

ABSTRACT

ZSM-5 zeolites have been modified by Chemical Vapour Deposition (CVD) and impregnation methods and the catalysts studied for the selective synthesis of para dialkylbenzenes.

A successive modification technique was used to coat the zeolite surface with layers of silica. The properties of the catalyst were studied as a function of the amount of silica deposited. The rate of sorption of o- and p-xylene was drastically reduced upon deposition of silica, but the surface area remained almost the same. As for the catalytic results, the activity dropped, para-selectivity improved and the B/DEB remained the same. The above results lead the conclusion that, by CVD, only the zeolite external surface and the pore mouth are modified leaving the internal structure intact. A trend in para-selectivity of PDEB > PET > PX was obtained with the silylated catalyst.

In alkylation of ethylbenzene, an aluminolanthanosilicate catalyst of ZSM-5 type showed higher para-selectivity on account of occluded lanthanum species inside the pores. The para-selectivity has been improved by modifying the catalyst with oxide of magnesium. The sorption, acidic, and catalytic properties of the modified catalyst were comparatively less.

Several alumionophosphates have been synthesized by modifying the synthesis parameters such as source of aluminium, crystallization period and temperature, concentration of the amine etc.

The medium pore aluminophosphate molecular sieve $\text{AlPO}_4\text{-11}$ has been synthesized by using additional templating agents such as n-dibutylamine and n-dipentylamine. The extended lengths of these molecules exceeds the unit cell c-dimension of the $\text{AlPO}_4\text{-11}$. Modelling and quantum chemical calculations results indicate conformational flexibility for the amine molecules due to rotational freedom along the N-C bond and the possibility to accommodate a terminal methyl group in the double 6-member side-pocket. Based

on MNDO calculations, the net charge on the nitrogen atom's in the amine molecules was found to be similar and independent of the dimension and nature of the alkyl group. Ammonia was chosen as a model amine molecule and its adsorption on bridging oxygen sites was studied. The results were extrapolated to understand the the nature of interaction of amine molecules with the AlPO_4 -11 framework. In addition to the above studies, ^{13}C CP MASNMR results provided evidence for the dynamic movement of the amine molecules inside the one-dimensional tubular channels of AlPO_4 -11.

X-ray diffraction pattern and NMR spectra showed different profiles on calcination and rehydration of AlPO_4 -11. The extra peaks in the NMR spectra which correspond to 20% of the total area under the signals have been attributed to the interaction of the T-site of the framework with water molecules. The T3 site of the AlPO_4 -11 framework corresponds to 20% of the total T-sites. The NMR results have been directly correlated to this i.e. the T3 sites are affected by water molecules.

The results of modelling studies are consistent with the NMR results. The values of the adsorption energies calculated indicated that the Al3 and P3 are the preferred sites for adsorption of water molecules. Also the larger T3-O-T angle poses minimum steric hindrance to the approaching water molecules.

In addition to studies on AlPO_4 -11, a cobalt substituted AlPO_4 -11 has been successfully synthesized. Isolated redox centres have been detected based on catalytic test reactions. The CoAPO -11 has been compared with MnAPO -11.

Literature data show that both VPI-5, the largest pore molecular sieve and AlPO_4 -8 crystallize from similar gel composition and hydrothermal treatment conditions. According to the present studies, VPI-5 transformed to AlPO_4 -8 even at 388 K as studied by X-ray diffraction and MASNMR studies. The studies led to a precursor-product relationship between the two. The organic-free VPI-5, AlPO_4 -H1 has been synthesized and its identity with VPI-5 re-established based on data from XRD and MASNMR spectral measurements. Transformation of H1 to AlPO_4 -8 like that observed in the case of VPI-5 has been confirmed. The present studies show that AlPO_4 -8 cannot be synthesized directly

without the thermal treatment of either VPI-5 or H1 and that no organic is needed for its synthesis.

An aluminophosphate probably having a layered structure has been crystallized by increasing the amine concentration in the synthesis system for VPI-5. Characterization by the different techniques indicates that it may have a layered structure.