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Activation of ZSM-5 Catalysts

The protonic form of the zeolite ZSM-5 has been shown to be an active catalyst for the conversion of a wide range of compounds into a product which contains a substantial proportion of aromatic components (*1*, *2*). Of the possible reactants, methanol has been studied in the greatest detail, but the other alcohols propanol, t-butanol, and 1-heptanol have also been successfully converted, as have hydrocarbon reactants such as propylene and the hexanes (*3*).

Nevertheless, previous work has also shown (*3*) that, using the protonic form of ZSM-5 prepared by thermal decomposition of the ammonium-exchange form, the activity for the conversion of ethanol or of ethylene to aromatic-rich hydrocarbon product was generally poor. Passage of ethanol over this catalyst at a typical reaction temperature of 673 K usually led to the generation of ethylene without any higher hydrocarbon products, although occasional batches of this catalyst resulted in the formation of substantial amounts of aromatic products. Likewise, passage of ethylene over the catalyst at a typical reaction temperature of 673 K usually gave a very low conversion to higher hydrocarbon products with the complete absence of aromatic products, although occasional batches of this catalyst resulted in the formation of substantial amounts of aromatic hydrocarbon products.

The behavior described above is to be compared to that reported by Derouane *et al.* (*4*) who reported that a ZSM-5 catalyst which had been converted into the protonated form by treatment with aqueous hydrochloric acid at 353 K was active at 673 K for the conversion of ethanol to aromatic-rich hydrocarbon product.

In view of these data it seemed probable that ZSM-5 catalysts, although being apparently identical when judged in terms of X-ray diffraction data (cf. (*3*, *5*)), could show substantial differences in activity for the conversion of ethanol or ethylene, depending on the method used to generate the protonated form.

The analytical data given by the two groups of workers (*3*, *4*) show that although the aluminum content of the initially prepared ZSM-5 samples was almost identical (3.14 and 3.17 wt%) for the two preparations, the hydrochloric acid treatment used by Derouane *et al.* (*4*) for protonation had removed nearly half the aluminum initially present.

From this comparison it is therefore not possible to say if the different activity of these two catalysts toward the conversion of ethanol or ethylene is due primarily to the different aluminum contents, or whether the two methods of protonation generated different actidity functions in the zeolite irrespective of possible differences in aluminum content.

Accordingly, we have examined the activity toward ethanol or ethylene conversion of ZSM-5 samples which have been subjected to various protonation procedures.

The experimental details were generally similar to those previously described (*3*), and this reference also gives details of the initial ZSM-5 preparation.

CATALYST PREPARATION

(*a*) *Protonation via ammonium exchange.* This sample, which is designated ZSM-5-H(1), was prepared by the method previously described (*3*). The ZSM-5 as initially prepared was repeatedly ex-

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changed with 1 *M* NH_4NO_3 solution at room temperature, and the ZSM-5-NH_4 was washed with water at room temperature and then heated in air at 770 K. Analysis gave: Na, 0.38 ± 0.01 wt%; Al, 3.14 ± 0.01 wt%; Cl, 0.1 ± 0.1 wt%.

(*b*) *Treatment with aqueous hydrochloric acid.* This sample, which is designated ZSM-5-H(2), was prepared by treating ZSM-5-H(1) with 0.6 *M* aqueous HCl at room temperature for 24 hr (38.5 cm^3 of HCl/g of zeolite). At the end of this treatment period the zeolite was recovered and dried overnight at 500 K. Analysis gave: Na, 0.14 ± 0.01 wt%; Al, 3.14 ± 0.01 wt%; Cl, 0.2 ± 0.1 wt%.

(*c*) *Treatment with aqueous nitric acid.* This sample, which is designated ZSM-5-H(3), was prepared by treating ZSM-5-H(1) with 0.6 *M* aqueous HNO_3 in a manner similar to that described for ZSM-5-H(2).

(*d*) *Treatment with aqueous hydrofluoric acid.* This sample, which is designated ZSM-5-H(4), was prepared by treating ZSM-5-H(1) with aqueous hydrofluoric acid in the manner described for ZSM-5-H(2).

(*e*) *Treatment with gaseous HCl under reaction conditions.* This treatment was carried out *in situ* in the flow reactor which was subsequently used to study reactant conversions. A sample of ZSM-5-H(1) was treated with a feed which was prepared by mixing anhydrous ethanol and aqueous 3 *M* HCl in such proportions that the feed contained 2 g of hydrogen chloride/100 g of feed. This feed was passed (in vaporized form) over the catalyst sample at 673 K for 4 hr at a total reactor pressure of 1 atm. The product from this treatment is designated ZSM-5-H(5). Analysis gave: Cl, 0.2 ± 0.1 wt%.

(*f*) *Treatment with 1,2-dichloroethane under reaction conditions.* This treatment was carried out in a manner similar to that used for ZSM-5-H(4), except that the feed to the zeolite in the reactor consisted of a mixture containing 96 wt% ethanol and 4 wt% 1,2-dichloroethane. The product from this treatment is designated ZSM-5-H(6).

REACTION OF ETHANOL AND ETHYLENE

In all cases the reactions were studied using a small stainless-steel microreactor which contained 0.1 g of catalyst. The feed was passed to the reactor via a preheater coil, and the reaction temperature in all cases was 673 K. Ethanol (anhydrous, AR grade) feed was supplied to the microreactor at a rate of 0.7 g hr^{-1} without the addition of a feed diluent. Ethylene (Phillips research grade) feed was supplied to the microreactor as a mixture containing 30 mole% ethylene and 70 mole% hydrogen or nitrogen at a total feed rate of 8.5 cm^3 min^{-1}. Hydrogen and nitrogen behaved identically as diluents. In all cases the total reactor pressure was 1 atm.

The proportions of the main classes of reaction products are summarized in Table 1 for ethanol reactant and in Table 2 for ethylene reactant after reaction time of 60 min.

As reported previously (*3*), the usual activity of ZSM-5-H(1) for ethanol was dominantly conversion to ethylene, although occasional batches of this catalyst resulted in the formation of substantial amounts of aromatic product. The ranges of product compositions resulting from this behavior are indicated in Table 1. Parallel to this, the usual activity of ZSM-5-H(1) for the conversion of ethylene was for relatively low overall conversion with dominant products in the C_3–C_5 range: an example of this behavior is given in Table 2.

In contrast to the activity of ZSM-5-H(1), all of the catalysts ZSM-5-H(2)–ZSM-5-H(6) *consistently* gave aromatic hydrocarbons as the dominant products from ethanol: the data in Table 1 show that in these cases aromatics made up not less than about 80 wt% of the total products. Although there are some minor variations, these aromatic products from ZSM-5-H(2)–ZSM-5-H(6) are all of roughly comparable composition except in the case of ZSM-5-H(4) where there was a large amount of C_{10+} aromatic.

TABLE 1

Reaction Products from Ethanol

Catalyst[c]	Reaction products[a,b] (wt%)							Conversion (mole%)
	C_1,[e] C_2	C_3–C_5	B	T	X	TMB	C_{10+}	
ZSM-5-H(1)[d]	50–100	0–25	← 0–25 total aromatics →					>95
ZSM-5-H(2)	5	4	0.5	9	36	40	5	>95
ZSM-5-H(3)	4	13	2	12	24	34	11	>95
ZSM-5-H(4)[f]	1	4	0	0	3	0	92	>95
ZSM-5-H(5)[f]	3	15	1	7	22	42	10	>95
ZSM-5-H(6)	1	10	1	10	27	46	5	>95

[a] C_1–C_5, aliphatic hydrocarbons; B, benzene; T, toluene; X, xylenes and ethylbenzene; TMB, trimethylbenzenes; C_{10+} aromatics of carbon number ≥10.

[b] Product distributions after about 60-min reaction starting with fresh catalyst. Reaction temperature 673 K.

[c] Catalyst identity, see text.

[d] Usual behavior; occasional samples gave product distributions similar to ZSM-5-H(2).

[e] Mainly ethylene.

[f] Small amounts (≤2%) of C_6 and C_7 aliphatics also produced.

With ethylene reactant, in contrast to the behavior of ZSM-5-H(1), the catalyst ZSM-5-H(2) consistently gave high overall conversion with most of the product being aromatic; an example is given in Table 2. Similar behavior to that of ZSM-5-H(2) was observed with ZSM-5-H(5) and ZSM-5-H(6).

CATALYST LIFETIME AND REGENERATION

Although, for comparative purposes, the data in Tables 1 and 2 are given for an on-stream time of 60 min, it was observed that the catalyst activity varied with on-stream time. With both ethanol and ethylene reactants on ZSM-5-H(2)–ZSM-5-H(6), the overall conversions remained high (≥95 mole%) for on-stream times up to about 4 hr at 673 K (Table 3); however, the nature of the aromatic products changed. In all cases as the on-stream time increased there was a trend for trimethylbenzenes (TMB) and C_{10+} aromatics to increase relative to benzene (B), toluene (T), and xylenes and ethylbenzene (X). Thus, for comparison with the data in Table 1, reaction of ethanol over ZSM-5-H(2) at 673 K for 2 hr gave an aromatic product of which about 80 wt% was TMB plus C_{10+}. This behavior is markedly different from that of methanol: in this case it was observed that reaction for 3 hr over ZSM-5-H(2) at 673 K gave aromatic products that were only about 30 wt% TMB plus C_{10+}.

TABLE 2

Reaction Products from Ethylene

Catalyst[c]	Reaction products[a,b] (wt%)						Conversion (mole%)
	C_3–C_5	B	T	X	TMB	C_{10+}	
ZSM-5-H(1)	68	4	7	11	4	7	28
ZSM-5-H(2)	10	1	32	45	6	6	97

[a] C_3–C_5 nonaromatic hydrocarbons; B, benzene; T, toluene; X, xylenes and ethylbenzene; TMB, trimethylbenzenes; C_{10+} aromatics of carbon number ≤10.

[b] Product distributions after about 60-min reaction starting with fresh catalyst. Reaction temperature 673 K.

[c] Catalyst identity, see text.

There is a parallel between the relative propensities of ethanol and methanol for the generation of TMB and C_{10+} aromatics and the rapidity of catalyst deactivation. In the case of ethanol (and ethylene), reaction times in excess of about 5 hr at 673 K always led to falling overall conversions. On the other hand, the reaction of methanol under these conditions resulted in only extremely slow catalyst deactivation, the methanol conversion remaining close to 100 wt% for many hours (several tens of hours).

TABLE 3

Reaction Products at Long Reaction Times[c]

Catalyst[b]/reactant	Reaction products[a] (wt%)							On-stream time (min)
	C_1, C_2	C_3–C_5	B	T	X	TMB	C_{10+}	
ZSM-5-H(2)/C_2H_5OH	1	8	0	7	29	50	5	260
ZSM-5-H(6)/C_2H_5OH	2	4	0	2	17	56	19	263
ZSM-5-H(2)/C_2H_4	—	11	0	5	25	57	2	285

[a] C_1–C_5, aliphatic hydrocarbons; B, benzene; T, toluene; X, xylenes and ethylbenzene; TMB, trimethylbenzenes; C_{10+}, aromatics of carbon number ≥ 10.

[b] Catalyst identity, see text.

[c] Reaction temperature 673 K.

Because of the onset of catalyst deactivation, in the ethanol reaction the runs were always terminated after not more than 5 hr on stream, followed by catalyst regeneration. Catalyst regeneration was effected by treatment in a stream of oxygen for 16 hr at 673 K. In all cases, this regeneration restored the catalyst to approximately its initial activity (with respect to conversion and product distribution), and it was found that at least four use/regeneration cycles could be carried out without significant change in catalyst performance.

Some evidence for the nature of this catalyst deactivation was obtained by comparing the sorption of *n*-hexane and of toluene on samples of fresh, deactivated, and regenerated catalyst. Sorption measurements were made at 293 K, at a relative pressure $p/p_0 = 0.5$, and after an equilibration period of 10 min, after which time the sorption was approximately constant. Prior to sorption measurement the samples were outgassed in vacuum at 620 K for 120 min. The data are given in Table 4. It is evident that catalyst deactivation was accompanied by a substantial reduction in sorptive capacity of the zeolite, but this capacity was restored by suitable regenerative treatment in oxygen.

DISCUSSION

From the above results we may summarize the following conclusions.

Treatment of ZSM-5-H(1) with dilute aqueous mineral acid (HCl, HF, or HNO_3) generates catalysts which have reproducible high activity for the conversion of ethanol or ethylene to aromatics.

The enhancement referred to above can be achieved without altering the Si/Al ratio of the ZSM-5. However, if more severe treatment with mineral acid is used (e.g. (*4*)) some aluminum may be removed, but the resultant catalyst still possesses enhanced activity for ethanol or ethylene conversion (at least judged in terms of *initial* activity).

Treatment with aqueous mineral acid (e.g., ZSM-5-H(2)) results in a protonated product with a lower sodium content than that produced via ammonium exchange.

TABLE 4

Sorption Data

Catalyst[b]	Treatment	Sorption[a] (mmole g^{-1})	
		n-hexane	Toluene
(A) ZSM-5-H(1)	fresh sample	1.23[c]	1.07[c]
(B) ZSM-5-H(6)	deactivated after 360 min on stream with ethanol reaction at 673 K	0.30	0.23
(C) ZSM-5-H(6)	sample (B) after regeneration, 30 min in O_2 at 773 K, 67 kPa	0.64	—
(D) ZSM-5-H(6)	sample (C) after further regeneration, 60 min in O_2 at 773 K, 67 kPa.	1.11	0.99

[a] Sorption data obtained after equilibration for 10 min under conditions indicated.

[b] Catalyst identity, see text.

[c] Values taken from Ref. (*3*).

This reduced sodium content may be associated with the enhanced catalytic activity. by the creation of more strongly acidic sites.

The enhanced activity does not depend upon the addition of F or Cl to the catalyst, since treatment with HNO_3 is effective and, for those samples treated with HCl, analysis revealed no significant increase in the Cl content.

An enhancement similar to that obtained by treatment of ZSM-5-H(1) with aqueous mineral acid may be achieved by treatment at 673 K with a feed stream containing ethanol mixed with HCl or 1,2-dichloroethane. In both cases we consider that the activating agent is gaseous HCl. In the case of a feed consisting of ethanol plus HCl, although reaction to form ethyl chloride is possible, the equilibrium constant at 673 K for the decomposition of ethyl chloride to HCl and ethylene is 79 atm. In the case of the feed containing ethanol and 1,2-dichloroethane, we note that at 673 K the equilibrium constant for the decomposition of 1,2-dichloroethane to HCl and vinyl chloride is 121 atm. In both cases HCl was detected in the reactor effluent.

The enhancements effected by the treatments summarized above are permanent in the sense that they survive regeneration of the catalysts in oxygen at 673 K.

Higher molecular weight products, including deactivating products, are produced more readily from ethanol than from methanol. This is presumably a consequence of the fact that ethanol supplies C_2 units for the growth of product molecules, whereas methanol supplies C_1 units.

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