

Acidity and catalytic activity studies on the benzylation of *o*-xylene using some rare-earth exchanged zeolite-Y

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The acidity of the various rare-earth exchanged zeolite-Y catalysts has been examined by titration method using Hammett indicators and is correlated with the catalytic activity of the samples in the benzylation of *o*-xylene.

Heterogeneous catalysis is gaining importance in the synthesis of chemical intermediates and fine chemicals. In the shift away from homogeneous catalysis, zeolites play a major role. The zeolite based catalysts are effective in meeting current industrial processing and more stringent environment pollution limits.

A number of rare-earth ions exchanged zeolites have been shown to be catalytically active for a wide range of chemical reactions such as hydrogenation, oxidation, isomerization and cracking of various organic feed stocks. The cations present in the non-framework or exchange positions can be substituted by other cations through ion-exchange. The exchange capacity is large in the case of materials with low Si/Al ratios¹. The catalytic properties of these catalysts depend on the nature, number and location of the rare-earth cations and the acidity of the zeolite framework.

Zeolite Y consists of linked truncated octahedra called 'sodalite units', which have a cage of diameter 6.5 Å (β cage) accessible through six-membered rings of oxygen atoms². These units are connected to two six-membered rings, giving rise to a hexagonal prism. The polyhedra formed in this way encloses a supercage (α -cage) with an internal diameter of 12.5 Å and accessible through four 12-membered rings of oxygen atoms with a free aperture of 7.4 Å.

Ion-exchange is found to have a profound effect on various cation-oxygen and O-O bond lengths. Occupancy of site 1 by small univalent, divalent or trivalent cations increases the free diameter of the six-

membered oxygen rings in the hexagonal prisms joining the sodalite cages, in zeolite-Y. It has been found that the RE-cations can stabilize the framework and increase the thermal stability of the framework of zeolite Y. When H-Y is exchanged with RE-ions, the catalytic activities are enhanced considerably due to the higher strength of acid sites generated by RE-ions^{3,4}.

Yashima *et al.*⁵ have carried out the alkylation of toluene by methanol to xylenes over La, Ce, Co, Ni and Sr exchanged zeolite Y and found that the amount of *para*-isomers in reaction products was higher than the predicted one. This is attributed to the sieve effect and peculiarities of adsorption interactions between reagent and catalyst.

This paper discusses the characteristics of rare-earth ions containing Y zeolites in the benzylation of *o*-xylene. We have exchanged zeolite-Y with various rare-earth ions like La, Sm and Dy.

Experimental

Na-form of zeolite-Y was supplied by United Catalysts India Ltd. Before exchanging with rare-earth chlorides, the zeolite samples were stirred with 0.1 M solution of sodium acetate for 24 h. It was then washed free of acetate ions, filtered and dried. They were then stirred with the corresponding rare-earth chloride solutions (1 M) for 24 h. The filtered zeolites were washed repeatedly with distilled water to remove the counter-ions, dried and sieved to get particles of 100-200 mesh size. They were then activated at 500°C for 2h. The rare-earth content in the exchanged zeolites was estimated by AAS (Hitachi-800) and the degree of ion-exchange was calculated. Crystallinity of the exchanged zeolites was checked by X-ray diffraction using Rigaku Model, D/MAX-VC, Japan, diffractometer. No loss of crystallinity was observed.

The acidity in zeolites is due to the presence of the trivalent metal atom in a tetrahedral bonding configuration in the frame-work, creating a net negative charge on the frame-work. When this charge is balanced by a cation, it imparts Brönsted acidity to the zeolite. The contribution of Brönsted acidity to total acidity is much more than that by Lewis acid centres (originating from the frame-work Al) or other

Table 1—Benzylation of *o*-xylene^a

Catalyst ^a	Conv. of BC ^b (wt. %)	Rate of BC conv ^c (mmol g ⁻¹ h ⁻¹)	Product distribution (wt.%) ^d		
			3, 4-DMDPM	2, 3-DMDPM	Others
La (52.8)-Y	63.99	6.02	93.41	6.51	0.83
Sm(53.7)-Y	46.74	4.39	96.8	3.2	0.23
Dy (51.8)-Y	42.69	4.02	93.38	6.62	0.55

^a Reaction conditions: catalyst (g)=0.5; catalyst/C₆H₅CH₂Cl (wt./wt.)=0.21, *o*-xylene/C₆H₅CH₂Cl (molar ratio)=5; *o*-xylene (mol)=0.09; Reaction time 4 h.
^b Percentage of cation-exchange is given in brackets.
^c BC=benzyl chloride (C₆H₅CH₂Cl)
^d Rate of BC conversion (mmol g⁻¹h⁻¹) is expressed as the amount of BC converted/wt. of the catalyst × reaction time (h)
^e 2, 4-DMDPM=2, 4-dimethyldiphenylmethane; 3, 4-DMDPM=3, 4-dimethyldiphenylmethane; others = consecutive products

metal ions⁶⁻⁹. Tanabe's method¹⁰ was used for the measurement of acidity of the zeolites. The samples were activated at 500°C for 2 h prior to each experiment. The samples responded to the following indicators: dimethyl yellow ($pK_a \leq 3.3$), methyl red ($pK_a \leq 4.8$) and bromothymol blue ($pK_a \leq 7.2$). The acidity was determined by titration with *n*-butylamine (Table 1).

The liquid phase catalytic runs were carried out batchwise in a mechanically stirred, 50 ml closed, glass reactor fitted with a reflux condenser, a thermometer and a septum for withdrawing the product samples. The temperature of the reaction vessel was maintained using an oil bath. In a typical run, appropriate amounts of *o*-xylene and benzyl chloride (5:1 molar ratio) were charged in the reactor along with 0.5 g catalyst. The reaction mixture was heated to 363K with stirring. Samples were withdrawn periodically and analysed using a gas chromatograph (HP 6890) fitted with a flame ionization detector and a capillary column (50 m × 0.2 mm) with methyl silicon gum. Some selected runs were analysed by GC-MS (Shimadzu-MS QP-2000A) for product identification. The composition of the reaction mixture was also determined by comparing their gas chromatograph with those of authentic samples.

Results and discussion

Table 1 shows the conversion of BC (wt.%), rate of BC conversion (mmol g⁻¹h⁻¹) and the product distribution (wt.%) obtained over various catalysts in the benzylation of *o*-xylene. Under identical reaction conditions, 3, 4-dimethyldiphenylmethane (3, 4-DMDPM) and 2, 3-dimethyldiphenylmethane (2, 3-

Table 2—Acidity of the rare-earth ions exchanged zeolites

Zeolite	H ₀ ≤3.3	H ₀ ≤4.8	H ₀ ≤7.2
La-Y	1.190	1.192	0.952
Sm-Y	1.168	1.158	0.847
Dy-Y	1.143	0.917	0.767

DMDPM) are the main reaction products. A significant amount of polybenzylated products (others) are also formed (Table 1). Both 2, 3-DMDPM and 3, 4-DMDPM are formed by parallel reactions while polybenzylated products arise from secondary consecutive reactions of mono-benzylated products¹¹.

Among zeolite catalysts, La-Y catalyses the reaction efficiently to 3, 4-DMDPM and it is found to be superior compared to other rare-earth exchanged zeolite catalysts. The conversion of BC, rate of BC conversion and selectivity for 3, 4-DMDPM over La-Y after 4 h of reaction time are found to be 63.99 wt.%, 6.02 mmol g⁻¹h⁻¹ and 93.41 wt.%, respectively. La-Y shows the maximum value of acidity (Table 2). The value of H₀ at pK_a 3.3 is found to decrease from 1.19 to 1.14 while moving from La-Y to Dy-Y. The corresponding decrease in the value of conversion is found to be from 63.99 to 42.69. Thus the conversion of BC is found to have a direct correlation with the acidity of the catalyst. We are unable to explain the appreciable decrease in catalytic activity due to small change in acidity when we change La by Sm. The selectivity for the major product (3, 4-DMDPM) is found to be almost same over the three zeolites studied.

In acid catalyzed reactions, the activity of the catalyst is not only directly proportional to the total

concentration of acid sites present on the catalyst but also to the concentration of acid sites with a given acid strength¹². In addition to acidity, the shape selectivity also influences both conversion and selectivity of the products in case of zeolite catalysis. The acidity can be influenced by the size of the cation which is exchanged. The pore size of the zeolite was found to be a critical parameter in order to ensure a good selectivity. It is concluded that the presence of strong Brönsted acid sites in the zeolite catalyst appears to be very important which protonates alkylating agent into an electrophile which then attacks the aromatic ring resulting in the formation of substituted products.

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