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On the Framework Hydroxyl Groups of H-ZSM-5 Zeolites

The structure and potential catalytic applications of ZSM-5 remain of great interest. A number of papers dealing with IR spectroscopy have reported that H-ZSM-5 has mainly two types of framework hydroxyl groups, absorbing at 3600–3605 and 3720–3740 cm^{-1}, respectively (*1*, *2*), while Kazansky *et al.* (*3*) have observed two bands at 3610 and 3745 cm^{-1}, respectively. Recently, Jacobs and von Ballmoos (*4*) suggested that highly crystalline H-ZSM-5 zeolites exhibit only a single type of framework hydroxyl group at 3600 cm^{-1} and that H-ZSM-5 samples of poorer quality show a second hydroxyl band at 3720 cm^{-1} to be assigned to extrazeolitic impurities. However, Védrine *et al.* (*5*) considered that it is misleading to try to identify the amorphous content of the sample by the 3720-cm^{-1} band in the case of H-ZSM-11. Here we present some infrared spectroscopic and adsorption data of several H-ZSM-5 samples prepared under different synthesis conditions in order to elucidate the dependence of the framework OH band on synthesis conditions.

The HZSM-5 samples listed in Table 1 have been shown to be well-crystallized ZSM-5 zeolites by X-ray powder diffraction, infrared lattice vibrational bands, and *n*-hexane adsorption capacity. The samples were prepared by calcination at 810 K of ZSM-5 as synthesized and subsequently repeated cation exchange with 0.5 *N* HCl or 1 *M* NH_4Cl solutions at 353 K. The self-supporting wafer (5–7 mg/cm^2) of HZSM-5 sample was evacuated to 10^{-5} Torr at 673 K in the IR cell. 4-Methylquinoline (Fluka, >97% GC) was dried over an activated 5A molecular sieve and further degassed before being introduced into the IR cell. The adsorption was carried out at 298 K and saturation vapor pressure (~10^{-3} Torr) of 4-methylquinoline for 2 hr. A computerized Nicolet 5DX FT spectrometer was used for recording the IR spectra at room temperature. In order to enhance the signal-to-noise ratio, 100 scans were accumulated and averaged for every spectrum prior to adsorption of 4-methylquinoline and after desorption (evacuation for 1 h) at various temperatures. The adsorption amounts of 1,3,5-trimethylbenzene (G.C. grade) on various HZSM-5 samples were measured by a high-vacuum gravimetric method.

Some of the framework hydroxyl group IR spectra of the HZSM-5 samples are shown in Fig. 1. It is obvious that some samples exhibit a very intense 3745-cm^{-1}

TABLE 1

Samples of H-ZSM-5

Sample[a]	Nitrogenous base used in synthesis	Si/Al (atom ratio)	Symbol[b]
1	Ethylamine	25.0	+
2	Ammonium hydroxide	25.0	×
3	Ammonium hydroxide	22.5	□
4	Tetrapropyl ammonium bromide	32.0	○
5	None	17.0	△
6	Ethylenediamine	23.5	▽
7	Tripropylamine and propyl bromide	32.6	■
8	Tetrapropyl ammonium bromide	44.4	●
9	Tripropylamine and propyl bromide	24.1	▲
10	*n*-Butylamine	26.9	▼

[a] Samples 1–6 were kindly supplied by Professor Juan Liang (Dalian Institute of Chemical Physics, Academia Sinica).

[b] Used in Figs. 2–5.

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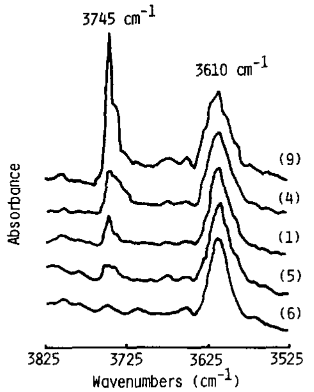

FIG. 1. OH band spectra of some HZSM-5 zeolites (numbers refer to the samples listed in Table 1).

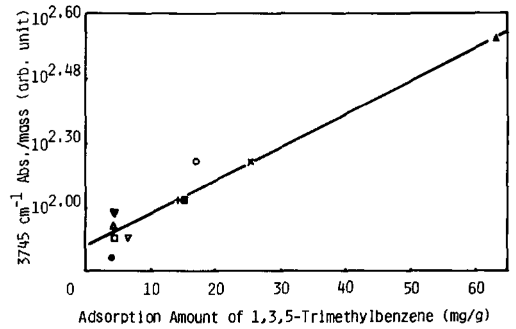

FIG. 3. The absorbance per unit mass of the 3745-cm^{-1} OH band vs the adsorption amount (303 K, P/P_s = 0.5) of 1,3,5-trimethylbenzene on various HZSM-5 samples.

band, while the others show only a single hydroxyl group band at 3610 cm^{-1}. The recorded wavenumbers of framework hydroxyl groups are in good agreement with the data of Kazansky *et al.* (*3*), namely, OH bands at 3745 and 36 10 cm^{-1}. It seems that the intensity of the 3745-cm^{-1} band relates neither to the purity of HZSM-5 nor to the type of nitrogenous base used in the synthesis; even the sample synthesized without using any nitrogenous base exhibits a very weak 3745-cm^{-1} band. Preliminary electron microscopic observations have revealed that the smaller the crystallites of HZSM-5, the more intense the 3745-cm^{-1} band (see Fig. 2). For convenience we may use the adsorption amount of 1,3,5-trimethylbenzene (molecule size ~0.75 nm) as the measure of the external surface of HZSM-5. The absorbance (per sample mass) of the 3745-cm^{-1} band is plotted against the adsorption amount of 1,3,5-trimethylbenzene (303 K, P/P_S = 0.5) in Fig. 3, and a straight line is found. Hence there exists a direct proportionality between the number of 3745-cm^{-1} OH groups and the external surface area of HZSM-5.

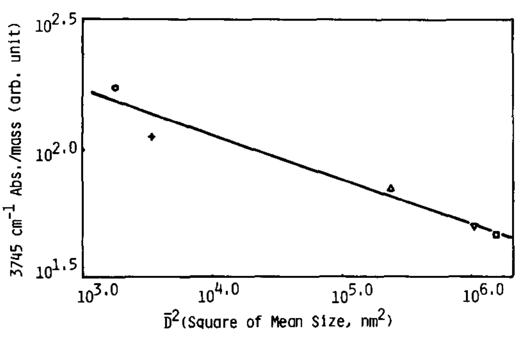

FIG. 2. The absorbance per unit mass of the 3745-cm^{-1} OH band vs the square of the mean crystallite size ($\bar{D}^2$) of HZSM-5 samples.

For further elucidation of the proportionality mentioned above, we recorded the IR spectra following 4-methylquinoline adsorption and subsequent desorption at various temperatures. The minimum diameter of the 4-methylquinoline molecule is about 0.65 nm, so it cannot enter the channels of crystallites of HZSM-5 at room temperature. Upon adsorption of 4-methylquinoline the intensity of the OH bands at 3610 and 3745 cm^{-1} decreases and new bands at 3300, 3224, 2958, 1600, 1513, and 1395 cm^{-1} due to 4-methylquinoline appear simultaneously. The OH band absorbance difference ($A_0 - A_T$) between the absorbance prior to adsorption and that after adsorption and then desorption at temperature T (in K) denotes the decrease in the number of OH groups caused by adsorbed 4-methylquinoline. Thus $(A_0 - A_T)/A_0$ may denote the coverage by the adsorbed 4-methylquinoline after desorption at temperature

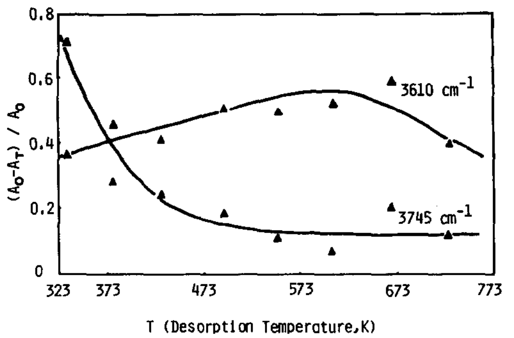

FIG. 4. Coverage by adsorbed 4-methylquinoline vs desorption temperature on HZSM-5 (sample (9)). A_0—absorbance prior to adsorption. A_T—absorbance after adsorption then desorption at temperature T.

T. The values of $(A_0 - A_{323})/A_0$ for the 3745-cm^{-1} band and the 3610-cm^{-1} band are 0.7 and 0.35, respectively (see Fig. 4). In view of the fact that the adsorption amount of 4-methylquinoline at 3745-cm^{-1} OH groups readily decreases on desorption, it can be said that most of the 3745-cm^{-1} OH groups are located at the external surface of HZSM-5 and a certain amount (~35%) of the 3610 cm^{-1} OH groups are at a place which is easily accessible to 4-methylquinoline at room temperature. It is interesting to point out that in contrast with the adsorption at the 3745-cm^{-1} OH groups the adsorption amount at the 3610-cm^{-1} OH groups slightly increases with increasing temperature of desorption from 323 to 673 K. This indicates that the 4-methylquinoline molecules migrate from 3745-cm^{-1} OH groups to 3610-cm^{-1} OH groups on desorption and that the adsorption at 3610-cm^{-1} OH groups needs some activation energy. The desorption of 4-methylquinoline from 3610-cm^{-1} OH groups starts to occur above ~725 K.

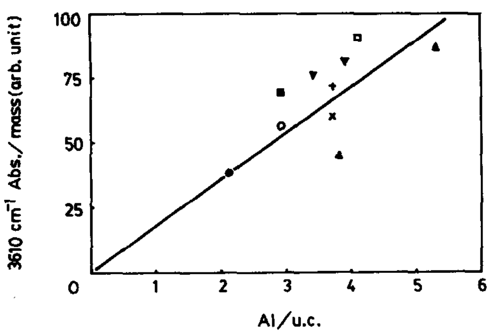

FIG. 5. The absorbance per unit mass of the 3610-cm^{-1} OH band vs the number of Al atoms in the unit cell of HZSM-5 samples.

Figure 5 shows that there is an approximately linear relationship between the absorbance (per unit mass) at 3610 cm^{-1} and the number of aluminum atoms in the unit cell of the various HZSM-5 samples studied. This means that the 3610-cm^{-1} OH band is related to the aluminum in the lattice of HZSM-5 in spite of the different intensities of the 3745-cm^{-1} OH band, indirectly showing nearly the same quality of these 10 HZSM-5 samples.

From the data presented above we can conclude that framework hydroxyl groups giving rise to the 3745-cm^{-1} band are due to terminal silanol groups SiOH exhibiting very weak acidity, and most of them are located at the external surface of HZSM-5. It seems to be incorrect to assign the 3745-cm^{-1} band to extrazeolitic impurities in the HZSM-5. The framework hydroxyl groups giving rise to the 3610-cm^{-1} band are due to Si–OH–Al groups, exhibiting very strong acidity as is usually suggested. Not all the 3610-cm^{-1} OH groups are located in the interior of crystallites; at least a certain amount (~35%) of strongly acidic 3610-cm^{-1} OH groups seems to be located at the external surface or near the pore mouths of tiny crystallites of HZSM-5.

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