The Degree of Crystallinity of ZSM-5 determined by Raman Spectroscopy

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A new procedure for determining the degree of crystallinity of ZSM-5 using the Raman peak at 382 cm^{-1} is proposed and is shown to be as accurate as the same parameter determined by X-ray diffraction and more acuate than that determined by infrared absorption measurements.

The degree of crystallinity of microporous materials is an important parameter from both scientific and technological viewpoints. This parameter has been usually determined by X-ray powder diffraction (XRD)[1,2] and to a lesser extent by infrared (IR) spectroscopy.[3] Only few articles, however, have reported Raman spectroscopy studies of zeolite structures and none of these addressed the degree of crystallinity. Amongst all zeolites studied by the above methods ZSM-5 has received most attention due probably to its unique skeleton topology and its high potential for applications,[4-6] however the results reported are of an empirical character and further investigation is necessary to specify how to utilise Raman spectroscopy

for determining the degree of crystallinity in these types of materials.

The aim of this communication is to report a new, more effective procedure for determining the degree of crystallinity of ZSM-5 by use of Raman spectroscopy and to compare the results thus obtained with the traditional XRD and IR absorption methods.

Five samples of ZSM-5 with differing degrees of crystallinity prepared by hydrothermal synthesis with NPr$_4$Br as organic template (for details see Refs. 7 and 8) were investigated by XRD (Philips APD-15 diffractometer with Cu-Kα radiation), IR spectrometry (Specord IR spectrometer on KBr pellets) and Raman spectroscopy (Dilor Microdil 28, 488 nm wavelength, spectral resolution of 5 cm^{-1}). Fig. 1 shows the Raman spectra of four of the samples studied, with a degree of crystallinity determined by XRD, α_{XRD}, of 0, 25, 45 and 100% in the spectral range 300–600 cm^{-1} which was found to be most sensitively influenced by the degree of crystallinity. Throughout this study the values of α_{XRD} were specified by the well-known method of Gulfax and Sand.[9] The parameter α_{XRD} is plotted along the abscissa in Fig. 2, while along the ordinate are plotted the values of the degree of crystallinity of the same samples determined by IR absorption, α_{IR} (□), and by Raman spectroscopy, α_R (○). The former values were calculated using the method proposed by Coudurier et al.[3] in which the degree of crystallinity α_{IR} has been defined as the ratio between the areas below the peaks at ca. 550 and 460 cm^{-1} in the IR absorption spectrum of the sample under study devided by the same ratio for a reference sample with α_{XRD} = 100%.

The parameter α_R, of interest in this study, is defined as the area of the peak at ca. 382 cm^{-1} in the Raman spectrum of the sample studied normalized to that in the spectrum of the
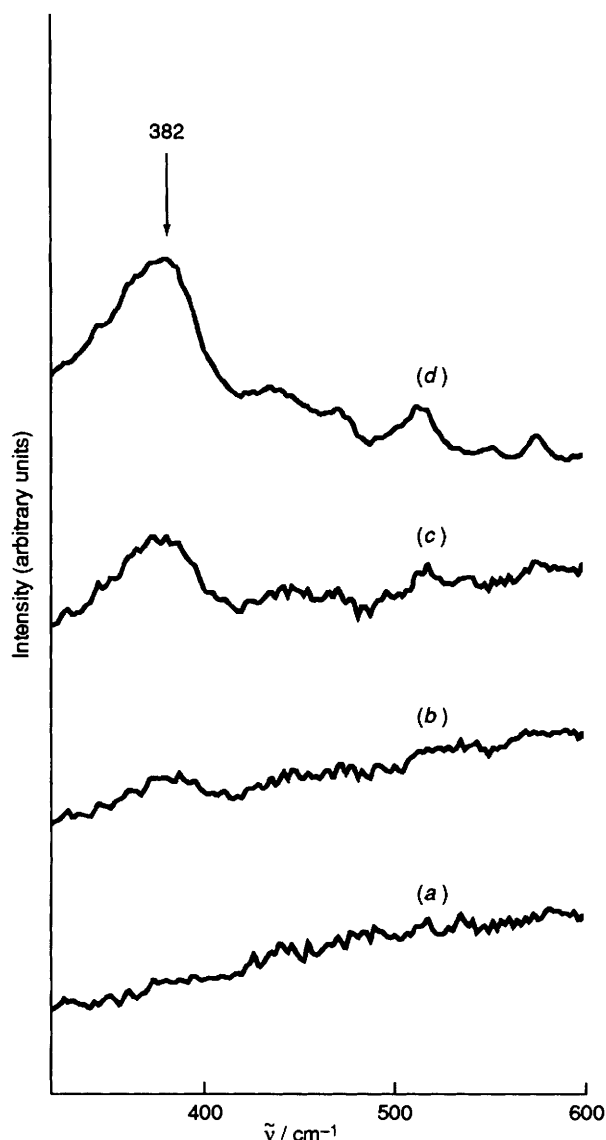

Fig. 1 Raman spectra of four ZSM-5 samples with differing degree of crystallinity as determined by X-ray analysis, α_{XRD}; (a) 0, (b) 25, (c) 45 and (d) 100% crystallinity
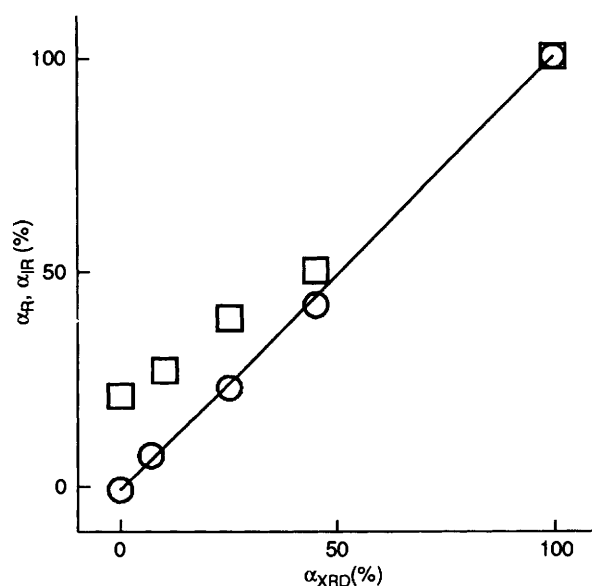

Fig. 2 Relationship between the degree of crystallinity of ZSM-5 determined by X-ray diffraction, α_{XRD} versus degree of crystallinity as determined by Raman spectroscopy, α_R (○), and by infrared absorption, α_{IR} (□)

reference sample. As discussed previously, our model calculations performed for a five-membered puckered ring of SiO_4 tetrahedra by the method described in ref. 10 leads to the assignment of the peak at 550 cm^{-1} in the IR spectrum of ZSM-5 to the *ca*. silicon–bridging oxygen-bond rocking mode in the ring, while that at *ca*. 382 cm^{-1} is due to a combined Si–O–Si and O–Si–O bending mode. These two peaks have already been discussed in the literature[3,4] and our modelling confirms to a great extent their previous identification. It is worth noting here that the IR-active mode with a wavenumber of *ca*. 550 cm^{-1}, usually related to the presence of double rings in the zeolite framework,[3] is in general characteristic of closed contours of covalent Si–O bonds and its parameters vary with the ring geometry.

As can be seen in Fig. 1, the peak at 382 cm^{-1} in the Raman spectrum of ZSM-5 is very sensitive to the degree of crystallinity. Although this peak has been shown to change from one zeolite to another of differing ring-size,[4] it has not been used until now for determining the degree of crystallinity of zeolites. Here we propose the Raman-active vibrational mode giving rise to this peak as a viable measure of the parameter *a*. As seen in Fig. 2, for ZSM-5 there is a one-to-one correspondence between the degree of crystallinity determined by X-ray diffraction, α_{XRD}, and that determined by the normalized area of the peak at 382 cm^{-1}, α_R, in the whole range studied. Comparison between the values of the degree of crystallinity of ZSM-5, as determined by IR absorption, α_{IR} and by Raman scattering, α_R, reveals that the latter is much

more accurate, especially in the low-crystallinity range (below *ca*. $\alpha = 50\%$), where the values of α_{IR} are systematically too high. The reason for this is that the IR absorption by both the crystalline zeolite and the non-crystalline silicate phase takes place in the same spectral range, seriously reducing the accuracy in determining the peak area.

In conclusion, it is shown that the degree of crystallinity of ZSM-5 determined by Raman spectroscopy using the area below the peak at 382 cm^{-1} is to a great extent equivalent to that determined by X-ray diffraction and is more accurate than measurements obtained by IR absorption spectroscopy.

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