Shape-selective isopropylation of naphthalene over dealuminated mordenites.
Increasing β-substitution selectivity by adding water

Andrew D. Schmitz and Chunshan Song [1]

Fuel Science Program, Department of Materials Science and Engineering, Pennsylvania State University,
209 Academic Projects Building, University Park, PA 16802, USA

Received 11 December 1995; accepted 28 March 1996

Isopropylation of naphthalene was examined over two dealuminated H-mordenites (HM) having SiO_2/Al_2O_3 molar ratio of 38 (HM38) and 74 (HM74). Experiments were done in batch reactors at 200°C. With propylene as the alkylating agent, selectivity for β-substitution of naphthalene increased when water was added, and reached a maximum with a water-to-catalyst mass ratio of 0.80 (ca. 45 mmol water/g-cat). Of particular importance was the increase in $\beta\beta$-selectivity to 2,6- and 2,7-diisopropylnaphthalene (2,6-DIPN and 2,7-DIPN) with added water. Without added water, $\beta\beta$-selectivities were 56 and 77% for HM38 and HM74, respectively. Selectivities to the highly desired 2,6-DIPN isomer were 37 and 54%, respectively. With added water, $\beta\beta$-selectivities increased to 90 and 95%, and 2,6-DIPN selectivities increased to 60 and 70% for HM38 and HM74, respectively. A large amount of added water always decreased the activity; however, mixed effects were observed for intermediate amounts of added water. Sorption of water on the catalyst surface seems to explain changes in isomer selectivity and catalytic activity. Coke deposits on the catalysts also decreased when water was added. Furthermore, it was shown that higher $\beta\beta$-selectivity could be obtained with isopropanol (*i*-PrOH) as the alkylating agent, rather than propylene, under the same conditions. Comparison experiments showed that this was due to water formed from *i*-PrOH.

Keywords: alkylation; mordenite; shape-selectivity; 2,6-diisopropylnaphthalene

1. Introduction

Shape-selective naphthalene alkylation has become an important research subject due to the demand for 2,6-dialkylnaphthalenes (2,6-DAN's). Selectively alkylated polycyclic aromatic hydrocarbons such as 2,6-DAN's can be used to make monomers of advanced polyester materials including polyethylene naphthalate, polybutylene naphthalate, and liquid crystalline polymers [1–3]. Previous reports have shown that hydrogen-mordenite (HM) catalysts are effective for the shape-selective isopropylation of naphthalene to produce 2-monoisopropylnaphthalene (2-MIPN) and 2,6-diisopropylnaphthalene (2,6-DIPN) [4–15].

Selective naphthalene alkylation over dealuminated HM was examined previously in this laboratory, using isopropanol (*i*-PrOH) [4] and propylene [5,6] as the alkylating agents. Compared to isopropylation using propylene, *i*-PrOH often afforded higher selectivity to 2,6-DIPN and higher 2,6-DIPN/2,7-DIPN ratio. Water can be formed from *i*-PrOH either by dehydration or by the bimolecular reaction between *i*-PrOH and naphthalene. We suspected that the increased 2,6-DIPN selectivity for *i*-PrOH alkylating agent was due to this byproduct water. This consideration prompted us to examine the effects of added water (or added *i*-PrOH) on naphthalene alkylation with propylene alkylating agent. Our objective was to understand the effects of water on isomer selectivity and catalyst activity. Combined use of partially dealuminated mordenites and added water (or added *i*-PrOH) was found to be an effective and inexpensive means to increase selectivity for 2-MIPN and 2,6-DIPN products.

2. Experimental

Na-M14 and NH_4-M38 mordenites were supplied as 9–10 μm average particle size powders from the PQ Corporation, Inc. The last two digits in the catalyst name give the SiO_2/Al_2O_3 molar ratio. Nitrogen BET surface areas were 466 and 512 m^2/g, and pore volumes were 0.31 and 0.30 cm^3/g for Na-M14 and NH_4-M38, respectively. NH_4-M38 had 0.07 wt% residual Na_2O. Na-M14 (6.24 wt% Na_2O) was treated with 1 M NH_4Cl at reflux, washed until free of chloride, and dried to generate the ammonium form (0.19 wt% Na_2O). H-mordenites were obtained by calcination in air at 465 °C. HM14 was stirred in 1 M HCl for 24 h at reflux temperature, washed free of chloride, dried, and calcined to generate HM74 (<0.01 wt% Na_2O, 583 m^2/g, and 0.35 cm^3/g). Catalyst samples were solubilized using lithium metaborate fusion for ICP-AES chemical analysis.

All chemicals were of high purity and used as sup-

---

[1] To whom correspondence should be addressed.

plied. Naphthalene (99%) and *i*-PrOH (99.5+%) were obtained from Aldrich Chemical, Inc. Propylene (99.5% minimum, polymer purity) was obtained from Matheson, Inc.

Catalyst tests were done at 200°C, for 2 h, in a 30 cm^3 stainless-steel microautoclave reactor. The reactor was attached to a mounting bracket and immersed in a fluidized sand bath heater while being vertically agitated (240 min^{-1}, 1 cm stroke). The standard reactor charge was 0.15 g freshly calcined catalyst, 1.0 g (7.8 mmol) naphthalene, 0.65 g (15.6 mmol) of propylene, and a variable amount of either water or *i*-PrOH (0–300 mg). The H_2O/Cat ratio (mmol/g) was determined from the masses of freshly calcined catalyst (neglecting residual moisture) and added water. To calculate the H_2O/Cat ratio for *i*-PrOH, it was assumed that *i*-PrOH reacts completely to give an equimolar amount of water as a byproduct. Two additional runs were done using *i*-PrOH (15.6 or 3.9 mmol) as the alkylating agent, without any added water.

At the end of the test, the reaction was quenched in cold water. After venting the gas headspace, acetone was used to wash the reactor contents onto a filter. Solution products were analyzed by GC-MS and GC-FID. For both GC instruments, the column was 30 m × 0.25 mm DB-17 (J&W Scientific), and the oven temperature program was 40–280°C at 4°C/min.

Thermal gravimetric analyses (TGA) were done on a Mettler TG50 thermobalance. Recovered catalyst samples were dried at 70°C, 10^{-2} Torr, before TGA. A fresh sample of HM38 catalyst, calcined and handled in the usual manner, was analyzed by TGA for comparison. Approximately 6 mg of each sample was loaded in an alumina crucible and heated 30–800°C, at 10°C/min, under 200 cm^3/min dry air flow.

3. Results

Under the conditions employed, greater than 97% of the alkylation products are isopropylnaphthalenes. Side reactions result in small amounts of alkylnaphthalenes that are not solely isopropyl-substituted. Mass balances are greater than 96% in all cases, with material losses being primarily attributed to carbonaceous deposits on the catalyst. β-substitution of naphthalene gives rise to the main products (fig. 1): 2-monoisopropylnaphthalene (2-MIPN) and two diisopropylnaphthalene (DIPN) isomers, 2,6-DIPN and 2,7-DIPN.

Naphthalene alkylation by propylene over HM38 catalyst, with various amounts of water added to the reactor, is shown in table 1 and fig. 2. Selectivities for 2-MIPN (β-selectivity), and 2,6-DIPN and 2,7-DIPN (ββ-selectivity) increase with added water as shown in fig. 2. With sufficient added water, β-selectivity climbs to ca. 80%, and selectivity for 2,6-DIPN rises from 37 to 63%, with a 19% increase in the 2,6-DIPN/2,7-DIPN isomer ratio. ββ-selectivity to 2,6- and 2,7-DIPN increases from 56 to 89%. Adding water beyond 45 mmol/g does not further increase %2,6-DIPN and has mixed effects on the 2,6-DIPN/2,7-DIPN ratio.

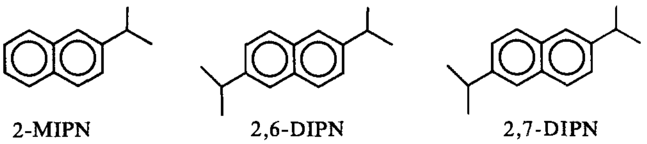


Fig. 1. Structures of β-substituted mono- and diisopropylnaphthalenes.

Naphthalene conversion decreases monotonically with the H_2O/Cat ratio. At 110 mmol/g, the catalyst is almost inactive. Monosubstitution of naphthalene occurs more rapidly than the second and subsequent additions; therefore, yields of polyalkylated naphthalene fall as the conversion decreases. Naphthalene conversion was found to be quite sensitive to the residual moisture level on the hygroscopic catalyst when no water was added. The catalysts were handled in ambient during reactor loading; consequently, scatter in conversion data was somewhat larger for runs with no added water. From TGA analysis, it is estimated that about 5.5 wt% moisture is adsorbed on HM38 and 4.5 wt% on HM74 during this exposure to ambient humidity. Data for tests with added water were reproducible as confirmed by duplication.

Table 2 and fig. 3 show the effects of added water on naphthalene isopropylation over the HM74 catalyst. Compared to HM38, HM74 shows higher β- and ββ-selectivities, and in particular, higher %2,6-DIPN. This is consistent with our earlier observations concerning the effects of HM dealumination on alkylation isomer selectivity [5,6]. A maximum in 2,6-DIPN selectivity is reached at ca. 45 mmol/g added water – the same maximum seen for the series of water-addition tests with the HM38 catalyst (table 1). Above 45 mmol/g added water, ββ-selectivity is roughly constant, but the 2,6-DIPN/2,7-DIPN ratio shows a downward trend.

Table 1
Selective naphthalene alkylation by propylene over HM38 with added water

H_2O/Cat (mmol/g)	Conv. (%)	Isomer selectivity (mol%)				
		MIPN	DIPN			
		2-	2,6-	2,7-	other	2,6-/2,7-
0	88	52	37	18	45	2.02
0	81	56	38	19	43	2.00
4.1	78	63	44	21	36	2.10
19.6	67	76	58	25	17	2.36
44.3	60	80	63	26	10	2.40
59.2	41	80	61	28	10	2.16
59.3	49	78	59	28	13	2.15
110.4	9	82	66	29	5	2.29
110.9	7	79	66	28	6	2.33

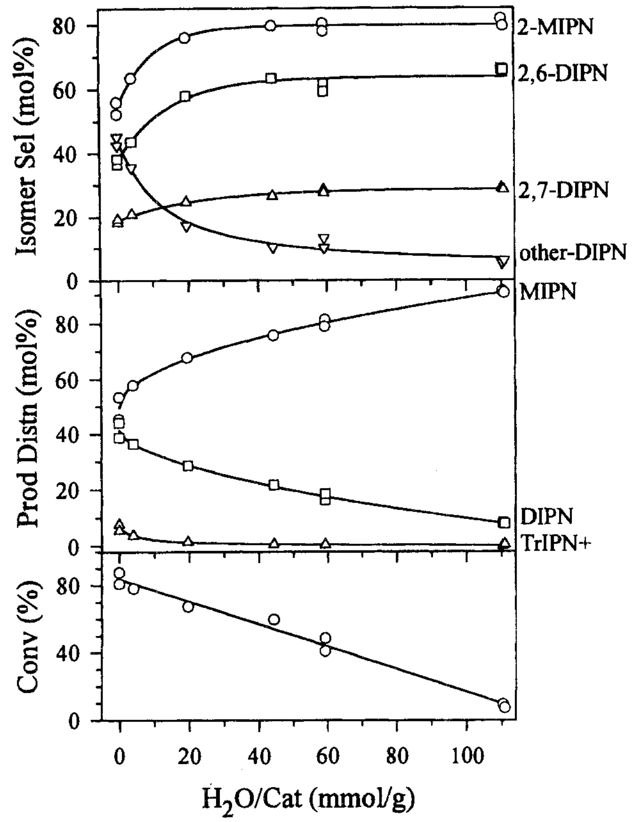


Fig. 2. Influence of added water on naphthalene alkylation with propylene over HM38 catalyst at 200°C.

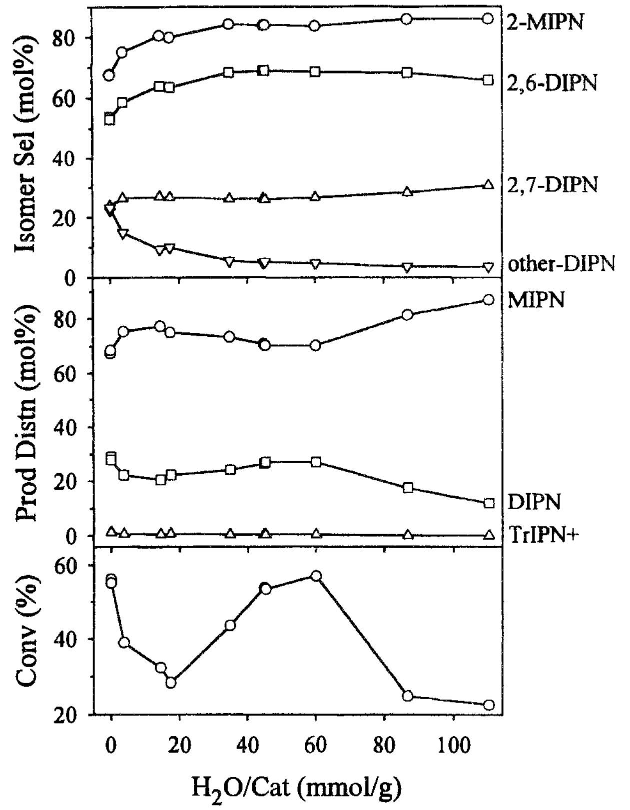


Fig. 3. Influence of added water on naphthalene alkylation with propylene over HM74 catalyst at 200°C.

Interestingly, added water shows mixed effects on naphthalene conversion for HM74. Small amounts of added water cause the catalyst activity to decrease, but a minimum is reached at about 20 mmol/g added water, and more added water results in higher conversion. We were surprised by these observations initially and performed duplicate experiments. Reproducibility of the trends shown in fig. 3 was confirmed. It seems that a poisoning mechanism is superseded by an activity-enhancing mechanism at intermediate H_2O/Cat ratios. In general, increase in conversion could be due to an increase in the number of active sites, higher activity per site, or inhibition of catalyst deactivation.

Table 2
Selective naphthalene alkylation by propylene over HM74 with added water

H_2O/Cat (mmol/g)	Conv. (%)	Isomer selectivity (mol%)				
		MIPN	DIPN			
		2-	2,6-	2,7-	other	2,6-/2,7-
0	56	68	54	24	22	2.26
0	55	67	53	24	23	2.22
3.7	39	75	59	26	15	2.22
14.4	32	80	64	27	9	2.37
17.4	28	80	63	27	10	2.38
34.8	44	84	68	26	6	2.61
44.8	54	84	69	26	5	2.62
45.3	53	84	69	26	5	2.65
60.1	57	84	68	27	5	2.56
86.9	25	86	68	28	4	2.41
110.2	23	86	66	31	4	2.15

Since the changes in product selectivity observed when water is added are often accompanied by large changes in conversion, it should be mentioned that the selectivities also change with conversion in the absence of water. In general, the yield of MIPN decreases and that of DIPN increases, and the selectivities to 2-MIPN and 2,6-DIPN decrease with increasing naphthalene conversion in the absence of water [6].

TGA analyses of the used catalysts clearly demonstrate that added water also retards carbon deposition, as shown in figs. 4 and 5. Only the high-temperature weight loss region is considered, where the primary reaction is oxidation of carbonaceous deposits (coke) in air. The curves are also normalized to a common origin to correct for variations in weight loss at low temperatures, particularly for differences in residual moisture and residual wash solvent. The fan-shaped patterns of figs. 4 and 5 describe a 25–30% decrease in coke deposits with added water.

Table 3 shows the data for naphthalene alkylation by *i*-PrOH on HM38 catalyst. When propylene is replaced with an equimolar amount of *i*-PrOH (i.e., naphthalene/alkylating-agent mol ratio of 0.5) β- and $\beta\beta$-selectivities increase significantly, but naphthalene conversion

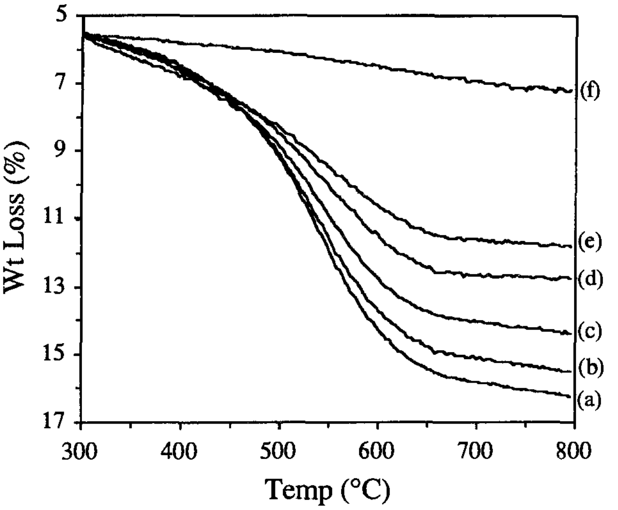


Fig. 4. TGA-derived weight loss profiles of used and fresh HM38 catalysts in air. (a)–(e) Oxidative removal of carbonaceous deposits on used catalysts from runs with the following added H_2O/Cat ratios (mmol/g): (a) 0; (b) 4.1; (c) 19.6; (d) 44.3; (e) 110.9. (f) Residual moisture in the freshly calcined catalyst.

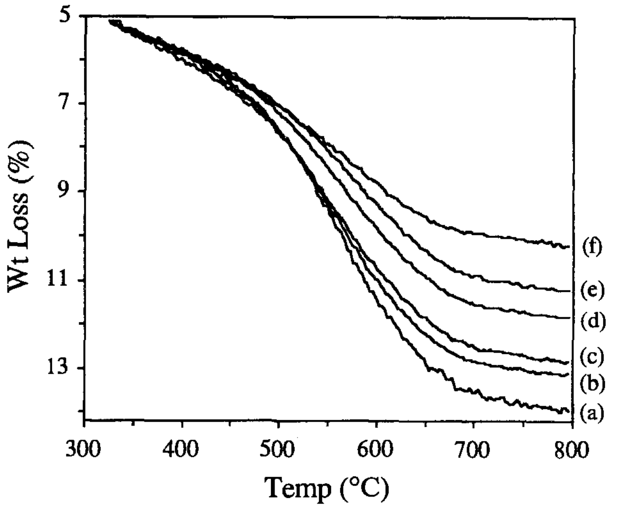


Fig. 5. TGA-derived weight loss profiles during oxidative removal of carbonaceous deposits used HM74 catalysts from runs with the following added H_2O/Cat ratios (mmol/g): (a) 0; (b) 3.7; (c) 14.4; (d) 34.8; (e) 60.1; (f) 110.2.

decreases (compare with zero added water data from table 1). Table 3 also shows that when the naphthalene/*i*-PrOH mol ratio is increased to 2.0, naphthalene conversion increases and both %2,6-DIPN and 2,6-DIPN/2,7-DIPN are very high. Song and Kirby [4] found similar results in their work on naphthalene isopropylation with *i*-PrOH, and suggested that adsorption of excess water or *i*-PrOH on catalyst sites might explain the activity differences. In fact, when the data in table 1 and table 3 are compared under similar H_2O/Cat ratios, the results are quite similar. (Complete reaction of *i*-PrOH, by dehydration or by bimolecular reaction with naphthalene, is assumed in the calculation of the H_2O/Cat ratios. It is noteworthy that no unreacted *i*-PrOH was observed in the GC's of the liquid products.) Apparently, naphthalene alkylation using *i*-PrOH is analogous to naphthalene alkylation using propylene with added water.

The role of byproduct water from *i*-PrOH was further investigated by adding *i*-PrOH to the naphthalene-plus-propylene system (table 4). Added water and added *i*-PrOH are compared in fig. 6. It can be seen that whether water is added directly, or generated in situ from *i*-PrOH, its effects on naphthalene alkylation over HM38 are very similar.

4. Discussion

HM38 activity decreases monotonically with H_2O/Cat (fig. 2). This suggests a fairly uniform distribution of Brønsted acid sites being passivated by water adsorption, probably involving interactions between water and acidic hydroxyl groups as shown in scheme 1. Yields of α-substituted isopropylnaphthalenes (1-MIPN and other-DIPN) decrease sharply in the range where H_2O/Cat equals 0–20 mmol/g. Due to size restrictions, α-substitution of naphthalene can only occur on external surface catalyst sites, and not within the HM micropores. Since the external surface of the catalyst constitutes only a small fraction of the total surface area, a small amount of added water is sufficient to deactivate these non-selective catalyst sites. Above 45 mmol/g added water, HM38 activity continues to decline, but there is little effect on isomer selectivity. It can be concluded that adsorption of water on the internal acid sites of HM38 has little effect on alkylation isomer selectivity.

Table 3
Selective naphthalene alkylation by isopropanol over HM38

Nap/*i*-PrOH mol ratio [a]	*i*-PrOH/Cat (mmol/g) [b]	Conv. (%)	Isomer selectivity (mol%)				
			MIPN	DIPN			
			2-	2,6-	2,7-	other	2,6-/2,7-
0.5	103	11	82	60	33	−7	1.81
2.0	25.9	37	85	64	25	11	2.51

[a] Reactor charge: 0.15 g HM38 catalyst, 1.0 g naphthalene, and the given amounts of *i*-PrOH to make the specified ratio.
[b] Also equivalent to the mmol water produced by reaction of isopropanol.

Table 4
Selective naphthalene alkylation by propylene over HM38 with added isopropanol

i-PrOH/Cat (mmol/g)[a]	Conv. (%)	Isomer selectivity (mol%)				
		MIPN	DIPN			
		2-	2,6-	2,7-	other	2,6-/2,7-
1.1	78	62	42	20	38	2.05
5.4	72	64	44	22	34	2.04
13.2	67	69	50	24	26	2.05
18.0	67	71	52	25	23	2.09
33.4	64	77	59	27	13	2.17

[a] Also equivalent to the mmol water produced by reaction of isopropanol.

HM38 and HM74 have considerably different activity patterns in response to added water (figs. 2 and 3). For HM74, the initial decrease in activity, which is accompanied by a decrease in α-alkylation, is attributed to passivation of external surface Brønsted acid sites. Conversion increases between H_2O/Cat approximately 20 and 45 mmol/g, concurrent with increases in %2,6-DIPN and 2,6-DIPN/2,7-DIPN ratio. This suggests that water addition generates new active sites for alkylation, and that the new active sites are located inside the shape-selective HM channels. Conversion finally decreases above 60 mmol/g water added due to deactivation of Brønsted acid sites within the micropores by adsorbed water.

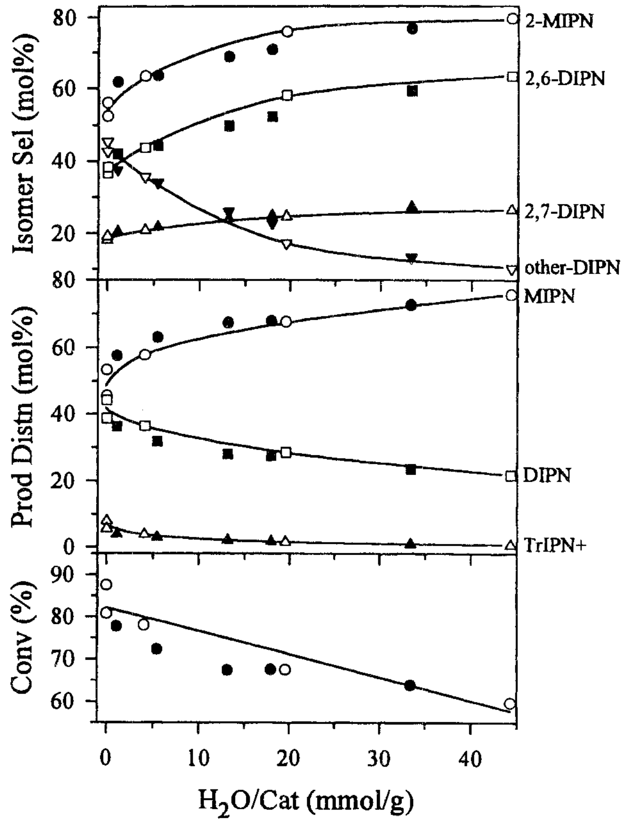
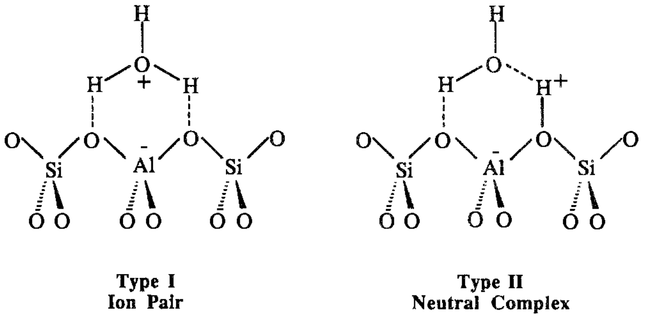


Fig. 6. Comparison of the effects of added water (open symbols) and added *i*-PrOH (filled symbols) on naphthalene alkylation with propylene over HM38 at 200°C.



Scheme 1. Interactions of Brønsted acid sites with water molecules.

Two questions that arise are: Why does water addition affect mordenite alkylation activity? and Why does catalytic activity increase in the range H_2O/Cat equals 20–60 mmol/g for HM74, but not for HM38? Concerning the acid characteristics of mordenites and their changes upon water addition, some observations reported in the literature [16–38] are relevant to the discussion here.

For HM38 mordenite, the decrease of activity upon water addition is apparently due to the passivation of active sites. It is known [16] that water may interact with Brønsted acid sites on the zeolite in two possible ways leading to two surface structures: an ion pair in which the proton is transferred from the Brønsted acid site to the water molecule to form a hydronium ion (H_3O^+), or a complex in which the water molecule hydrogen bonds at the Brønsted acid site but no proton transfer occurs. Some researchers indicated that addition of water to an H-form zeolite leads to formation of hydronium ion H_3O^+ [17,18], while other studies favor the hydrogen-bonded form [19–21] or the partially protonated form [22]. Recent experimental study by Cheetham and Thomas and their co-workers [23] and the quantum chemical calculations by Sauer and co-workers [16,24,25] have established that both hydronium ion form and hydrogen-bonded form are present upon interaction of water with Brønsted OH on zeolite surface. Scheme 1 is consistent with these recent findings.

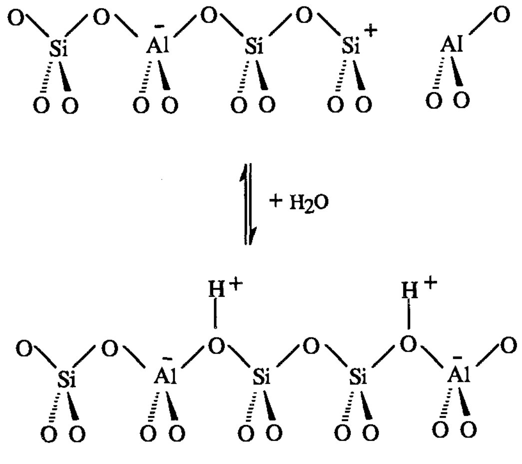
Dumesic et al. [26–28] found that a non-dealuminated H-mordenite (HM13) has a homogeneous distribution of Brønsted acid sites with very few strong Lewis acid sites. It is known that the addition of water and heating can convert Lewis acid sites to Brønsted acid sites [29], although little or no previous study has knowingly adjusted the water/catalyst ratio as a method for controlling the selectivity/activity of shape-selective alkylation over zeolite catalysts. In their IR study of pyridine and water adsorption on HM ($SiO_2/Al_2O_3 = 12$), Lefrancois and Malbois [30] observed both Lewis and Brønsted acid sites; added water completely converted the Lewis acid sites to Brønsted acid sites at 200–300°C.

For HM with SiO_2/Al_2O_3 of ca. 32, Cannings [31] used IR to show that strong Lewis acid sites are slowly converted to Brønsted sites in the presence of water vapor. In summary, the above-mentioned studies show that water adsorption on HM can be dissociative, forming new Brønsted acid sites from Lewis sites.

In general, dealumination of H-mordenite decreases total acidity and generates strong acid sites at the expense of weak and intermediate strength sites; consequently, dealuminated HM has both Brønsted and Lewis acid sites [32–37]. It has been suggested that the Lewis acid sites of HM involve tricoordinate aluminum and silicon [31,37]. Ammonia adsorption on the strong Lewis acid sites of dealuminated HM is dissociative; whereas, molecular adsorption occurs on weaker Lewis sites and Brønsted sites [32,33]. Scheme 2 illustrates a possible mechanism for dissociation of water on the Lewis acid sites of HM that is consistent with these earlier suggestions [29–31,37].

In the present work, it is expected that dissociative adsorption of water will occur on the relatively small number of Lewis sites contained on HM38. However, dissociative adsorption becomes more important for the more dealuminated sample, HM74, which should have a higher percentage of strong Lewis acid sites. In addition, it is known that hydrophobicity of mordenite increases with increasing SiO_2/Al_2O_3 ratio [38]. Therefore, the internal surface of HM74 is expected to be more hydrophobic than that of HM38.

The following model is proposed for water adsorption on HM74: (1) In the range where $H_2O/Cat = 0–20$ mmol/g, primarily, adsorption of water occurs on Brønsted acid sites, particularly those on the catalyst's external surface. Naphthalene conversion and non-selective alkylation reactions decrease due to passivation of catalyst sites (as also observed for the HM38 catalyst). (2) At higher partial pressures of water ($H_2O/Cat = 20–60$ mmol/g), water diffuses into the micropores and adsorbs dissociatively on strong Lewis sites, converting them to Brønsted acid sites. Naphthalene conversion increases in this range because more Brønsted acid centers are generated, having appropriate acid strength to supply protons for the formation of carbocation intermediate involved in the alkylation. (3) Water added beyond $H_2O/Cat = 60$ mmol/g decreases the number of acid sites available for catalyzing the alkylation reaction, either by adsorption on Brønsted acid sites, or by capillary condensation.



Scheme 2. A model for illustrating dissociation of water on Lewis sites.

We now understand that *i*-PrOH alkylating agent behaves as propylene with added water. When propylene is replaced with an equivalent amount of *i*-PrOH (line 1, table 3), there appears to be too much in situ generated moisture, and the 2,6-DIPN/2,7-DIPN ratio is only 1.81. Conversely, naphthalene/*i*-PrOH mol ratio of 2.0 gives a high 2,6-DIPN/2,7-DIPN ratio and again, high overall $\beta\beta$-selectivity. Under these conditions, the H_2O/Cat ratio is 25.9 mmol/g, which is nearly the optimum moisture level found for alkylation by propylene (table 1). Coincidence of the data for added water and added *i*-PrOH in fig. 6 gives additional support to the argument that enhanced β-isomer selectivity with *i*-PrOH is due to byproduct water.

There have been several accounts of improved selectivity in isopropylation of polycyclic aromatic hydrocarbon involving deactivation of acid sites on the external surfaces of HM. For isopropylation of biphenyl over HM, Sugi and co-workers [39,40] found improved 4,4′-diisopropylbiphenyl (4,4′-DIPB) selectivity under high propylene pressure. They concluded that adsorption of propylene on external surface acid sites inhibits isomerization of 4,4′-DIPB. We have shown that the adsorption of propylene on HM also passivates acid sites that are active for isomerization of 2,6-DIPN [10]. Deposition of cerium oxide on the external surfaces of HM was also found by Sugi et al. [11] to improve 2,6-DIPN selectivity. Furthermore, Moreau and coworkers [13] obtained higher selectivity for 2,6- and 2,7-DIPN in the isopropylation of naphthalene when the HM external surfaces were silanated. Clearly, deactivation of HM external surface acid sites improves alkylation selectivity. Our work shows that this can be accomplished simply by adding water. A more elaborate approach involving expensive reagents and/or catalyst pretreatment may not be necessary.

Mordenite has a unidirectional, non-interconnecting channel structure. A major concern with this type of catalyst is diffusion impedance and pore blockage by coke deposits. Coking is generally more severe for HM having low SiO_2/Al_2O_3 ratio. The TGA patterns in figs. 4 and 5 show that addition of water retards coking by about the same magnitude for both HM38 and HM74. Therefore, the presence of water slows deactivation due to carbon deposition irrespective of dealumination level.

The changes in catalytic properties for HM38 upon addition of water are somewhat similar to the changes induced by dealumination [6]. This is probably because both water addition and chemical dealumination results in less reactions on the external surface. Hydrochloric acid treatment removes aluminum to yield a silica-rich external surface [41]. Water addition passivates the Brønsted acid sites on the external surface. Both treatments decrease external surface-catalyzed non-selective reactions.

5. Conclusions

Addition of modest amounts of water is beneficial to naphthalene isopropylation over mordenites in several regards: increased selectivity for substitution at the β-carbons of naphthalene, increased catalytic activity under certain conditions, and decreased rate of carbon deposition on the catalyst. Improved β-isomer selectivity with *i*-PrOH alkylating agent is due to the water produced from the alcohol. The combined use of partially dealuminated mordenites and added water is an effective and inexpensive means to increase 2-MIPN and 2,6-DIPN selectivities in the isopropylation of naphthalene. This approach has significant practical applications in production of 2,6-DIPN.

Acknowledgement

We would like to acknowledge the encouragement and support of Professor Harold Schobert at the Pennsylvania State University. We would also like to thank the PQ Corporation, Inc. for graciously providing the mordenite starting materials with detailed analytical data.

References

[1] C. Song and H.H. Schobert, Fuel Process. Technol. 34 (1993) 157.
[2] C. Song and H.H. Schobert, Am. Chem. Soc. Div. Fuel Chem. Prepr. 40 (1995) 249.
[3] D. Fraenkel, M. Cherniavsky, B. Ittah and M. Levy, J. Catal. 101 (1986) 273.
[4] C. Song and S. Kirby, Micropor. Mater. 2 (1994) 467.
[5] A.D. Schmitz and C. Song, Am. Chem. Soc. Div. Fuel Chem. Prepr. 39(4) (1994) 986.
[6] A.D. Schmitz and C. Song, Am. Chem. Soc. Div. Fuel Chem. Prepr. 40(4) (1995) 918.
[7] J.A. Horsley, J.D. Fellmann, E.G. Derouane and C.M. Freeman, J. Catal. 147 (1994) 231.
[8] P. Moreau, A. Finiels, P. Geneste, F. Moreau and J. Solofo, Am. Chem. Soc. Div. Fuel Chem. Prepr. 40 (1995) 913.
[9] S.-J. Chu and Y.-W. Chen, Ind. Eng. Chem. Res. 33 (1994) 3112.
[10] A.D. Schmitz and C. Song, Catal. Today (1996), in press.
[11] Y. Sugi, J.-H. Kim, T. Matsuzaki, T. Hanaoka, Y. Kubota, X. Tu and M. Matsumoto, in: *Zeolites and Related Microporous Materials: State of the Art 1994*, Stud. Surf. Sci. Catal., Vol. 84, eds. J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Elsevier, Amsterdam, 1994) p. 1837.
[12] Y. Sugi and M. Toba, Catal. Today 19 (1994) 187.
[13] P. Moreau, A. Finiels, P. Geneste and J. Solofo, J. Catal. 136 (1992) 487.
[14] A. Katayama, M. Toba, G. Takeuchi, F. Mizukami, S.-i. Niwa and S. Mitamura, J. Chem. Soc. Chem. Commun. (1991) 39.
[15] J.D. Fellmann, J. Saxton, P.R. Wentrcek, E.G. Derouane and P. Massioni, US Patent No. 5,026,942 (1991).
[16] J. Sauer, Science 271 (1996) 774.
[17] B.C. Gates, *Catalytic Chemistry* (Wiley, New York, 1992) ch. 5.
[18] L. Merchese, P.A. Wright, J. Chen and J.M. Thomas, J. Phys. Chem. 97 (1993) 8109.
[19] J. Sauer, C. Kolmel, F. Haase and R. Ahlrichs, in: *Proc. 9th Int. Zeolite Conf.*, Montreal 1992, eds. T. van Ballmoos et al. (Butterworth–Heinemann, Boston, 1993) pp. 679–685.
[20] A.G. Pelmenschikov and R.A. van Santen, J. Phys. Chem. 97 (1993) 10678.
[21] R.A. van Santen and G.J. Kramer, Chem. Rev. 95 (1995) 637.
[22] L.M. Parker, D.M. Bibby and G.R. Burns, Zeolites 13 (1993) 107.
[23] L. Smith, A.K. Cheetham, R.E. Morris, L. Marchese, J.M. Thomas, P.A. Wright and J. Chen, Science 271 (1996) 799.
[24] F. Haase and J. Sauer, J. Am. Chem. Soc. 117 (1995) 3780.
[25] M. Krossner and J. Sauer, J. Phys. Chem. (1996), in press.
[26] B.E. Spiewak, B.E. Handy, S.B. Sharma and J.A. Dumesic, Catal. Lett. 23 (1994) 207.
[27] S. B. Sharma, B.L. Meyers, D.T. Chen, J. Miller and J.A. Dumesic, Appl. Catal. A 102 (1993) 253.
[28] D.T. Chen, S.B. Sharma, I. Filimonov and J.A. Dumesic, Catal. Lett. 12 (1992) 201.
[29] C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice* (McGraw-Hill, New York, 1991) ch. 7.
[30] M. Lefrancois and G. Malbois, J. Catal. 20 (1971) 350.
[31] F.R. Cannings, J. Phys. Chem. 72 (1968) 4691.
[32] N. Cardona-Martinez and J.A. Dumesic, Adv. Catal. 38 (1992) 149.
[33] I.V. Mishin, H. Bremer and K.-P. Wendlandt, in: *Catalysis on Zeolites*, eds. K. Kalló and Kh.M. Minachev (Stillman, Boca Raton, 1988) ch. 9.
[34] A. Auroux and Y.B. Taarit, Thermochim. Acta 122 (1987) 63.
[35] A.L. Klyachko, G.I. Kapustin, T.R. Brueva and A.M. Rubinstein, Zeolites 7 (1987) 119.
[36] A.L. Klyachko, G.I. Kapustin, G.O. Gionti, T.R. Brueva and A.M. Rubinstein, Kinet. Catal. 26 (1985) 613.
[37] G.I. Kapustin, L.M. Kustov, G.O. Glonti, T.R. Brueva, V.Yu. Borovkov, A.L. Klyachko, A.M. Rubinstein and V.B. Kazanskii, Kinet. Catal. 25 (1984) 959.
[38] U.Y. Chen, J. Phys. Chem. 80 (1976) 60.
[39] Y. Sugi, X. Tu, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim and M. Matsumoto, Am. Chem. Soc. Div. Fuel Chem. Prepr. 40 (1995) 908.
[40] X. Tu, M. Matsumoto, T. Matsuzaki, T. Hanaoka, Y. Kubota, J.-H. Kim and Y. Sugi, Catal. Lett. 21 (1993) 71.
[41] R. Szostak, *Molecular Sieves* (Van Norstrand Reinhold, New York, 1989) ch. 1.