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Synthesis of high-silica [Al]-SSZ-31 by a steam-assisted conversion method and its catalytic performance in the isopropylation of biphenyl

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Synthesis of high-silica [Al]-SSZ-31 zeolite by a dry-gel conversion method was performed and the catalyst was tested for the isopropylation of biphenyl with propylene. In the case of the small-scale synthesis, the product phase was found to be dependent on the alkali concentration of the initial gel, and a phase change from BEA to SSZ-31 to MFI was observed with time at the optimum alkali concentration. In the case of the large-scale synthesis, temperature had a profound effect on the crystallization of SSZ-31. A phase transformation from BEA to SSZ-31 was observed when the crystallization temperature was changed from 150 °C to 175 °C. [Al]-SSZ-31 was active in the isopropylation of biphenyl and selectively catalyzed the production of the least bulky isomers. Biphenyl conversion decreased with increasing silica to alumina ratio while selectivity remained nearly constant. Triisopropyl isomer yields were high in the case of lower silica to alumina ratios.

Introduction

Zeolites and other related molecular sieves are prepared by conventional hydrothermal methods.[1–3] Over the past few years new crystallization methods for zeolite synthesis using the so called dry method have been developed and studied by various research groups.[4–21] Although the detailed synthetic procedures, as well as the names coined for the methods used, varied somewhat in different cases, the basic concept of the procedures was the conversion of an amorphous solid gel to crystallized zeolite materials in the presence of a vapor phase. The source of the vapor is water or a mixture of water and organic compounds. Dong and coworkers[4,5] first reported the synthesis of ZSM-5 in the presence of vapors of ethylenediamine, triethylamine and water. Later, this method was investigated by Kim *et al.*[6] (who first named it as the 'vapor-phase transport' or VPT method) and Matsukata *et al.*[7,8] to synthesize various phases such as MFI, ANA, MOR, FER, *etc.* It was Matsukata and coworkers who first referred to the method as dry-gel conversion (DGC) and synthesized aluminosilicate zeolites such as BEA with various silica to alumina ratios.[9–11] The gel, prepared and dried with a non-volatile structure-directing agent (SDA) such as tetraethylammonium hydroxide (TEAOH), was crystallized in the presence of water vapor, and later this crystallization method was named steam-assisted conversion (SAC).[12] Both SAC and VPT methods are types of DGC. Following the SAC method, Bandyopadhyay *et al.* synthesized borosilicate zeolites such as [B]-BEA, MFI and MTW,[13,14] and recently aluminophosphate and silicoaluminophosphate molecular sieves such as $AlPO_4$-5, SAPO-5, $AlPO_4$-11, and SAPO-11.[16] ZnAPO-34 was also synthesized by Zhang and Gavalas.[17] Titanium-substituted zeolites such as [Ti]-BEA[18,19] and [Ti]-NU-1[20] have also been synthesized by Tatsumi *et al.* Apart from being an alternative synthesis route, the DGC method possesses some advantages over conventional hydrothermal methods. It enables dry-gel transformation to zeolite in high yield and involves nearly complete conversion of gel to zeolite. It also generates less waste for disposal, allows for reductions in reactor volume, and could be utilized in the continuous production of zeolites.[7,9] Moreover in some cases, the dry method was found to be essential, or at least beneficial, for the formation of particular phases and properties other than those obtained by the hydrothermal method.[11,15,19,22]

The Friedel–Crafts alkylation of aromatic compounds is very industrially important for the preparation of various synthetic intermediates for fine-chemicals, and SSZ-31, which is a one-dimensional, large-pore, high-silica zeolite, could be utilized for such shape-selective catalysis of bulky aromatics. The synthesis of all-silica SSZ-31 was reported by Zones *et al.*,[23] and the framework silicon was difficult to substitute by other atoms. Lobo *et al.* have proposed a model for the structure of SSZ-31;[24] it has a large number of faults with an intergrowth of mainly four different polymorphs, a structure closely related to NCL-1[25] and OU-1,[11] and also related to ZSM-12, Beta and SSZ-24. The synthesis of a borosilicate version of SSZ-31 and post-synthesis modification to its aluminosilicate version have also been studied using different starting materials and SDAs.[23,26–28] OU-1, which is basically similar to SSZ-31, was reported to be synthesized from a phase transformation of BEA using TEAOH as SDA.[11] In our previous short communication,[15] we reported the synthesis of [Al]-SSZ-31 by a DGC method and showed a similar, but faster, type of phase change. In the present study, the detailed investigation of the synthesis of [Al]-SSZ-31 using 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide as the SDA has been studied by the DGC method. The synthetic behavior, influence of various factors during the synthesis, and thorough characterization of the samples were the main objectives of this study. As far as the catalytic activity is concerned, there are hardly any reports of catalytic reactions over [Al]-SSZ-31 in the literature. Shape-selective isopropylation of biphenyl to produce industrially useful intermediates such as 4,4′-diisopropylbiphenyl (4,4′-DIPB) has been extensively studied over zeolites like mordenite.[29–34] In the present paper, in addition to its synthesis, the catalytic

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performance of the [Al]-SSZ-31 samples prepared with various silica to alumina ratios has been examined in the isopropylation reaction of biphenyl.

Experimental

Preparation of the structure-directing agent $Et_3N^+(CH_2)_6N^+Et_3(OH^-)_2$

Triethylamine (37.2 g, 368 mmol) was added to a solution of 1,6-dibromohexane (24.4 g, 96 mmol) in acetone (170 ml), and the whole mixture was refluxed for about 50–60 h. After the reaction, the mixture was filtered and washed with acetone (200 ml) and the solvent removed *in vacuo* to give a white solid (38.9 g) which was dissolved in methanol (25 ml) by heating to 60 °C. After cooling to room temperature, crystals separated out slowly. Diethyl ether (200 ml) was slowly added to encourage crystals to develop. The crystals were collected by filtration and washed with benzene (80 ml), and finally dried *in vacuo*. 1,1,1,8,8,8-Hexaethyl-1,8-diazoniaoctane dibromide was obtained as colorless plates (37.4 g, 87%).

Diaion® SA10A (OH) (Mitsubishi Chemical Co.) anion exchange resin (185.5 g, corresponding to a 275 mmol exchange capacity) was added to a solution of the dibromide salt (15.3 g, 34.3 mmol) in distilled water (200 ml) and the whole mixture was gently stirred at room temperature for 24 h. After filtration, the aqueous solution was concentrated to 134.3 g to give 0.235 mmol g^{-1} of 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide ($R^{2+}(OH^-)_2$) based on titration of the resulting solution with 0.05 N standard HCl solution.

Synthesis of [Al]-SSZ-31 by DGC on a small scale

A typical procedure for the smaller scale (10 mmol of SiO_2) synthesis of [Al]-SSZ-31 by the DGC method was as follows: 8.51 g (2 mmol) of $R^{2+}(OH^-)_2$ solution (0.235 mmol g^{-1}) was mixed with 0.1 g (0.84 mmol) of a 32 wt% aqueous solution of NaOH and stirred for 15 min followed by the addition of 1.5 g colloidal silica (Snowtex® 40, Nissan Chemical Co.), which consists of 0.6 g (10.0 mmol) of SiO_2, and the mixture was stirred for 30 min. To this mixture, 9 mg (0.026 mmol) of $Al_2(SO_4)_3$, dissolved in 2.2 ml of distilled, deionized warm water, was added and the final mixture was stirred for another 2 h. The gel was then dried for about 1 h over an oil bath at 80 °C with continuous stirring. When the gel became thick and viscous, it was manually stirred using a Teflon rod and stirring was continued until it dried (approximately 45 min). A white solid was formed which was ground into a fine powder and divided into two parts, each part being poured into a small Teflon cup (20 mm × 20 mm I.D.). The cup was placed in a Teflon-lined autoclave (23 ml) with the support of a Teflon holder. Small amounts of external bulk water (*ca.* 0.2–0.3 g per 1 g of dry gel), which was the source of the steam, were contained at the bottom of the autoclave in such a manner that the external bulk water never came into direct contact with the dry gel. The autoclave was kept in a convection oven at 175 °C and autogenous pressure for 24–48 h. The final gel composition was: SiO_2–$0.2R^{2+}(OH^-)_2$–0.084NaOH–$0.0026Al_2O_3$. Afterwards, the autoclave was quenched with cold water, and the zeolite powder was removed from the cup, washed thoroughly with water and dried at room temperature.

Synthesis of [Al]-SSZ-31 by DGC on a large scale

Due to the requirement for larger amounts of sample in order to test the catalytic activity, [Al]-SSZ-31 was also synthesized on a large scale by the DGC method. A typical large scale procedure (40 mmol of SiO_2) was as follows: in the same sequence as described above, 33.0 g (8.0 mmol) of $R^{2+}(OH^-)_2$ solution (0.242 mmol g^{-1}) was mixed with 0.42 g (3.36 mmol) of a 32 wt% aqueous solution of NaOH, followed by the addition of 6.0 g colloidal silica (Snowtex® 40), containing 2.4 g (40 mmol) of SiO_2, and the mixture was stirred for 30 min. Next, 48 mg (0.14 mmol) of $Al_2(SO_4)_3$ was dissolved in 8.8 ml of distilled, deionized warm water and added to the above mixture, the resultant mixture being stirred for a further 2 h. The gel was then dried for about 5 h over an oil bath at 80 °C with continuous stirring. The dried and powdered gel was divided into two parts and each part was poured into a medium-sized Teflon cup (55 mm × 37 mm I.D.). This cup was placed in a Teflon-lined autoclave (125 ml) with the support of a Teflon holder. A small amount of external bulk water (*ca.* 0.2–0.3 g per 1 g of dry gel) was present at the bottom of the autoclave. The autoclaves were kept in a convection oven at 150 °C for 48 h followed by 175 °C for 12 h. The final gel composition was: SiO_2–$0.2R^{2+}(OH^-)_2$–0.084NaOH–$0.0035Al_2O_3$. Afterwards, the autoclave was quenched with cold water, and the crystals were washed thoroughly with distilled water and dried at room temperature.

Calcination and post-synthesis treatment

To remove the organic SDA occluded inside the pores, the as-synthesized zeolite sample was kept in a muffle furnace, and heated in a flow of air (100 ml min^{-1}). The temperature was raised from room temperature to 540 °C over a period of 7 h, and maintained at this temperature for 4 h. The temperature was raised again to 600 °C over a period of 4 h, and kept at this temperature for another 4 h. Finally the sample was cooled to room temperature under ambient conditions.

The calcined sample (Na-form) was refluxed with ammonium nitrate solution for 12 h with stirring. The mass of ammonium nitrate was the same as that of zeolite, and the H_2O : zeolite ratio was 50 : 1 (w/w). The zeolite was filtered, and this process was repeated twice more after which it was washed thoroughly with water and dried overnight at room temperature. Finally the NH_4-form of the zeolite was calcined in a flow of air for 8 h at 550 °C to obtain the H-form.

Physicochemical characterization

Powder X-ray diffraction (XRD-6000, Shimadzu) with CuKα radiation ($\lambda = 1.5418$ Å) was applied to determine the crystallinity and phase purity of the as-synthesized and calcined samples. Elemental analyses were performed using inductively coupled plasma (JICP-PS-1000 UV, Leeman Labs Inc.). The crystal size and morphology of the samples were investigated by scanning electron microscopy (SEM) using a Philips XL30 microscope. Nitrogen adsorption measurements were carried out on a BELSORP 28SA gas adsorption apparatus. Thermal analyses of the as-synthesized samples were performed on a Shimadzu DTG-50 analyzer. Acidity measurements were performed by temperature programmed desorption of ammonia on a BEL TPD-66 apparatus. ^{13}C CP MAS NMR and ^{27}Al MAS NMR spectra of the as-synthesized samples were recorded on a Varian UNITY Inova 400 FT-NMR spectrometer.

Catalytic reactions

Isopropylation of biphenyl (BP) with propylene over [Al]-SSZ-31 was carried out in a 100 ml autoclave (SS 316). A typical reaction procedure was as follows: the catalyst (0.5 g) and BP (15.4 g, 100 mmol) was placed inside the autoclave and the equipment was purged with nitrogen. The temperature of the autoclave was raised slowly to the desired point (typically 250 °C) and propylene gas was introduced at 0.8 MPa, the pressure of propylene being kept constant throughout the reaction (4 h). After completion of the reaction, the autoclave was cooled and the reaction product was filtered and diluted with 200 ml toluene. Approximately 1.5 ml of solution was taken from the total bulk products and diluted with toluene (1.5–6.0 ml) and then analyzed by gas chromatography (Shimadzu GC-14A; column: Ultra-1, 25 m × 0.3 mm). Products were identified using GC–MS (Shimadzu QP 5000).

The products encapsulated inside the zeolite pore were analyzed as follows: the catalyst was filtered off after the reaction, washed with 200 ml acetone, and dried overnight at 110 °C. Then it was dissolved in 1.5 ml HF (47 wt% solution) under ice-cooling, and the resulting solution was basified with potassium carbonate until the effervescence stopped. After repeated extraction of the organic layer with dichloromethane (20 ml × 3), the solvent was removed *in vacuo*. Finally the residue was dissolved in 5 ml toluene and analyzed by GC and GC–MS in a similar way to the bulk product.

Results and discussion

Synthesis and characterization

The XRD pattern of a typical as-synthesized [Al]-SSZ-31 sample prepared at optimum synthetic conditions and gel composition is shown in Fig. 1. The XRD pattern showed a pure SSZ-31 phase with high crystallinity. While investigating the small scale synthesis the alkali concentration in the starting gel was found to be critical for the synthesis of a pure SSZ-31 phase. Within the range of $NaOH/SiO_2 = 0.05–0.12$, pure SSZ-31 was obtained. A mainly MFI phase was formed below (*ca.* 0.03) and above (*ca.* 0.15) this range. When the synthesis was investigated with time at an optimum $NaOH/SiO_2$ ratio of 0.084, the SSZ-31 phase was found to be formed through a phase change of BEA. As shown in Fig. 2, at shorter synthesis times (6 h) a BEA phase formed and was converted to a SSZ-31 phase with time (12 h), and this phase was stable up to 48 h. Finally, a mixture of SSZ-31 and MFI was obtained with prolonged synthesis time (56 h). At lower $NaOH/SiO_2$ (0.03), a pure MFI phase was obtained after a longer synthesis time (Fig. 3), whereas at higher $NaOH/SiO_2$ (0.15), a pure BEA phase was obtained at a shorter synthesis time (8 h) and converted with time to a mixture of an SSZ-31 and MFI phase (Fig. 4). The results indicate that formation of a pure SSZ-31 phase is favored by a phase change from BEA at a medium alkali concentration. Similar kinds of phase transformation of high-silica BEA to OU-1 were observed by Rao *et al.*;[11] however, the phase transformation from BEA to SSZ-31 in the present case was much faster (within 12 h) compared to that from BEA to OU-1 (60 h). It is also noticeable that apart from the desired SSZ-31 phase, pure [Al]-MFI and pure [Al]-BEA phases could also be obtained using lower and higher NaOH contents in the starting gel, respectively.

The phase-change phenomenon of BEA to SSZ-31 was more suitably explored while synthesizing [Al]-SSZ-31 on a larger scale. When the large-scale synthesis was attempted at 175 °C, only an MFI phase crystallized after 36 h, whereas at 150 °C, a BEA phase was observed at 46 h and this phase was unchanged even after 78 h. Accordingly, the gel was initially heated at 150 °C for 48 h and then subsequently heated at 175 °C for 12 h, which resulted in the formation of a pure SSZ-31 phase (Fig. 5). This procedure was reproducible and [Al]-SSZ-31 was synthesized by this method on a large scale with varying silica to alumina ratios. Following this procedure, pure [Al]-SSZ-31 was synthesized with silica to alumina input ratios of 184, 284 and 384. ICP analysis of these samples showed output ratios of 136, 176 and 251, respectively. However, a BEA and MFI phase was formed at lower (*ca.* 100) and higher (*ca.* 800) input

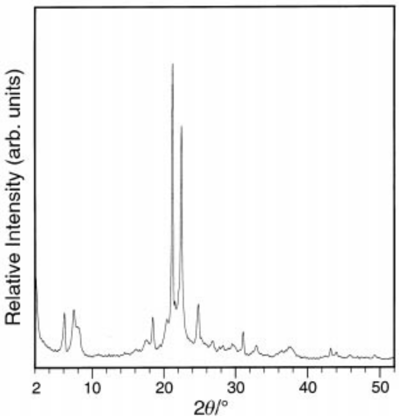

Fig. 1 XRD pattern of as-synthesized [Al]-SSZ-31.

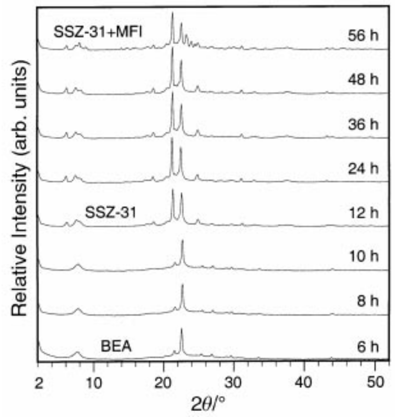

Fig. 2 XRD patterns with time course of as-synthesized samples at $NaOH/SiO_2 = 0.084$.

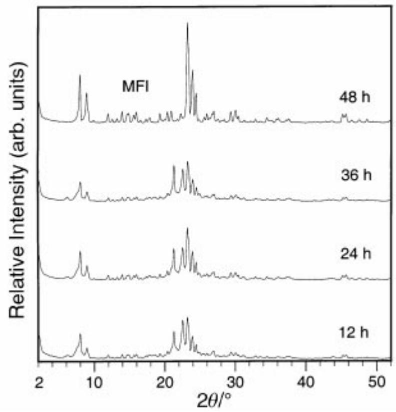

Fig. 3 XRD patterns with time course of as-synthesized samples at $NaOH/SiO_2 = 0.03$.

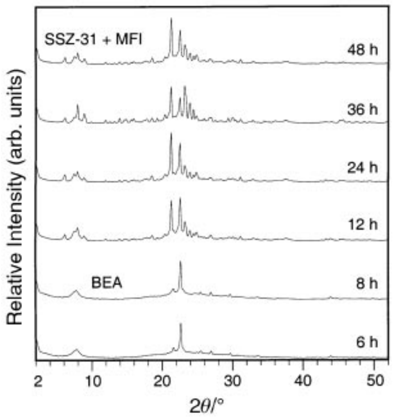

Fig. 4 XRD patterns with time course of as-synthesized samples at $NaOH/SiO_2 = 0.15$.

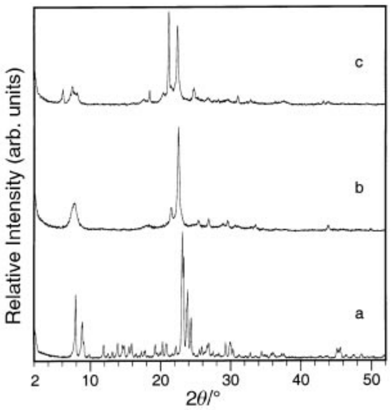

Fig. 5 XRD patterns of as-synthesized [Al]-SSZ-31 (prepared by the larger scale route) at: (a) 175 °C, 36 h; (b) 150 °C, 46 h; (c) 150 °C, 48 h then 175 °C, 12 h.

ratios, respectively. When the synthesis was carried out at 150 °C for longer time (60 h) and switched over to 175 °C (12 h), an impure phase of cristobalite was observed with the SSZ-31 phase. A similar result was noticed when the synthesis was prolonged at 175 °C (24 h) after changing from 150 °C.

The synthesis results were also influenced by the source of silica. Snowtex 40 showed the best results for the preparation of SSZ-31, while Cab-O-Sil M-5 (fumed silica, Cabot) and Ludox AS-40 (colloidal silica, Du Pont) yielded mainly MFI phase. The presence of a small amount of NaOH at different concentrations in the colloidal silica source may have played some role.

The XRD patterns of the as-synthesized samples obtained after different times, their corresponding ^{13}C CP MAS NMR spectra, and for comparison, the NMR spectra of the SDA are depicted in Fig. 6. The spectra of the products obtained at 6 h (BEA) and 10 h (SSZ-31 + BEA) very closely resemble that of the SDA. However, in the later synthesis stages (12–48 h) where pure SSZ-31 phase was obtained, two new peaks around 12 and 46 ppm were observed. One possibility for this could be due to the partial formation of triethylamine *via* Hoffmann degradation of the SDA. However, these peaks suddenly appeared from 12 h and there was almost no change of their intensity afterwards. Moreover, there was no sign of formation of these peaks in the mixed phase of SSZ-31 and BEA obtained at 10 h. Thus we believe that these extra peaks could have come from the structural and environmental factors of SSZ-31 rather than partial degradation of the SDA. Nevertheless, the close resemblance of the NMR throughout the synthesis time with that of SDA indicated the intactness of the SDA inside the zeolite pore. The CHN analysis of the as-synthesized sample showed $N^+/Si = 0.054$. Considering polymorph A of SSZ-31 having 28 T atoms per unit cell, it was observed that one unit cell contained 1.5 N^+, or in other words 0.75 SDA molecules, which means the SDA was well packed inside the pore.

The TPD of NH_3 profiles of the H-form of [Al]-SSZ-31 samples with various silica to alumina ratios are shown in Fig. 7. In all cases, deconvolution indicated there were three stages of NH_3 desorption with peak maxima at around 170 °C, 270 °C and 450 °C. The first peak (peak I) appearing at 170 °C resulted from the desorption of strongly physisorbed NH_3, mainly on the external surface of the zeolite. The second peak (peak II), at 270 °C, was attributed to the desorption of NH_3 from weak Brönsted and Lewis sites. The third peak (peak III), at 450 °C, was due to the desorption of NH_3 from strong Brönsted sites. Such observations of desorption of NH_3 from different acidic sites have been reported previously by various researchers.[35–37] In our present study total acid concentrations of 0.21, 0.03 and 0.02 mmol g^{-1} were measured for samples with silica to alumina ratios of 136, 176, and 251, respectively. It can be noticed that there are some differences in the TPD profile. In the case of samples with $SiO_2/Al_2O_3 = 136$ particularly, the contribution of peak I is greater than that of the other two samples, and this was reflected in its higher total acid concentration compared to the other two samples.

The ^{27}Al MAS NMR spectrum of the as-synthesized [Al]-SSZ-31 sample (Fig. 8) showed a single peak at 52.2 ppm,

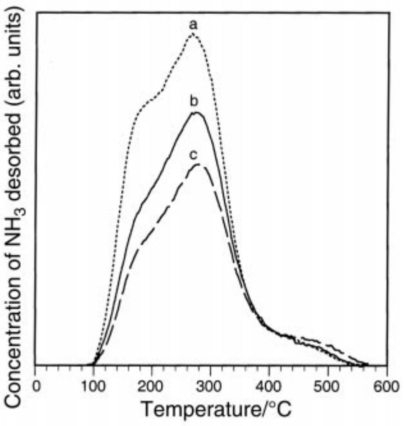

Fig. 7 NH_3-TPD profile of the H-form of [Al]-SSZ-31 samples with (a) $SiO_2/Al_2O_3 = 136$, (b) $SiO_2/Al_2O_3 = 176$, (c) $SiO_2/Al_2O_3 = 251$. In each case, peaks are observed at 170 °C (peak I), 270 °C (peak II), and 450 °C (peak III).

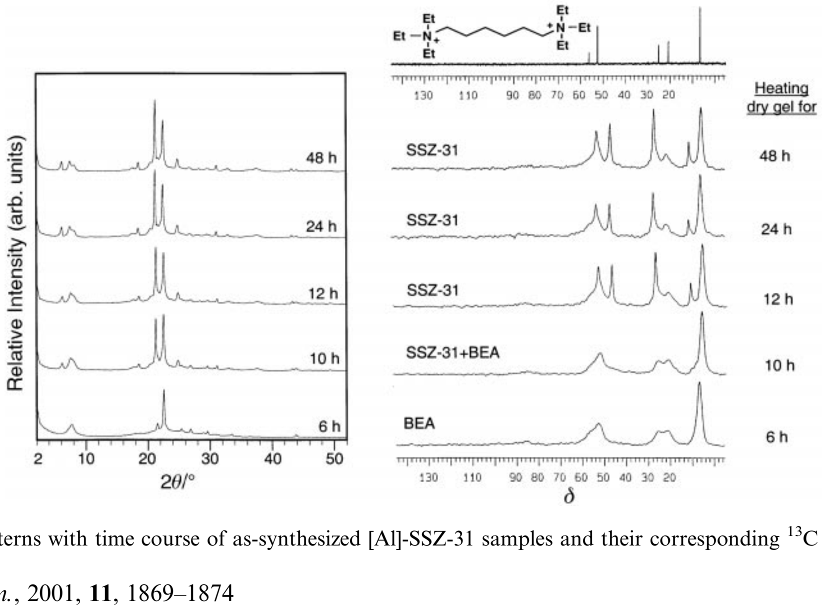

Fig. 6 XRD patterns with time course of as-synthesized [Al]-SSZ-31 samples and their corresponding ^{13}C CP MAS NMR.

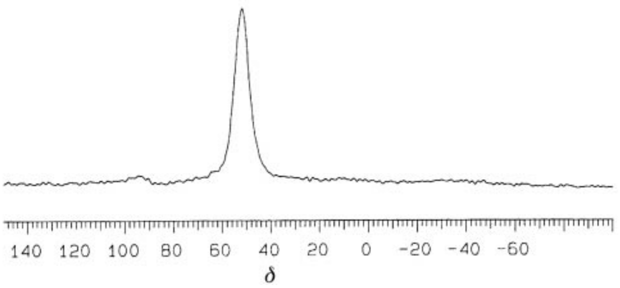

Fig. 8 ^{27}Al MAS NMR spectrum of as-synthesized [Al]-SSZ-31.

indicating the tetrahedral framework nature of Al and the absence of any octahedral species. The N_2 adsorption isotherm of calcined [Al]-SSZ-31 possessed a micropore volume of 0.128 $cm^3\ g^{-1}$, and a BET surface area of 445 $m^2\ g^{-1}$. The elemental analysis of the samples measured by ICP showed that a major portion of the gel phase was converted to the zeolite phase; around 80% of the silica to alumina ratio of the starting gel being retained in the as-synthesized sample. The yield of the [Al]-SSZ-31 samples was higher (about 75 to 90%) than that of [B]-SSZ-31 synthesized by the hydrothermal method (65%).

Catalytic reaction

[Al]-SSZ-31 was tested for its catalytic activity in the isopropylation of biphenyl using propylene as an alkylating agent. SSZ-31 was found to be active and showed selectivity towards 4,4′-diisopropylbiphenyl (DIPB) among the diisopropyl isomers and towards 4-isopropylbiphenyl (4-IPBP) among the monoisopropyl isomers. 4,4′-DIPB formed with the consumption of 4-IPBP leading to an accumulation of 2-, and 3-IPBP. The high selectivity for 4,4′-DIPB among the DIPB isomers showed that isopropylation proceeded *via* a consecutive mechanism; biphenyl was isopropylated predominantly to 4-IPBP and isopropylation of 4-IPBP produced 4,4′-DIPB in the second stage.[38] Fig. 9 shows the effect of silica to alumina ratio on conversion and selectivity of 4-IPBP as well as 4,4′-DIPB for bulk and encapsulated products. As conversion is related to acid concentration, it can be seen that with increasing silica to alumina ratio (decreasing acid concentration) conversion decreased. The conversion decreased from 68% to 28% when the silica to alumina ratio was increased from 136 to 251. However, selectivity for 4,4′-DIPB remained nearly constant. Encapsulated products showed higher selectivity for 4,4′-DIPB than bulk products for all three ratios, indicating that shape selective alkylation may be predominant within the pores. Figs. 10a and b show the effects of silica to alumina ratio on the product distribution in the isopropylation of biphenyl for both bulk and encapsulated products. On comparing bulk and encapsulated products, we observe that triisopropylbiphenyl yields were low in encapsulated products, indicating that unidimensional channels of SSZ-31 exhibited some spatial restrictions and prevented further isopropylation of DIPB isomers. As discussed earlier, the NH_3-TPD result showed that [Al]-SSZ-31 with a silica to alumina ratio of 136 had a higher total acid concentration. Correspondingly, triisopropyl isomer yields were relatively higher in the bulk products for a silica to alumina ratio of 136 (Fig. 10a). However, encapsulated products showed low yields of triisopropyl isomers, we can assume that there were more acidic sites on the external surface of [Al]-SSZ-31 with a silica to alumina ratio of 136, giving more triisopropyl isomers in the bulk products. In our previous studies we have reported isopropylation of biphenyl over mordenite,[33,38] and that triisopropyl isomers are generally produced by external acid sites in the case of mordenite.[38,39] Triisopropyl isomers were low for both bulk and encapsulated products in cases of SSZ-31 samples with silica to alumina ratios of 176 and 251, suggesting few external active sites. In the case of mordenite, the selectivity increased with increasing silica to alumina ratio. We do not observe a similar pattern in the present case because the silica to alumina ratios compared are on the higher range and not similar to that of mordenite. It may be noted that the synthesis of [Al]-SSZ-31 directly by a conventional hydrothermal method was rather difficult;[23] however, the dry-gel method enables us to successfully incorporate aluminium in the range $100 < SiO_2/Al_2O_3 < 800$. From our results it is clear that [Al]-SSZ-31 is acidic in nature

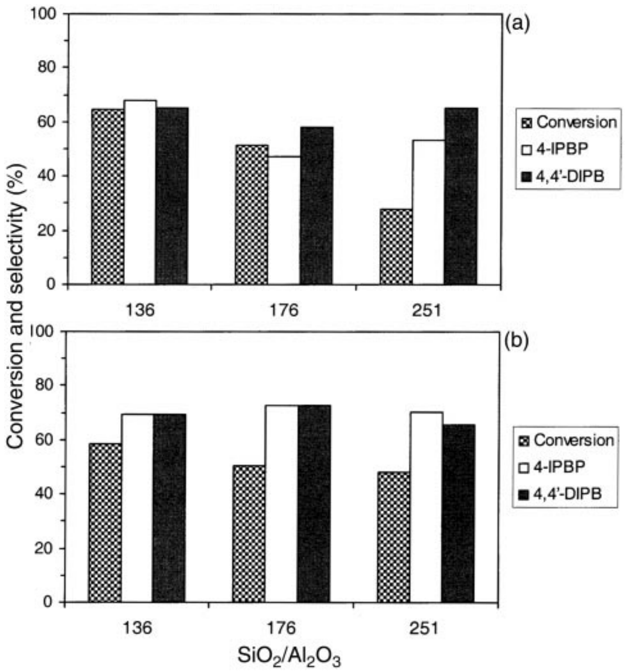

Fig. 9 Effect of SiO_2/Al_2O_3 ratio on conversion and selectivity in the isopropylation of biphenyl for (a) bulk and (b) encapsulated products over SSZ-31. Reaction conditions: 100 mmol biphenyl; 0.5 g catalyst; temperature 250 °C; pressure 0.8 MPa; reaction time 4 h.

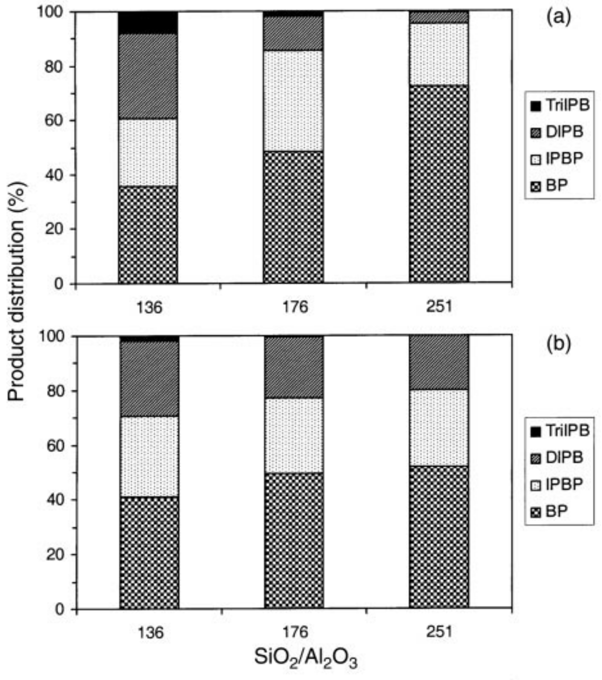

Fig. 10 Effect of SiO_2/Al_2O_3 ratio on product distribution in the isopropylation of biphenyl for (a) bulk and (b) encapsulated products over SSZ-31. Reaction conditions: 100 mmol biphenyl; 0.5 g catalyst; temperature 250 °C; pressure 0.8 MPa; reaction time 4 h.

and shows selectivity towards 4,4′-DIPB; however, the selectivity is low compared to that of mordenite.

Conclusion

A steam-assisted conversion method was successfully utilized for the direct synthesis of [Al]-SSZ-31 with various silica to alumina ratios using 1,1,1,8,8,8-hexaethyl-1,8-diazoniaoctane dihydroxide as the structure-directing agent. The alkali content in the starting gel influenced the phase selection, and the optimum range was found to be $0.05 \leqslant NaOH/SiO_2 \leqslant 0.12$ for a pure SSZ-31 phase. A phase change from BEA to SSZ-31 to MFI was observed with the time course of the synthesis at optimum NaOH content. ^{13}C CP MAS, and ^{27}Al MAS NMR of the as-synthesized sample showed the intactness of the SDA inside the pore and the tetrahedral framework nature of Al, respectively. The TPD of NH_3 showed increasing total acid concentration with decreasing silica to alumina ratio. [Al]-SSZ-31 was found to be active in the shape-selective alkylation of biphenyl by propylene. The selectivity for 4-IPBP was higher among the mono-isopropylbiphenyl isomers and that for 4,4′-DIPB was higher among the DIPB isomers. The conversion decreased with increasing silica to alumina ratio, however the selectivity remained almost constant. Bulk products showed relatively high amounts of triisopropylbiphenyl as compared to encapsulated products; furthermore, the selectivity for 4,4′-DIPB in encapsulated products was high suggesting that shape selective alkylation may be predominant within the pores.

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