Effects of decrease in number of acid sites located on the external surface of Ni-SAPO-34 crystalline catalyst by the mechanochemical method

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In order to improve shape selectivity of the methanol to ethylene conversion and mitigate coke formation, the acid sites located on the external surface of Ni-SAPO-34 crystals were neutralized by the intrinsic mechanochemical method. Ni-SAPO-34 crystals were mixed in an agate mortar with basic alkaline or alkaline earth metal oxides supported on microspherical non-porous silica. Their catalytic performances in methanol conversion were enhanced, especially in the case of BaO-modified catalyst. The reason was verified by adopting the cracking of *t*-butylbenzene, which could not access into the pore channel due to its bulky molecular size. These changes in the reaction performance consistently could be ascribed to the decrease of the acid sites on the external surfaces.

Keywords: shape selectivity, acid sites, external surface, methanol conversion, coke formation, mechanochemical neutralization

1. Introduction

An alternative and effective route of ethylene synthesis now increases its importance. Recently, studies on ethylene synthesis using SAPO-34 having the homologous structure of CHA were reported by several research groups [1–6]. However, as CHA has large cavities inside the crystal channel structure, it involves a risk of rapid coke formation as chabazite catalysts have [7], when the intrinsic strength and concentration of acid sites inside the cavity are too high. By the incorporation of Ni into the framework of the SAPO-34 structure, the acid strength could be weakened [3]; however, the coke formation still remained at the external surface of the crystals, owing to its small restriction for the growth of fused-ring aromatics, i.e., the precursors of aromatic coke.

Many researchers have performed studies to overcome this problem [7–10], but it has not been resolved as yet. Inui et al. [11–13] reported that the acid sites located on the external surface of Ga-incorporated MFI-type metallosilicate were reduced by Pt-ion exchange and successive heat treatment resulting in a marked reduction of coke deposit due to hydrogen spill-over through the Pt particles at the portholes. Recently, they extended their work by a selective neutralization of acid sites located on the outer surface of H-ZSM-5 crystals [14] and H–Ga silicate crystals [15] and confirmed its neutralization effect on the methylation reaction of methylnaphthalene, respectively.

In our previous paper [16], it was demonstrated that the amount of coke deposited sensitively depended on the acid-site density of the external surface of Ni-SAPO-34 crystals in the methanol to light olefin conversion reaction. Also, acid sites of the external surface decreased the selectivity to ethylene from methanol owing to the non-restricted oligomerization at the solid surfaces.

In the present study, therefore, the mechanochemical neutralization method was adopted to neutralize the acid sites on the external surface of Ni-SAPO-34 crystal, with the intention to reduce the coke formation and increase the shape selectivity in methanol conversion.

2. Experimental

2.1. Catalyst preparation

The preparation procedure of catalysts is shown in figure 1. The gel composition of the Ni-SAPO-34 crystal was 0.20 Al_2O_3 : 0.20 P_2O_5 : 0.06 SiO_2 : 0.0015 NiO : 0.20 $(TEA)_2O$: 10 H_2O, and it was synthesized by the rapid crystallization method [17]. The obtained crystal was calcined at 600 °C for 3 h in air to remove the organic template before neutralization.

Neutralization of the acid sites on the external surface was conducted as follows: a 70 wt% portion of Ni-SAPO-34 crystalline particles were manually milled in an agate mortar for 30 min with a 3 wt% portion of a basic metal oxide such as MgO, CaO, BaO, or Cs_2O supported on a 27 wt% portion of microspherical non-porous silica particles of 0.3–1.5 μm in diameter (PS-3, Onoda Cement). As the reference catalyst, a 70 wt% portion of Ni-SAPO-34 was mixed with 30 wt% of PS-3. These samples were then tabletted and calcined at 600 °C for 30 min in air followed by crushing and sieving to 20–24 mesh to provide the reaction. The five kinds of catalysts were designated as cats.

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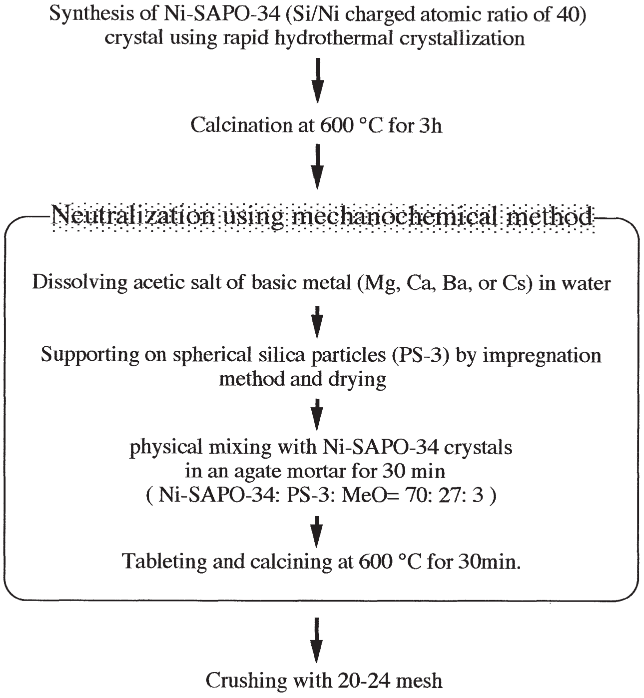


Figure 1. Preparation procedure of catalyst.

1 (none), 2 (CaO), 3 (MgO), 4 (BaO), and 5 (Cs_2O) for the modified oxides, none, CaO, MgO, BaO, and Cs_2O, respectively.

2.2. Characterization

Synthesized Ni-SAPO-34 crystals were identified by powder X-ray diffraction analysis (XRD), by using a Shimadzu XD-DI with nickel filtered Cu Kα radiation (30 kV, 30 mA) at an angle of 2θ range from 50 to 5°.

Morphology of the PS-3, Ni-SAPO-34 crystals, and the mixture of the former with the metal-oxide-loaded PS-3 were observed by Hitachi S-2500CX scanning electron microscope (SEM).

Acidic properties of the catalysts were measured by temperature-programmed desorption (TPD) of pre-adsorbed NH_3 or 4-methylquinoline, using a Rigaku micro thermo-gravimetric analyzer Thermoflex TG 8110 equipped with a thermal analysis station TAS 100, and the TPD profiles were obtained from the differential of the integral curve of weight loss from 80 to 600 °C at a constant heating rate of 10 °C/min in a 50 ml/min N_2 flow.

The amount of coke deposited on the catalyst after the reaction was measured by temperature-programmed oxidation (TPO) by using a Shimadzu DT-40 thermo-gravimeter at a heating rate of 10 °C/min in a 40 ml/min air flow. The profiles were obtained by the same way as described for TPD, and the coke contents were calculated from the weight loss in a temperature range from 300 to 800 °C.

2.3. Reaction method

Methanol conversion was carried out in an ordinary fixed flow-type apparatus. A 0.325 g portion (0.35 ml) of catalyst was packed into a quartz tubular reactor having 5.0 mm inner diameter, and a reaction gas, composed of 15 mol% methanol and 85 mol% N_2, was allowed to flow with a gaseous hourly-space velocity (GHSV) of 500 h^{-1} at a temperature range from 300 to 450 °C for 1–5 h on stream.

Catalytic cracking of t-butylbenzene was carried out at 450 °C to evaluate the effect of the neutralization on the

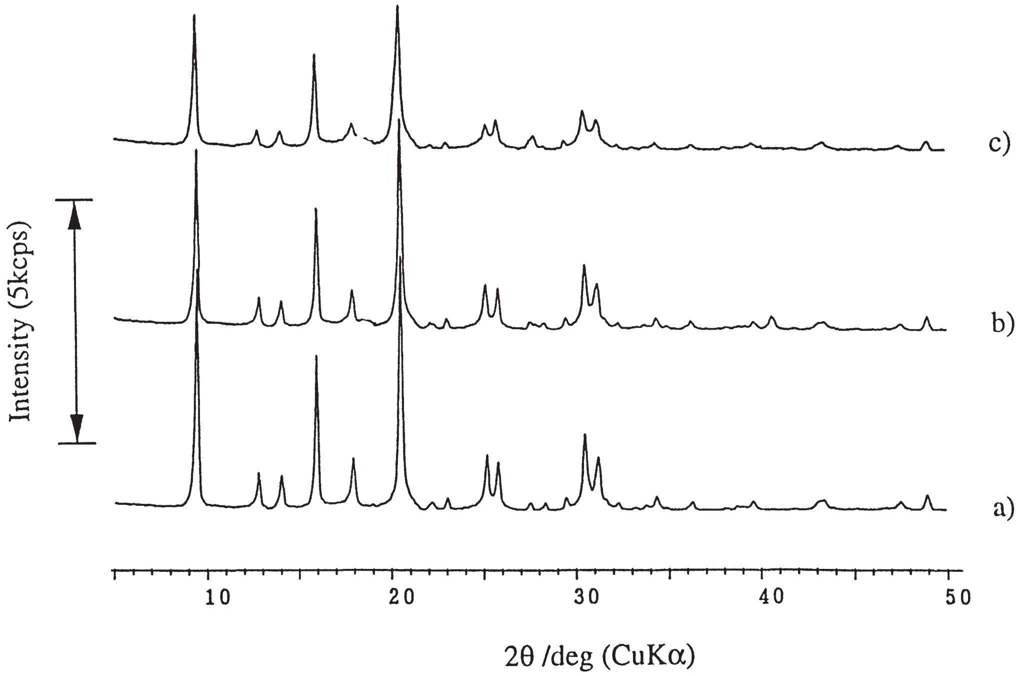
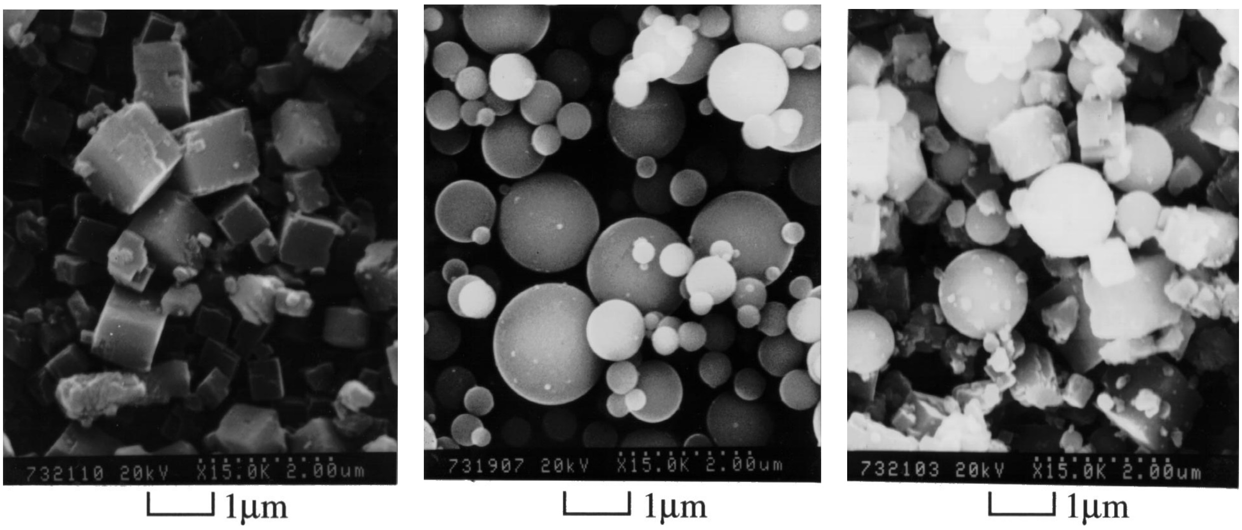


Figure 2. XRD patterns of cats. 1 (none) (a), 4 (BaO) (b) and 5 (Cs_2O) (c).



(a) (b) (c)

Figure 3. SEM photographs of Ni-SAPO-34 (a), PS-3 (b) and cat. 4 (BaO) (c).

activity of the outer surface of crystalline particles. A 0.5 g portion of catalyst was used. t-butylbenzene was fed to an evaporator by a microtube pump, was diluted to 20 mol% with N_2, and fed to the catalyst with a GHSV of 1000 h^{-1}.

The products were analyzed by three FID-type gas chromatographs, Shimadzu GC7A, 12A, and 14A. Analyses for methanol and dimethyl ether, C_1–C_4 hydrocarbons, gasoline range hydrocarbons, and CO_x were carried out by using columns Porapak T, VZ-10, silicon OV-101, and activated carbon, respectively. The deposited coke was determined by combustion using micro-thermogravimetric analyzer Shimadzu DT-40.

2.4. Coke deposited

The amount of deposited coke was measured by TPO. A 20 mg portion of a sample was placed in a sample pan and heated from 300 to 800 °C at a constant heating rate of 10 °C/min in a 40 ml/min air flow. A 20 mg of α-alumina was used as the reference.

3. Results and discussion

3.1. Physical properties of the catalysts

The XRD patterns for the catalysts are shown in figure 2. The peak for the modified catalysts almost coincided with that of the unmodified one. However, in the case of Cs_2O modification, the peak intensity decreased considerably. This is ascribed to permeation of Cs_2O into the inside of the Ni-SAPO-34 particle, causing a structural damage of some part of crystals.

The SEM photographs for Ni-SAPO-34, the spherical silica support (PS-3), and cat. 4 (BaO) are shown in figure 3. The crystals of Ni-SAPO-34 synthesized by the rapid crystallization method were in the form of uniform cubes of 1 μm, and the diameters of spherical particles of PS-3 were 0.3–0.8 μm. The morphology of the cat. 4 (BaO) implies that Ni-SAPO-34 crystals were sufficiently mixed with spherical silica particles and, therefore, the BaO supported on the microspherical silica could contact the external surface of Ni-SAPO-34 crystals.

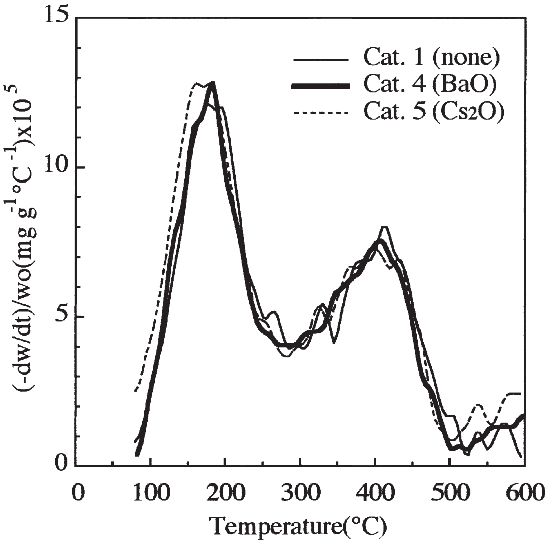


Figure 4. NH_3-TPD profiles for Ni-SAPO-34 crystalline catalysts modified with basic oxides (MeO).

The NH_3-TPD profiles for modified and unmodified catalysts are shown in figure 4. These profiles consist of two peaks; one appears at a low-temperature range around 150–200 °C and another appears at a high-temperature range around 350–450 °C. The low- and high-temperature peaks correspond to the weak and strong acid sites, respectively. The peak intensity and width were not changed in modified catalysts compared with unmodified. The acidic properties of Ni-SAPO-34 crystals modified with different basic oxides are presented in table 1. As shown, for all catalysts except for cat. 5 (Cs_2O), the amounts of NH_3 adsorption

Table 1
Acidic properties of Ni-SAPO-34 catalysts modified with basic oxides.

Catalyst	Adsorption amount of NH_3 (mmol/g)	Adsorption amount of quinoline (mmol/g)	BET surface area (m^2/g)
Cat. 1 (none)	1.571	0.102	323
Cat. 3 (MgO)	1.570	0.099	324
Cat. 4 (BaO)	1.543	0.095	320
Cat. 5 (Cs_2O)	1.313	0.080	314

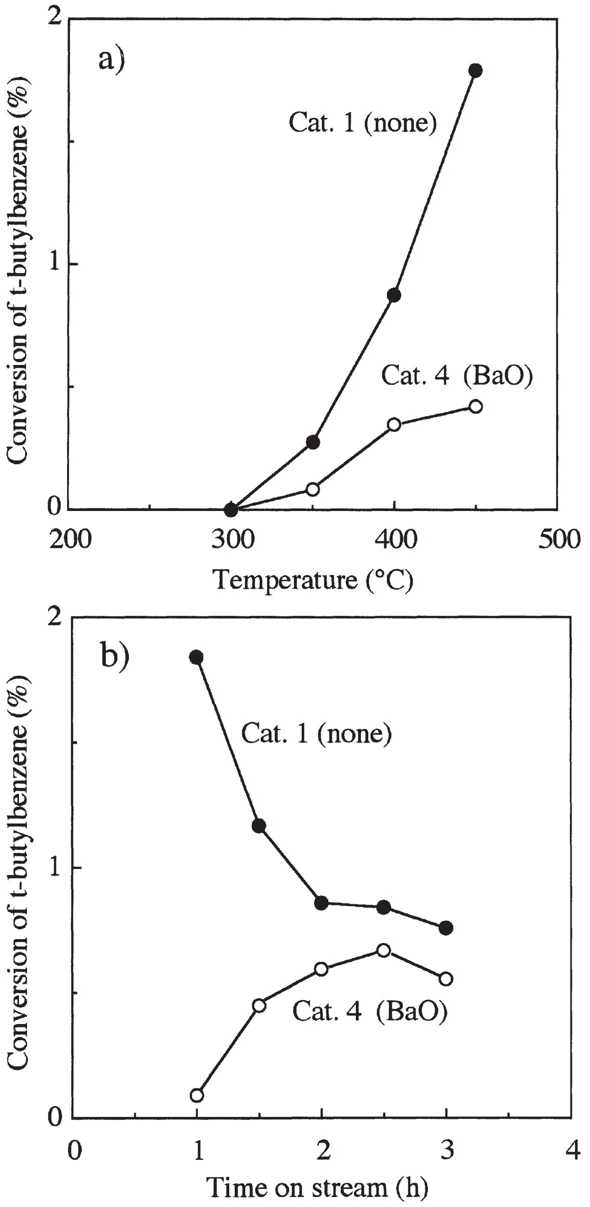


Figure 5. Effect of temperature (a) and time on stream (b) on the conversion of t-butylbenzene. Reaction conditions: 20 mol% t-butylbenzene, 80 mol% N_2, temperature 450 °C, GHSV 1000 h^{-1}.

were similar. However, from the data of quinoline TPD, it is recognized that with increase in the basicity of the supported material, i.e., MgO $<$ BaO $<$ Cs_2O, the acidity on the external surface decreased. On the other hand, for cat. 5 (Cs_2O), the acid amount in the crystals was remarkably reduced. This is ascribed to the permeation of basic material in the crystals, whereby the acid sites on the internal surface were partly neutralized.

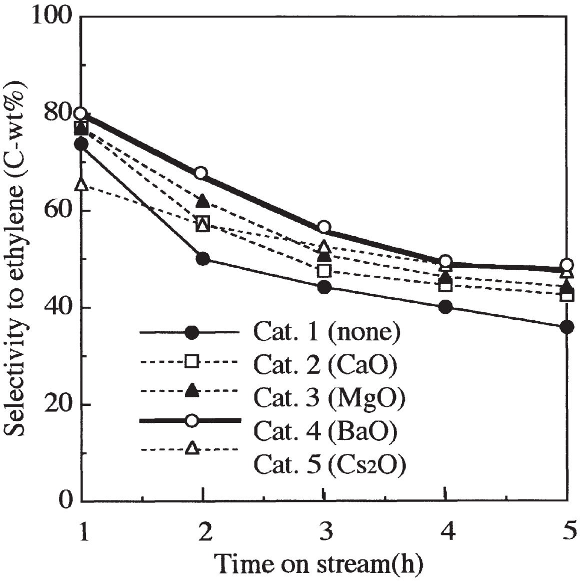


Figure 6. Effect of time on stream on the methanol to ethylene conversion on various Ni-SAPO-34s modified with different basic oxides. Reaction conditions: 15 mol% MeOH, 85 mol% N_2, GHSV 500 h^{-1}, 425 °C.

To estimate the effect of neutralizing acid sites on the external surface, cracking of t-butylbenzene on cat. 4 (BaO) and cat. 1 (no base additive) was carried out. Effect of reaction temperature and time on stream on the conversion are shown in figure 5 (a) and (b), respectively. On both catalysts, the conversion of t-butylbenzene was very low. However, as shown, the conversion of t-butylbenzene on cat. 4 (BaO) was obviously lower than that on cat. 1 (none). The conversion of t-butylbenzene on cat. 1 (none) decreased with an increase in time on stream. These results explain that the acid sites on the external surface of Ni-SAPO-34 crystals was significantly neutralized with BaO ingredient by the mechanochemical method.

3.2. Methanol conversion

Figure 6 shows the changes in ethylene selectivity as a function of time on stream on the catalysts modified with different basic oxides. The modified catalysts exhibited higher selectivity to ethylene and longer catalyst life relative to the unmodified catalyst. Especially when BaO was used as the modifier, this effect was the largest. In table 2, the product distribution for methanol conversion shown in figure 6 is shown. Selectivity to ethylene on both catalysts decreased with increase in time on stream. An important result is the decrease of the yield of over C_5. In consequence, the deactivation was moderated on cat. 4 (BaO) compared with on cat. 1 (none). In particular, it is significant that the prolonged catalytic life with the modified catalysts indicates that the formation of coke on the external surface decreased. On the other hand, selectivity to ethylene with the modified catalysts is always higher

Table 2
Change of the products with an increase of time on stream in methanol conversion on unmodified and modified Ni-SAPO-34s.

Catalyst	Time on stream (h)	Methanol conversion (%)	Distribution of products (C wt%)						
			DME	C_1	C_2–C_4	$C_{2=}$	$C_{3=}$	$C_{4=}$	$C_{5\sim}$
Cat. 1 (none)	1	100	0	6.51	1.92	73.00	11.13	5.24	2.50
	2	100	0	6.34	3.96	56.10	28.36	6.98	4.30
	3	100	0	5.28	3.80	44.70	31.50	11.78	3.44
	4	100	0	6.42	3.67	40.50	34.05	11.33	4.04
	5	94.0	3.52	9.53	3.25	36.70	34.51	8.97	3.52
Cat. 4 (BaO)	1	100	0	3.74	1.29	80.72	10.25	3.81	0.20
	2	100	0	3.54	2.18	67.00	22.96	3.16	1.15
	3	100	0	4.23	3.45	56.10	28.55	6.64	1.74
	4	100	0	5.10	3.73	49.07	30.60	9.31	2.26
	5	100	0	4.12	4.31	47.02	31.25	10.63	2.69

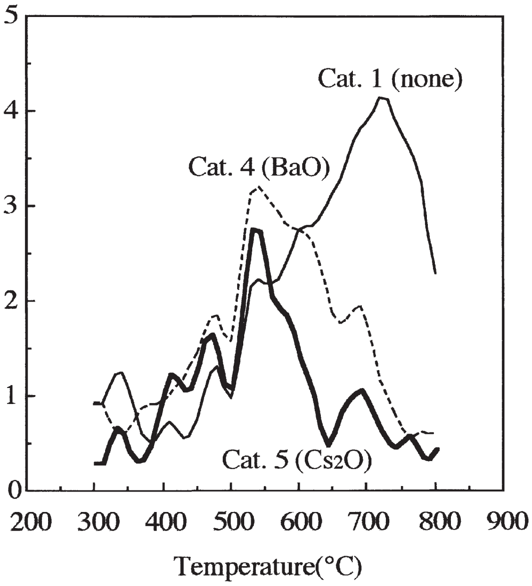


Figure 7. TPO profiles for coke deposited on Ni-SAPO-34 catalysts modified with basic oxides. Reaction conditions: 15 mol% MeOH, 85 mol% N_2, GHSV 500 h^{-1}, 425 °C, time on stream 3 h.

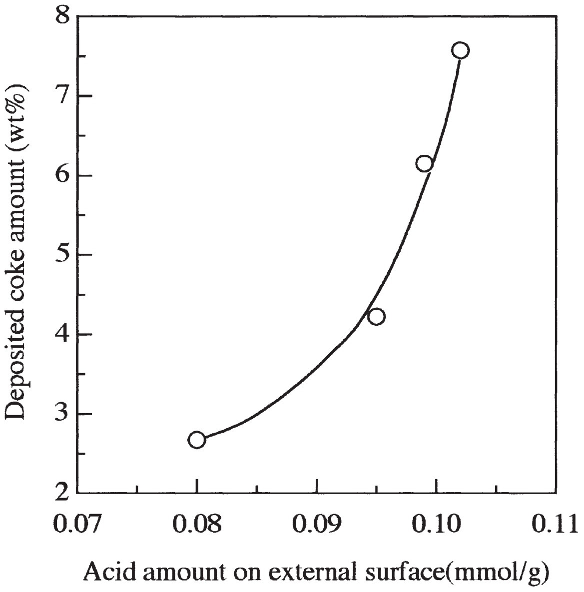


Figure 8. Relation between the deposited coke amount and the acid amount on external surface.

than that over the unmodified catalysts. Ethylene is selectively produced on the internal acid sites due to narrow pore structure [16], while non-selective reaction occurs on the external acid sites. Therefore, the neutralization of the external acid sites increased ethylene selectivity. On both catalysts, ethylene selectivity was decreased with an increase in time on stream. This is ascribed that the pore mouths of the crystal were gradually blocked by coke, and the internal acid sites, which are responsible for selective ethylene synthesis.

After the reaction for 3 h, the amounts of coke deposited on the catalysts were analyzed by TPO and the profiles are shown in figure 7. Compared with unmodified catalyst, the amount of coke deposited on the modified catalysts decreased indicating that the number of acid sites located on the external surface decreased. Furthermore, on the catalysts modified by stronger basic compounds such as Cs_2O, the amount of coke was reduced to half of that of the unmodified catalyst.

In the previous report [16], it was suggested that the deactivation observed on Ni-SAPO-34 crystalline catalysts could be attributed to the coke deposition which occurred on the external surface of the crystals. In fact, as shown in figure 8, the amount of deposited coke is closely related to the acid site concentration on the external surface of crystals.

4. Conclusion

Acid sites on the external surface of Ni-SAPO-34 crystals could be selectively neutralized by the mechanochemical method with basic oxides supported on the microspherical non-porous silica. In methanol conversion, the modified Ni-SAPO-34 catalysts exhibited a higher selectivity to ethylene and longer catalyst life than the unmodified one, corresponding to the decrease of coke formation on acid sites located on the external surface of the crystals.

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