the nonacidic extraframework aluminium are identical. This third type of methoxy species has been reported by Kubelkova et al. [3] in AIHY and AIH-ZSM-5 samples by methanol adsorption. The most striking observation in this in situ infrared study was the ease of the formation of the extraframework aluminium bound methoxy species at such low temperatures as 423 K upon methanol ad-

sorption; while such a species could be observed upon dimethyl ether adsorption at higher temperature of 523 K.

4. Conclusions

Assignment of the infrared bands observed in the spectra of dimethyl ether adsorbed on H-ZSM-5 samples under reaction conditions has been clarified. In particular an extraframework aluminium bound methoxy species is generated from dimethyl ether adsorption, and also from methanol adsorption. Therefore the infrared spectra of adsorbed methanol and dimethyl ether reported previously [2,7–9] can now be rationalized in terms of three types of methoxy groups: Brønsted acid sites bound methoxy species (SiOCH_3Al), external silanol bound methoxy species (SiOCH_3), and extraframework aluminium bound methoxy species (AlOCH_3).

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