Probing the Dynamics of Methylated Benzenes Adsorbed on Zeolite ZSM-5 by Quasielastic Neutron Scattering

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The motion of *p*-xylene adsorbed within the framework of zeolite ZSM-5 is much less constrained than that of the *o*- and *m*-isomers.

The zeolitic molecular sieve ZSM-5[1] is used in many important catalytic processes and has been the subject of intense research efforts. The zeolite is highly siliceous (with Si : Al ratio of above *ca.* 15) and has two intersecting intracrystalline channel systems: channels 5.6 × 5.3 Å in diameter are running in the (010) direction and 5.5 × 5.1 Å channels in the (100) direction.[2] ZSM-5 can be readily synthesized in the presence of a structure-directing template, typically tetrapropylammonium bromide. The catalytically active H^+ form of the zeolite is produced by calcining the ammonium form of the zeolite at >550 °C.

Catalytic reactions on zeolites are intimately involved with molecular dynamics and shape selectivity.[3–5] The external surface of a typical zeolite crystallite is only *ca.* 1% of the total Brunauer-Emmett-Teller (BET) surface area, and thus the vast majority of catalytic sites are confined inside the crystallite. Since the zeolitic apertures are restricted in size, the probabilities of forming various products are determined to a great extent by molecular dimension and configuration. Product selectivity occurs when, from various species formed within the channels and cavities, only some can diffuse out of the crystallite and appear as reaction products; larger product species must first be converted to smaller molecules. An example of this is *p*-xylene, which can diffuse out of zeolite ZSM-5 while *o*- and *m*-xylenes can do so less readily.[4,5]

In the course of our recent ^{13}C magic-angle-spinning NMR[6,7] studies of the catalytic conversion of methanol to petrol over zeolite H-ZSM-5 we have found that the amounts of toluene and *m*-xylene in the products are small, and that the relative abundance of the various methylbenzenes in the adsorbed phase shows that an additional kind of shape selectivity occurs within the intracrystalline space. It does not rely on the ability of species to enter or to leave the crystal, nor on the size of the transition state: isomerisation is sterically restricted within the crystallite at the active site itself. Selectivity of this kind is similar to the action of enzymes, and we shall refer to it as 'active site shape selectivity'.

In order to probe the question of molecular mobility of organic molecules adsorbed on zeolite ZSM-5 we have resorted to quasielastic neutron scattering. The very high neutron scattering cross-section of the proton compared with nuclei of other elements present in the molecular sieve makes inelastic neutron scattering and quasielastic neutron spectroscopy convenient tools for the dynamics of adsorbed organics.[8] Variable-temperature ^{2}H NMR spectroscopy of static samples containing deuteriated adsorbates is another line of inquiry which we are following.

The present ZSM-5 had the unit cell formula $Na_{5.5}Al_{5.5}Si_{90.5}O_{192}$ and thus Si : Al = 16.5. Samples of 4 g each were thoroughly dehydrated at 400 °C for 24 h, cooled to 77 K, and contracted in a vacuum line with a known, and carefully adjusted, volume of toluene, *o*-, *m*- and *p*-xylene vapour at 12 torr pressure and at room temperature for 24 h. The sample container was then tightly sealed and warmed up to room temperature for transport to the Institut Laue-Langevin, Grenoble. Prior to the experiments, the sample container was very gradually cooled to the desired temperature. This procedure ensured a homogeneous distribution of the adsorbate over the sample. The amount of substance adsorbed on the samples was determined volumetrically. There could be no capillary condensation, since the quantity of substance adsorbed was well below sorption capacity of ZSM-5 at this temperature. Scattering experiments were performed using the time-of-flight spectrometers IN5 and IN4. A range of neutron wavelengths were used, allowing us to investigate the effect of energy resolution on the results.

We first measured quasielastic scattering from samples of *p*- and *o*-xylene adsorbed on ZSM-5 at elevated temperatures on the spectrometer IN5. With *p*-xylene at an incident wavelength of 6 Å very little quasielastic scattering was observed over the temperature range 300 to 500 K in the ±1 meV energy window corresponding to the wavelength used. The signal-to-noise ratio was insufficient to allow us to analyse the weak quasielastic scattering in terms of a single Lorentzian lineshape of variable intensity and width and a delta function to mimic the residual elastic line. We can only say that the measured quasielastic linewidth is almost constant with temperature but varies with Q, which is indicative of molecular diffusion rather than reorientation. For *o*-xylene we collected data over a similar temperature range and found the quasielastic component to be even weaker and narrower than for the *para*-isomer (see Fig. 1 for data at 450 K). We note that both samples had a large Debye–Waller factor, *ca.* 1 Å^2, that is the attenuation of scattered signal with temperature and angle. This indicates that the organic undergoes large amplitude motions and/or moves over considerable distances. The total amount of all three xylenes adsorbed on the host framework was identical. At first glance it would seem reasonable to conclude that, because of its shape, *p*-xylene would move through the intracrystalline space more readily than *o*-xylene, thereby giving a more intense quasielastic component. If both molecules experience a similar potential, they would have similar Debye-Waller factors.

In an attempt to find the origin of the large Debye-Waller factor, the samples were then studied on the lower resolution spectrometer IN4 at a range of temperatures with neutrons of 16 meV incident energy. Results from the sample loaded with p-xylene with the empty zeolite scattering subtracted are shown in Fig. 2. The amount of quasielastic scattering increases rapidly with Q, and it is readily seen why so little quasielastic scattering was observed in the much narrower

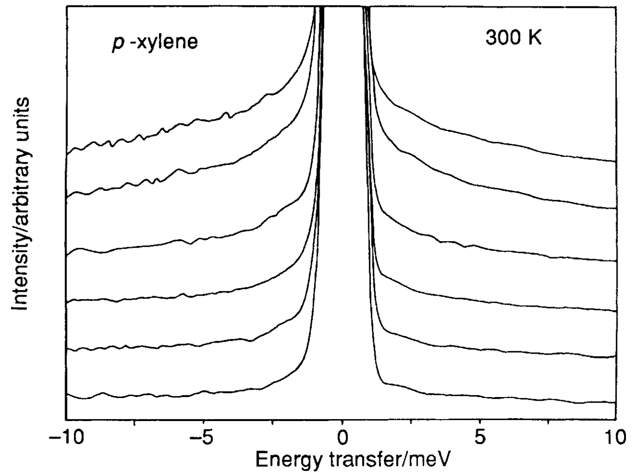

Fig. 2 Scattered intensity, corrected for container scattering, of adsorbed *p*-xylene measured on the IN4 spectrometer at 300 K. The value of Q increases for the six plots from the bottom to the top of the figure.

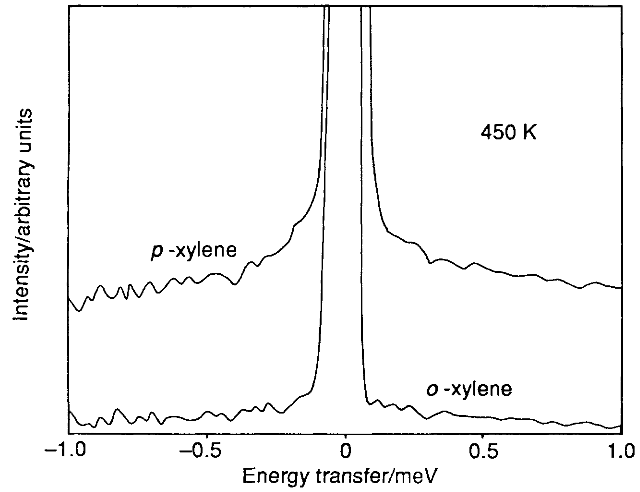

Fig. 1 Scattered intensity, corrected for container scattering, of *o*- and *p*-xylene adsorbed on zeolite ZSM-5. The spectra were measured at 450 K on the IN5 spectrometer with neutrons of 6 Å wavelength.

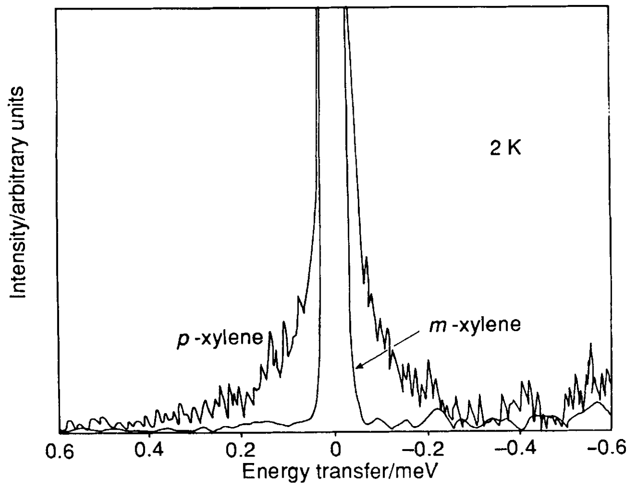

Fig. 3 Scattered intensity, corrected for container scattering, of adsorbed *m*- and *p*-xylene. The spectra were measured at 2 K on the IN5 spectrometer with neutrons of 9 Å wavelength.

energy window of the spectrometer IN5. The peak shape can be fitted reasonably well with a Lorentzian function which is consistent with quasielastic scattering rather than a distribution of inelastic features.

This result prompted us to look again at these materials on IN5 with its higher energy resolution but at lower temperatures. Figure 3 shows that the results for *o*- and *m*-xylene after subtraction of the signal from pure zeolite are very different. The spectrum of *m*-xylene is essentially an unbroadened resolution function. In contrast, the *p*-xylene shows a marked broadening even at 2 K. Since at this temperature the molecules are well localised within the zeolite channel system, the origin of this low-temperature broadening must be quantum mechanical, and probably arises from tunnelling transitions of the methyl groups.[9] These have been well studied in a variety of materials. The fact that no single transition is observed in our samples implies that the carrier is located at a number of different sites within the zeolite. The tunnelling frequency is a sensitive probe of the strength of the interaction between the host and the adsorbate and we can hope to derive a detailed picture of these interactions from our measurements.

The difference between the *p*- and *m*-xylene is borne out by the temperature dependence of the spectra. At low resolution *p*-xylene shows a marked quasielastic component of increasing intensity with increasing temperature but of constant width between 20 and 200 K. On the other hand, in *m*-xylene there was no sign of quasielastic scattering until about 100 K.

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