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Towards a Green Synthesis of LAB's: Effect of Rare Earth Metal Ions on the Benzene Alkylation with 1-Dodecene over NaFAU-Y Zeolites

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Chemically modified microporous materials can be prepared as robust catalysts suitable for application in vapor phase processes such as Friedel-Crafts alkylation. In the present paper we have investigated the use of rare earth metal (Ce^{3+}, La^{3+}, RE^{3+}, and Sm^{3+}) exchanged Na-Y zeolites as catalysts for the alkylation of benzene with long chain linear 1-olefin; 1-dodecene. Thermodesorption studies of 2,6-dimethylpyridine adsorbed catalysts (in the temperature range 573 to 873 K) show that the rare earth zeolites are highly Brönsted acidic in nature. A perfect correlation between catalyst selectivity towards the desired product (2-phenyldodecane) and Brönsted acid sites amount has been observed.

1. Introduction

Responsible care and sustained development have been the paradigms of industrial production. Therefore, the process has to be optimized in terms of energy efficiency, chemical utilization, and waste minimization [1, 2]. The manufacture of fine and speciality chemicals in traditional processes has commonly been associated with the large quantities of toxic waste [3]. Use of traditional catalysts such as mineral acids, strong bases, and toxic metal reagents is widespread and has many drawbacks including handling difficulties, inorganic contamination of the organic products, formation of large volumes of toxic waste and very poor reaction selectivity leading to unwanted isomers and other side-reaction products. Again, the normal work-up procedure for the reaction employing these catalysts involves a water quench that prevents the acid being used again. In addition, since the catalysts are irreversibly lost, the overall atom efficiency is very low and hence is not cost effective. Thus, these traditional catalysts are marked by high E-factor and low atom efficiency. Consequently, a judicious choice for a safe acid catalyst for the alkylation reaction attains significance.

These problems can be largely overcome if genuinely catalytic, heterogeneous alternatives to environmentally unacceptable catalytic systems can be developed. Solid acid catalysts are the best alternatives. They include heteropoly acids [4], sulphated zirconia [5], acidic clays [6], $AlCl_3$ or $ZnCl_2$ supported on mesoporous clays or MCM-41 type materials [7, 8], and acidic zeolites [9–11]. Although many of these are active, the lack of selectivity for Linear Alkyl Benzene's (LAB's) and stability to process time are serious problems. A successful solid acid catalyst demands activity, selectivity, reusability and stability towards cocking, etc. so as to be economical compared to HF acid [1, 2]. Zeolites showed higher selectivity for the 2-

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phenyl isomer [12]. The selectivity for the desired product (2-phenylalkane) strongly depended on the chain length of the 1-olefin over a given catalyst. In the present paper we discuss the alkylation of benzene with 1-dodecene over a series of solid acid catalysts. High chemical and thermal stability of the systems, high activity, reusability and resistance to deactivation coupled with its eco-friendly nature makes rare earth exchanged zeolites a superior choice of catalyst for the synthesis of LAB's over the conventional catalysts such as HF or $AlCl_3$.

2. Materials and instrumentation

2.1. Starting materials

Sodium exchanged zeolite was prepared by ion exchanging the pure H-Y zeolite (Sud-Chemie India Ltd.) with 0.1 M sodium chloride solution (0.05 moles of NaCl/g of zeolite obtained from SD-Fine Chemicals, India) at room temperature for 3 times. Rare earth exchanged forms were prepared by ion exchanging Na-Y with a 0.5 M rare earth nitrate solution (0.025 moles of nitrate/g of zeolite, obtained from Indian Rare Earths Ltd. Udyogamandal, Kerala, India) at 353 K for 24 h. It was then filtered, washed with de-ionized water followed by drying at 383 K in an air oven over night. All the samples were then calcined at temperatures from 423 to 773 K, and at 773 K for 5 h with a heating rate of 12 K per minute with a constant air blowing over the sample (60mL/min) [13, 14]. H-mordenite was a product from Zeolyst International New York, USA with a Si/Al ratio of 19. SiO_2- Al_2O_3 was prepared using well-known chemical routes in the laboratory [15].

2.2. Catalysts characterization

The percentage of metal ion exchanged and framework Si/Al ratio were determined by EDX using a JEOL JSM-840 A (Oxford make model l6211 with a resolution of 1.3 eV). Structural information was obtained from XRD performed using a *Rigaku D-max C X*-ray diffractometer with Ni-filtered Cu Kα radiation and IR performed using a *Nicolet Impact 400FT IR* spectrometer. Solid-state NMR experiments were carried out using a *Bruker DSX-300* spectrometer at resonance frequencies of 78.19 MHz for ^{27}Al and 59.63 MHz for ^{29}Si. For all the experiments a standard 4 mm double-bearing *Bruker* MAS probe was used. A sample rotation frequency of 7 KHz for ^{27}Al and ^{29}Si with a single pulse excitation corresponding to $\pi/2$ flip angle was used. The pulse length for the experiments was 10 ms and 4 ms for ^{27}Al and ^{29}Si respectively whereas the pulse delays were 2 s, and 5 s. The surface area and pore volume measurements were performed by low temperature nitrogen adsorption with the help of a *Macromeritics Gemini* surface area analyzer. Acid structural properties were determined by temperature programmed desorption (TPD) of ammonia with a conventional equipment. For the Brönsted acid amount determination by thermodesorption method, the activated samples (about 10 mg) were equilibrated with 2, 6–dimethyl pyridine vapors. The samples were equilibrated for 48 hours under vacuum. 2, 6–DMP desorbed in the temperature range 573–873 K was monitored using *TGAQ 50 V2.34* thermal analyzer (*TA Instruments* make) in presence of nitrogen at a heating rate of 20 K/min.

2.3. Reaction procedure

Reaction was carried out in a fixed-bed, down-flow reactor made of glass with 0.6 cm internal diameter and 30 cm height. Catalysts (1500 mg) were activated (773 K) for 12 hours in presence of oxygen, allowed to cool to room temperature in dry nitrogen and then heated to reaction temperature (448 K) where it was kept for one hour to stabilize. The reaction mixture (99% 1-dodecene obtained from *Lancaster Chemical Company* was used without further purification. Benzene obtained from *SD Fine Chemicals* was used after purification with sulphuric acid and 10% sodium carbonate) was fed into the reactor in presence of dry N_2 to provide inert atmosphere. Products were collected at third hour and were analyzed with a *Chemito GC1000* gas chromatograph equipped with a SE-30 capillary column (oven temperature 353-503 K, injector temperature 373 K, detector temperature 373 K). The products were further analyzed with GCMS using a *Shimadzu-5050* instrument provided with a 30 m HP-30 capillary column of cross linked 5% phenylmethylsilicone. The MS detector voltage was 1 kV. The m/z values and relative intensity (%) are indicated for the significant peaks. (Conditions: column temperature was adjusted between 323-533 K with a heating rate of 10 K/minute, injector: 513 K and detector: 563 K).

3. Results and discussion

3.1. Physicochemical characterization

A detailed study of the characterization of the present catalyst systems has been already reported elsewhere [16, 17]. The unit cell composition of different zeolite samples is listed in Table-I. X-ray diffraction and infrared spectral studies confirms the inertness of the zeolite framework towards moderately high ion exchange temperatures. Consistent with the earlier reports, it is clear that parent as well as rare earth exchanged zeolites crystallizes into cubic unit cell with F3dm space group. Fourier Transform infrared spectroscopy shows uniform transmittance patterns for the parent and rare earth exchanged zeolites. Rare earth exchanged zeolites and Na-Y zeolite show bands characteristic of faujasite type of zeolites in the framework region. The spectra show major shifts in the framework vibrations of Na-Y zeolite upon rare earth exchange as evidenced from Table-I. IR spectra and X-ray diffraction measurements showed that rare earth Na-Y zeolites are crystalline and present well-defined structures.

^{27}Al MAS NMR spectra of dehydrated zeolites show a main central peak around 58 ppm (Na-Y = 60.12, CeNa-Y= 55.17, and LaNa-Y = 56.09 ppm) corresponds to tetra-coordinated framework aluminium. For the as-exchanged rare earth zeolites, a small peak at/around 0 ppm is observed confirming the presence of extra-framework aluminium (hexa-coordinated). A small peak at/around 30 ppm is due to penta-coordinated aluminium in the zeolite structure. These spectra have been thoroughly discussed in our earlier report [16].

^{29}Si MAS NMR spectra of H-Y, Na-Y, as-exchanged CeNa-Y and LaNa-Y zeolites show a sharp peak around 95±5 ppm. The main central peak in the spectra of the samples show shoulder peaks corresponding to Si (nAl), where n = 3, 2, and 1. The central peak must be due to a Q^4 silicon atom. Exchanging H^+ ions with Na^+, Ce^{3+}, and La^{3+} results in a high field shift of Si (nAl) signals, indicating a change in the local geometry of SiO_4 tetrahedra in presence of heavy cations. Details are reported elsewhere [17].

The important physicochemical characteristics of different zeolites employed in the present study are summarized in Table-II. The acid strength distribution of the parent and various rare earth exchanged zeolites are presented in Table-II. This table describes the distribution of acidity in three temperature regions of 373–473 K (weak acid sites), 473–673 K (medium acid strength) and 673–873 K (strong acid sites). Hence, NH_3-TPD presents the acid site distribution in zeolites rather than the total acidity. Amount of ammonia desorbed by each sample varies with the nature of rare earth cation present. All the rare earth exchanged samples invariably show high value of acidity. CeNa-Y and SmNa-Y have the maximum acidity and pure Na-Y the least. However, for all the rare earth exchanged zeolites the amount of ammonia desorbed in the high temperature region (673-873 K) is low.

The Brönsted acid amount obtained from the thermodesorption of 2, 6-DMP is shown in Table-II. 2, 6-DMP desorption clearly shows the variation of Bönsted acidity with the exchange of sodium with rare earth metal cations. Brönsted acidity of Na-Y is 0.18 mmol/g of the catalyst and that of as-exchanged CeNa-Y and RENa-Y is 0.74 and 0.69 mmol/g respectively. This increase in Brönsted

TABLE I Chemical composition, important framework vibrational modes, and the amount of 2,6-DMP desorbed from the parent and different rare earth exchanged zeolites

Zeolite	Chemical composition[a]	Assymetric stretch (cm^{-1})EL or IT[b]	Symmetric stretch (cm^{-1}) EL or IT[b]	Double ring[c] (cm^{-1})	T-O bend[d] (cm^{-1})
H-Y	$H_{76.5}\ Al_{76.5}\ Si_{115.5}\ O_{384}$	1050	771	570	457
Na-Y	$Na_{78.5}\ Al_{78.5}\ Si_{113.5}\ O_{384}$	1058	791	571	460
CeNa-Y	$Ce_{10.7}\ Na_{44.3}\ Al_{76.4}\ Si_{115.6}\ O_{384}$	1078	777	578	468
LaNa-Y	$La_{10.5}\ Na_{45.0}\ Al_{78.5}\ Si_{115.5}\ O_{384}$	1073	767	573	465
RENa-Y[e]	$La_{9.38}\ Ce_{1.21}\ Pr_{2.72}\ Nd_{3.10}\ Na_{27.27}\ Al_{78.5}\ Si_{115.5}\ O_{384}$	1074	779	577	468
SmNa-Y	$Sm_{8.1}\ Na_{52.4}\ Al_{78.5}\ Si_{115.5}\ O_{384}$	1073	778	579	469

a. As determined by Energy Dispersive X-ray analysis.
b. EL, External linkage; IT, internal tetrahedra.
c. D^6R double ring units.
d. T= Si, Al.
e. RENa-Y is a mixed rare earth exchanged zeolite with La^{3+} as the main counter cation and small amounts of Ce^{3+}, Pr^{3+} and Nd^{3+} etc.

TABLE II Physicochemical characterization of pure H-Y, binder free Na-Y and its rare earth exchanged analogues calcined at 773 K

	Acid amount (mmol/g)				Textural properties[b]		
Zeolite	weak[a]	medium	strong	Total acid amount (mmol/g)	BET surface area (m^2/g)	Pore volume (m^3/g)[c]	Brönsted acid sites amount (mmol/g)[d]
H-Y	0.69	0.41	0.33	1.43	398	0.266	0.39
Na-Y	0.59	0.12	0.05	0.77	254	0.232	0.18
CeNa-Y	1.45	0.59	0.20	2.24	484	0.296	0.74
LaNa-Y	0.92	0.42	0.13	1.48	441	0.287	0.56
RENa-Y	0.70	0.68	0.46	1.83	468	0.291	0.69
SmNa-Y	1.21	1.09	0.34	2.64	498	0.302	0.71

a. Ammonia desorbed in the temperature range 373–473 might contain some physisorbed ammonia too.
b. As determined from low temperature nitrogen adsorption isotherm.
c. Total pore volume measured at 0.9976 P/P0.
d. As determined by thermodesorption of 2,6-dimethylpyridine in the temperature range 573 to 873 K.

acidity on exchange with rare earth cations is in lines of several well-established methods of generating Brönsted acid sites in the pores or cavities of a zeolite. Decrease of Brönsted acidity in the case of LaNa-Y must be due to the increased migratory tendency of La^{3+} cations from the large cages to the small cages and subsequent formation of BAS that are not accessible for probe molecule compared with the Ce^{3+} ions. This observation is in good agreement with the results from NH_3 TPD studies, thermodesorption of 2,6-DMP and different MAS NMR studies. From Table-II, we conclude that there is a perfect correlation between the amount of ammonia desorbed in NH_3-TPD studies and the amount of 2,6 DMP desorbed in the temperature range 573-873 K.

3.2. Alkylation of benzene with 1-dodecene

Three classes of solid acids have been used in this work for the alkylation of benzene with 1-dodecene. They include; 1) pure H-Y, 2) rare earth exchanged NaFAU-Y zeolites, 3) silica-alumina. Under the reaction conditions, marginal heat effects due to exothermic nature of the reaction were observed. During the reaction, temperature was varied in the range 3-5 K.

The results of the benzene alkylation with 1-dodecene over various as-exchanged zeolites along with mordenite, and SiO_2-Al_2O_3 under well-optimized conditions are presented in Table-III. Na-Y zeolite is near inefficient as an alkylation catalyst. 1-dodecene conversion increases as the Na^+ ions get preferentially exchanged with rare earth cations. However, the overall conversion of 1-dodecene over rare earth exchanged zeolites is rather small compared to pure H-Y. Among different rare earth exchanged zeolites, cerium exchanged zeolite exhibit maximum conversion of olefin and selectivity for the 2-phenyl isomer. Silica-alumina performs far inferior to pure H-Y or as-exchanged rare earth zeolites. LaNa-Y and RENa-Y RENa-Y is a mixed rare earth exchanged zeolite with La^{3+} as the main counter cation and small amounts of Ce^{3+}, Pr^{3+} and Nd^{3+} etc. exhibit almost similar activity and selectivity. H-Y and rare earth exchanged forms generate more di-substituted products compared with mordenite. Dialkylation was maximum over pure H-Y zeolite and was least over mordenite. As-exchanged zeolites produce almost identical amounts of di-dodecylbenzene.

HFAU-Y has a 3-D interconnecting pore systems with super cages of 1.18 nm connected by circular 12-ring 0.74 nm windows [18]. HMOR has a bi-directional pore system with parallel circular 12-ring channels (0.65x0.70 nm) and elliptical 8-ring channels (0.26x0.57). However, it practically functions as unidirectional pore system as the 8-ring channels, in effect, are inaccessible for most organic compounds [19]. Here, the product selectivity appears to play a major role. On the other hand, silica-alumina does not have a regular pore structure.

Parent Na-Y zeolite shows very low activity and selectivity for the conversion of 1-dodecene to 2-phenyl isomer. The effect of sodium ions on the activity of Brönsted type of zeolites in acid catalyzed reactions has been recognized very early especially in the case of faujasite type of zeolites. It was proposed that the residual Na^+ ions have a poisoning effect on the acidity i.e.: a particular Na^+ ion, present within the decationated zeolite, has a neutralizing effect over a large number of the existing protons [20-21]. The effect of residual Na^+ ions is to weaken the Brönsted acid sites, without actually neutralizing more than one Brönsted site per Na^+ ion. Pure Na-Y possess very small acid amount. Subsequent exchange of Na^+ ions by rare earth cation improves the acid structure dramatically. An increased Brönsted acid strength (it is well known that rare earth cations produce Brönsted acidity in zeolites; see Table-II) would increase the lifetime of the intermediate carbocation generated by taking proton from zeolite by the C_{12} olefin. This improves the chances of addition of the carbocation to the benzene molecule, thus improving the alkylation of benzene with 1-dodecene [20]. Consistent with the increase in the Brönsted acidity, all the rare earth exchanged zeolites exhibits better conversion of 1-dodecene and selectivity for 2-phenyldodecane than the pure binder free Na-Y zeolite. A comparison of acid sites amounts of pure H-Y and various as-exchanged zeolites reveals that in general the as-exchanged zeolites show weak desorption peaks at high temperature reagions. This might be the reason for their reduced overall conversion of 1-dodecene. Improvement in the porous network (see surface area and pore volume in Table-II), and the number of active sites per unit area [ratio of total acid amount from NH_3-TPD and surface area; ($mmol/m^2$); not shown] of Na-Y zeolite upon exchange with rare earth metal ions might be the reason for the improved selectivity for 2-phenyldodecane.

To compare the activity of different as-exchanged rare earth Na-Y zeolite systems with standard catalytic systems, alkylation of benzene with 1-dodecene was performed over H-mordenite and silica-alumina. Mordenite shows much higher activity and selectivity for this reaction (86.5 and 54.5% respectively). This variation in activity is due to their structural difference (see previous discussion). In the case of mordenite, shape selectivity appears to play an important role in producing maximum 2-phenyl isomer. Silica-alumina with their weak acid structural properties and non-regular pore structure, exhibit low conversion of 1-alkene selectivity for the desired isomer.

3.3. Time on stream studies

Though zeolites possess very high activity and selectivity for the production of 2- phenyl isomers, they are not very stable towards the drastic reaction conditions [22–24]. We have carried out the alkylation reaction for 14 h

TABLE III Alkylation of benzene with 1-dodecene – variation of catalysts

Zeolite	Alkene conversion	2-phenyldodecene	Monoalkylated[a]	Heavy[b]
H-Y	81.9	39.2	92.8	7.2
Na-Y	10.2	40.1	96.1	3.9
CeNa-Y	75.1	46.4	94.3	5.7
LaNa-Y	67.6	44.6	93.9	6.1
RENa-Y	66.8	45.6	93.4	6.6
SmNa-Y	71.7	46.3	94.9	6.1
H-MOR[c]	86.5	54.5	94.1	5.9
SiO_2-Al_2O_3[c]	30.2	30.2	95.3	4.7

Reaction temperature: 448 K; amount catalyst: 1500 mg; benzene to 1-dodecene molar ratio: 20:1; time on stream: 3 h; constant flow of nitrogen: (10 mL/h).

a. Include 3, 4, 5, and 6 phenylalkane isomers.

b. Include dodecene dimers, didodecylbenzene, alkyltetralines, skeletal isomerization products (<2%), and some other polymeric products. Also, lower hydrocarbons formed during the reaction through the cracking of 1-dodecene (occurred to a very limited extent), which reacts with benzene to form lower alkyl benzenes [16].

c. H-mordenite used as a model catalyst was a product from Zeolyst International New York, USA with a Si/Al ratio of 19.

d. SiO_2- Al_2O_3 was prepared using well-known chemical routes in the laboratory [17].

continuously over H-Y and CeNa-Y zeolites and products were collected at intervals of every hour. The results of deactivation studies are depicted in Figure 1. For H-Y zeolite, conversion of 1-dodecene attains a maximum after 4 h (82.8%) and then starts to deactivate (conversion was 52.1% after 14 h). However, the selectivity for the 2- phenyl isomer increases slowly with time and reaches maximum after 14 h (45.1%). CeNa-Y undergoes rather slow deactivation compared to H-Y.

Conversion was 76.5% at forth hour and 59.2% at the end of the reaction and the corresponding selectivity for 2-phenyalkane was 46.9 and 50.9%. H-Y underwent 37.1% deactivation whereas, CeNa-Y 22.6% in 14 h. The improvement in the 2-phenyldecane content with time is clearly due to the blocking of unwanted pores of the catalyst upon coking. It practically prevents the diffusion of isomerized products like 3, 4, 5 or 6-phenyldodecane coming out of the zeolite pores. This increase in the 2-phenyl isomer content with time could also be due to the transalkylation reaction between benzene molecule and bidodecylbenzene and tridodecylbenzene in the zeolite pore mouth [25]. The increase in the 2-phenyl isomer production strongly supported by the fact that there is corresponding decrease in the in the dialkylate formation with time.

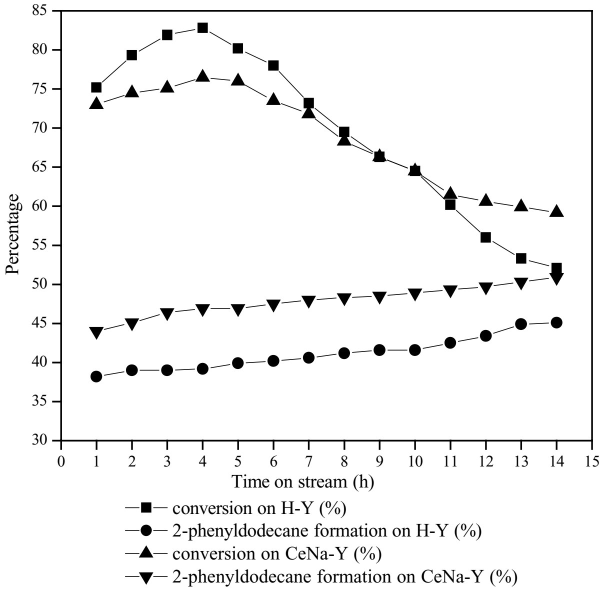

Figure 1 Effect of time on stream (TOS, h) in the total conversion of 1-dodecene and selectivity for 2-phenyldodecane during the alkylation benzene with 1-dodecene on H-Y and CeNa-Y zeolites.Reaction temperature: 448 K; amount catalyst: 1500 mg; benzene to 1-dodecene molar ratio: 20:1; weight hour space velocity: 2.48 h_{-1}; constant flow of nitrogen: (10 mL/h).

We have found that the deactivated H-Y and rare earth zeolites (in fact other solid acids too) can be partially regenerated by solvent extraction to remove most of the 'heavy' products followed by oxidative treatment at the activation temperature.

The deactivated zeolite (we have studied CeNa-Y) is extracted with benzene to remove the products from the catalyst surface. Further washed with de-ionized water, dried at 383 K overnight and regenerated by activating to 773 K at a heating rate of 12 K per minute and at 773 K it was maintained for 5 h. Regenerated CeNa-Y converted 73.8% 1-decene under similar reaction conditions.

4. Conclusion

Benzene alkylation with 1-dodecene was carried out over H-Y, Na-Y, and various rare earth (Ce^{3+}, La^{3+}, RE^{3+}, and Sm^{3+}) exchanged Na-Y zeolites, H-mordenite, and silica-alumina. The present method for the synthesis of mono-dodecylbenzene gives more than 90% yield. A perfect correlation between the amount of 2,6-DMP desorbed in the 573-873 K temperature range and yield of

2-phenyldodecane have been derived in the case of rare earth exchanged Na-Y zeolites. Time on stream (TOS) studies confirms the superior resistance of rare earth zeolites towards catalysts deactivation. Catalyst stability is high and can be carried out continuously. These catalysts are reused and the processes produce no drained waste and the catalysts hence used are highly environmentally friendly.

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