para-Selectivity of a Highly Siliceous ZSM-5 Zeolite Modified with Arsenic(III)

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A highly siliceous ZSM-5 zeolite treated with $AsCl_3$ vapour at 673 K exhibited a high *para*-selectivity (94.1%) for the alkylation of ethylbenzene with ethanol.

It has been reported that HZSM-5 zeolites modified with oxides of Mg,[1–4] P[2–4] or B[2–4] exhibit a high *para*-selectivity for alkylations of alkylbenzenes. Kaeding *et al.* have proposed that the high *para*-selectivity of modified ZSM-5 zeolites is due to 'product selectivity,' namely the intracrystalline diffusivity of the *para*-isomer being much higher than that of the other two isomers.[2] We have reported that metallosilicates with the MFI zeolite structure exhibit higher *para*-selectivities for the ethylation of ethylbenzene than HZSM-5,[5] and that the weaker acid sites on the catalysts with the MFI structure provide higher *para*-selectivity, because in the narrow pores the isomerization of the *para*-isomer produced primarily is suppressed to some extent through 'restricted transition-state selectivity' and requires strong acid sites, compared with the alkylation.[4,5]

Many studies have investigated the replacement of silicon or aluminium in the framework of synthetic zeolites with elements such as B, Be, Cr, Ce, Fe, Ga, P, Ti, V or Zr.[6] These molecular sieves are generally synthesized hydrothermally. Yamagishi *et al.* have reported that some atoms can be introduced into defect sites of the framework by treatment with metal chlorides at elevated temperatures, the so-called 'atom-planting method.'[7] In the alkylation of ethylbenzene with ethanol, Sb-HZSM-5 zeolite prepared by the atom-planting method showed a high *para*-selectivity (90.4%).[5]

We now report the preparation of highly siliceous ZSM-5 zeolite modified with arsenic(III) (As-HZSM-5) by the atom-planting method and discuss the *para*-selectivity of the As-HZSM-5 zeolite for the alkylation of ethylbenzene with ethanol.

The detailed procedure for the atom-planting method has been described.[7] As-HZSM-5 zeolite was prepared by treatment of siliceous HZSM-5 zeolite (Si/Al = 870) with $AsCl_3$ vapour (11 kPa) at 873 K for 2 h. The amount of As in the bulk of As-HZSM-5 zeolite was 0.17 mmol g^{-1}.

IR spectroscopy was used to examine the introduction of As into the framework of highly siliceous HZSM-5 zeolite. The IR spectra for the parent HZSM-5 and the As-HZSM-5 zeolites are depicted in Fig. 1. The HZSM-5 showed only one band at 3740 cm^{-1} due to non-acidic silanol groups. The IR spectrum for As-HZSM-5 zeolite exhibited a new band at 3678 cm^{-1} together with the band at 3740 cm^{-1}. In the IR spectrum of pyridine adsorbed on the As-HZSM-5 at 373 K, we observed an absorption band at 1545 cm^{-1} which was attributed to pyridinium ion, while the absorption band at 3678 cm^{-1} disappeared. This indicates that acidic OH groups may be generated by the introduction of As^{3+} into the framework by the atom-planting method.

The alkylation of ethylbenzene with ethanol on As-HZSM-5 zeolite was carried out at 673 K. The detailed reaction procedure was as described.[3] The *para*-selectivity [the fraction of the *para*-isomer in the diethylbenzene (DEB) produced], changed with *W*/*F* ratio and diethylbenzene yield. In order to compare the *para*-selectivities of As-HZSM-5, HZSM-5 modified with 5 wt% P oxide [P(5)HZSM-5] and HZSM-5 zeolites, the *para*-selectivities at an almost constant yield of diethylbenzene (15–20%), *i.e.*, at an almost constant alkylation activity, were determined and are summarized in Table 1. The almost constant alkylation activity was achieved by adjusting *W*/*F*. The *para*-selectivity of As-HZMS-5 zeolite, 94.1%, was higher than those of P(5)HZSM-5 and HZSM-5.

Adsorption measurements for *p*- and *o*-xylenes on As-HZSM-5, P(5)HZSM-5 and HZSM-5 zeolites were carried out. The relative *o*-xylene adsorption velocity (V_{ROA}) was obtained from the ratio of the amount of *o*-xylene adsorbed at 180 min to that of *p*-xylene adsorbed at infinite time.[4,5] The

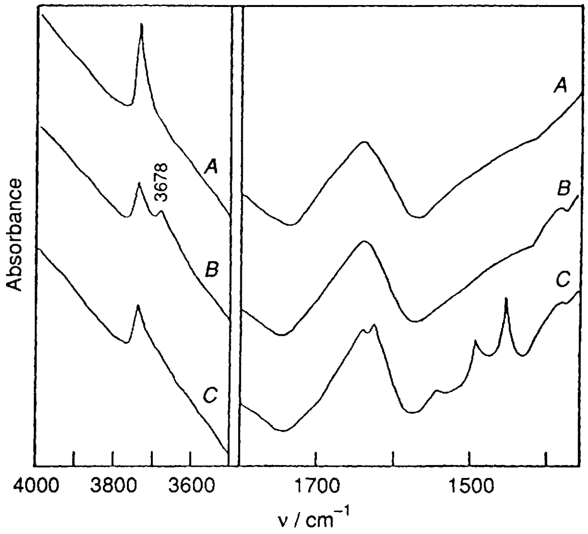

Fig. 1 IR spectra for the parent highly siliceous HZSM-5 and As-HZSM-5: (*A*) parent HZSM-5; (*B*) As-HZSM-5; (*C*) As-HZSM-5 after pyridine adsorption

Table 1 Alkylation,[a] adsorption and NH_3-TPD measurements

Catalyst	*W*/*F* /g h mol^{-1}	DEB yield (%)	*para*-selec. (%)	V_{ROA}	T_{max}/K
As-HZSM-5	10.7	15.3	94.1	0.524	458
P(5)HZSM-5	21.4	16.3	89.8	0.233	483
HZSM-5	3.57	19.8	43.2	0.639	563

Reaction temp. 673 K; partial pressures of ethylbenzene and ethanol, $P_{EB} = P_{EtOH} = 0.2$ atm.

V_{ROA} value may correspond to the 'tortuosity' of the pores of the zeolites or to the effective pore dimension. The V_{ROA} value for As-HZSM-5 was comparable with that for HZSM-5 and much higher than that for P(5)HZSM-5, while the *para*-selectivity for As-HZSM-5 was much higher than that of HZSM-5 and higher than that of P(5)HZSM-5 (Table 1). These facts suggest that the pore tortuosity of zeolites is not so important in improving the *para*-selectivity in this alkylation, as suggested previously.[4,5]

NH_3-TPD (temperature-programmed desorption) measurements for the zeolites examined here were carried out.[4,5] The peak position (T_{max}) in the NH_3-TPD profile may be correlated with the strength of acid sites, a lower temperature for the peak corresponding to weaker acid strength. The As-HZSM-5 and P(5)HZSM-5 zeolites each exhibited only one peak at 458 and 483 K, respectively (Table 1). The peaks for these two modified zeolites appeared at much lower temperatures than that for HZSM-5. Thus, the weaker acid strength leads to higher *para*-selectivity, as suggested in the previous paper.[4,5]

In conclusion, the As-HZSM-5 zeolite, whose acid strength is weak, exhibits a high *para*-selectivity (94.1%) for the alkylation of ethylbenzene with ethanol.

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