Shape-selective alkylation of biphenyl over H-[Al]-SSZ-31 with propylene

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Isopropylation of biphenyl (BP) over [Al]-SSZ-31, a large-pore, one-dimensional zeolite has been studied. Effects of temperature, pressure and SiO_2/Al_2O_3 ratio were examined. SSZ-31 was found to be an active catalyst in the isopropylation of biphenyl with propylene. The selectivity for 4-isopropylbiphenyl (4-IPBP) and 4,4′-diisopropylbiphenyl (4,4′-DIPB) was high among isopropylbiphenyl (IPBP) and diisopropylbiphenyl (DIPB) isomers, respectively, indicating SSZ-31 shows shape-selective catalysis. The selectivity for 4,4′-DIPB decreased with temperature increase; correspondingly the selectivity for thermodynamically more stable isomers (3,3′- and 3,4′ DIPB) increased with temperature. The yield of IPBP isomers decreased while that of DIPB isomers increased with temperature increase. Pressure showed less effect on conversion; however, increase in pressure suppresses the isomerization of 4,4′-DIPB to 3,3′- and 3,4′-DIPB. Conversion decreased with increase in SiO_2/Al_2O_3 ratio. At low SiO_2/Al_2O_3 ratio of 136, relatively high triisopropylbiphenyl (TriIPB) isomers were formed in bulk products and their amount decreased with increase in SiO_2/Al_2O_3 ratio.

KEY WORDS: [Al]-SSZ-31; isopropylation; biphenyl; 4-IPBP; 4,4′-DIPB and TriIPB

1. Introduction

Zeolites have gained considerable importance in acid catalysis due to their shape-selective nature [1–3]. Medium-pore zeolites *viz*. ZSM-5, have been studied extensively and found to be effective catalysts in acid catalysis of mononuclear aromatics [2]. Recently, much attention has been focused on large-pore zeolites. Large-pore zeolites are important acid catalysts in the Friedel–Crafts alkylation of relatively bulky polynuclear aromatics such as biphenyl (BP) and naphthalene (NP) [4–6]. Shape-selective alkylation over zeolites is known to yield symmetrically dialkylated polynuclear aromatics [7]. 4,4′-dialkylbiphenyls are synthetic intermediates for the preparation of biphenyl-4,4′-dicarboxylic acid, which is a very important monomer for the production of liquid crystalline polymers and engineering plastics [8]. Methylation [7], ethylation [9] and isopropylation [10] have been studied over zeolites. We have studied the isopropylation of biphenyl over a number of large-pore zeolites *viz*. H-Y, H-L and H-mordenite (HM) [3]. Futhermore, isopropylation on dealuminated as well as modified mordenite has also been studied extensively [6,11,12].

SSZ-31 is a one-dimensional, large-pore, high-silica zeolite with pore dimensions 8.6 Å × 5.7 Å [13]. Zones *et al*., first reported all-silica SSZ-31 [14]. The synthesis of boron substituted SSZ-31 followed by conversion to its aluminosilicate form has been studied using a number of structure-directing agents [14–16]. Recently, we reported the direct synthesis of [Al]-SSZ-31 by the dry-gel conversion method [17] and this method proved to be convenient for catalyst preparation. SSZ-31 being a large-pore zeolite and acidic in nature, can find applications in alkylation of polynuclear aromatics. In this study, we explore the catalytic performance of H-[Al]-SSZ-31 in the isopropylation of biphenyl.

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2. Experimental

2.1. Synthesis

[Al]-SSZ-31 was synthesized by the dry-gel conversion (DGC) method using 1,1,1,8,8,8-hexaethyl-1,8-diazonaoctane dihydroxide ($R^{2+}(OH^-)_2$) as structure-directing agent by a procedure reported elsewhere [16]. Samples with three input SiO_2/Al_2O_3 ratios 184, 284 and 384 were synthesized, which resulted in samples with SiO_2/Al_2O_3 ratios 136, 176 and 251, respectively. A typical synthesis procedure was as follows: to 0.42 g (3.36 mmol) of 32 wt% aqueous NaOH solution, 33 g (8 mmol) of $R^{2+}(OH^-)_2$ solution (0.242 mmol g^{-1}) followed by 6.01 g (40 mmol) of colloidal silica (Snowtex 40, Nissan Chemical Co.) were added. The mixture was stirred for about 15 min. Aluminum sulfate, 0.048 g (0.104 mmol) dissolved in warm water (8.88 g), was added to the above solution under stirring. The gel was stirred for about 1 h at room temperature. The final gel composition was: SiO_2–$0.2R^{2+}(OH^-)_2$–$0.084NaOH$–$0.0035Al_2O_3$–$61H_2O$. This gel was then dried at 80 °C to complete dryness. The dried gel was weighed, divided equally into two parts, and transferred into Teflon cups which were placed in autoclaves containing water (0.2 g water per gram of gel) at the bottom. The autoclaves were then

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heated at 150 °C for 48 h, followed by heating at 175 °C for another 12 h in a convection oven. The autoclaves were quenched with cold water and the product formed was filtered, washed with distilled water and dried overnight to give as-synthesized material.

2.2. Calcination and post-synthesis treatment

As-synthesized [Al]-SSZ-31 was calcined in a flow of air (100 ml min^{-1}) at 550 °C. The calcined material was converted to H-form by repetitive ion-exchange at 80 °C, three times, with ammonium nitrate solution (catalyst : NH_4NO_3 : H_2O wt ratio 1 : 1 : 50).

2.3. Catalytic reactions

The reactions were carried out in a batch reactor (100 ml SUS-316) under constant propylene pressure in the temperature range 225–325 °C. The pressure was varied from 0.1 to 0.8 MPa. A typical procedure is as follows: the autoclave containing 0.5 g [Al]-SSZ-31 and 15.4 g (100 mmol) biphenyl was flushed with nitrogen before heating. When the desired temperature, typically 250 °C, was attained, propylene was introduced up to 0.8 MPa in the autoclave. This propylene pressure was maintained throughout the reaction (4 h). After the reaction, the autoclave was cooled, the catalyst was filtered and washed with 200 ml toluene. Approximately 1.5 ml solution was taken from the total bulk products and diluted with toluene (1.5–6.0 ml). Products obtained after the reaction were identified by GC-MS (Shimadzu QP5000), and analyzed by a gas chromatograph (Shimadzu 14A) equipped with an Ultra-1 capillary column (25 m × 0.3 mm).

2.4. Measuruments

Phase purity of the samples was examined by X-ray diffraction (Shimadzu XRD 6000 diffractometer; Cu Kα (λ = 1.5418 Å)) and the output silica to alumina ratio was determined by inductively coupled plasma spectroscopy (ICP; 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.

3. Results and discussion

3.1. Effect of SiO_2/Al_2O_3

The catalysts used in the reaction were crystalline and without any impurity. SEM showed that all the samples had particle size less than or equal to 1 μm. The BET adsorption isotherm for all the samples was typically a type I curve indicating the absence of mesopores within the samples.

The isopropylation of biphenyl with propylene over H-[Al]-SSZ-31 yielded mixtures of isopropylbiphenyls (IPBPs), diisopropylbiphenyls (DIPBs) and triisopropylbiphenyls (TriIPBs) [3,6,12].

From figure 1 and table 1 it is evident that conversion of biphenyl decreases with increase in SiO_2/Al_2O_3 ratio; however, the decrease is not very significant. In case of mordenite we observed that above SiO_2/Al_2O_3 = 100, conversion remained nearly constant [3] (table 1) so we may assume that the conversion is not dependent on SiO_2/Al_2O_3 ratio for isopropylation of biphenyl in high silica to alumina region. Synthesis of [Al]-SSZ-31 with a ratio below 100 was difficult by the dry-gel conversion method so comparison over a wide range of SiO_2/Al_2O_3 ratio was not possible. From table 1 we observe that TriIPB yield is high for the sample with SiO_2/Al_2O_3 = 136 as compared to samples with

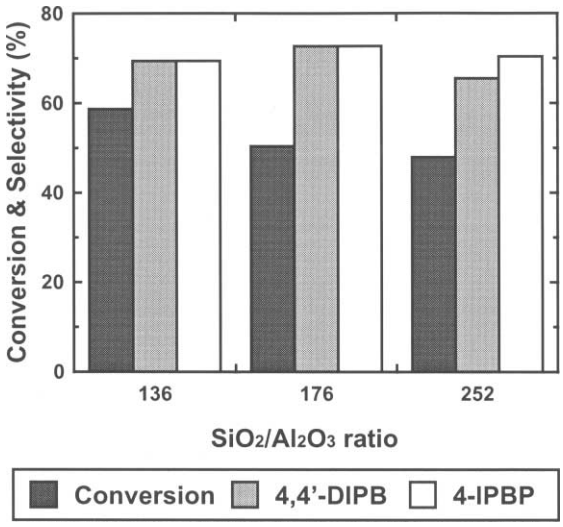

Figure 1. Effect of SiO_2/Al_2O_3 ratio on the conversion and selectivity in the isopropylation of biphenyl. Reaction conditions: BP 100 mmol, catalyst 0.5 g, propylene pressure 0.8 MPa, reaction time 4 h.

Table 1
Effect of SiO_2/Al_2O_3 ratio on isopropylation of biphenyl over SSZ-31 and mordenite.[a]

Zeolite	SiO_2/Al_2O_3[b]	Conv. (%)	Yield (%)			Selectivity for IPBP (%)			Selectivity for DIPB (%)		
			IPBP	DIPB	TriIPB	2-	3-	4-	4,4′-	3,4′-	3,3′-
SSZ-31	136	64.4	39.1	49.1	11.8	2.2	10.4	67.7	65	8.4	7.9
SSZ-31	176	51.6	71.8	24.9	3.3	22.4	30.4	47.1	57.9	29.9	8.5
SSZ-31	251	27.6	83.9	15.3	0.8	18.3	28.5	53.2	65.2	26	15.3
HM	128	71.9	34.9	63.8	1.3	2.6	36.9	60.5	87.1	10.2	0.9
HM	206	72.7	34.0	64.6	1.4	1.8	37.6	60.6	88.1	10.8	0.8

[a] Reaction conditions: BP 100 mmol, catalyst 0.5 g, reaction time 4 h.
[b] Measured by ICP analysis.

SiO_2/Al_2O_3 176 and 251. We assume that in the case of the sample with $SiO_2/Al_2O_3 = 136$, more active sites may be present on the surface of the catalyst leading to non-selective reactions.

Table 1 also reveals that the selectivities for 4,4′-DIPB are nearly constant for all the samples. Assuming that the selective alkylation predominates within the pores of the zeolite, the above result suggests that the number of active sites within the zeolite pores may be nearly the same for high SiO_2/Al_2O_3 region. Similarly in the case of the mordenites with $SiO_2/Al_2O_3 = 128$ and 200 (table 1), with increase in SiO_2/Al_2O_3 ratio, the selectivities for 4-IPBP and 4,4′-DIPB remain nearly the same. In contrast to mordenite, the yield of IPBP increases with SiO_2/Al_2O_3 in the case of SSZ-31, suggesting that further isoproplylation of 4-IPBP to 4,4′-DIPB is retarded to a certain extent at high SiO_2/Al_2O_3 ratio.

3.2. Effect of temperature

Figure 2 summarizes the effect of temperature on isopropylation of biphenyl over [Al]-SSZ-31. As expected conversion increased with temperature increase while the selectivity for 4,4′-DIPB decreased. However, increase in pressure had less effect on conversion. As evident from figure 2, the conversion and yield of DIPBs increase and yield for IPBPs decreases with temperature increase at the temperatures tested. These results suggest that dealkylation may be low in the case of [Al]-SSZ-31 even at high temperatures and pressure. This behavior was contradictory to what we observed for HM wherein at temperatures higher than 300 °C, the IPBPs yield increased while the DIPBs yield decreased at temperatures >300 °C [3]. As evident from figure 1, the selectivity for 4,4′-DIBP decreases with increase in temperature, and selective formation of 4,4′-DIPB was observed below 275 °C. Analogous to the case of HM, the selectivities for 3-IPBP and 3,4′-DIPB isomers were found to increase with temperature increase. This observation suggests that 4,4′-DIPB isomerizes to 3,3′- and 3,4′-DIPB, which are known to be thermodynamically more stable [3]. Selectivity for TriIBPs increased with temperature, which may be due to non-selective reactions occurring on the external surface of the catalyst or due to less steric hindrance in SSZ-31 zeolite pores [3,18]. Among the IPBPs, the selectivity for 3-IPBP increased with temperature increase while those for 4- and 2-IPBP isomers decreased.

3.3. Effect of pressure

Conversion of biphenyl remained nearly constant with pressure. As evident from figure 3, yields of both IPBP and DIPB isomers remained constant with pressure. However, pressure did seem to affect the selectivities for 3,3′- and 3,4′-DIPB. At low pressure (0.1 MPa) the selectivity for these isomers was high and decreased with increase in pressure. Correspondingly the selectivity for 4,4′-DIPB increased with increase in pressure. A study on the effect of propylene pressure on the stability of 4,4′-DIPB was carried out (figure 4). In absence of propylene, 4,4′-DIPB isomer-

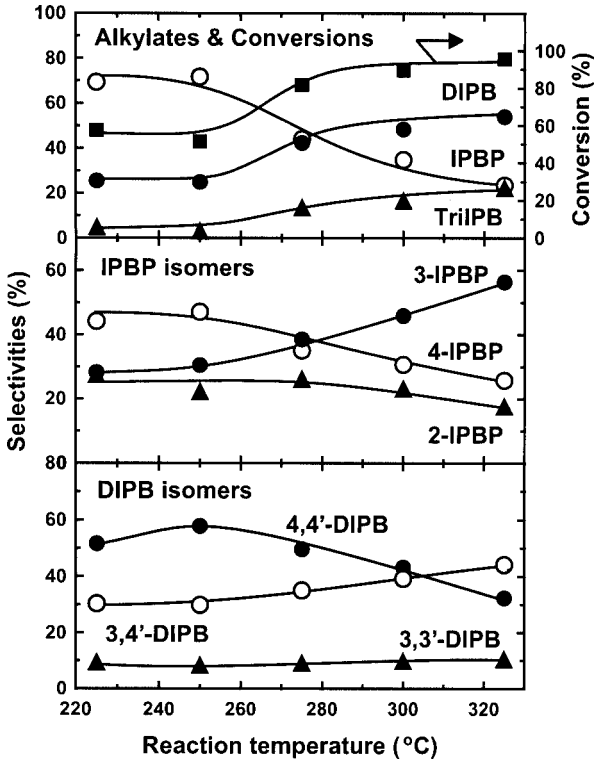

Figure 2. Effect of temperature on the isopropylation of biphenyl over [Al]-SSZ-31. Reaction conditions: BP 100 mmol, catalyst 0.5 g, propylene pressure 0.8 MPa, reaction time 4 h.

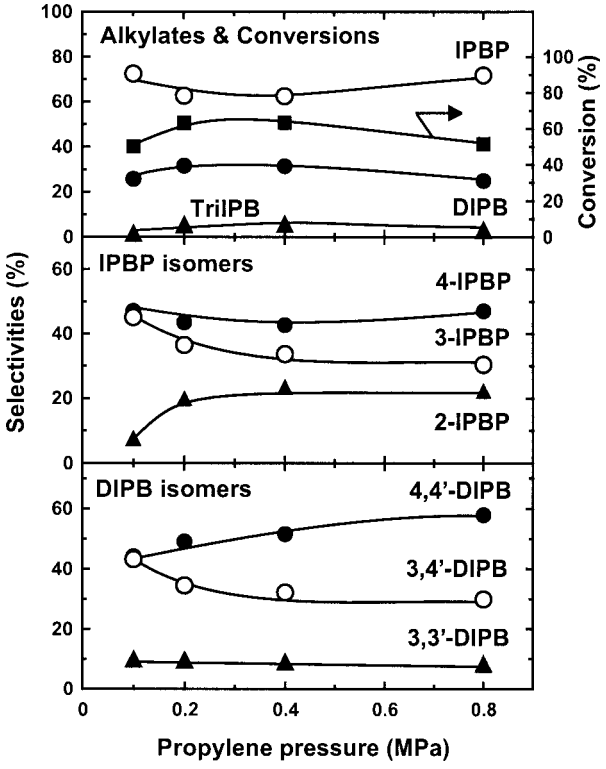

Figure 3. Effect of pressure on the isopropylation of biphenyl over [Al]-SSZ-31. Reaction conditions: BP 100 mmol, catalyst 0.5 g, temperature 250 °C, reaction time 4 h.

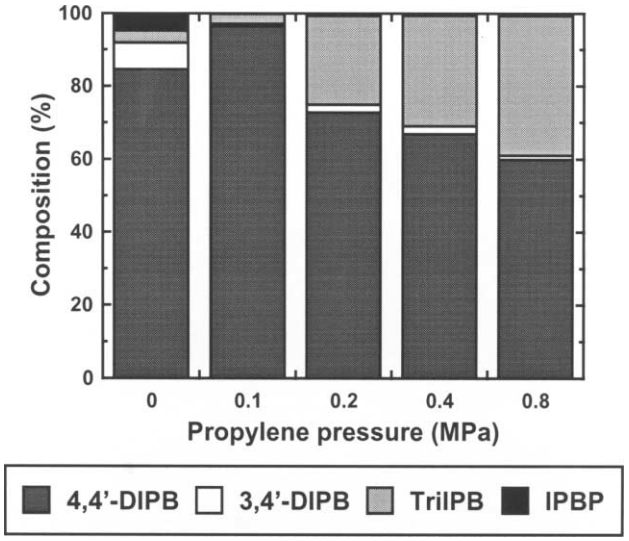

Figure 4. Isomerization of 4,4′-DIPB in the presence of propylene pressure over [Al]-SSZ-31. Reaction conditions: 4,4′-DIPB 50 mmol, catalyst 0.5 g, temperature 250 °C, reaction time 4 h.

ized easily to 3,3′- and 3,4′-DIPB even at 250 °C. Furthermore, IPBPs were formed by dealkylation in absence of pressure or at low propylene pressure. Increase in propylene pressure controlled the isomerization of 4,4′-DIPB. We observed similar behavior in case of HM [3]. Takahata and co-workers also observed a decrease in isomerization of 4,4′-DIPB at high propylene pressure [19]. Analogous to HM, further isopropylation was observed in small amounts over SSZ-31. The yields of TriIPBs were slightly higher in SSZ-31 as compared to HM probably due to its larger pores and/or due to reactions occurring on the external surface.

From the above results we can assume that shape-selective isopropylation occurred to yield predominantly the least bulky 4-IPBP among the IPBP isomers, and 4,4′-DIPB among the DIPBs over SSZ-31. 4,4′-DIPB yielded with the consumption of 4-IPBP leading to accumulation of 3-IPBP. The high selectivity for 4,4′-DIPB among the other DIPB isomers showed that isopropylation proceeds *via* a consecutive mechanism that is: biphenyl was isopropylated predominantly to 4-IPBP, which was further isopropylated producing 4,4′-DIPB in the second stage.

4. Conclusion

[Al]-SSZ-31 is found to be active in the alkylation of biphenyl by propylene. Analogous to HM, among the IPBP isomers the selectivity for 4-IPBP is high and that of 4,4′-DIPB is high among the DIPB isomers. These results suggest that [Al]- SSZ-31 is selective for 4,4′-DIPB; however, the selectivity is low as compared to HM. The relatively low selectivity may be due to the large pores of SSZ-31 or may be due to the fact that the reaction inside the pores may be slower in the case of SSZ-31 than in the case of mordenite. Diffusion of the substrates and products may be slow in the one-dimensional pores of SSZ-31, and reaction may also be taking place on the external surface to a certain extent. On the other hand, mordenite has 12/8-ring intersections and this helps in diffusion leading to smoother introduction of the alkylating agent and biphenyl and also effective diffusion of the products.

In the case of SSZ-31, the yields of IPBPs decrease while that of DIPBs increase with temperature at 0.8 MPa pressure. Conversion increases with increase in temperature while the selectivity for 4,4′-DIPB decreases. At high temperature 4,4′-DIPB isomer formed isomerises to 3,3′- and 3,4′-DIPB which are thermodynamically more stable. Pressure has a profound effect on the isomerization of 4,4′-DIPB. Isomerization of 4,4′-DIPB is reduced considerably at high propylene pressures. Three different SiO_2/Al_2O_3 ratios were examined. Conversion decreases with increase in silica to alumina ratio; however, the decrease is not very significant. The selectivity for 4,4′-DIPB remained nearly constant. At $SiO_2/Al_2O_3 = 136$, more TriIPB isomers are formed, probably due to a larger number of active sites on the surface.

Further investigation on the nature of these active sites and effect on encapsulated products and modification of catalyst is under consideration and will be discussed in future.

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