Direct Measurement of Interaction Energy between Solids and Gases. IV. Acidic and Catalytic Properties of Amorphous and Crystalline Alumino-silicates

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Surface acidities and acid strength distributions of amorphous silica–alumina, Y-type faujasite and mordenite have been examined by measuring the differential heats of adsorption of ammonia. The number of acid sites with adsorption heats higher than 70 kJ/mol increased in the order: $NH_4Y > NH_4M > RENH_4Y >$ silica–alumina. On the other hand, the order of the acid strength was: $NH_4M > RENH_4Y >$ silica–alumina $> NH_4Y$. The high catalytic activities of zeolites for cumene cracking and toluene disproportionation were correlated with acid strength, Brönsted acidity, and electrostatic effect.

Zeolite have been shown to be more active than amorphous silica–alumina catalysts for many reactions. Miale *et al.*[1] compared the relative rates of hexane cracking reaction by a wide variety of zeolite catalysts with those by amorphous silica–alumina catalysts. They showed the superior activity of zeolite catalysts, that is, the relative rate, compared with silica–alumina taken as 1, was more than 10000. Plank *et al.*[2] showed the high activity of zeolite catalysts for gas oil cracking. Venuto and co-workers have shown that zeolites can catalyze a wide range of organic reactions.[3] In a previous paper,[4] the cumene cracking activities were measured for several FCC catalysts and the present authors concluded that the higher activity of zeolite-cracking catalysts could not be explained only by an acidity increase. Tung[5] proposed the time variant Brönsted acidity of zeolite catalysts to explain their high activity compared with that of amorphous silica–alumina. The nature of active centers of zeolite catalysts has been reviewed recently.[6]

In this work, cumene cracking and toluene disproportionation reaction were measured over amorphous silica–alumina, Y-faujasite and mordenite. The results of activity were correlated with acid strength distribution, IR spectra of adsorbed pyridine and electrostatic effects evaluated from nitrogen adsorption.

Experimental

Materials. The solid acids used in this study were shown in Table 1. Silica–alumina (Al_2O_3 contents, 28 wt %), Na-type mordenite and rare-earth(RE)exchanged Y-faujasite supplied by Catalysts and Chemicals Ind. Co. Ltd. NH_4M and $RENH_4Y$ were prepared by a conventional cation exchange procedure with NH_4NO_3 solution and then calcined in air at 600 °C and 400 °C for 3 h, respectively. NH_4Y, prepared by an ion exchange with NH_4Cl solution of NaY-faujasite supplied by Linde Co. was calcined in air at 400 °C for 3 h. The degree of ion-exchange was determined by flame photometry. All the catalysts were used as granule of 28—60 mesh.

Table 1. Surface area, SiO_2/Al_2O_3 molar ratio and the degree of exchange of solid acid catalysts

	SA[a]	NH_4Y	$RENH_4Y$	NH_4M
Surface area ($s/m^2\ g^{-1}$)	511	595	451	430
SiO_2/Al_2O_3 molar ratio	4.3	5.0	4.82	10.9
Ion exchange/%	—	96.0	96.3[b]	98.1

a) Silica–alumina. b) 64.0% rare earth and 32.3% NH_4^+ exchanged.

Apparatus and Procedure. Experimental procedures and analysis of differential heats of adsorption of ammonia to estimate the acidity and acid strength distribution were carried out as described in a previous paper.[7] The same apparatus was used to measure the heat of adsorption of nitrogen and argon on solid acid catalysts. Each catalysts received a heat treatment at 400 °C under a pressure of 1.3×10^{-3} Pa for 5 h before calorimetric measurements.

The infrared absorption spectra of the adsorbed pyridine on solid acid catalysts were recorded on Hitachi infrared spectrometer model EPI-G3 by use of a conventional *in situ* cell connected to a vacuum line. The catalysts were pressed into a wafer with a thickness of about 10 mg/cm² and heat-treated at 400 °C under a pressure of 1.3×10^{-3} Pa for 4 h. The infrared spectra were measured at 25 °C.

The catalytic reactions were carried out in a pulse reactor system. The apparatus and experimental procedure were described in detail in a previous paper.[4] The catalysts were pretreated at 400 °C for 4 h in a stream of helium gas as a carrier. The helium flow rate during the pretreatment was 30 cm³/min. The catalyst bed used in a cumene cracking reaction consisted of 20 mg catalysts diluted with 130 mg of catalytically inert quartz beads and the reaction was carried out at 300 °C and at a helium flow rate of 60 cm³/min. Toluene disproportionation reaction was carried out at 400 °C and at a helium flow rate of 30 cm³/min over 150 mg of catalysts. The catalytic activity was estimated by means of a conversion rate of cumene and toluene.

Results

Catalytic Activity. The cumene cracking and toluene disproportionation activities over mordenite, Y-faujasite and silica–alumina are shown in Table 2. $RENH_4Y$ had higher initial activity for cumene cracking than NH_4Y and NH_4M. A large drop in conversion with an increase in the pulse number was observed over NH_4M, indicating the formation of non-volatile residue which left portions of the active site inaccessible to the reactants. NH_4M showed higher activity for toluene disproportionation and the order of activity was: $NH_4M > RENH_4Y > NH_4Y >$ silica–alumina in agree-

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Table 2. CUMENE CRACKING[a] AND TOLUENE DISPROPORTIONATION[b] ACTIVITY OVER SILICA–ALUMINA, NH_4Y, $RENH_4Y$, AND NH_4M

	Cumene conversion/%[c]	Cumene conversion/%[d]	Toluene conversion/%[e]
SA	3.5	0	0
NH_4Y	68.9	48.3	5.5
$RENH_4Y$	83.0	37.1	18.6
NH_4M	71.1	10.5	56.9

a) React. temp: 300 °C, 60 cm³ of He/min. b) React. Temp: 400 °C, 30 cm³ of He/min. c) Conversion of the first pulse (5 μl). d) Conversion of the pulse (5 μl) after 180 μl of the reactant was charged. e) Average conversion of the first 5 pulses (2 μl × 5).

ment with the results of Nakano *et al.*[8] Conversions of cumene or toluene over amorphous silica–alumina were slight or none under these reaction conditions.

Differential Heats of Adsorption of Ammonia. In Fig. 1, the differential heats of adsorption of ammonia on silica–alumina, NH_4Y, $RENH_4Y$, and NH_4M are shown. The nature of differential heat curves of silica–alumina and NH_4Y has been discussed previously.[7] The differential heat curve of $RENH_4Y$ showed the existence of strong acid sites of heats of adsorption higher than 105 kJ/mol compared with that of NH_4Y, but the number of acid sites between adsorption heats of 80—100 kJ/mol decreased markedly. Initial heat of NH_4M was higher than 150 kJ/mol and the differential heat curve was very similar to that of $RENH_4Y$.

The acid strength distributions of these solid acid catalysts are shown in Fig. 2. The maximum distributions were observed at *ca.* 98 kJ/mol for mordenite and Y-faujasites and the other maximum distributions were also observed at 110 kJ/mol and 77, 120 kJ/mol for $RENH_4Y$ and NH_4M, respectively. Silica–alumina possessed a maximum distribution at 105 kJ/mol.

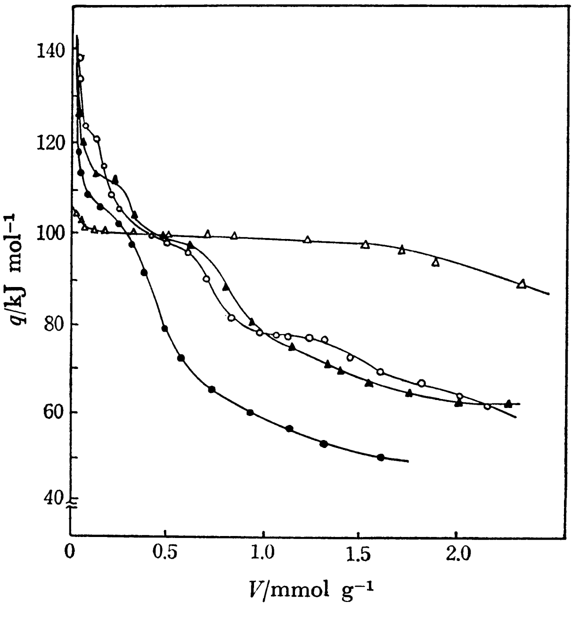

Fig. 1. Heats of adsorption of ammonia on solid acid catalysts at 25 °C.
-△-: NH_4Y, -▲-: $RENH_4Y$, -○-: NH_4M, -●-: SA.

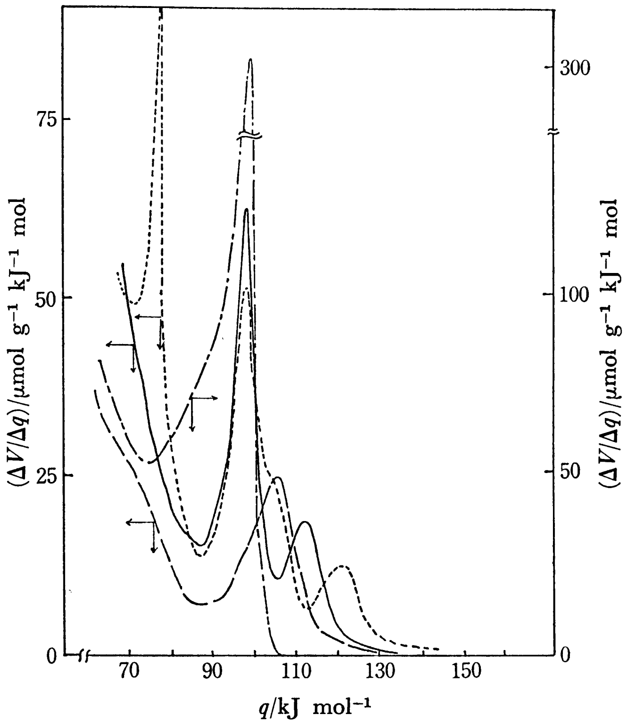

Fig. 2. Acid site distributions of solid catalysts.
----: NH_4M, -·-·: NH_4Y, ——: $RENH_4Y$, —–—: SA,

Infrared Spectra of Adsorbed Pyridine. Infrared spectra of pyridine on silica–alumina and zeolites are shown in Fig. 3. The adsorbed pyridine has strong and

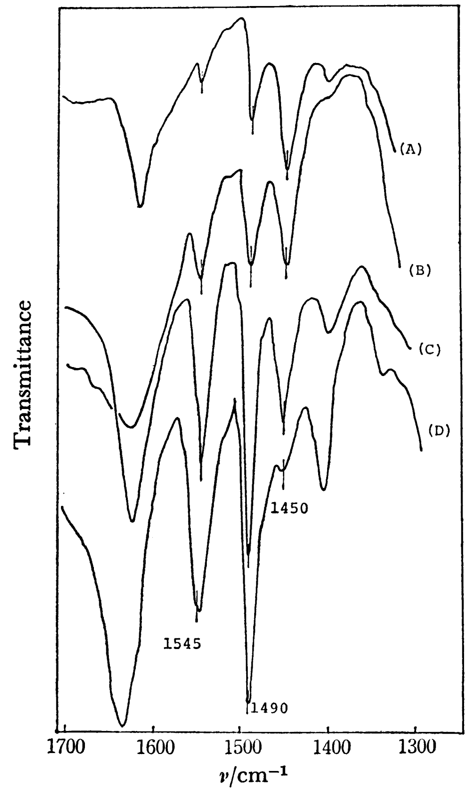

Fig. 3. Spectra of adsorbed pyridine on solid acids after pyridine dosing at 25 °C and evacuating at 150 °C for 1 h, (A) SA; (B) NH_4M; (C) $RENH_4Y$; (D) NH_4Y.

sharp bands characteristic of pyridinum ions (B-Py) at 1545 cm^{-1} and coordinately-bonded pyridine (L-Py) at 1450 cm^{-1}. In these spectra, the hydrogen-bonded species were removed by evacuation at 150 °C for 1 h, which was confirmed by the disappearences of their characteristic absorption bands at 1593 and 1438 cm^{-1}. It is apparent that the fraction of L-Py was higher in silica–alumina than in zeolites. The exchange with rare-earth cations in RENH$_4$Y results in a formation of Lewis acid sites and enhances the acid strength as shown in Fig. 2. The band near 1443 cm^{-1} due to pyridine interacted with the rare-earth cations could not be observed after the evacuation at 150 °C. Strong adsorption band of L-Py was observed on NH$_4$M in contrast with the results of Yashima *et al.*[9]

Heats of Adsorption of Nitrogen and Argon. The integrated heats of adsorption of nitrogen and argon on silica–alumina, NH$_4$Y, RENH$_4$Y, and NH$_4$M are collected in Table 3. They were taken up to 20—35 μmol/g of the amount adsorbed for zeolites and about 10 μmol/g for silica–alumina. The order of integral heats was: NH$_4$M>RENH$_4$Y>NH$_4$Y>silica–alumina. For zeolites, this order coincides with that of acid strength in Fig. 2. A large difference in adsorption heats between argon and nitrogen was observed over NH$_4$M.

TABLE 3. HEAT OF ADSORPTION OF NITROGEN AND ARGON ON SOLID ACIDS (q/kJ mol^{-1})

	SA	NH$_4$Y	RENH$_4$Y	NH$_4$M
N$_2$	6	11.8	14.5	23.1
Ar	5	9.0	10.1	16.8

Discussion

A high activity of zeolites has led to suggestions that the active sites such as Brönsted acid sites, Lewis acid sites and electrostatic fields on crystalline alumino-silicates are considerably different from those on amorphous alumino-silicates. Oblad[10] has compared the acidic nature of zeolite cracking catalysts with that of silica–alumina and concluded that the activity of zeolites was related to the intrinsic "protonic acidity" of the alumino-silicate lattice.

The present authors have previously shown that the cumene cracking activity over amorphous silica–alumina had a linear correlation with the number of acid sites higher than 70 kJ/mol of adsorption heats of ammonia.[4] The surface acidities obtained from Fig. 1 are 0.65, 1.32, 1.56, and 3.95 mmol/g for silica–alumina, RENH$_4$Y, NH$_4$M, and NH$_4$Y, respectively. An increase in acid strength in RENH$_4$Y can be explained by inductive effects of rare-earth cation on the acidic hydroxyl groups. These values suggest that the excellent activity of zeolite catalysts for cumene cracking can not be explained only in terms of acidity increase. However, the existence of strong acid sites in NH$_4$M and RENH$_4$Y leads to a large aging of cumene cracking activity, *i.e.*, the formation of non-volatile residue.

It is evident that the catalysts such as NH$_4$M and RENH$_4$Y which possessed stronger acid sites showed higher conversion for toluene disproportionation, indicating that the reaction was effectively promoted by strong acid sites, *i.e.*, the sites having the heat of adsorption of ammonia higher than *ca.* 100 kJ/mol. However, it is difficult to explain the difference in activities for toluene disproportionation between silica–alumina and NH$_4$Y in terms of acid strength.

Differential heats in Fig. 1 contain both the interaction of ammonia with Brönsted and with Lewis acid sites, and it is difficult to differentiate these two sites from heat curves. The relatively homogeneous acid sites at 98 kJ/mol in adsorption heats of NH$_4$Y in Fig. 2, combined with the results of infrared spectra, can probably attributed to protonic acid sites because of the existence of weak band of L-Py in Fig. 3. The apparent ratios of the peak height of L-Py to B-Py, compared with that of silica–alumina taken as 1, were 0.57, 0.19, 0.03 for NH$_4$M, RENH$_4$Y, and NH$_4$Y, respectively. If we assume that the number of Brönsted acid sites is equal to that of Lewis acid sites in silica–alumina, the Brönsted acidities of silica–alumina, NH$_4$M, RENH$_4$Y, and NH$_4$Y should be 0.32, 0.99, 1.11, and 3.82 mmol/g, respectively. Brönsted and Lewis acid sites concentration of the solid acids were summarized in Table 4. If Brönsted rather than Lewis acid sites are the seats of activity for toluene disproportionation as mentioned by Benesi,[11] the absence of activity over silica–alumina must somewhat be due to its small Brönsted acidity and this is also true for cracking activity. The higher initial activity over RENH$_4$Y for cumene cracking can be related to its relatively strong acid sites and larger number of Brönsted acid sites.

It has long been believed that the zeolite surfaces were heteropolar. Therefore, molecules occuluded within the zeolite framework are subject to its electrostatic field. Huang *et al.*[12] obtained the isosteric heat of adsorption of krypton from adsorption isotherms and discussed the surface electrostatic effects associated with lattice cations of Y-faujasites. They concluded that the existence of bivalent cations on zeolite surface had no influence on the adsorption of krypton because of its smaller contribution to polarization energy. Meanwhile the use of nitrogen molecules should be suitable for studies of electrostatic effects of solid surfaces because of its large quadrupole moment and relatively large polarizability.

If we can assume that the polarizability of nitrogen is almost the same as that of argon, the difference of

TABLE 4. BRÖNSTED AND LEWIS ACID SITES CONCENTRATION MEASURED BY THE INFRARED SPECTRA OF ADSORBED PYRIDINE

	Catalysts			
	SA	NH$_4$M	RENH$_4$Y	NH$_4$Y
Acidity/mmol g^{-1}	0.65	1.56	1.32	3.95
L-Py/B-Py	1	0.57	0.19	0.03
B-sites[a]/mmol g^{-1}	0.32	0.99	1.11	3.82
L-sites[b]/mmol g^{-1}	0.33	0.57	0.21	0.13

a) The number of Brönsted acid sites. b) The number of Lewis acid sites.

adsorption heats between them is probably due to the quadrupole-electrostatic field gradient interaction. Therefore, the higher adsorption heats of nitrogen on $RENH_4Y$ compared with that on NH_4Y can be ascribed to the contribution of quadrupole interaction of nitrogen with rare-earth cations. It is noteworthy that the order of integral heats of nitrogen coincides with that of activity for toluene disproportionation. These facts indicate that the cages and channels of zeolitic crystalline structure are characterized by the existences of high electrostatic field and its gradient, and therefore they act as strong polarizing agents for hydrocarbon transformation reactions.

It may be concluded from the present work that the acidity of zeolite catalysts appears to be the same kind as silica–alumina but differs in both quantity and quality of acid sites. Acid strength distributions of each solid acids obtained from differential heats of adsorption of ammonia are extensively different depending upon their crystalline structure and the existence of cations. The acid sites having the adsorption heats of ammonia higher than *ca.* 100 kJ/mol are effective for toluene disproportionation at 400 °C and these values are considerably high compared with the effective acid strength for cumene craking. Heats of adsorption of nitrogen indicate the high electrostatic field over zeolite surfaces. The low Brönsted acidity as well as the low electrostatic effects probably correlate with the low activity of amorphous silica–alumina.

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