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Cumene Cracking Over Aluminum-Deficient Large-Port Mordenites

HARVEY S. BIERENBAUM, SUBHAVADH CHIRAMONGKOL,
AND ALVIN H. WEISS

Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

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Cumene cracking activities have been measured over a series of acid-leached, large-port hydrogen-exchanged mordenites ranging in alumina content (on anhydrous basis) from 11.2% (commercial H^{ex}-mordenite) to 0.1% Al_2O_3 at both differential and integral conversions. Although elemental and morphological analyses of the latter material have previously shown it to be of silicic acid composition with a mordenite crystal structure, sufficient Brönsted acid exchange sites remain to produce an active catalyst. Differential conversion results, which are considered more representative of intrinsic cracking activity than those at integral conversion, showed the 0.1% Al_2O_3 content mordenite to be less active, however, than 1.4, 1.9, and 11.2% alumina catalysts, a fact which is interpreted to mean that Brönsted acid sites are counted either by cracking activities or alumina content in the 0.1 to 1% Al_2O_3 region. At integral conversions, the initial cracking activity of the 0.1% Al_2O_3 catalyst approached that of H^{ex}-mordenite, a phenomenon attributed to a limitation on conversion imposed by the rate of mass transfer to the surface of the catalysts. However, in all cases, the 0.1% alumina mordenite had a much lower rate of activity decline than H^{ex}-mordenite and, after a short time on-stream at integral conversion levels, the low alumina material was the more active catalyst. Although the essential nature of the center of catalytic activity, i.e., the Brönsted acid site, did not change as a result of the drastic quantity of alumina removed, the lower density of acid sites in the lowest alumina catalyst reduced the rate of Brönsted catalyzed condensation to higher molecular weight species (capable of blocking micropores) relative to the rate of desorption of these compounds. Helping in this direction of lower fouling rate would be the enhancement of desorption of heavy products as a result of the acid treatment having opened the pore structure.

INTRODUCTION

Since the first International Conference on Molecular Sieves, mordenite, a silica-rich (Si/Al $\sim$ 6) zeolite, has increasingly become a subject of scientific investigations, as pointed out by Burbidge *et al.* (*3*). In general, initial activity for cracking is high but activity maintenance is very poor.

Several authors have studied the catalytic properties of acid-leached mordenites. Beecher *et al.* (*2*) and Voorhies *et al.* (*17*) investigated the hydrocracking of *n*-decane and decalin over 0.5% palladium impregnated mordenites with Si/Al ratios up to 46.5. Both studies showed the acid-leached mordenites had higher hydrocracking activities than the material with conventional Si/Al ratios. Topchieva *et al.* (*16*) studied cumene cracking in a pulsed microreactor over H^{ex}-mordenites acid leached to a maximum Si/Al ratio of 18. The data obtained (*16*), but not presented, implied results similar to those of (*2*) and (*17*), i.e., the lower alumina content materials had the higher catalytic activity. Eberly and Kimberlin (*5*) reported an increase in cumene cracking activity of H^{ex}-mordenite upon removal of alumina to a Si/Al ratio of 64. They also noted there was little difference in the rate of activity decline between the original and leached catalysts. On the other hand, Weller and Brauer (*18*) found *n*-hexane cracking activity went through a maximum for a series of mordenites dealuminated to Si/Al ratios only as high as about 9. Piguzova *et al.* (*13*) found similar maxima in *n*-decane cracking activity at a Si/Al ratio of about 9. They also found isomerization activity for *n*-pentane and *o*-xylene decreased in the Si/Al range of 9.45 to 14.3.

Considerable work has been done on cumene cracking over both amorphous silica–alumina (*10–12*) and molecular sieve zeolites (*6, 14, 15*). In regard to cumene product distribution, Murakami *et al.* (*10*) and Pansing and Malloy (*11*) found isomers of diisopropylbenzene in addition to benzene and propylene after cracking over silica–alumina gel. Richardson (*15*) found that besides benzene and propylene, toluene, ethyl benzene, styrene, and alpha-methylstyrene were formed during cumene cracking over various ion-exchanged faujasite catalysts. Although cumene cracking over H^{ex}-mordenite has been studied by Topchieva *et al.* (*16*), Eberly and Kimberlin (*5*), and Keough (*7*), all of the products were not shown.

The present work is for the purpose of extending the background in this area to Si/Al ratios as high as 600 (practically pure hydroxylated silica in a mordenite structure) and to define minor as well as major product activities and selectivities. Details on synthesis and the elemental and morphological properties of the catalysts we have investigated can be obtained from Chang (*4*). Preliminary studies on these catalysts by Kranich *et al.* (*8*) list physical and chemical properties, adsorption and diffusion characteristics, butene isomerization, and our differential conversion cumene cracking activities. Integral studies on butenes isomerization showed the same phenomenon of passing through an activity maximum as reported by Weller and Brauer (*18*).

EXPERIMENTAL METHODS

Materials. Prepurified grades of compressed air (Linde, 99.99%), helium (Airco, 99.996%), and hydrogen (Airco, 99.5%) were used. Prior to use, hydrogen was passed over a palladium Deoxo catalyst to remove trace oxygen. Water and carbon dioxide were removed from all gases by passage over Drierite and then Ascarite.

Cumene from two sources was used. After purification, analyses were Eastman, 99.8%, and Phillips Petroleum Co. Research Grade, 99.94%.

The Eastman material was treated to remove polar materials by refluxing with calcium hydride and distilling. Impurities remaining were α-methylstyrene, ethylbenzene, and substances corresponding to three unidentified chromatographic peaks. Purified Eastman cumene was used for most of the differential conversion studies.

Phillips' cumene was purified according to the chromatographic method described by Maatman *et al.* (*9*). This cumene was sealed in bottles with Teflon lined septa and used in less than 1 week. α-Methyl styrene was the only impurity found. The purified Phillips' cumene was used for a portion of the differential conversion study and for all of the integral conversion work.

Catalyst cracking activity decline was sensitive to cumene quality. Cumene purified by the Maatman procedure, but which was exposed to air prior to use, resulted in catalyst activity falling from initially 33% to 2% conversion after 17 g of cumene/g of H^{ex}-mordenite catalyst had been processed. Similar operation with purified cumene protected from air caused an activity decline from 33 to 30%.

Equipment. The reactor used was a $\frac{1}{4}$ × 0.010-in. wall × 7.75-in. long stainless steel tube with a $\frac{1}{8}$-in. stainless steel thermowell in the center of the reactor tube. The reactor was inserted in a 4 × 2 × 0.625-in. aluminum bronze block and heated by two 150-W cartridge heaters 0.375-in. o.d.

The block and reactor tube were located in the center of a 6 × 4 × 2-in. firebrick (K38) which was further wrapped with 5 layers of aluminum foil. The entire reaction unit was placed in the oven of a Perkin-Elmer 880 FID Gas Chromatograph, as shown in Fig. 1.

The temperature of the block was maintained to a precision of ±3°F. Isothermal

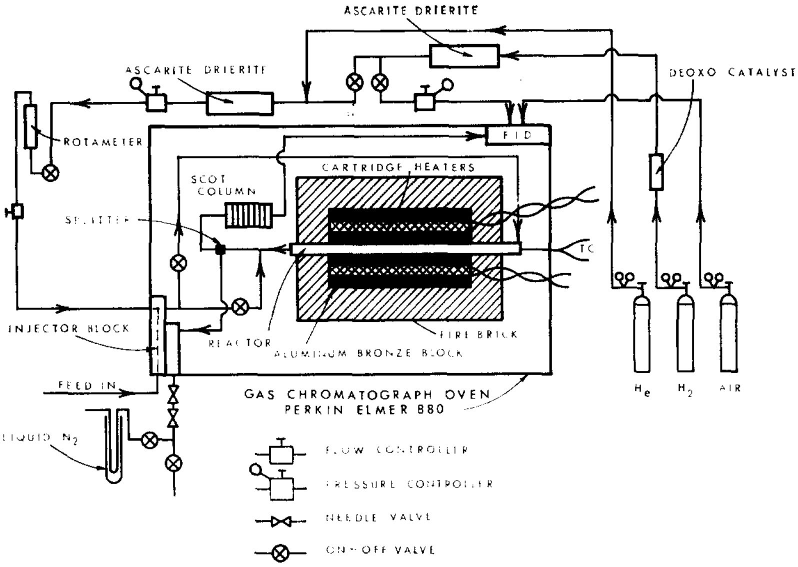


FIG. 1. Microreactor unit.

lengths of maximum reaction temperature were found to be 1.5 to 2.0 in. in length and independent of the flow rate of carrier gas. Total pressure ranged from 2.5–4.2 psig.

Analytical. Analyses of reaction products were obtained by passing a part of the reactor effluent through a 50 ft × $\frac{1}{32}$ in. × 0.02 in. Perkin-Elmer SCOT column of stationary phase *m*-bis(*m*-phenoxy-phenoxy)-benzene and Apiezon L. Since the reactor was in series with the column, the reaction gas was the carrier gas being used—either H_2 or He. The column was programmed at 4°C/min from an initial temperature of 80 to 175°C. Trace product styrene was not adequately resolved from the cumene peak well enough to permit quantitative or qualitative observation. Xylenes were invariably present in such minor amounts that their production could not be meaningfully quantitated.

Products more volatile than benzene were identified by using continuous, rather than pulsed, operation. Product gas emerging in steady flow from the splitter vent shown in Fig. 1 was collected in a Hamilton, 1 ml, gas-tight, flow-through syringe. The trapped gas was injected into a Varian Aerograph Series 1200 FID chromatograph equipped with an $\frac{1}{8}$ in. × 10 ft column packed with "Durapak" *n*-octane/Porasil C. Resolution of methane, propane, propylene, *n*-butane, and butenes, but not ethane, from ethylene was obtained. The cumene was pumped by a syringe pump at the rate of 0.22 liquid ml/h into the septum of the Perkin-Elmer chromatograph while He or H_2 rate was 280 STD ml/min over 22.5 mg of 0.1% Al_2O_3 catalyst at a reaction temperature of 680°F.

Catalyst preparation. Catalysts for differential cumene conversion studies were made by manually shaking 0.04 g of catalyst powder which had been dried for 2 hr at 200°C with similarly dried 20 to 40 mesh quartz sand in a 1-oz vial at a 1000:1 weight ratio. A portion of this mixture (0.4 g containing 4×10^{-4} g of active catalyst) was placed in the reactor isothermal zone with quartz sand packed in the remainder of the reactor.

Integral cumene conversion studies (10–40%) were made using 0.0225 g of dried catalyst powder which was weighed directly into the reactor and sandwiched between plugs of Pyrex wool which were in turn held in place by quartz sand.

Reactor operation. Catalysts used for both differential and integral conversion experiments were pretreated for 15.5 hr at 1000°F and with a carrier gas flow rate of 40 ml/min. At the end of the pretreatment period the temperature was lowered to 680°F and the carrier gas flow rate was raised to 275 to 285 ml/min over the catalyst.

Small catalyst loadings (0.4 mg) were aged by serial injections of 5.19 ± 0.25-μl quantities of cumene into the carrier gas stream from a spring loaded Hamilton CR 700-20 liquid injection syringe until the appropriate cumulative amount of cumene was passed over the catalyst. Liquid product analyses were made for each injection.

Large catalyst loadings (22.5 mg) were aged in a continuous feed mode by pumping cumene from the syringe pump at a rate of 0.22 ml/hr. Pumping was periodically interrupted and the catalyst activity was measured with 5-μl pulses of cumene.

RESULTS AND DISCUSSION

Activity. Figure 2, an expanded initial activity plot of conversion to the only major liquid product—benzene—shows that at integral conversion near 0.4, cracking activities of H^{ex}-mordenite, 1.4% and 0.1% Al_2O_3 catalysts did not diminish greatly at 680°F in the course of catalyst operation to 2.5 g of cumene/g of catalyst. The catalysts were pretreated in He; and the switching of carrier gas from He to H_2 and back to He had no significant effect on cracking activity.

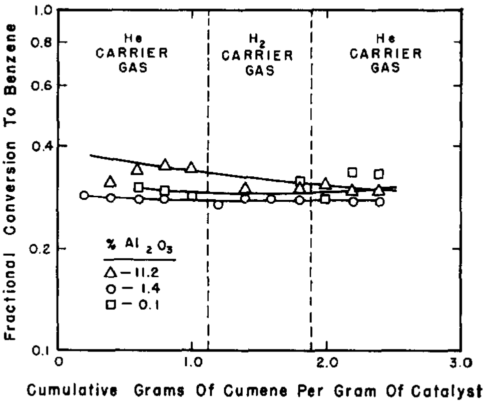


FIG. 2. Effect of carrier gas on cumene conversion to benzene for catalysts pretreated in helium. Similar initial activities at integral conversion levels at 680°F.

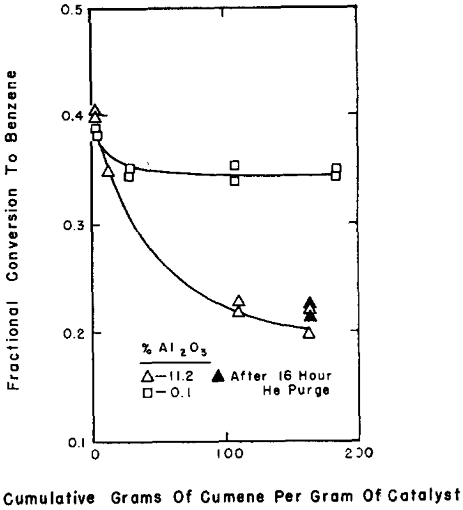


Fig. 3. Effect of aging on cumene conversion to benzene at integral conversion levels of 680°F.

It was sometimes, but not consistently, observed that measurable adsorption of the first pulse to a catalyst was had. Subsequent adsorption was within the accuracy of chromatographic material balances (±2.7%). Consequently, it is felt that the initial activities of the catalysts are best quantitatively estimated by extrapolation of fractional conversion to zero time using aging curves of longer duration, such as Fig. 3. These values are 0.385 and 0.410 fractional conversion, for 5-μl cumene pulses at 680°F over 22.5 mg quantities of 0.1% and 11.2% Al_2O_3, respectively. They are compared in Table 1 as a function of catalyst quantity to our earlier results (*8*) with 0.4-mg quantities which showed that at *differential*, rather than *integral*, conversions, the initial cracking activity was significantly higher for H^{ex}-mordenite, 1.9%; and 1.4% Al_2O_3, than it was for the 0.1% Al_2O_3 catalyst.

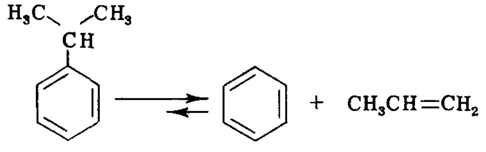
The results obtained with 22.5 mg of

TABLE 1

INITIAL CUMENE CRACKING ACTIVITY 5 μl AT 680°F, He CARRIER

Catalyst quantity (mg)	Initial fractional conversion	
	0.1% Al_2O_3	11.2% Al_2O_3
0.4	0.002	0.018
22.5	0.385	0.410
50	0.578	0.625
125	0.710	0.790

catalyst were suspiciously near the equilibrium cumene conversion of 0.408 calculated for 680°F, 17.9 psia, and plug cumene flow. Experiments were then made with larger catalyst quantities, 50 and 125 mg, and the conversions obtained are also listed on Table 1. A conversion as high as almost twice equilibrium—0.790—was obtained. This indicates that chromatographing was significant enough in the reactor that the reverse reaction in the 0.4-conversion range could be neglected and that the activity data obtained at that conversion level are a reasonable approximation of the forward reaction mainly



(1)

The similarity of the integral conversions (in the 0.4 conversion range, at least) for 0.1 and 11.2% Al_2O_3 can then be interpreted as being the result of transport limitations to these highly active catalysts, rather than equilibrium limitations.

Conducting a 12 hr, 1000°F heat treatment on an H^{ex}-mordenite catalyst pretreated in H_2 and aged to a level of 55 g/g restored activity to 50% of the initial level. This experiment suggests that both reversibly adsorbed higher molecular weight species and irreversible fouling products were on the catalyst. The reversibly adsorbed species are apparently not removed by purging with He at reaction temperature of 680°F for 16 hr. Figure 3 shows no significant conversion change can be noted.

Aging at integral conversion levels on H_2 pretreated mordenite confirmed our previously published differential conversion results (*8*) that H^{ex}-mordenite activity may still have been declining slightly at 155 g/g as shown on Fig. 3. H_2 pretreated H^{ex}-mordenite and 0.1% Al_2O_3 show similar initial conversion activity, but disparate activity after aging. In both differential and integral studies, activity decline rates of 0.1% Al_2O_3 catalysts are less marked than those of 1.4 and 1.9% Al_2O_3 and H^{ex}-mordenite.

It is important to realize that there is no change in cracking mechanism when the carrier gas is switched from helium to hydrogen. Table 2 lists data which show that propylene is the major product in cumene cracking at the 680°F initial activity condition studied with either H_2 or He carrier gas. The consequence is that benzene yield is a measure of Brönsted acidity and is independent of hydrogen presence. This would not be the case if free radical hydrodealkylation processes were also significant (rather than trace) at our conditions.

Figure 4 is an activity plot of fractional conversion to benzene versus percentage Al_2O_3 in the catalyst plotted at a catalyst aging of 75 g of cumene/g of catalyst. The integral conversion data show that increasing alumina content results in an apparent slight decrease in cracking activity. In contrast to this, the differential conversion data, also plotted at 75 g of cumene/g of catalyst, indicate that cracking activity increases from the 0.001 fractional conversion level for 0.1% Al_2O_3 catalyst to approximately 0.01 fractional conversion for catalysts containing 1.4, 1.9, and 11.2%

TABLE 2
CUMENE CRACKING AT 680°F OVER 0.1% Al_2O_3

	Gas analysis (%)	
	Cracking in He	Cracking in H_2
CH_4	0.00	1.18
C_2's	1.09	1.04
C_3H_6	91.0	93.9
C_3H_8	5.48	2.52
C_4's	2.81	1.39

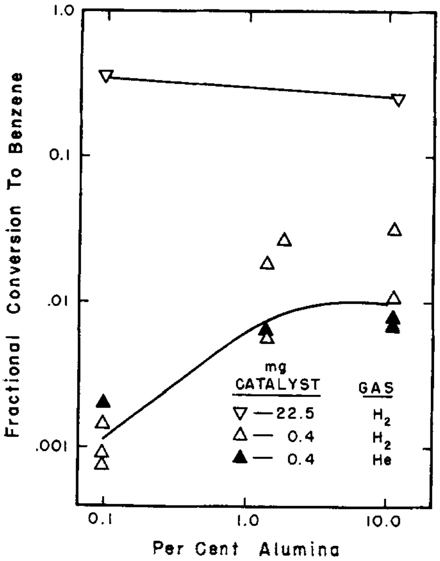


FIG. 4. Effect of Al_2O_3 content on catalytic activity at integral and differential cumene conversion levels at 680°F and 75 g of cumene/g of catalyst.

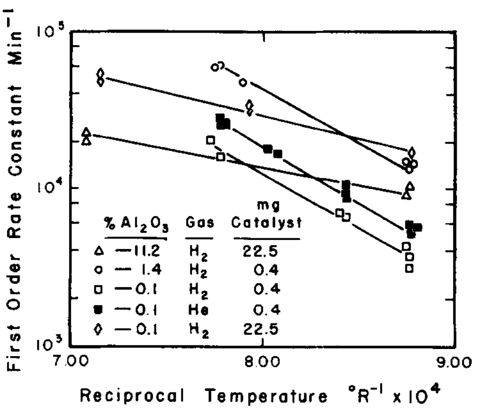


FIG. 5. Temperature dependence of first order rate constant for cumene dealkylation to benzene at integral and differential conversion levels.

Al_2O_3. We did not study catalysts in this work between 1.9 and 11.2% Al_2O_3, the range in which other authors observed activity increases or maxima. Our results do not preclude activity enhancement in that region.

It should be noted that every point on Fig. 4 represents a different charge of catalyst. In the case of the 0.4-mg catalyst loadings, this small catalyst charge resulted in an uncertainty of mass as great as ±40% with a corresponding uncertainty for comparison of different individual catalyst charges. However, the very small charge allowed study of intrinsic activity at differential conversion levels while operating at a temperature of practical interest which was high enough to avoid desorption problems.

Figure 5 is an Arrhenius plot of the first order rate constant at steady state activity. The differential conversion studies are for catalysts containing 0.1 and 1.42% Al_2O_3 since the H^{ex}-mordenite did not reach a steady differential conversion activity after as much as 150 g of cumene/g of catalyst. Each line represents a separate catalyst loading. Therefore, because of the possible charging inaccuracy, no quantitative conclusion comparing absolute catalyst activity should be drawn on the basis of these few curves which are presented solely for illustrating the temperature dependence of the cracking activity. Catalysts exhibit the identical activation energy of 17 kcal/mole irrespective of whether operation is in He or H_2 and also independent of alumina content.

At high conversions, activation energies are 7.2 kcal/mole, both for 11.2 and 0.1% alumina, aged for more than 150 g/g to almost steady state activity. The higher activation energy of the differential study can be considered more representative of the intrinsic activation energy since it compares well with the 20.6 kcal/mole obtained by Pansing and Malloy (*11*) for cumene cracking on silica–alumina catalysts and not too unfavorably with values ranging from 20 to 34 kcal/mole reported by other authors (*6*, *15*, *16*) for a variety of faujasite catalysts. It should be pointed out, however, that use of the phrase "intrinsic activation energy" does not preclude the possibility of unavoidable pore diffusion limitations since Thiele moduli have been shown to be high for mordenite catalysts in a similar reaction, such as hydrocracking (*2*).

Catalysts on which we obtained an integral conversion level activation energy of 7.2 kcal/mole showed little, if any, initial cracking activity difference (e.g., Fig. 4) between 0.1 and 11.2% Al_2O_3 materials. This lack of initial distinguishability, as well as

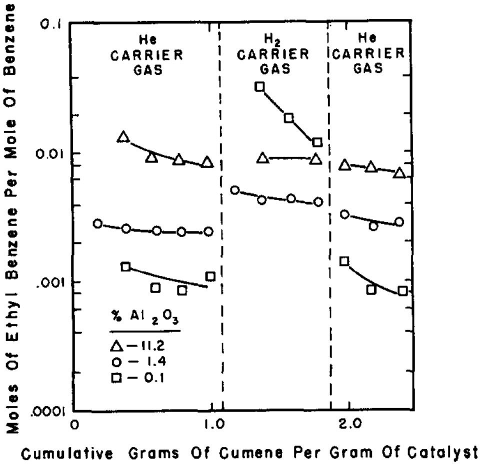


FIG. 6. Effect of carrier gas on selectivity for cumene conversion to ethylbenzene at 680°F.

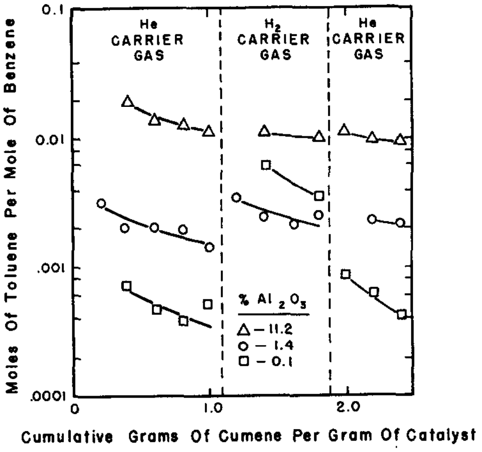


FIG. 7. Effect of carrier gas on selectivity for cumene conversion to toluene at 680°F.

the low value of activation energy, also supports our suggestion that our integral conversion data are strongly influenced by the rate of transfer of cumene from the gas phase to the surface of the catalyst. Eberly and Kimberlin (*5*) found an activation energy of 11 kcal/mole for 2.46 and 12.0% Al_2O_3 H^{ex}-mordenites at 400–550°F, where the magnitude of reaction rates may not have reached a transport controlling level.

Selectivity. The integral conversion studies, while not useful for intrinsic activity determination, did permit analyses of trace products and the determination of selectivity phenomena.

Initial ethylbenzene selectivity* is plotted as a function of catalyst aging in Fig. 6. A similar plot for toluene is provided in Fig. 7. For both of these species, selectivity increases with alumina content in He, but a reversal occurs in H_2. The sensitivity of the production of these compounds to the presence or absence of H_2 is an indication that their formation proceeds by a free radical mechanism, as suggested by Richardson (*15*).

On the other hand, initial diisopropylbenzene selectivity, as shown in Fig. 8, is effectively independent of operation in either He or H_2. Figure 9 shows the same behavior for *n*-propylbenzene. These would then be considered Brönsted acid catalyzed reactions, similar to the reaction for benzene production.

Figure 10 is a plot showing the effect of aging in H_2 on selectivity to ethylbenzene, toluene, *n*-propylbenzene, and diisopropylbenzenes. It is shown that while the selectivities to the first three trace products are initially higher for H^{ex}-mordenite, they fall to levels lower than those for the 0.1% alumina content material, the fall being particularly rapid for ethylbenzene and toluene. The fact that the slope of the selectivity curves for toluene and ethyl-

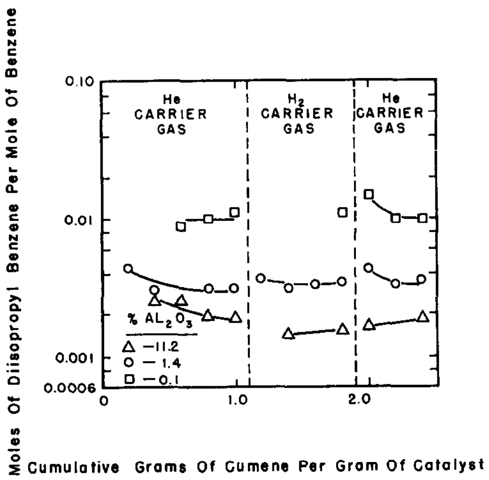


FIG. 8. Effect of carrier gas on selectivity for cumene conversion to diisopropylbenzene at 680°F.

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* Selectivity is defined as moles of trace product per mole of benzene product.

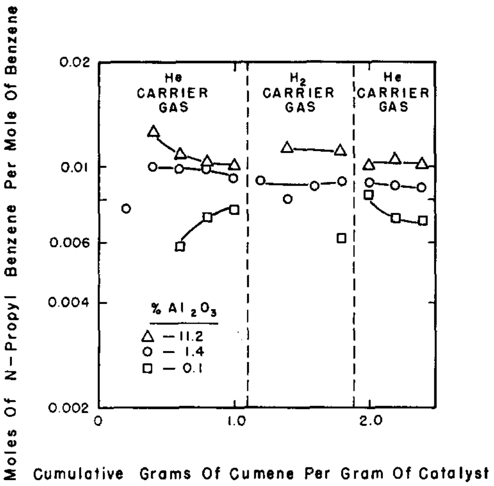

FIG. 9. Effect of carrier gas on selectivity for cumene conversion to *n*-propylbenzene at 680°F.

benzene on H^{ex}-mordenite are so different from zero may be taken as further proof that their formation is by a mechanism different than that for benzene production. The rate of decline of Brönsted activity has been shown by Richardson (*15*) to be different from that of free radical activity on the same faujasite catalyst. The practically zero slopes exhibited by the toluene and ethylbenzene selectivity curves on 0.1% Al_2O_3 mordenite may be taken as evidence of overall catalyst stability, since production of benzene is relatively constant. The effect of aging on selectivity both for disproportionation to diisopropyl benzenes and for isomerization to *n*-propylbenzene is small. The relatively low slope of these selectivity curves obtained for H^{ex}-mordenite is, in effect, the Brönsted catalyzed nature of isomerization, disproportionation, and cracking, since selectivity is defined in terms of benzene production.

It should also be noted that the absolute amount of diisopropylbenzenes was found to be much less over H^{ex}-mordenites than 0.1% Al_2O_3. In view of the fact that three much heavier molecular weight species, as yet unidentified were produced only by H^{ex}-mordenite, catalyst activity decline of the H^{ex}-mordenite is closely related to the formation of Brönsted catalyzed higher molecular weight disproportionation and/or condensation products.

CONCLUSIONS

Activity. The intrinsic activity of H^{ex}-mordenite is greater than that for 0.1% Al_2O_3 mordenite. This can be explained by the vastly greater number of acid sites in the H^{ex}-mordenite which are directly related to alumina content. However, mass transfer limitations at integral conversion levels, as well as the low activity decline rate of the

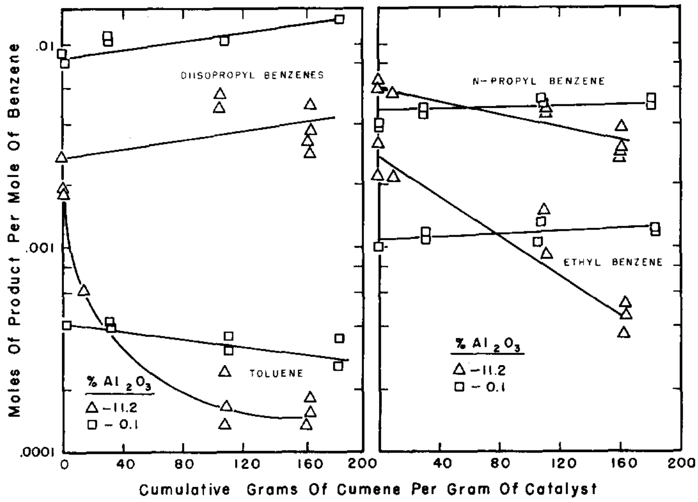

FIG. 10. Effect of aging on selectivity for cumene conversion to ethylbenzene, toluene, *n*-propyl-, and diisopropylbenzenes at 680°F in hydrogen.

low alumina material, have combined to give it the appearance of similar activity to that of H^{ex}-mordenite before aging and greater activity after aging. Activity enhancement of maxima in the intermediate (2.46 to 12%) alumina content range found by others can be explained by a greatly decreased resistance for diffusion created during the dealumination process, either by increasing the effective micropore diameter of the mordenite or removal of amorphous material which is thought to block some of the mordenite micropores (*5*). This would be analogous to the behavior noted by Barrer and Coughlan (*1*), who found that nonpolar krypton adsorbed on acid-leached clinoptilolite, but did not on the untreated material. The pore structure may have been opened in the 0.1% Al_2O_3 mordenite, but there are just too few acid sites remaining to produce as active a catalyst.

Mechanism. Although there are significant differences in trace product selectivities between the 0.1% Al_2O_3 catalyst and H^{ex}-mordenite, the major reaction of cumene at the conditions we have studied is cracking to produce benzene and propylene. It is concluded that a Brönsted acid catalyzed reaction is the primary method of dealkylation in both H^{ex}-mordenite and mordenites dealuminated to materials containing two orders of magnitude less Al_2O_3 than the starting compound.

Trace products ethylbenzene and toluene appear to be created by free radical induced reactions, while the formation of *n*-propylbenzene and diisopropylbenzenes is brought about by a mechanism similar to that for benzene production. It may be possible that the severe acid and thermal treatments used in synthesis have either added or exposed trace metal compound impurities (*8*), which catalyze free radical hydrodealkylations that produce toluene and ethylbenzene from cumene.

Activity decline. The low alumina catalyst displays a surprising stability of catalytic activity, even at the same initial integral reaction rate as H^{ex}-mordenite. We believe that this stability is due to the lower density of acid sites in the low alumina catalyst, which reduces the rate of condensation to high molecular weight species relative to the rate of desorption of these compounds. The larger pore structure of the low-alumina catalyst would then be synergistic in decreasing fouling rate, as condensation products release from the microstructure would be enhanced.

ACKNOWLEDGMENTS

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