JOURNAL OF CATALYSIS 59, 26–36 (1979)

The Disproportionation of Toluene over a HY/β-AlF$_3$/Cu Catalyst

1. Preparation and Characterization

L. E. ANEKE, L. A. GERRITSEN, P. J. VAN DEN BERG,[1] AND W. A. DE JONG

Laboratory of Chemical Technology, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Received May 30, 1977; revised June 16, 1978

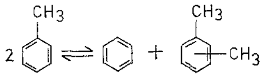
The preparation, characterization, and testing of a catalyst consisting of 72 wt% HY zeolite, 18 wt% β-AlF$_3$, and 10 wt% Cu for the conversion of toluene into benzene and xylenes are described. The effect of β-AlF$_3$, copper, and the activation temperature on the activity, selectivity, and stability of the catalyst were investigated. The results demonstrate that the catalyst shows satisfactory performance and reveal that 500°C is its optimum activation temperature. Texture determinations and activity measurements suggest that disproportionation activity is localized in the transitional pores of the catalyst and that the micropores only serve to collect heavy reaction products which would otherwise lead to deactivation. The results of ammonia adsorption combined with the effect of activation temperature on activity indicate that Brønsted acid sites formed during activation are responsible for the activity. It appears that only about 10% of the surface sites on freshly activated catalyst are acidic.

NOMENCLATURE

Symbol	Description
B, T, X, M	Benzene, toluene, xylenes, methane
g	Ammonia adsorption (ml/g)
P	Partial pressure (atm)
q_{st}	Isosteric heat of adsorption (kcal/mol)
S	Selectivity
S_a	Adsorption entropy (cal/mol·K)
S_{BET}, S_L, S_t, S_m	Specific surface area (m^2/g)
V_G, V_t	Pore volume (ml/g)
W/F	Space time (g·hr/mol)
ξ	Degree of conversion
θ	Surface coverage
Π	Total pressure (atm)

INTRODUCTION

The disproportionation of toluene:



$$\Delta H_r = 0.8 \text{ kJ/mol toluene (800 K)}$$

was first reported in 1884 by Anschütz (*1–3*), who refluxed toluene at atmospheric pressure with aluminum chloride as catalyst. Since that time, many liquid-phase studies have been carried out over metal halides acting as classical Friedel–Crafts catalysts (*4–7*). The reaction also proceeds in the vapor phase over solid acidic catalysts, such as silica–alumina and natural or synthetic zeolites (*8–10*).

However, mordenite and faujasite are known to be superior in many respects to silica–alumina (*11*). Mordenite (*12, 14*), rare-earth-exchanged X zeolite (*11, 13*), and cation-exchanged Y zeolite (*15, 16*)

---

[1] To whom correspondence should be directed.

0021-9517/79/100026-11$02.00/0

possess the highest activity for this reaction. Unfortunately, many of these initially very active catalysts show a low selectivity for disproportionation as a result of hydrodealkylation and cracking reactions. Furthermore, the rate at which their activity declines owing to coke formation is usually so fast that their activity all but disappears within a few hours. Accordingly, the trend in the development of improved toluene disproportionation catalysts has shifted toward the use of composite catalysts (*17*).

Satisfactory activity and stability have been claimed for combinations such as alumina–aluminum fluoride (*18*), mordenite–aluminum fluoride (*20*), clinoptilolite–aluminum fluoride–copper (*26*) and mordenite–aluminum fluoride–copper (*19*).

This study deals with the preparation, characterization, and performance of a HY/β-AlF$_3$/Cu toluene disproportionation catalyst. Its performance in terms of activity, selectivity, and stability is compared with that of known catalysts. Subsequently, the effect of β-AlF$_3$ and Cu content on catalyst performance is investigated. Nitrogen physisorption and mercury porosimetry are employed to characterize the texture of the catalyst and ammonia chemisorption to determine its acidity.

EXPERIMENTAL

Materials. The sodium Y zeolite, SK-40, was purchased from Union Carbide Corp. in the form of pellets with binder and as a powder without binder. Other chemicals (copper nitrate, aluminum chloride, ammonium chloride, and ammonium fluoride) were reagent grade products. The two silica–aluminas, which were studied along with the zeolite-based catalysts, were obtained from AKZO Chemie (Ketjen, Amsterdam). The first, 5P, is a low-alumina (15% alumina) sample which had been subjected to steam treatment by the manufacturer. The second, 3P, is similar to the first type, except that it was not treated with steam. The hydrogen mordenite, Zeolon 100, was obtained from Norton Co., U.S.A.

The toluene, analytical grade, was used without further purification. Ammonia, nitrogen, and hydrogen were of chemically pure quality. The ammonia, whose purity was verified by gas chromatography to be 99.92%, was used without further purification. The nitrogen and hydrogen were passed over a copper on silica (BASF BTS R3-11) catalyst to remove traces of oxygen and over molecular sieve 3A to remove moisture.

Preparation of catalysts. The silica–aluminas and the hydrogen mordenite were used without further treatment. The ammonium form of SK-40 with binder was prepared by exchanging the Na$^+$ ions for NH$_4^+$ ions by three successive immersions of 25-g batches in a 2.23 *N* NH$_4$Cl solution (250 ml). During each exchange, the resulting slurry was heated under reflux for 2 hr, with thorough stirring. After the final exchange the zeolite was filtered off, washed free of chloride and sodium ions with deionized water, and then dried overnight in an oven at 110°C. Analysis of the NH$_4$Y zeolite by atomic absorption spectrophotometry showed that the unit cell composition had changed to $\mathrm{Na_{4.6}(NH_4)_{51.4}(AlO_2)_{56}(SiO_2)_{136} \cdot }n\mathrm{H_2O}$. This corresponds to a degree of ammonium ion exchange of 91.8%. A higher level of exchange was not attempted in order not to damage the crystalline structure of the zeolite.

The β-AlF$_3$ was prepared by a double decomposition reaction between solutions, in deionized water, of stoichiometric quantities of aluminum chloride (120.7 g $\mathrm{AlCl_3 \cdot 6H_2O}$ in 250 ml) and ammonium fluoride (55.6 g NH$_4$F in 150 ml). The resulting solution was clear, presumably as a result of the preponderance of the soluble α-form of aluminum fluoride; it was partially

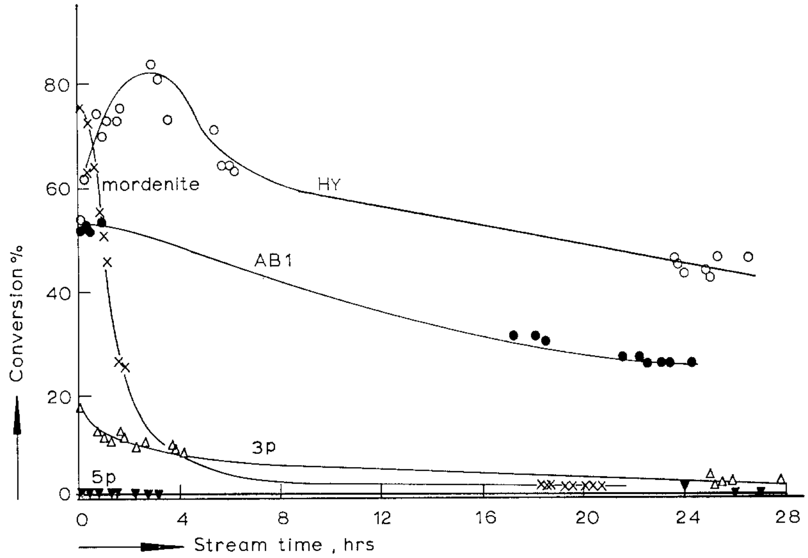


FIG. 1. Comparison of the activity of various catalysts.

evaporated and allowed to stand for 2 days. The white precipitate formed on standing was filtered off, washed with deionized water, and dried at 110°C. X-ray diffraction analysis showed that it was ammonium aluminum fluoride, NH_4AlF_4, formed according to the equation:

$$4NH_4F + AlCl_3 \rightarrow NH_4AlF_4 + 3NH_4Cl.$$

Chemical analysis also showed that it was contaminated with excess ammonia and about 0.5% chloride. After calcination at 500°C for 24 hr, chemical analysis showed it to be free of ammonium ions. X-ray diffraction analysis of the residue confirmed that it was β-AlF_3 with an average crystallite size of 18.5 mm (185 Å), formed according to:

$$NH_4AlF_4 \rightarrow \beta\text{-}AlF_3 + NH_3 + HF.$$

Catalysts containing NH_4Y and β-AlF_3 were prepared by adding the required quantity of NH_4AlF_4 to a suspension in deionized water of the ammonium Y zeolite. The mixture was heated and stirred in order to mix the two components intimately, evaporated almost to dryness, and further dried at 110°C.

Catalysts consisting of NH_4Y and copper were prepared in a similar manner by mixing the zeolite with copper nitrate dissolved in deionized water. Catalysts containing the three components were similarly prepared.

The NH_4AlF_4 and $Cu(NO_3)_2$ were dissociated at 500°C under flowing hydrogen to β-AlF_3 and CuO during activation before the start of an experimental run. The CuO was reduced by the hydrogen to Cu.

Equipment. The catalytic performance measurements were carried out in a standard continuous flow apparatus at 1 atm total pressure.

The hydrogen was purified from oxygen and water and metered by a flow controller. The hydrogen passed through a saturator filled with toluene, immersed in a thermostatically controlled water bath. The hydrogen–toluene stream then flowed through heated tubes to the reactor, which was placed in an electrical oven.

Product samples were separated in a chromatographic column containing bentone and diisodecylphthalate on Chromosorb W, and analyzed catharometrically.

Nitrogen adsorption measurements were carried out in a micro-BET apparatus at −196°C according to the method described by Lippens and co-workers (*27*). The system containing the catalyst sample was evacuated for 16 hr at 350°C before measurement of each adsorption isotherm (*21*).

A mercury penetration porosimeter, operating pressure range 0 to 3500 atm, was used for the mercury penetration measurements. The appropriate corrections for mercury compressibility were applied (*22*). Further details on the instrument used and on the theory of its applications are available in the literature (*23*).

The ammonia adsorption measurements were carried out in a temperature-programmed thermobalance. A baffle plate was installed just above the furnace in order to minimize the effects of convection currents on the furnace temperature.

Procedure. The catalyst, particle size 0.21 to 0.42 mm, was activated in a hydrogen flow by heating the reactor from room temperature to 230°C at the rate of 1°C/min and maintaining the latter temperature for 2 hr. The temperature was then raised to 500°C at the rate of 2°C/min and held at this value for 18 hr. The catalyst was then tested at standard conditions of 500°C and 1 bar total pressure. The hydrogen/toluene ratio was 16.7 mol/mol, and W/F was 859 g cat·hr/mol toluene.

The mole fractions of the components were calculated by the method of internal normalization in which toluene was used as the internal standard. The following three reactions accounted for the components present in the product:

$$2T \rightleftarrows B + X \quad \text{(toluene disproportionation)}$$

$$T + H_2 \rightarrow B + M \quad \text{(toluene hydrodealkylation)}$$

$$2X \rightleftarrows T + TMB \quad \text{(xylene disproportionation)}$$

where T, B, X, M, and TMB stand for toluene, benzene, xylenes (equilibrium ratios), methane, and trimethylbenzenes (also present in equilibrium ratios). If Y stands for the mole fraction of a particular component in the product, the conversion of toluene defined as the fraction of toluene in the feed converted by all reactions, is

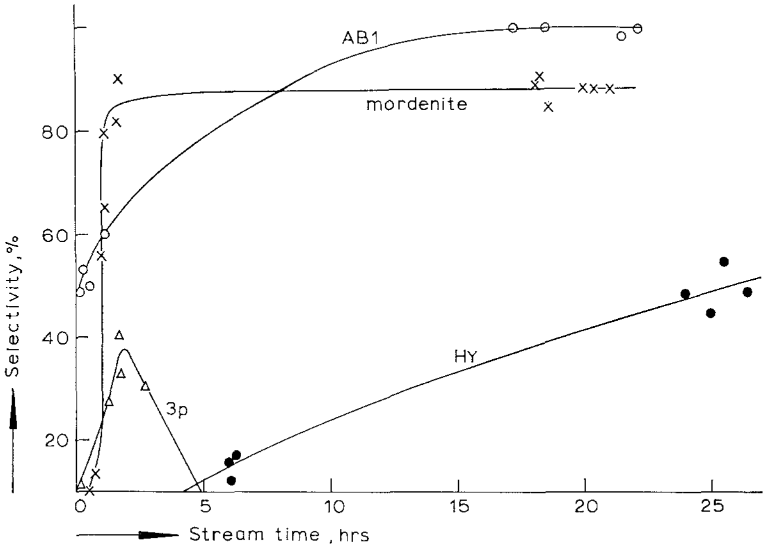


FIG. 2. Comparison of the selectivity of various catalysts.

TABLE 1

Toluene Disproportionation Performance of the Catalysts[a]

Catalyst		Toluene disproportionation performance	
No.	Description	Total conversion (%)	Selectivity (%)
4	$HY/AlF_3/Cu$ used 0.1 hr	33	25
5	$HY/AlF_3/Cu$ used 2 hr	42	85
6	$HY/AlF_3/Cu$ used 1½ months	25	92
7	Silica–alumina (steamed)	2	0
8	Silica–alumina (not steamed)	15	70

[a] Reaction conditions: $\Pi = 10$ atm, $T = 500°C$, H_2/toluene = 16.7 mol/mol, W/F = 176 g·hr/mol.

given by:

$$\xi = \frac{(Y_{\mathrm{B}} + Y_{\mathrm{X}} + Y_{\mathrm{TMB}})100}{(Y_{\mathrm{B}} + Y_{\mathrm{X}} + Y_{\mathrm{X}} + Y_{\mathrm{TMB}})}\ \%.$$

The disproportionation selectivity, defined as moles of toluene converted by disproportionation divided by the moles of toluene converted by all reactions, is given by

$$S = \frac{2(Y_{\mathrm{X}} + 2Y_{\mathrm{TMB}})100}{(Y_{\mathrm{B}} + Y_{\mathrm{X}} + Y_{\mathrm{TMB}})}\ \%.$$

For the ammonia adsorption measurements, about 10 mg of catalyst was activated for 24 hr in the thermobalance with a mixture of hydrogen (60 ml/min) and nitrogen (108 ml/min). Mixtures of nitrogen and ammonia were then passed through. The balance was calibrated at the beginning of each series of ammonia adsorption measurements (*21*).

RESULTS

Catalytic activity. The activity and selectivity of a composite catalyst, designated AB1 (72 wt% HY + 18 wt% β-AlF_3 + 10 wt% Cu), are compared with those of HY zeolite, H mordenite, and the silica–aluminas 5P and 3P in Figs. 1 and 2. The results show that the activity of H mordenite is high initially, but it decreases rapidly. The selectivity of this catalyst for toluene disproportionation is rather high. The two silica–aluminas show a very low activity and selectivity for this reaction. The steamed sample is a particularly poor catalyst, with very little activity and zero selectivity. The composite catalyst AB1 is less active than HY zeolite but it is nevertheless the best toluene disproportionation catalyst among the five because of its reasonable activity coupled with a high selectivity. Because of coke formation the activity of AB1 is not quite stable under the test conditions with respect to time, but this can be improved by working at higher pressures (see Table 1 and (*21*)).

A catalyst without binder shows the same catalytic properties as AB1.

Effect of β-AlF_3. The aluminum fluoride content on HY zeolite was varied between 0 and 17 wt%. Table 2 summarizes the results on activity and selectivity. It is clear that the catalyst with the highest β-AlF_3 content (17 wt%) is the most stable and initially also the most selective, although its activity is low compared with the other catalysts.

Effect of copper. Table 3 contains the results for catalysts consisting of varying amounts of copper on HY zeolite. These results show that the catalysts containing 8 and 12 wt% copper are reasonably active and selective even after 50 hr of stream time. Catalysts with copper percentages different from these are much less selective and stable, the main reaction of toluene over them being hydrodealkylation rather than disproportionation.

Effect of activation temperature on AB1. Catalysts activated according to the procedure previously described but at four

TABLE 2

Effect of β-AlF_3 Content on Conversion (ξ) and Selectivity (S)

Catalyst	β-AlF_3 on HY zeolite (%)	At 2 hr		At 50 hr		At 100 hr		At 140 hr	
		ξ (%)	S (%)	ξ (%)	S (%)	ξ (%)	S (%)	ξ (%)	S (%)
1	0	84	2	27	70	13	84	12	85
2	5	74	4	28	77	16	89	14	89
3	9	54	46	20	84	13	86	11	86
4	17	20	84	6	88	6	88	6	88

different temperatures (400, 450, 500, and 540°C) were tested for toluene disproportionation activity at standard conditions, except for the reaction temperature, which was 450°C. The results are shown in Fig. 3. The catalyst activated at 540°C showed very little activity. The catalyst activated at 400°C had the highest initial activity but also the highest rate of deactivation. The catalyst activated at 500°C showed a lower initial activity than the one activated at 450°C, but also a lower deactivation rate.

A similar trend is observed for the selectivity which increases with activation temperature but above 500°C decrease again.

Nitrogen adsorption measurements. The texture data determined by low-temperature nitrogen adsorption measurements are given in Table 4. The isotherms of the zeolite-based catalysts and the steamed silica–alumina were of Type I according to the BET classification. The adsorption data were fitted to the Langmuir isotherm and used to calculate the specific surface areas. The fit was excellent and it was assumed, as usually, that the cross-sectional area of a nitrogen molecule at liquid nitrogen temperature is 0.162 nm^2 (16.2 $Å^2$). The unsteamed silica–alumina showed a Type IV isotherm and the BET method was therefore used to calculate its surface area. The pore volumes (V_G) of the zeolite-based catalysts and the steamed silica–alumina were determined by the Gurvitsch rule, the density of the adsorbed nitrogen being taken as 0.8081 ml/g. V_G is the volume of the pores with radii less than about 10 nm (100 Å). The t-method of De Boer *et al.* (*28*, *29*) was used to estimate the micropore volume (V_t), the micropore area (S_m), and the transitional pore area (S_t), of the microporous cata-

TABLE 3

Effect of Copper Content on Conversion (ξ) and Selectivity (S)

Catalyst	Cu on HY zeolite (%)	At 0 hr		At 2 hr		At 25 hr		At 50 hr	
		ξ (%)	S (%)	ξ (%)	S (%)	ξ (%)	S (%)	ξ (%)	S (%)
1	0	55	41	84	2	46	48	27	70
2	2	56	36	83	0	10	56	2	0
3	3	53	52	82	0	17	68	6	62
4	6	68	0	85	0	12	78	6	85
5	8	73	5	82	4	33	80	13	71
6	12	40	46	66	6	27	70	17	81
7	25	50	15	82	0	11	55	3	30

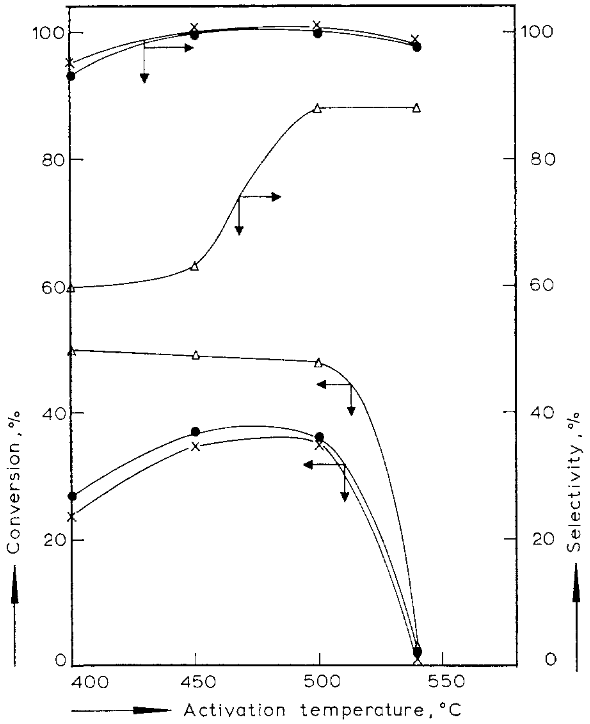


FIG. 3. Effect of activation temperature on conversion and selectivity of catalyst AB1. △, performance at $t = 0$ hr; ●, performance at $t = 20$ hr; ×, performance at $t = 28$ hr.

lysts (No. 1–7). S_t is the area of pores with diameters between 2 and 20 nm. S_m is the area for pores less than 2 nm.

Mercury penetration measurements. The pore size distribution of the NaY zeolite, of catalyst AB1 and of a catalyst used

TABLE 4

Texture of the Catalysts

Catalyst		S_L (m^2/g)	S_{BET} (m^2/g)	V_G (ml/g)	S_t (m^2/g)	S_m (m^2/g)	V_t (ml/g)
No.	Description						
1	NaY zeolite	546	—	0.193	25	454	0.178
2	NH_4Y zeolite	648	—	0.229	25	618	0.204
3	HY/NH_4AlF_4/Cu-oxide	370	—	0.129	65	243	0.093
4	HY/β-AlF_3/Cu	491	—	0.171	98	308	0.116
5	HY/β-AlF_3/Cu used 2 hr	270	—	0.094	77	154	0.053
6	HY/β-AlF_3/Cu used 1½ months[a]	144	—	0.048	70	24	0.010
7	Silica–alumina (steamed)	146	—	0.049	71	20	0.010
8	Silica–alumina (unsteamed)	—	400	—	—	—	—
Method		Langmuir method	BET method	Gurvitsch rule	t-method	t-method	t-method

[a] After 1½ months the conversion and selectivity under standard conditions were 25 and 92%, respectively.

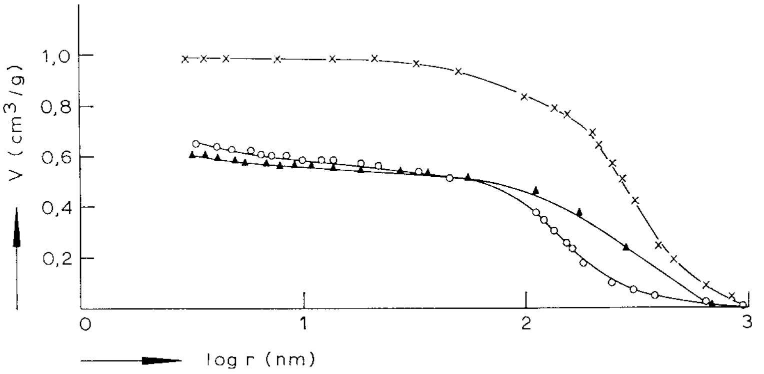


FIG. 4. Pore size distribution of NaY zeolite, AB1, and a used catalyst.

for 1 week is shown in Fig. 4. The cumulative pore volume V is plotted as a function of the pore radius r (in nanometers). The mercury porosimeter used in this study could not fill pores with radii less than 2.2 nm (22 Å); consequently the micropores of the catalyst were not penetrated and are therefore not evident in Fig. 4.

Ammonia adsorption on catalyst AB1. The ammonia adsorption isotherms on AB1 and silica–alumina 3P were measured between 300 and 500°C from 0 to 300 mm Hg. Calculation shows that no capillary condensation has taken place in the micropores of the catalyst under the conditions of our measurements. The isotherms were shown elsewhere (*21*) to obey the Freundlich equation. From the maximum ammonia adsorption, the number of acid sites at 450°C on freshly activated AB1 was calculated to be 3.54×10^{20} sites/g or 7.21×10^{17} sites/m² (*21*). With this value the percentage of the total sites (corresponding to S_L in Table 4) that are acidic at 450°C on the activated catalyst was computed to the 11%. From the amounts of adsorbed ammonia it follows

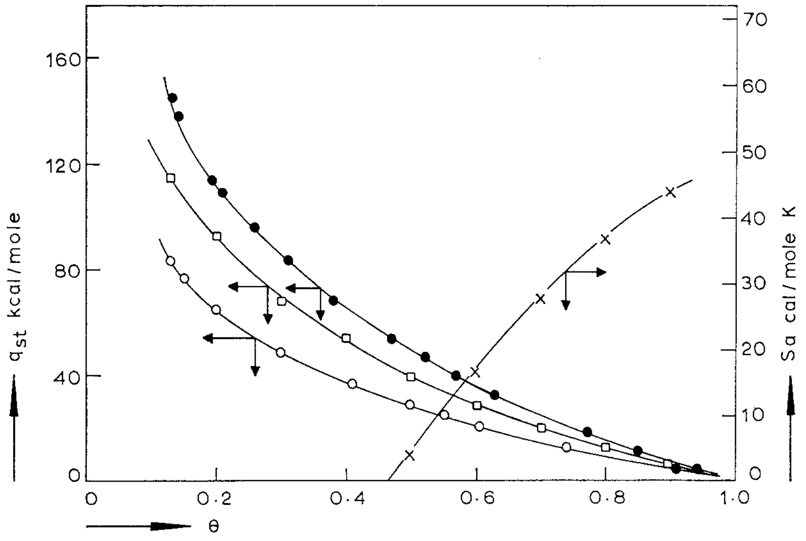


FIG. 5. Isosteric heats, q_{st}, and adsorption entropies, S_a, of ammonia on AB1. ●, 430 to 450°C; ○, 450 to 470°C; □, average.

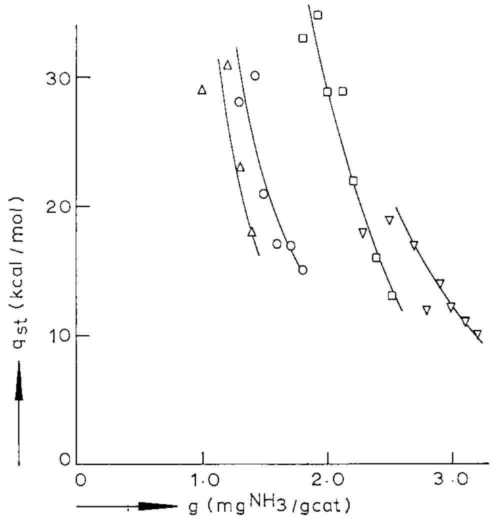


Fig. 6. Isosteric heats of ammonia adsorption on silica–alumina 3P. △, 450 to 500°C; ○, 400 to 500°C; □, 350 to 400°C; ▽, 300 to 350°C.

that AB1 is more acidic than silica–alumina by a factor 2.

Figure 5 shows the isosteric heats, q_{st}, and adsorption entropies, S_a, of ammonia on AB1 while the isosteric heats on silica–alumina 3P are given in Fig. 6. For silica–alumina the isosteric heat is plotted as a function of the quantity of ammonia adsorbed, because the Freundlich plot gives straight lines which do not converge. So it is not possible to estimate the maximum adsorption of ammonia. The Temkin plot is not applicable either; a negative heat of adsorption was found. Nevertheless Fig. 6 shows a decrease of q_{st} as a function of g as postulated by the Temkin and Freundlich theories of adsorption. Figures 5 and 6 show that, at comparable adsorption values, AB1 shows higher heats of adsorption than the silica–alumina sample and, therefore, possesses sites with nigher acid strengths.

The type of acid sites present on AB1 was investigated by comparing the ammonia adsorption capacity of catalyst samples activated at different temperatures with their toluene disproportionation performance. The results are presented in Table 5. The adsorption capacity drops by 70% after activation at 550°C instead of 500°C. Injection of a small quantity of water virtually restores its ammonia adsorption capacity to its original level. Similarly, the activity of the catalyst activated at 550°C has all but disappeared, but addition of a small quantity of water partly restores the activity.

DISCUSSION

Table 4 shows that when catalyst AB1 (No. 4) is used for 2 hr for toluene dis-

TABLE 5

Effect of Activation Temperature on Ammonia Adsorption Capacity and Toluene Disproportionation Performance of AB1

	Activated at 500°C	Activated at 550°C	Activated at 550°C then water-treated
Ammonia adsorption (mg/g)[a]	5.0	1.5	5.2[b]
Toluene disproportionation performance			
Total conversion (%)	51	2	11
Selectivity (%)	57	0	100[c]
Reaction pressure: 1 atm			
W/$F_{toluene}$: 859 g·hr/mol			
H_2/toluene: 16.7 mol/mol			

[a] P_{NH_3} = 245 mm Hg; total pressure = 1 atm; nitrogen flow rate = 193 ml/min.

[b] After injection of 1.0 μl water.

[c] After injection of 0.3 ml water.

proportionation, the micropore volume (V_t) and the micropore surface area (S_m) decrease to about half their original values. At the same time, the transitional pore area undergoes a comparatively less pronounced decrease from 98 to 77 m^2/g. The same trend is observed in the catalyst which was used for $1\frac{1}{2}$ months (No. 6). Although it is still catalytically active (Table 1), its micropore volume (Table 4) has all but disappeared (0.01 ml/g), which suggests that the micropores collect heavy reaction products; the decrease in the transitional pore area from 98 to 70 m^2/g is small in comparison and seems to indicate that the seat of catalytic activity is in the transitional pores.

The catalytic performance tests (Figs. 1 and 2) demonstrate that more and more active sites are eliminated as the reaction proceeds (progressively lower conversion) and that the remaining sites are the ones that are active for toluene disproportionation (progressively higher selectivity). Apparently the most active sites are eliminated first; these sites are responsible for the most important side reactions, hydrodealkylation and cracking of toluene. The elimination of the active sites and the resulting progressive decrease in activity can most probably be attributed to coke formation.

The best activation temperature for catalyst AB1 appears to be 500°C. Above this temperature the performance of the catalyst clearly deteriorates. This can be explained on the basis of the formation of Brønsted and Lewis sites on the catalyst during activation (*12*, *25*). At a certain water content, dissociation of hydrate water occurs, leading to the formation of protons which combine with lattice oxygen atoms in the catalyst to form hydroxyl groups that act as Brønsted acid sites. Still further loss of water, as the temperature of activation increases above 500°C, results in dehydroxylation of the catalyst and the formation of inactive and possibly also Lewis acid sites. This hypothesis is in agreement with the results of others (*31*) on the nature of the active sites on HY zeolite.

Copper and β-AlF_3 in combination improve the performance of HY zeolite; the optimum composition of such a catalyst seems to be 72 wt% HY, 18 wt% β-AlF_3, and 10 wt% copper. It is not clear how the beneficial effect of β-AlF_3 and Cu on the selectivity and stability can be accounted for.

Ammonia adsorption measurements suggest that only about 10% of the surface sites on freshly activated AB1 are acidic. Its acidic properties are consistent with the hypothesis that its high performance for toluene disproportionation is due to its acidity. The lower acidity and acid strength of silica–alumina are thought to be responsible for its lower performance.

ACKNOWLEDGMENTS

The contributions of R. A. Betcke and R. A. van Iddekinge to the performance of the experiments are gratefully acknowledged.

REFERENCES

1. Anschütz, R., and Immendorff, H., *Ber. Deut. Chem. Ges.* **17**, 2, 2816 [1884).
2. Anschütz, R., and Immendorff, H., *Ber. Deut. Chem. Ges.* **18**, 1, 657 (1885).
3. Anschütz, R., *Ann. Chem.* **235**, 150 (1886).
4. Nightingale, D. V., *Chem. Rev.* **25**, 329 (1939).
5. Brown, H. C., and Smoot, C. R., *J. Amer. Chem. Soc.* **78**, 2176 (1956).
6. Pitzer, K. S., and Scott, D. W., *J. Amer. Chem. Soc.* **65**, 803 (1943).
7. Schriesheim, A., *J. Org. Chem.* **26**, 3530 (1961).
8. Natanson, and Kagan, *J. Phys. Chem. USSR* **17**, 381 (1943).
9. Given, P. H., and Hammick, D. L., *J. Chem. Soc.*, 1779 (1949).
10. Izumi, Y., and Shiba, T., *Bull. Chem. Soc. Japan* **37** (12), 1797 (1964).
11. Matsumoto, H., and Morita, Y., *Bull. Japan Petrol. Inst.* **10**, 8 (1968).
12. Benesi, H. A., *J. Catal.* **8**, 368 (1967).
13. Venuto, P. B., Hamilton, L. A., Landis, P. S., and Wise, J. J., *J. Catal.* **5**, 81 (1966).

14. Yashima, T., Moslehi, H., and Hara, N., *Bull. Japan Petrol. Inst.* **12**, 106 (1970).
15. Jacobs, P. A., Leeman, H. E., and Uytterhoeven, J. B., *J. Catal.* **33**, 31 (1974).
16. Wang, K. M., and Lansford, J. H., *J. Catal.* **24**, 262 (1972).
17. Gutberlet, L. C., and Bertolacini, R. J., U.S. Patent 3, 548, 020 (1970).
18. Toyo Rayon Kabushiki Kaisha, Tokyo, Dutch Patent No. 6706218 (1970).
19. Toyo Rayon Kabushiki Kaisha, Tokyo, Dutch Patent No. 6817615 (1968).
20. Otani, S., Iwamura, T., Hayashi, S., Ogawa, D., and Kanaoka, M., U.S. Patent No. 3, 597, 492 (1971).
21. Aneke, L. E., "Kinetics of the Vapour-Phase Catalytic Disproportionation of Toluene," Dissertation, Delft, 1976.
22. Scholten, J. J. F., *in* "Porous Carbon Solids" (R. L. Bond, Ed.), p. 225. Academic Press, New York and London, 1967.
23. De Wit, L. A., and Scholten, J. J. F., *J. Catal.* **36**, 36 (1975).
24. Tanabe, K., "Solid Acids and Bases." Academic Press, New York and London, 1970.
25. Moscou, L., and Lakeman, M., *J. Catal.* **16**, 173 (1970).
26. Toyo Rayon Kabushiki Kaisha, Tokyo, Dutch Patent No. 6817616 (1968).
27. Lippens, B. C., Linsen, B. G., and de Boer, J. H., *J. Catal.* **3**, 32 (1964).
28. De Boer, J. H., Lippens, B. C., Linsen, B. G., Broekhoff, J. C. P., Heuvel, A. v.d., and Osinga, Th. J., *J. Colloid Interface Sci.* **21**, 405 (1966).
29. Broekhoff, J. C. P., and Linsen, B. G., *in* "Physical and Chemical Aspects of Adsorbents and Catalysts" (B. G. Linsen, Ed.), p. 1. Academic Press, New York and London, 1970.
30. Gati, G., and Knözinger, H., *in* "Proceedings. 5th International Congress on Catalysis (Florida 1972)," p. 819. North-Holland/American Elsevier, New York and Amsterdam, 1973.
31. Ward, J. W., *J. Catal.* **9**, 225 (1967).