Modification of H-Mordenite by a Vapour-phase Deposition Method

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Depositing $Si(OMe)_4$ from the vapour phase onto H-mordenite reduces the size of pore exits in the zeolite but leaves the acid sites unaltered.

Recently, new methods of zeolite modification have been proposed, which have opened new opportunities for catalyst design.[1,2] One such modification method, the silanation of H-mordenite by depositing $Si(OMe)_4$ from the vapour phase is reported in this communication.

Methyl orthosilicate (*ca.* 8 Torr) was admitted onto evacuated H-mordenite (HM, supplied from Norton Zeolon 100H) at 593 K, and the gradual increase in weight of the zeolite was measured *in situ* by a quartz microbalance. Silicated HM was obtained after 1—2 h, and was then calcined at 673 K for 3 h in an oxygen stream to yield two types of catalyst, SiHM(1) (weight increase 2.2%) and SiHM(2) (2.7%). The i.r. spectrum of the silicated HM revealed absorptions due to CH (2900, 2700, and 1505 cm^{-1}) and CO_3^{2-} species (1595, 1450, and 1385 cm^{-1}), but all of these absorptions were removed easily by the calcination procedure.

Acid profiles of the catalysts were evaluated by measurement of the temperature programmed desorption (TPD) of adsorbed ammonia.[3] The TPD spectra showed two peaks, 'low' and 'high', and the maximum temperatures were located at *ca.* 423 and 683 K. The maximum temperatures and amounts of desorbed ammonia on the SiHM were, however, almost the same as on the HM; the acid sites of the HM were thus unaltered by the silanation.

Adsorption experiments were carried out both with H_2O and with *o*-xylene as adsorbate in order to investigate the physical characteristics of the mordenites (Table 1). Modified HM and HM itself adsorbed H_2O to a similar extent, but the adsorption capacity for *o*-xylene was much reduced on SiHM, indicating that the larger molecule (kinetic diameter† of *o*-xylene = 6.3 Å) could not enter the pore of the SiHM. One can conclude from both measurements that the silicate interacts only with the exterior of the mordenite, reducing the pore exit size but leaving the internal structure unchanged.

The catalytic activity of the SiHM in the disproportionation of toluene was then tested, and it was found to be shape-selective[2] owing to the above mentioned structural characteristics (Table 1). Selective disproportionation to *p*-xylene on SiHM was higher than on HM at the low conversion levels investigated where secondary isomerization of the xylenes produced was relatively unimportant.

Table 1. Properties of the mordenites.

		HM	SiHM(1)	SiHM(2)
NH_3 desorbed[a]/ mmol g^{-1}	'low' peak	0.41	0.33	—
	'high' peak	0.87	0.87	—
Adsorption capacity[b]/ mmol g^{-1}	H_2O	9.60	—	9.80
	o-xylene	0.52	—	0.04
% Selectivity for *p*-xylene[c]		31	78	65

[a] In the TPD experiments the catalyst used was first evacuated at 773 K. NH_3 (7.3 kPa at equilibrium) was pre-adsorbed and the catalyst was then evacuated at 373 K for 45 min. A programmed increase in catalyst temperature of 2.5 K min^{-1} from 373 K was used for the TPD measurements. [b] At 293 K. [c] In the toluene disproportionation the conversion of toluene was 2% under the conditions used (573 K; weight of catalyst : total flow rate = 8.1—0.4 g h mol^{-1}; toluene: N_2 = 1 : 5).

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† Kinetic diameter is defined as the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy.