

## Lewis acidity of rare earth exchanged zeolites

S Sugunan\*, J Bindhu, Disha & V Jessey  
Department of Applied Chemistry  
The Cochin University of Science &  
Technology, Kochi 682 022, India

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The Lewis acidity of yttrium and dysprosium exchanged zeolite Y and ZSM-5 has been determined by titration method using Hammett indicators. The acidity of the Y form increases with increase in concentration of the rare earth cation in the Y zeolite. It is independent of the amount of the rare earth ion for ZSM-5. The data have been correlated with the activity of these zeolites for the esterification of butanol using acetic acid.

The special thermal stability associated with rare earth exchanged zeolites enables them to find a large number of applications in industry. The catalytic activity of such rare earth exchanged zeolites depend on both the rare earth cation and the support. But a systematic study of the surface properties of these catalysts is lacking. Rare earth oxides are in general considered as bases<sup>1</sup>, and are also used as catalysts in a number of processes. Rare earths supported in zeolites are often used. The application of zeolite as an industrial catalyst is mainly due to its acidity. Incorporation of other cations into the zeolite changes its acidity. Acidity of the cation exchanged zeolites is mainly due to the Lewis acid sites. In this note we report the acidity of zeolite Y and ZSM-5 exchanged with rare earth element yttrium and dysprosium. The catalytic activity of these zeolites towards an esterification reaction is also reported as a test towards the acidity of these catalysts.

### Experimental

All solvents were purified before use. Sodium form of both ZY and Z ZSM-5 were supplied by United Catalysts India Ltd. Chlorides of yttrium and dysprosium were supplied by Indian Rare Earths Ltd., Udyogamandal. Before exchanging with rare earths 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 rare earth chloride solutions of different concentration for 24 h. The rare earth exchanged zeolites were powdered and sieved to get particles of

100-200 mesh size. They were then activated at 500°C for three hours.

The acidity was determined by titrating 0.1 g of the catalyst suspended in benzene against standard solutions of *n*-butylamine in benzene using the standard procedure<sup>2</sup>. At the end point basic colour of the indicator appeared. Since the titre for a 2 h experiment was found to be the same as that for a 24 h experiment titre values after 2 h were accepted. Some disadvantages of the method are that (i) water must be rigorously excluded, since water itself may react and alter the acidic character of the solid; and (ii) the usual colour change is difficult to observe when the sample itself is coloured or dark. In spite of these limitations, this method readily enables a determination of relative acid strength.

To study the catalytic activity 1 g of the catalyst, 0.5 g acetic acid and 5 g *n*-butanol were taken in a 25 cc round bottomed flask fitted with a reflux condenser. The reaction temperature was maintained at 98.0°C. The reaction was followed by product analysis by means of a Varian 3400 Gas Chromatograph.

The surface area of the samples were determined by BET method using Carla Erba Sorptomatic series 1800.

### Results and discussion

The acid strength of zeolites can be measured by a variety of methods including base titration using Hammett indicators, temperature programmed desorption of bases, NMR and IR spectroscopy. The acidity and basicity of these rare earth exchanged zeolites were measured by titration method using Hammett indicators of various *pKa* values. The following Hammett indicators were used. (The *pKa* values are given in brackets). Crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), neutral red (6.8), bromothymol blue (7.2) and 4-nitroaniline (18.4). The rare earth exchanged zeolites responded only to dimethyl yellow, methyl red and bromothymol blue towards acidity. No basic sites were detected with these indicators. The data are given in Table 1.

The acidity of zeolites depends on the coordination of Al and on the chemical nature of its neighbours. In zeolites it is generally accepted that the

Table 1—Acidity and catalytic activity of rare earth exchanged zeolites (Dy Y - dysprosium exchanged zeolite Y, Y Y - yttrium exchanged zeolite, Dy ZSM-5 - dysprosium exchanged zeolite ZSM-5 and Y ZSM-5 - yttrium exchanged zeolite ZSM-5)

Catalyst	Surface area $\text{m}^2\text{g}^{-1}$	Acidity ( $\text{m mol g}^{-1}$ )			Catalytic activity $10^8$ $k_1(\text{s}^{-1}\text{m}^{-2})$
		$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$	
NaY	347.15		0.247	0.272	3.99
0.05 Dy Y	347.20	4.388	5.025	5.654	3.86
0.10 Dy Y	347.05	5.025	6.276	7.538	3.97
0.20 Dy Y	349.25	6.282	8.158	9.423	4.26
0.50 Dy Y	348.30	7.538	10.668	11.923	11.05
Na ZSM-5	270.57	5.025	6.276	6.903	30.78
0.05 Dy ZSM-5	275.99		8.166	8.777	21.80
0.10 Dy ZSM-5	281.41		8.150	8.786	22.80
0.15 Dy ZSM-5	292.25		8.794	9.404	23.20
0.05 Y Y	347.15	5.017	5.644	6.771	4.84
0.10 Y Y	350.93	6.898	8.153	9.407	5.41
0.15 Y Y	348.12	7.525	8.780	10.030	6.26
0.20 Y Y	349.70	8.153	11.288	11.915	13.67
0.05 YZSM-5	276.29		8.161	8.788	24.00
0.10 YZSM-5	280.41		8.161	8.788	27.00
0.20 YZSM-5	291.25		8.161	8.788	29.00

Bronsted acid site is the -OH bridging a framework Si to a framework Al<sup>2</sup>. The dehydroxylation of alumina hydrate creates coordinately unsaturated sites which are the origin of Lewis acidity of these zeolites.

These are several factors that can influence the exchange of rare earth cations for Na<sup>+</sup> in zeolites like pH, time and concentration. The sodium form of zeolite Y in aqueous media produces basic pH (8.0-9.5) which is above the hydrolysis point of rare earth ions. This can lead to the precipitation of rare earth hydroxide on both the inner and outer surfaces of the zeolite. Hence the pH of the zeolite solution was adjusted with HCl to 5.0. The framework of ZY is generally resistant to structural degradation in acidic media. But partial dealumination may occur. The removal of Al from the lattice leads to decrease in the ion exchange capacity. Protons may compete with exchanging cations and influence the exchange level and ion distribution. Earlier studies<sup>2</sup> on the exchange equilibrium with Gd<sup>3+</sup> as a function of pH of the solution revealed that the exchange process is fairly similar over the pH range 3-5. Earlier studies<sup>3,4</sup> on cation exchange isotherms had also revealed that 24 h were required to obtain an exchange equilibrium

due to the size of the hydrated rare earth cation. Hydrated ion radius<sup>5</sup> of Y<sup>3+</sup> is 3.19 Å and that of Dy<sup>3+</sup> is 3.16 Å. There was no spectroscopic evidence for framework dealumination that may be associated with acidic condition. At room temperature the hydrated rare earth cations are restricted to the super cage because of their size. The most probable position is the center of the 12 ring opening of the super cage in ZY<sup>6-8</sup>. Cations in this position may act as obstacles for other cations. It has been reported that at an exchange level of 50% which corresponds to 1.2 Gd<sup>3+</sup> ion per super cage half of all the 12 rings would be occupied<sup>2</sup>. Studies using TPD of ammonia and base titrations using Hammett indicators reveal that there is a distribution of acid sites in zeolites. These are ascribed to cation (Al and rare earth) in different environments and the number of ions or molecules coordinated to the cations. Increased interaction of Al with a given Al site corresponds to weaker acidity. Stronger acidity is associated with isolated Al sites in a silica rich environment. In rare earth exchanged ZY Dy<sup>3+</sup> occupies the center of the 12 ring opening of the super cage. The number of such cages occupied by the rare earth cation increases as the rare earth

content increases. The rare earth cation is probably coordinated to three O atoms and three water molecules in the first coordination sphere at room temperature<sup>9-11</sup>. Even at the activation temperature of 500° dehydroxylation may not be complete giving rise to some Bronsted acidity due to the OH groups attached to the rare earth cation.

ZSM-5 systems have three dimensional pore structure<sup>12</sup> comprising of 10 tetrahedron rings with windows of diameter 5.1-5.6 Å. It generates two types of pore systems, one consisting of zigzag channels of near circular cross section and the other of straight channels with elliptical cross section. Because of the larger radius of the hydrated rare earth cation the number of such cations responsible for Lewis acidity and consequently the number of Bronsted acid sites due to coordinated OH groups to the metal ions remains almost constant. The strength of the acid sites also remains constant. This may be the reason for the independence of acidity with change in concentration of rare earth cation in the exchange solution.

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