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Aluminum Insertion into High-Silica Zeolite Frameworks

II. Binder Activation of High-Silica ZSM-5

INTRODUCTION

Zeolite catalysts are normally manufactured by embedding the zeolite crystals in a matrix, usually a metal oxide such as alumina, to impart mechanical strength. This matrix, or binder, is usually assumed to be essentially an inert component of the catalyst. Recent evidence indicates that this is not the case for high-silica ZSM-5 bound with alumina. Interestingly, alumina binding has been found to enhance the catalytic activity of the zeolite for numerous reactions. This paper discusses the binder activation of high-silica ZSM-5 for *n*-hexane cracking, propylene oligomerization, lube hydrodewaxing, and methanol conversion to hydrocarbons.

The catalytic activity of high-silica ZSM-5 zeolite is enhanced when the zeolite is bound (wet-mulled and extruded) with Al_2O_3. This effect is demonstrated herein for four acid-catalyzed reactions: *n*-hexane cracking, propylene oligomerization, lube oil dewaxing, and methanol conversion to hydrocarbons. Binding with Al_2O_3 results in an increase in the zeolite ion-exchange capacity. This is attributed to Al migration from the binder into the zeolite framework, and tetrahedral coordination therein.

EXPERIMENTAL

Materials. High-silica ZSM-5 samples used in this study were synthesized according to the method of Argauer and Landolt (*1*) and had SiO_2/Al_2O_3 = 1,600, 26,000, and 38,000. These zeolite preparations will be referred to below as Samples A, B, and C, respectively.

α-Alumina monohydrate was obtained from Kaiser Aluminum Corporation.

The zeolite samples were composited with alumina binder by the following procedure: (1) wet-mulling the as-synthesized zeolite with alumina, (2) extrusion, (3) calcination at 538°C, NH_4^+ exchange, (4) calcination at 538°C.

Apparatus and procedures. Catalytic evaluations were done using equipment and procedures described elsewhere (*2–7*).

Temperature-programmed NH_3 desorption (TPAD) was carried out using a du Pont 951 thermogravimetric analyzer equipped with an automatic titrimeter assembly, as described by Kerr and Chester (*12*).

RESULTS AND DISCUSSION

n-Hexane cracking. The cracking activities of various catalysts with and without alumina binder were evaluated by determining the first-order rate constants for *n*-hexane cracking at 538°C. Data are expressed in terms of α activity (*2, 3*) which is the value of the rate constant for a given catalyst relative to that of an equal volume of a standard amorphous silica–alumina catalyst. Data showing the effect of alumina binder on two zeolite Samples A and B are listed in Table 1. The effect of steaming at 427°C on Sample A is also shown. Binding with alumina increased the α activity of Sample A from 4.0 to 7.7, and that of Sample B from 0.02 to 1.4. The activity of the alumina-bound Sample A was further enhanced by steaming (760 Torr H_2O) at 427°C, with the α increasing to 15.0 after 15 hr, and to 17.6 after 18 hr. By comparison, the activity of the unbound zeolite was changed little after steaming for 18 hr at 427°C.

Propylene oligomerization. The oligo-

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TABLE 1

n-Hexane Cracking[a]

Zeolite sample	Zeolite SiO_2/Al_2O_3	Alumina binder	Steam treatment[b] (hr)	Activity[c] (α)
A	1,600	No	0	4.0
A	1,600	No	18	5.0
A	1,600	Yes	0	7.7
A	1,600	Yes	15	15.0
A	1,600	Yes	18	17.6
B	26,000	No	0	0.02
B	26,000	Yes	0	1.4

[a] 100 Torr nC_6 in He; 538°C.

[b] 760 Torr H_2O; 427°C.

[c] Based on a catalyst bulk density of 0.43 cm^3/g in the absence of binder, and 0.55 cm^3/g in the presence of binder.

merization of light olefins to distillate range hydrocarbons over ZSM-5 has been reported by Garwood (*7*). The effect of binder on the activity of Sample C for propylene oligomerization was studied, following the experimental procedure of Garwood (*7*). Results may be seen in Table 2. Reaction conditions were 204°C, 35–48 atm, 0.5 WHSV, and data were taken after 24 hr on stream. In the absence of alumina binder, the activity of Sample C was low, giving 16% conversion, mostly to light products. A dry, physical mixture of Sample C with alumina showed no activity enhancement. However, when the mixture was wet-mulled and extruded, a substantial increase in activity was evident. Conversion rose to 77%, yielding 71.9% liquids containing 56% 165°C+ distillate range product. In a control experiment, not shown in Table 2, the alumina binder itself was found to be inactive for liquid hydrocarbon synthesis under similar reaction conditions.

Lube dewaxing. Catalytic lube dewaxing is a process based on the shape-selective properties of ZSM-5, wherein high-molecular-weight *n*- and monomethyl paraffins are removed from lube basestocks through cracking (*8*). Low pour point oils are thereby produced. A waxy lube raffinate (343–538°C b.p., 46°C pour point) was reacted over Sample C, either physically mixed or extruded with alumina. Reaction conditions were 343°C, 28 atm (under hydrogen), and 1.6 LHSV. The experimental apparatus was similar to that described by Chen (*5*). Experimental results are summarized in Table 3. It is apparent that the physical mixture (dry-mixed) of zeolite with alumina is inactive while the extrudate gave 15% conversion, reducing the pour point from 46 to −7°C. These results are especially significant in that they show the binder-activated zeolite to be shape selec-

TABLE 2

Propylene Oligomerization[a] (Zeolite Sample C)

	Pure zeolite	Physical mixture with binder	Extrudate	
$C_3^=$ conversion, wt%	16	15	77	77
Yields, wt%				
$C_1 + C_2$	0.1	0.5	—	0.3
$C_3^=$	84.0	85.5	22.7	22.6
C_3	7.9	13.3	2.4	1.8
$C_4 + C_5$	8.0	0.7	3.0	3.0
C_6^+	<0.1	<0.1	71.9	72.3
	100.0	100.0	100.0	100.0
165°C⁺ distillate, % of liq. pdt.	—	—	56	—

[a] 204°C; 35–48 atm; 0.5 WHSV (on zeolite).

TABLE 3

Catalytic Lube Dewaxing[a] (Zeolite Sample C)

		Physical mixture with binder	Extrudate
Avg. catalyst temp., °C		344	344
Time on stream, days		0.8	0.8
Yields, wt%			
$C_1 + C_2$		—	<0.1
C_3		—	0.9
C_4		—	2.5
C_5		—	1.8
C_6—343°C		1.3	9.4
343°C⁺ Lube		98.7	85.1
Lube properties	Charge		
Gravity, °API	29.1	29.5	28.4
Specific gravity	0.8811	0.8789	0.8849
Pour point, °C	>46	>46	−7
Kinetic viscosity, cSt			
40°C	—	—	95.08
100°C	9.91	—	10.77
Viscosity index	—	—	96.30

[a] 28 atm (H_2); 1.6 LHSV (on zeolite).

tive, that is, the active sites are situated inside the zeolite pore system.

Methanol conversion to hydrocarbons. The catalytic conversion of methanol to hydrocarbons forms the basis of the Mobil MTG (methanol-to-gasoline) process (*6, 9, 10*). This reaction involves essentially the complete dehydration of methanol, with recombination of the resultant C_1 fragments to form a mixture of hydrocarbons with the average formula $[CH_2]$. Although the detailed mechanism of the reaction remains uncertain at present (*10*), it is known to be catalyzed by strong acids, particularly zeolites. Among the zeolites, ZSM-5 is the most effective yet discovered for the reaction. Sample B, as pure crystal and alumina extrudate, was tested for the methanol conversion reaction at 370°C, 1 atm, 1 LHSV, using the procedure of Chang and Silvestri (*6*). Results are summarized in Table 4. As seen, the reaction is also subject to binder effects, with a fourfold increase in conversion from 1.8 to 8.0% upon extrusion of the zeolite crystals with alumina.

Binder effect on ion-exchange capacity. The ion-exchange capacities of Samples A and B were measured by TPAD both before and after extruding with alumina. As indicated by the data in Table 5, the exchange capacities of both samples were significantly higher after extrusion. Further increase in exchange capacity resulted from steaming.

TABLE 4

Methanol Conversion to Hydrocarbons[a]
(Zeolite Sample B)

	Pure zeolite	Extrudate
Conversion, %	1.8	8.0
Hydrocarbons, wt%		
$C_1 + C_2$	16.9	17.0
$C_2^=$	1.3	15.2
C_3	6.1	1.8
$C_3^=$	11.9	19.7
$C_4 + C_4^=$	28.1	29.2
C_5^+	35.1	17.1
	100.0	100.0

[a] 370°C; 1 atm; 1 LHSV (on zeolite).

TABLE 5

Binder Effect on Ion-Exchange Capacity

Zeolite sample	Alumina binder	Steam treatment[a] (hr)	NH_4^+ capacity[b] (meq/g)
A	No	0	0.02
A	Yes	0	0.08
A	Yes	15	0.15
B	No	0	0.0013
B	Yes	0	0.06

[a] 760 Torr H_2O; 427°C.
[b] On zeolite.

SUMMARY AND CONCLUSIONS

The activation of high-silica ZSM-5 as a result of binding with alumina has been demonstrated using four different catalytic reactions: *n*-hexane cracking, propylene oligomerization, lube dewaxing, and methanol conversion to hydrocarbons. These reactions are all acid catalyzed. It follows therefore that new acid sites are created during extrusion with alumina. Consistent with this is the observed increase in exchange capacity as measured by TPAD. That these sites are truly intrazeolitic, and not associated with some new aluminosilicate phase formed at the grain boundaries, is attested through the further observation that the activated zeolite catalyzed lube dewaxing, a reaction known to depend critically on the shape-selectivity characteristics of the zeolite (*8*). These activation effects are observable over a broad range (for typical practical ranges of binder concentration see, for example, Ref. (*13*)) of Al_2O_3 binder concentration.

Experiments comparing the effects of wet vs dry binding indicate that the mode of Al transfer is through a soluble Al species rather than a solid–solid reaction. Framework substitution would then occur by reaction with SiOH groups, in a manner similar to the action of Al halides upon high-silica ZSM-5 as described in Part 1 of this study (*11*).

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