

## Uses of I.R. Spectroscopy in identifying ZSM Zeolite Structure

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The study of i.r. lattice vibrational bands ( $400\text{--}1200\text{ cm}^{-1}$ ) for different types of zeolites with different particle sizes indicates, when synthesising a ZSM-type zeolite, that (i) the presence of a band at *ca.*  $550\text{ cm}^{-1}$  in addition to the one at  $450\text{ cm}^{-1}$  shows that ZSM-type zeolite crystallites may have been formed, even if X-ray diffraction shows nothing, and (ii) the absence of the  $550\text{ cm}^{-1}$  band unambiguously shows that such a zeolite has not been formed.

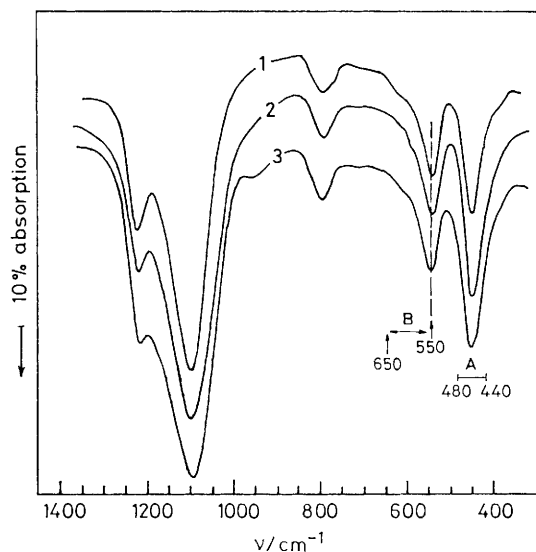
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In a recent study<sup>1</sup> the crystallisation of a ZSM-type zeolite was followed by X-ray powder diffraction (X.R.D.) and by i.r. spectroscopy. It was clearly shown that although the X-ray diffraction pattern of the sample was characteristic of an amorphous material, the i.r. spectra along with catalytic

measurements indicated that the material behaved like well crystallised ZSM-5 zeolite. The results were interpreted in terms of the presence of small ZSM-5 zeolite crystals (diameter less than 8 nm) in an amorphous matrix. The purpose of this communication is to emphasise further the

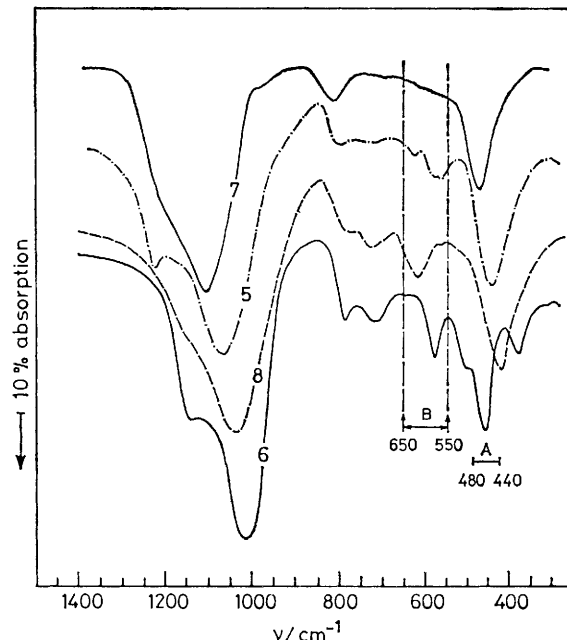
**Table 1.** Some X.R.D., transmission electron micrographic, and i.r. characteristics of different zeolites or silica samples.

Sample no.	Zeolite type	Chemical analysis Al/(Si + Al)	X.R.D. pattern	Transmission micrographs (shape and size in nm)	I.r. data	
					Vibrational frequency ( $\nu/\text{cm}^{-1}$ ) for band A	Optical density ratio A : B ( $\pm 0.02$ )
1	ZSM-5	0.042	Excellent	Parallelepipeds (500—2000)	550	0.72
2	ZSM-11	0.023	Excellent	Spheroids <sup>a</sup> ( $\approx 6000 \pm 2000$ )	551	0.60
3	ZSM-11	0.019	Bad	Spherulitic <sup>a</sup> ( $600 \pm 200$ )	548	0.41
4	Silicalite	0.001	Excellent	Parallelepipeds (1000—2000)	550	0.56
5	Z (zeolon)	0.20	Excellent	—	560, 578, 630	0.24
6	Y (Union Carbide)	0.29	Excellent	(Several thousands)	580, 500	0.51
7	SiO <sub>2</sub>	0	—	—	—	0
8	ZK-19	0.22	Excellent	—	620	0.31

<sup>a</sup> Ref. 11.**Figure 1.** I.r. spectra of KBr pellets of samples no. 1 (ZSM-5), 2 (ZSM-11,  $\phi$  ca. 6  $\mu\text{m}$ ), and 3 (ZSM-11,  $\phi$  ca. 0.6  $\mu\text{m}$ ).

use of i.r. spectroscopy and X-ray diffraction patterns for probing the crystallisation of zeolites. Accent will be on the various experimental aspects which may lead to misinterpretation.

ZSM-type (-5 and -11), silicalite, and ZK-19 (phillipsite) zeolite samples were prepared<sup>2</sup> in our laboratory. Amorphous silica and Y-type zeolite samples were commercial samples from Degussa, Grande Paroisse, and Union Carbide respectively. The i.r. spectra were recorded on a Perkin Elmer 580 spectrometer using the KBr pellet technique. X-Ray diffraction (Cu-K<sub>2</sub> radiation), high-resolution transmission electron microscopy, and micro-diffraction were used to characterise the zeolites. Also studied were their adsorption capacities for n-hexane and catalytic properties for the conversion of methanol into higher hydrocarbons and gasoline-type mixture, and for the alkylation of toluene. The i.r. spectra in the framework absorption region are shown in Figures 1 and 2 while the ratios of optical densities of the A (550—650) and B (440—480  $\text{cm}^{-1}$ ) bands are given in Table 1. These spectra are typical of silicate materials, with absorption bands at 1200—1150 (sh), 1100—1020 (vs), 800—700 (mw), 650—550 (m), 480—440  $\text{cm}^{-1}$  (s). According to the Flanigen-Khatami-

**Figure 2.** I.r. spectra of KBr pellets of samples no. 5 (mordenite Z), 6 (Y-zeolite), 7 (SiO<sub>2</sub>), and 8 (ZK-19 zeolite).

Szymanski correlation,<sup>3</sup> the absorptions near 1100, 700, and 450  $\text{cm}^{-1}$  are assigned to internal vibrations of the Si, AlO<sub>4</sub> tetrahedra and are also observed in silica or quartz. The 650—550  $\text{cm}^{-1}$  band was empirically assigned to the presence of double-rings of tetrahedra<sup>3</sup> in the framework. From normal co-ordinate calculations of a model of D4R or D6R units<sup>4</sup> this assignment appears reasonable. Attributing these bands to external vibration modes of chainlets of tetrahedra<sup>5</sup> allows one to explain their presence in all zeolites (particularly ZSM-5 and ZSM-11) and in many silicates.<sup>6</sup> The 1200—1150  $\text{cm}^{-1}$  band due to an external asymmetrical stretching vibration<sup>3</sup> was observed at a high frequency for samples such as ZSM or mordenite (1230  $\text{cm}^{-1}$ ). This frequency shift could be correlated to a high silica ratio<sup>7</sup> or to the presence of five-membered rings.<sup>8</sup>

As silica does not show any absorption near 550  $\text{cm}^{-1}$  the A : B band ratios may be a good probe to characterise the presence of a zeolite framework, since for very small particles

X.R.D. is useless. X.R.D. may even be erroneous since one may wrongly conclude, in the absence of any pattern,<sup>1</sup> that the material is not ordered. Quantitative i.r. data are not very accurate but for a well crystallised ZSM-type sample the A:B ratio is close to 0.7. If amorphous silica is present, one would expect this ratio to be less than 0.7 for ZSM-5 and less than 0.6 for ZSM-11 in proportion to the amount of disordered silica.

An interesting case is given in Table 1, sample 3. The X.R.D. pattern is very poor (only very small and broad peaks are observed at  $2\theta = 22$  and  $25^\circ$ ) while the A:B ratio is 0.41 and the n-hexane adsorption capacity is 8 compared to 11 (% by wt) for the pure ZSM-11 sample (sample 2).<sup>9</sup> Catalytic properties for the conversion of methanol into gasoline-type mixture are also typical of the ZSM-type<sup>2,10</sup> reaction but this indicates little since the presence of amorphous silica has only a small influence.<sup>10</sup> High resolution transmission electron micrographs and microdiffraction have shown<sup>11</sup> that each grain of sample (diameter  $\phi = 600$  nm) is formed by the aggregation of very small zeolite particles ( $\phi$  ca. 5–10 nm). This is consistent with the poor X.R.D. pattern. I.r. data (A:B ratio 0.4 instead of 0.6) and n-hexane absorption values (8 instead of 11% by wt) seem to indicate that roughly 30% of the sample remains amorphous, presumably as amorphous silica.<sup>11</sup>

It is interesting that Y-type zeolite also gives an intense absorption band near  $550\text{ cm}^{-1}$  (Table 1) whose position changes with the Al content.<sup>7</sup> This shows that one cannot use the A band alone, a reasonable premise according to ref. 1, as a criterion to conclude that the material is ZSM-type zeolite. Even though framework vibrational spectra contain much information about the structural characteristics of the zeolite frameworks, i.r. spectroscopy cannot take the place of X.R.D. to determine the structure of a sample. Indeed, i.r. spectroscopy is concerned with short-distance order which is only slightly different for zeolites of the same group. Nevertheless, the absence of the i.r. band at ca.  $550\text{ cm}^{-1}$  definitely indicates that ZSM-type zeolite is not present in the sample.

Our conclusion is that i.r. spectroscopy in the lattice vibrational modes region is of great use, particularly when X.R.D. fails owing to the presence of very small crystallites, and may even give an approximate estimation of the crystallinity. However one has to be cautious about assuming from this the nature of the zeolite. The i.r. technique has to be used along with other techniques such as X.R.D. analysis, electron microscopy at high resolution, electron microdiffraction, and capacity of adsorption of hydrocarbons and inorganic molecules to characterise fully the degree of order of a zeolite lattice.

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