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Synthesis, characterization and catalytic properties of ferri- and gallo-silicate analogues of zeolite NCL-1

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Ferri- and gallo-silicate analogues of NCL-1, a high silica large pore zeolite, have been synthesized and characterized through spectroscopic methods (XRD, IR, ESR and solid state MAS NMR), ion exchange capacity, adsorption (*n*-hexane, 1,3,5-trimethylbenzene and water), BET surface area and catalytic activity and selectivity in Brønsted acid catalyzed conversion of 1,3,5-trimethylbenzene measurements. These data were compared with those exhibited by Al-NCL-1 analogue. During 1,3,5-trimethylbenzene (mesitylene) isomerization into 1,2,4-trimethylbenzene (pseudocumene), the conversion decreased in the order: Al- > Ga- > Fe-NCL-1 (at the same reaction temperature, WHSV and time on stream). However, the selectivity for pseudocumene and isomerization selectivity (vis-á-vis disproportionation) followed the reverse order at comparable conversion level.

Keywords: ferri-silicate; gallo-silicate; zeolites; molecular sieves; synthesis; mesitylene isomerization

1. Introduction

The modification of physico-chemical and catalytic properties of zeolites via framework replacement of Al by some other metal ions is well established [1–3]. The incorporation of Fe^{3+} in a number of medium and large pore zeolite frameworks has been reviewed recently [3,4]. Gallo-silicate analogues of various zeolites structures such as MFI [5], MEL [6], TON [7], EUO [8], BEA [9,10] etc. have been reported. Recently, we have synthesized a new high silica large pore zeolite NCL-1 [11–14]. Although the crystallographic structure of zeolite NCL-1 is not yet known, the adsorption and catalytic test reactions clearly rank NCL-1 as a large pore zeolite, the effective void space being comparable to that of MOR [12,14].

Now, we report the synthesis, characterization and catalytic properties of ferri-silicate (Fe-NCL-1) and gallo-silicate (Ga-NCL-1) analogues of zeolite NCL-1. Both, the Fe-NCL-1 and Ga-NCL-1 are characterized by various spectroscopic techniques (such as XRD, IR, ESR and MAS NMR), ion exchange and sorption capacities method. Finally, the catalytic activity and selectivity of the Fe- and Ga-NCL-1 (vis-á-vis Al-analogues) in isomerization and disproportionation of 1,3,5-trimethylbenzene have been studied.

2. Experimental

2.1. Synthesis

The Fe-NCL-1 samples (A and B) were prepared after modifying the procedure, reported for NCL-1 zeolites [11,12], according to our general and convenient method for preparing ferri-silicate molecular sieves using a complexing agent [2,16]. In a typical Fe-NCL-1 preparation, an alkali solution containing 1.5 g NaOH in 20 g water was added to a slurry of 9 g fumed silica (Sigma-5130) in 60 g water. This mixture was stirred for 45 min at 298 K (solution A) before adding it slowly, under vigorous stirring, to a solution B, containing the required amount of ferric sulfate and oxalic acid in water (0.53 or 0.28 g of $Fe_2(SO_4)_3 \cdot 9H_2O$ in 20 g water to yield Si/Fe ratios 80 or 150, respectively, oxalic acid/Fe = molar ratio 1.5). The mixture was stirred for 15 min before adding to it a solution C containing 3.42 g of hexamethylene bis (triethylammonium bromide) in 15 g water. Finally, 1.0 and 1.1 g sulfuric acid (96%) in 30 g water was added to the gel having Si/Fe ratios 80 and 150, respectively. The resultant reaction mixture was stirred for 1 h and then placed in an autoclave. The crystallization was conducted in a 100 ml stainless steel autoclave at 443 ± 2 K under agitation (60 rpm).

Similarly, Ga- and Al-silicates were also prepared where instead of $Fe_2(SO_4)_3 \cdot 9H_2O$ and oxalic acid, $Ga_2(SO_4)_3$ (0.41 g, sample C or 0.21 g, sample D) or $Al_2(SO_4)_3 \cdot 16H_2O$ (0.3 g, sample E or 0.16 g, sample F) was added. Further, the amount of sulfuric acid used was 0.85 g (samples C and E) or 1.1 g (samples D and F). For comparison, pure silica polymorph, Si-NCL-1 (sample G) was also prepared according to the reported method [11,12]. The rest of the procedure was the same as mentioned above. The crystallization time (days) was 10 (samples A, C and E), 7 (samples B, D and F) or 3 (sample G).

After crystallization, the solid was filtered, washed thoroughly with deionized water, dried and finally cal-

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cined carefully in flowing dry air at 823 K (heating rate 2°C $\min^{-1}$). The yield of crystalline solid (based on SiO_2/M_2O_3 in gel) ranged between 85 and 90% for all the samples. The Na-form of the ferri- and gallo-silicates was converted into ammonium form by treatment with 1 M ammonium acetate solution. Finally, catalytically active H-form was obtained by calcining the ammonium form at 783 K for 16 h in a flow of dry air.

2.2. Characterization

The chemical analyses were performed by wet chemical as well as by atomic absorption methods (Hitachi Z-800). The crystalline phase identification was carried out by XRD (Rigaku, D Max/III-VC model using Cu Kα radiation). The zeolites were further characterized by scanning electron microscopy (Cambridge, Stereoscan 400), ESR (Bruker E-2000) and IR (Nicolet, KBr pellet technique). The solid state MAS NMR measurements (for ^{29}Si and ^{71}Ga) were carried out using a Bruker MSL 300 spectrometer. For ^{29}Si and ^{71}Ga, tetramethylsilane and $Ga(NO_3)_3 \cdot xH_2O$ were taken as external standards, respectively. Other details are given in ref. [12]. Calcined samples were also characterized by BET surface area and gravimetric adsorption (Cahn balance) measurements. The ion exchange capacities (K^+/MO_2^-, molar ratio, M = Fe^{3+}, Ga^{3+} and Al^{3+}) of calcined H/Fe-NCL-1, H/Ga-NCL-1 and H/Al-NCL-1 were determined by treating the Na-form of the samples with aqueous solution of KCl at 343 K for 3 h. The pH of the solution was maintained between 7 and 8 by adding a few drops of KOH solution. The exchange procedure was repeated thrice. Then, the catalyst was analyzed for K by wet chemical analysis.

Isomerization of 1,3,5-trimethylbenzene to 1,2,4-trimethylbenzene was carried out at atmospheric pressure using a down flow fixed bed tubular silica reactor (i.d. = 10 mm, length 30 cm) using binder-free H-form of the catalyst (particle size = 0.5–0.6 mm). Reaction products were analyzed by gas chromatography (HP-5880) using capillary column (silicon gum) and flame ionization detector.

3. Results and discussion

3.1. Characterization

The Si/M molar ratio (M = Fe, Ga and Al) of the reactant gels as well as the final crystalline solids are given in table 1. Because of the use of Al-free and highly pure fumed silica, the Al concentration in Fe- and Ga-NCL-1 samples was found to be negligible ($SiO_2/Al_2O_3 > 3000$) and could not be detected by AAS. The color of the as-synthesized and calcined ferri-silicate was almost white indicating the absence of brown iron oxide outside the zeolite crystals. The X-ray powder diffraction patterns of Fe-NCL-1, Ga-NCL-1 and Al-NCL-1 samples were typical of NCL-1 zeolites [11–13]. The crystallinity of Fe- and Ga-NCL-1 samples (with respect to Al-NCL-1 samples) was ca. 94 and 96%, respectively. The scanning electron micrographs of Ga-, Fe- and Al-NCL-1 exhibited the absence of amorphous material. The particles of all the three samples consist of a long bundle of needle shaped crystallites, typical of NCL-1 morphology [12,13]. The framework IR bands (in the region of 300–1300 cm^{-1}) of calcined Fe-, Ga- and Al-NCL-1 samples (fig. 1) are characteristic of NCL-1 zeolites. A minor shift towards lower wavenumber, exhibited by samples A and C, vis-á-vis E, may arise due to the replacement of Al by heavier Fe and Ga in NCL-1 framework [2,3].

The ESR spectrum of Fe-NCL-1 (fig. 2) shows two signals, one around $g = 4.3$ and the other at 2.0. These signals are characteristic of ferri-silicate molecular sieves and have been discussed in detail earlier [2,3]. Although an ESR signal around $g = 4.3$ cannot be used to confirm the presence of Fe^{3+} in zeolite lattice positions, the observation of such a signal is a necessary consequence of such a presence and may provide additional support to any postulate of isomorphous substitution of aluminum by iron [3]. Fig. 3 depicts ^{29}Si and ^{71}Ga MAS NMR spectrographs exhibiting a single peak at $\delta = 112$ ppm (Si(4Si)) and at $\delta = 148$ ppm (Ga^{3+} in Td environment) respectively. Al-NCL-1 (sample E) gave a

Fig. 1. Framework IR spectra of calcined NCL-1 samples, curves a–c refer to samples B, D and F, respectively.

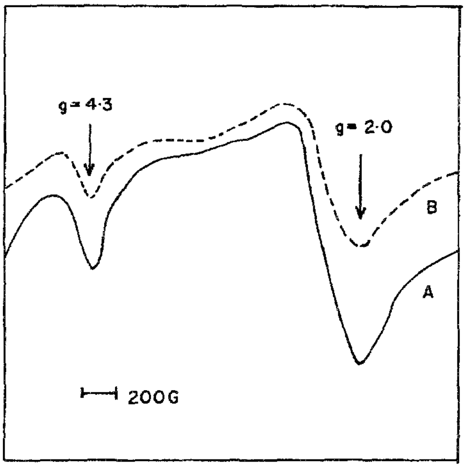


Fig. 2. ESR spectrum of Fe-NCL-1, curves a and b refer to as-synthesized and calcined samples, respectively.

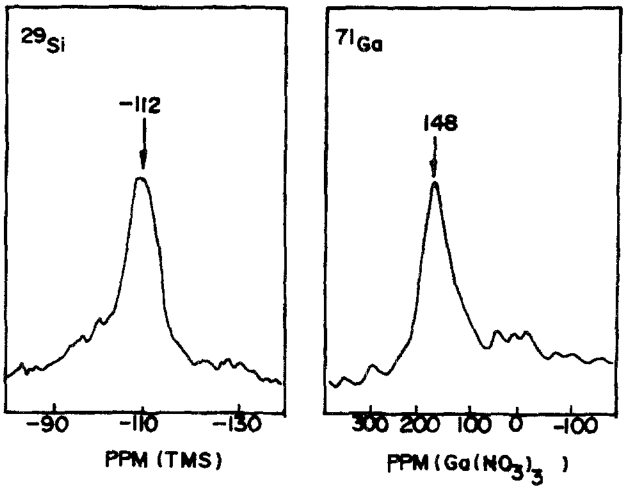


Fig. 3. ^{29}Si and ^{71}Ga MAS NMR of Ga-NCL-1 (sample C).

^{27}Al signal at $\delta = 51$ ppm (with respect to $Al(NO_3)_3{\cdot}6H_2O$) in accordance with earlier data [12].

The equilibrium sorption capacities of calcined H/Ga-NCL-1, H/Fe-NCL-1 and H/Al-NCL-1, for *n*-hexane, 1,3,5-TMB and water, estimated at 298 K and $p/p_0 = 0.5$, are listed in table 1. The comparability of sorption values of Fe-, Ga- and Al-NCL-1 and those reported earlier for NCL-1 zeolite indicates the absence of occluded material inside the zeolite channels. The BET surface area of these Fe- and Ga-NCL-1 samples was also similar to that reported for Al-analogues (table 1).

The values of the ion exchange capacities (K/Al, K/Ga or K/Fe molar ratio) exhibited by different samples are given in table 1. The ion exchange capacity of the zeolite can be taken as convincing, semiquantitative evidence for the isomorphous substitution of Fe, Ga, and Al in the lattice [2,3]. The observed ion exchange capacity in the present study strongly supports the presence of most of the Fe^{3+} and Ga^{3+} ions in the framework of zeolite NCL-1.

3.2. Catalysis

Acid catalyzed isomerization and disproportionation of 1,3,5-trimethylbenzene (1,3,5-TMB) was carried out over Fe-, Ga- and Al-NCL-1 (samples A, C and E, respectively). The 1,2,4-TMB is an industrially important starting material for the production of trimellitic acid/anhydride which is used in the manufacture of plasticisers, polyestermides and high temperature resistant polyimide [15]. Fig. 4 depicts the effect of reaction temperature on (i) TOF, moles of 1,3,5-TMB converted per mole of M^{3+} (M = Fe, Ga and Al) per hour (I) and (ii) selectivity for 1,2,4-TMB among total products (II). (The conversion of 1,3,5-TMB over Al-, Ga- and Fe-NCL-1 was 9.6, 16.5 and 20.1 wt%, respectively, under the same experimental conditions (temperature = 563 K, WHSV = 3.5 h^{-1} and time on stream = 30 min). Further, the selectivity of 1,2,4-TMB for Al-, Ga- and Fe-NCL-1 was 61.0, 70.0 and 78.0 % respectively.) The 1,2,3-TMB was formed in very small quantities ($\leqslant 2\%$). As expected, with the increase in the reaction temperature the conversion increases, whereas the selectivity for 1,2,4-TMB decreases slightly. The activity of the catalysts decreases as: Al- > Ga- > Fe-

Table 1
Physico-chemical properties of Fe- and Ga- and Al-NCL-1 analogues of zeolite NCL-1

Sample		Si/M molar ratio		K^+/M ratio	Surf. area [a] (m^2/g)	Sorption capacity (wt%)		
symbol	name	gel	product			*n*-hexane	1,3,5-TMB	water
A	Fe-NCL-1	80	88	0.70	320	6.6	4.6	5.0
B	Fe-NCL-1	150	175	0.72	328	6.5	4.8	4.9
C	Ga-NCL-1	80	85	0.81	318	6.4	4.7	5.0
D	Ga-NCL-1	150	153	0.87	313	6.6	4.5	4.9
E	Al-NCL-1	80	83	0.89	318	6.8	4.7	5.2
F	Al-NCL-1	150	157	0.91	323	6.9	4.8	4.6
G	Si-NCL-1	> 3000	> 3000	–	339	7.0	4.8	3.8

[a] From N_2 adsorption ($p/p_0 = 0.005$–0.01).
[b] Gravimetric adsorption at 298 K and $p/p_0 = 0.5$.

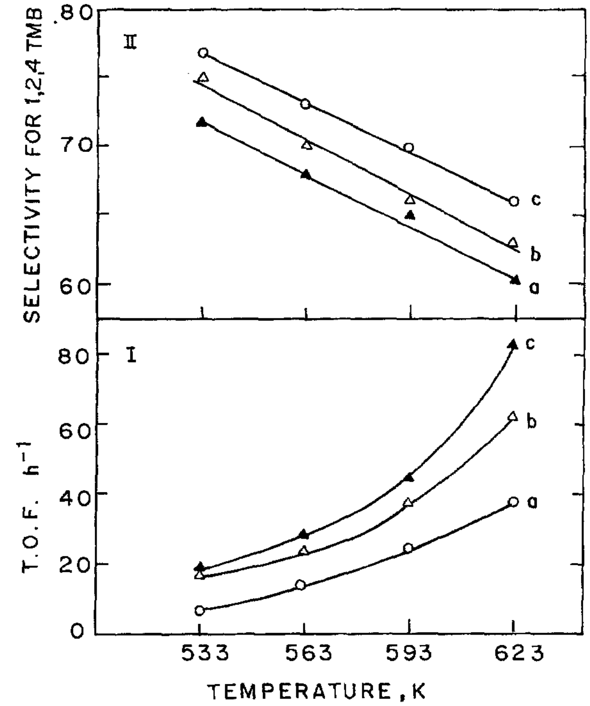


Fig. 4. Effect of reaction temperature on TOF and 1,2,4-TMB selectivity over Fe-, Ga- and Al-NCL-1 (samples A, C and E, curves a–c, respectively) in the conversion of 1,3,5-TMB. WHSV = 3.5 h^{-1}, TOS = 30 min.

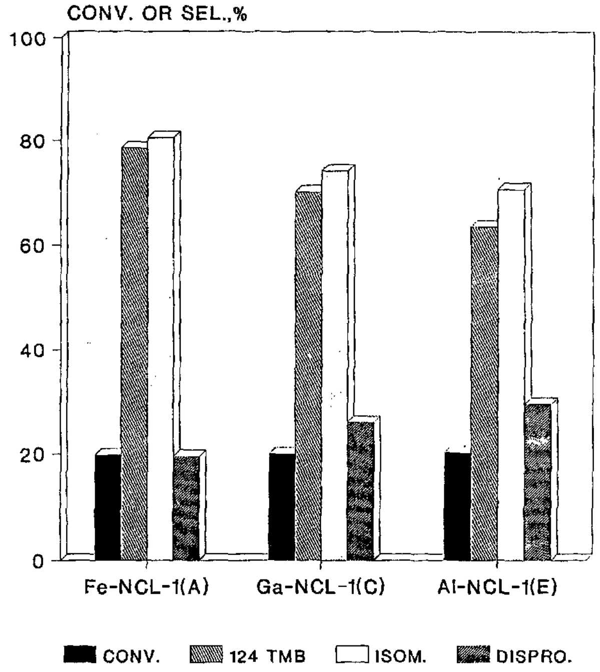
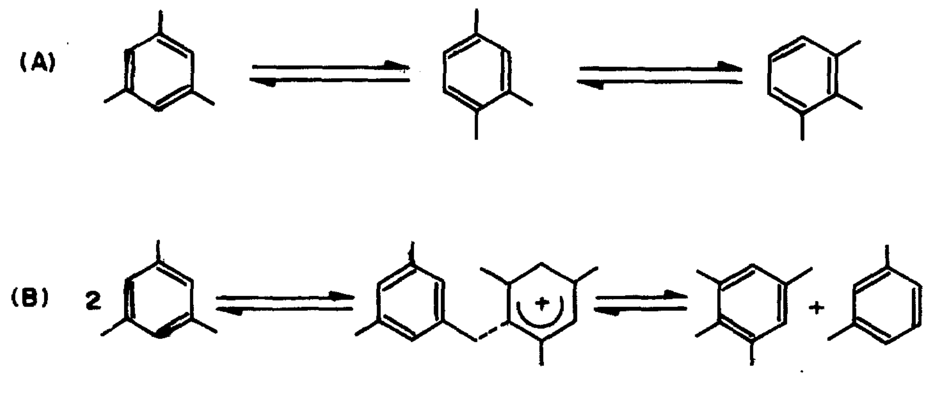


Fig. 5. Comparison of selectivities for 1,2,4-TMB and isomerization (vs. disproportionation) exhibited by Fe-, Ga- and Al-NCL-1 (samples A, C and E) at comparable conversion level. Temperature = 563 K, feed rate = 3.5 g h^{-1}, and TOS = 30 min, catalyst weight on anhydrous basis (g) = 2.1 (sample A), 1.3 (sample C) or 1.0 (sample E).

NCL-1, while the selectivity for 1,2,4-TMB follows the reverse trend in accordance with the fact that the acid strength of isomorphously substituted zeolites decreases in the following order: Al- > Ga- > Fe-silicate [2,3,16]. Fig. 5 compares the selectivities for 1,2,4-TMB and isomerized (moles of 1,2,4-TMB + 1,2,3-TMB), vis-á-vis disproportionated (moles of tetramethylbenzenes) products exhibited by samples A, C and E at the same temperature and feed rate and at similar conversion level (obtained by varying the amount of the catalyst). At comparable conversion, the selectivity for both 1,2,4-TMB and isomerization products decreases as: Fe- > Ga- > Al-NCL-1 in accordance with the view that isomerization selectivity (vis-á-vis disproportionation) increases with the decrease in acid strength for a given zeolite structure [6,17].

Collins et al. have reported [18], based on extensive kinetic studies on isomerization and disproportionation of trimethylbenzenes over LaY zeolites, that the isomerization of TMB occurs mainly via classical 1,2 methyl shift. The disproportionation products (tetramethylbenzene and xylenes) are formed by intermolecular methyl-group transfer via a diphenylmethane type intermediate [19] from one TMB molecule to another. A plausible reaction path (both isomerization and disproportionation) is depicted in scheme 1. Since NCL-1 is also a large



Scheme 1.

pore zeolite, the 1,2 methyl shift may be predominately occurring during 1,3,5-TMB isomerization.

4. Conclusions

The synthesis, characterization and catalytic properties of crystalline ferri-silicate as well as gallo-silicate analogues of zeolite NCL-1 have been studied. The ferri- and gallo-silicates were free of Al ($SiO_2/Al_2O_3 > 3000$). A minor shift in the IR bands towards lower frequency, the ESR signal at $g = 4.3$ and significant ion exchange capacities suggested the presence of well dispersed Fe^{3+} ions in the framework. A ^{71}Ga MAS NMR signal at $\delta = 148$ ppm suggests the presence of Ga in Td framework positions. The color of the as-synthesized and calcined samples was white indicating the absence of ferric oxide in Fe-NCL-1. The significant catalytic activity of Al-free samples of H/Fe-NCL-1 and H/Ga-NCL-1 in 1,3,5-TMB (mesitylene) isomerization provided strong evidence for the presence of iron and gallium in framework positions. The selectivity for isomerization (vis-á-vis disproportionation) products follows the order: Fe- > Ga- > Al-NCL-1. The activity (TOF) follows the reverse order.

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