JOURNAL OF CATALYSIS 79, 176–184 (1983)

Effects of Seed Materials on a Zeolite and Its Performance of Methanol Conversion

T. INUI, N. MORINAGA, T. ISHIHARA, T. KANIE, AND Y. TAKEGAMI

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received July 8, 1982; revised September 3, 1982

The effects of highly dispersed, fine powders on the preparation of zeolite catalysts for olefin synthesis from methanol have been studied. The addition of finely ground, preformed zeolite as seed crystals in the zeolite synthetic process resulted in the production of zeolite that had 1/70 the volume of zeolite prepared by standard methodology. Olefin selectivity and the effective lifespan of zeolite catalysts prepared with seed crystals were increased in comparison to catalysts prepared without seed crystals. Similar effects were obtained when finely pulverized alumina was used for zeolite synthesis. Improvements in the selectivity and life are discussed on the basis of various physical properties.

INTRODUCTION

The synthesis of lower olefins from C_1 compounds has gained importance as an alternative method for producing hydrocarbons that are normally obtained by thermal cracking petroleum naphtha. Mobil Oil Co. has developed a new type zeolite catalyst, ZSM-34 (*1*), that catalyzes the production of ethylene and propylene from methanol with high selectivity, more than 75 wt%, but seems to have a short catalytic life due to coke formation (*2*). The Mobil patent technique for producing zeolite catalysts requires relatively large amounts of the conditioning agent for crystallization and also requires long crystallization times at a moderate temperature.

Recently, we have introduced several improvements into the Mobil procedure so that a shorter crystallization time and less conditioning agent are required for the preparation of ZSM-34 type catalysts (*3*, *4*). Using small amounts of tetramethylammonium hydroxide as the crystallization agent, the crystallization time has been shortened to only 2 h at 187°C (*3*); furthermore, by using seed crystals, the catalyst life has been prolonged to twice the normal lifespan. In the present report, we have analyzed the role of seed zeolite and crystallization nuclei upon the preparation of zeolite catalysts and their subsequent performance.

EXPERIMENTAL

Preparation of zeolite. The standard procedure for the preparation of zeolite was as follows: solution A was a 30 wt% (0.32 mol SiO_2) silica-sol solution (cataloid SI 350, Shokubai Kasei Co.). Solution B was a mixture of 6.6 g NaOH (0.17 mol), 2.3 g KOH (0.040 mol), 2.8 g $NaAlO_2$ (0.034 mol), 1.4 g tetramethylammonium hydroxide (TMAH) (0.016 mol), and 45 g H_2O (2.5 mol). While vigorously stirring solution B in an ice bath with a Homo-Mixer (Tokushuki Kako Kogyo Co.) at ca. 6000 rpm, 65 g of solution A was added.

The molar ratios of the formed gel mixture were Si/Al = 9.4, (Na + K)/Al = 7.18, and K/(Na + K) = 0.19. The mixture was then heated for 2 h at 187°C in an autoclave. The formed zeolite was washed with water, dried at 110°C, and calcined at 540°C for 3.5

0021-9517/83/010176-09$03.00/0

h under an air stream. The zeolite catalyst was used without further treatment.

Preparation of zeolite in the presence of seed materials. Seed materials were prepared by separately grinding the following materials in an agate mortar: preformed zeolite, prepared as mentioned above, a 1 : 3 w/w mixture of γ- and α-alumina powders, Linde MS-5A, active carbon, magnesium oxide, and an ion-exchange resin, Amberlite IRA-400 (Organo Co.). Each seed material was suspended in solution B prior to the addition of solution A. Preparation of zeolite with seed crystals was carried out at a 1/10 scale of the standard method; mixing was done manually.

Reaction procedure. Methanol conversion was carried out in an ordinary flow reactor at atmospheric pressure. A 150 mg, ca. 0.2 cm^3, portion of pulverized catalyst was packed into a Pyrex tublar reactor, inner diameter 5 mm. Diluted methanol vapor, methanol 12 mol%, N_2 88%, was passed through the catalyst bed at 400°C with a gas space-velocity of 1000 h^{-1}. The gaseous products were analyzed by an FID gas chromatograph.

Characterization of zeolite. The crystalline shapes of the zeolite were observed with a Hitachi-Akashi scanning electron microscope, MSM-102, with magnification ranges of 1,000 ~ 30,000. BET surface areas were measured with using a Shimadzu micro-TG-20 by a continuous flow method using He as the carrier gas and one-point method of N_2 adsorption at liquid-nitrogen temperature. X-Ray diffraction patterns were obtained with a Rigaku Denki Geigerflex-2013. Thermogravimetric analysis of noncalcined zeolite was carried out in an air stream using a Rigaku Denki TG-DSC-8002. Adsorption at 20 ~ 30°C and desorption at 80°C of *n*-hexane and iso-pentane were carried out by a continuous flow method using a Shimadzu micro TG-20 equipped with a gas-flow controlling system. Effective diffusivity was calculated from a linear plot of the desorption rate versus log of the elution time (*5*).

RESULTS AND DISCUSSION

Change in Catalytic Activity during Methanol Conversion

Methanol was converted to hydrocarbons using catalysts prepared by the standard method at a reaction temperature of 400°C. The product distribution during the course of the reaction is shown in Fig. 1. As the reaction proceeded, the rate of production of olefins such as ethylene, $C_{2=}$, propylene, $C_{3=}$, and butene, $C_{4=}$, increased gradually; but the rate of methane, C_1, production did not change. The rates of paraffin production, propane, C_3, and butane, C_4, tended to decrease during the reaction period. After about 3.5 h, the formation of olefins decreased suddenly, and formation of dimethylether, DME, was observed; furthermore, the rate of decrease in hydrocarbon formation at this time, 3.5 h, was somewhat dependent upon the carbon number of the respective olefin product (Fig. 1). The decrease in C_4 olefin production was almost immediate after 3.5 h of reaction; the decrease in C_2 and C_3 olefins was more gradual. However, there was little or no change in methane formation after 3.5 h of reaction. In view of the fact that the color of the catalyst changed from white to gray ~ gray-

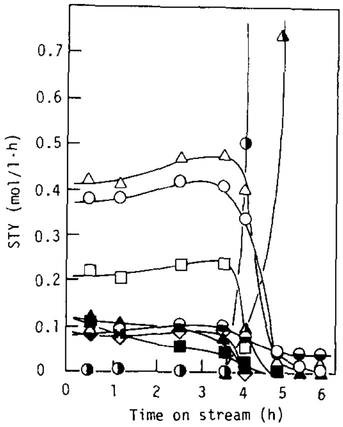


FIG. 1. Change in space–time yields on the nonseeded zeolite with time on stream. △, C_3H_6; ○, C_2H_4; □, C_4H_8; ▲, C_3H_8; ■, C_4H_{10}; ◒, CH_4; ⬘, $C_{5<}$; ◑, DME; **Δ**, CH_3OH.

TABLE 1

The Effect of the Amount of Seed Crystals Added on the Total Amount of Each Hydrocarbons Yielded

Seed crystals added (wt%)	Product yield (mol/liter)								ΣHC (mol/liter)	RC (mol/liter)	Catalyst life[a] (h)
	C_1	$C_{2=}$	C_3	$C_{3=}$	C_4	$C_{4=}$	$C_{5<}$	$C_2 \sim C_4$ olefins			
0	0.39	1.54	0.40	1.73	0.28	0.86	0.31	4.13	5.51	2.3	6.0
2.3	0.78	2.92	0.75	3.33	0.26	1.91	0.74	8.16	10.69	3.2	8.0
4.5	0.69	2.26	0.21	3.52	0.17	2.18	0.88	7.96	9.91	4.3	8.0
9.0	0.95	2.81	0.13	4.09	0.13	2.83	1.03	9.73	11.97	3.9	11.0
18.2	0.91	3.15	0.46	3.37	0.32	1.97	0.69	8.49	10.87	3.3	7.0

[a] Time until the beginning of DME formation.

black and also in view of the above mentioned changes in the product distribution over the duration of the reaction, it can be suggested that the gradual accumulation of carbonaceous matter blocked the pores of the catalyst and eventually caused a rapid decrease in catalytic activity. Formation of DME, which is an intermediate product of methanol to hydrocarbon conversion, began to decrease after 5.5 h on the catalyst surface indicating an almost total inhibition of catalytic activity due to carbon deposition. The increase in olefin selectivity and the decrease in paraffin selectivity seen after about 2 h of reaction can also be attributed to the blockage of pores within the zeolite particles due to carbon deposition.

The amount of residual carbon, RC, that had accumulated on the catalyst surface after 5.5 h of reaction was 18 mol/liter of catalyst. When the RC was removed by burning in an air stream at 500°C, the activity of the catalyst was completely restored. Such a tendency for deactivation was observed for all catalysts examined. The total amount of each hydrocarbon produced [$\Sigma C_{2=}$ (mol/liter) with total amount of ethylene] and the amount of total hydrocarbons produced per unit volume of catalyst up until the beginning of DME formation [ΣHC (mol/liter) for the total amount of all hydrocarbons] have been defined as the effective catalyst life per cycle.

Effects of Seed Crystals on Catalyst Formation and Performance

When catalysts were prepared in the presence of zeolite seed crystals as de-

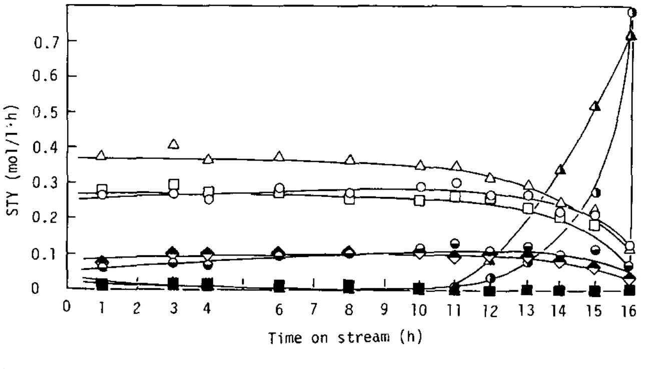
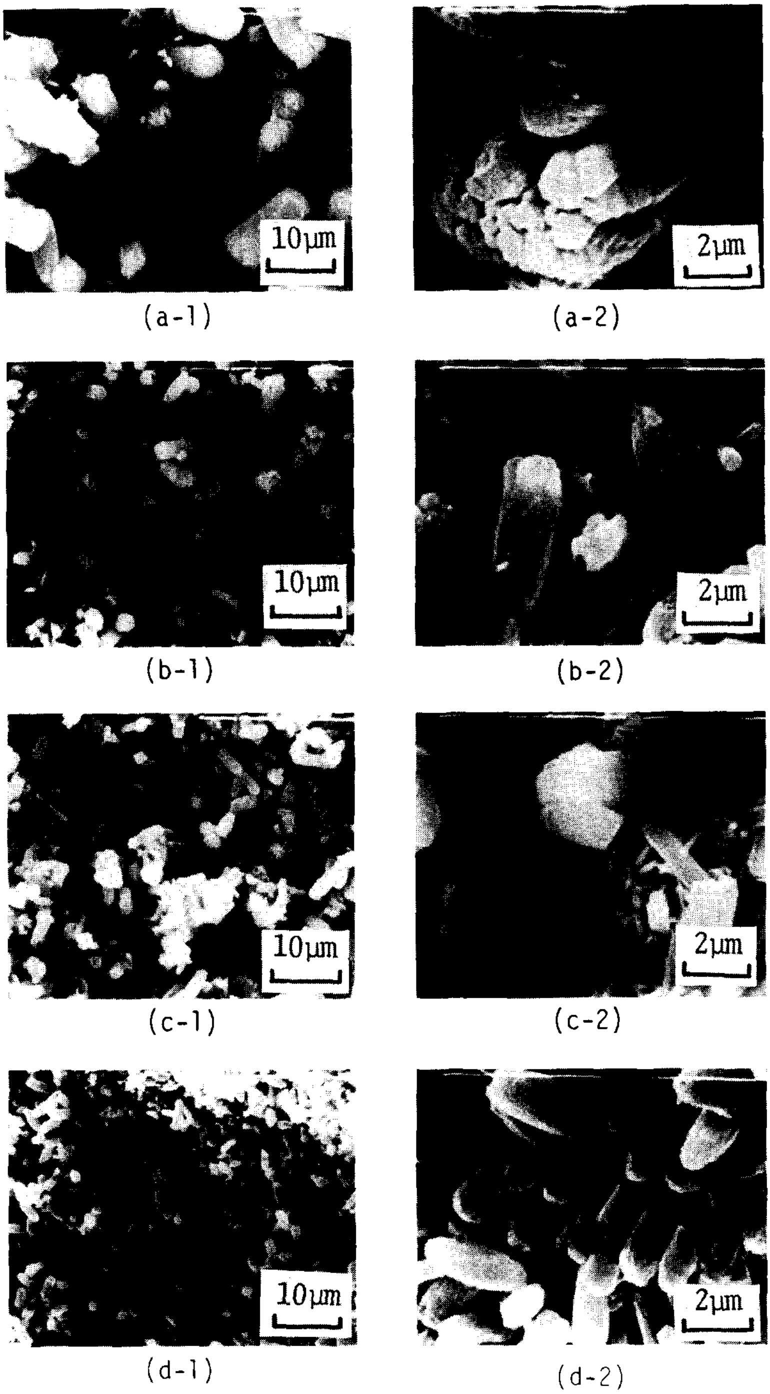


FIG. 2. Change in space–time.yields on the seeded zeolite with time on stream. △, C_3H_6; ○, C_2H_4; □, C_4H_8; ▲, C_3H_8; ■, C_4H_{10}; ◒, CH_4; ◈, $C_{5<}$; ◑, DME; Δ, CH_3OH.



(a-1) (a-2)

(b-1) (b-2)

(c-1) (c-2)

(d-1) (d-2)

FIG. 3. Scanning electron micrographs of seeded and nonseeded zeolites. Seed crystals added (wt%): (a) 0; (b) 2.3; (c) 4.5; (d) 9.0.

scribed in the experimental section, the resulting catalysts had longer effective lifespans; moreover, olefin selectivity was increased in comparison to the olefin selectivity of catalysts prepared without seed crystals (Table 1 and Fig. 2). Maximum lifespan and maximum olefin selectivity were obtained when catalysts were prepared in the presence of 9 wt% seed zeolite, however, both lifespan and olefin selectivity were decreased when more than 9 wt% seed zeolite was added to the crystallization solution. The amount of RC was increased in the catalysts prepared with seed crystals resulting in prolonged catalyst lifespans. The increased capacity for carbon deposition may be explained by the increase in total outer surface area of the catalysts. As can be seen in the scanning electron micrographs (Fig. 3), when seed zeolite had been added, small, cylindrical zeolite of uniform size was obtained; and each small cylindrical particle seems to have been composed of fine, stick-shaped crystals. The sizes of zeolites prepared by the addition of various amounts of seed zeolite to the zeolite crystallization solution are shown in Fig. 4. Size was calculated assuming a cylindrical shape. The size of cylindrical zeolite particles prepared by the addition of 9 wt% seed crystals to the crystallization solution was about 1/70 of the size of crystals of nonseeded zeolite. The size of the individual, stick-shaped crystals of the seeded zeolite was also smaller than that of nonseeded zeolite. When catalysts were prepared in the presence of 18 wt% of seed crystals, various shapes and size of zeolite were obtained; however, the average size of formed crystals did not change from those of zeolite formed in the presence of 9 wt% seed crystal. BET-surface areas for seeded and nonseeded zeolites differed only to a minor degree (Fig. 4). The amounts of adsorption n-hexane were clearly decreased for zeolite formed with seed crystals; however, the effective diffusivity for n-hexane was increased for zeolite formed with seed crystals (Fig. 5). These facts suggest that zeolite formed in the presence of seed crystals had smaller pore diameters and shorter pore lengths.

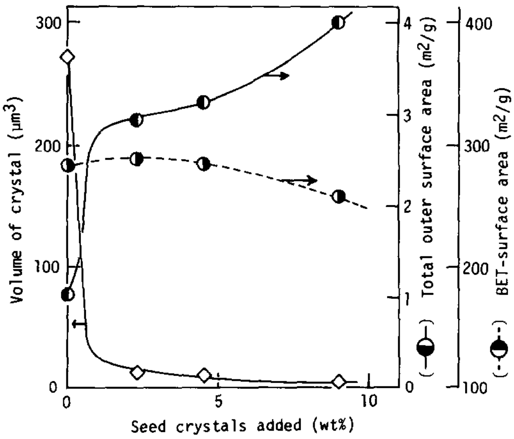


FIG. 4. Change in size of zeolites with the amounts of seed crystals.

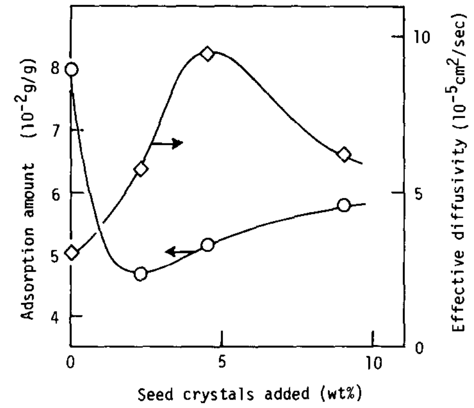


FIG. 5. Change in adsorption and diffusion of n-hexane for zeolites with the amounts of seed crystals.

Figure 6 show diagrams of differential thermogravimetric analyses for zeolites formed with and without seed crystals. The low- and high-temperature peaks correspond to dehydration of zeolite crystal and burning off of TMAH, respectively. The dehydration rate of seeded zeolite was larger compared with that for nonseeded zeolite indicating that dehydration proceeded more smoothly with smaller sized crystals.

The X-ray diffraction patterns (XRD) of the zeolites described in this study and that

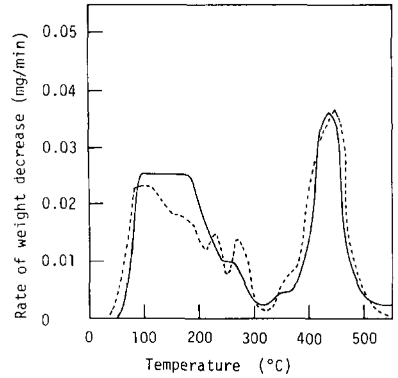


FIG. 6. TG profile for seeded and nonseeded zeolites. Solid line, seeded; dotted line, nonseeded.

of ZSM-34 (*1*, *2*) are compared in Fig. 7. XRD of zeolites prepared in the presence of 9 wt% seed crystals are clearly different from those of ZSM-34 as well as those from other zeolites prepared without seed crystals. These results are interpreted to mean that a crystalline structure different from that of ZSM-34 had been formed due to a greatly increased crystallization rate and differences in the ratio of incorporated silica and alumina by virtue of the combination of the crystallization conditions of our previous report (*3*) and the use of seed crystals. The XRD of the zeolite with 9 wt% addition of seed crystals has the feature of offretite mixed with small amounts of sodalite, and differs not only from the XRD of ZSM-34 but also those of T (*6*), ZX-4 (*7*), Fu-1 (*8*), Nu-1 (*9*), and ZSM-4 (*10*) which have been synthesized using TMAH.

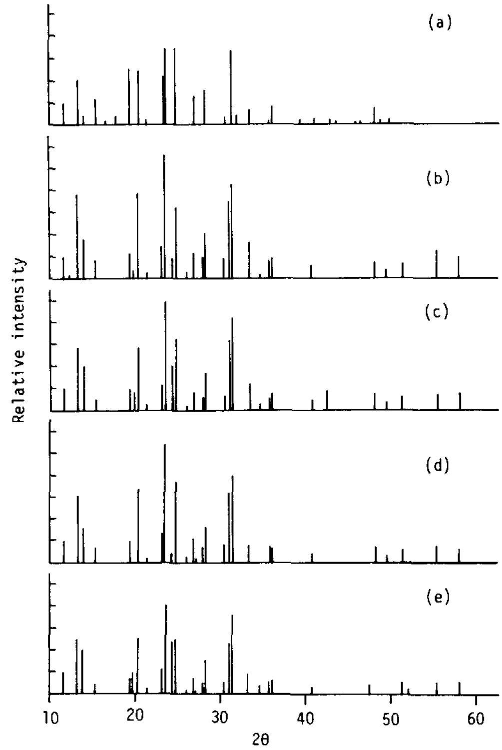


FIG. 7. X-Ray powder diffraction patterns for ZSM-34 and the seeded and nonseeded zeolites. (a) ZSM-34, seed crystals added (wt%): (b) 0; (c) 2.3; (d) 4.5; (e) 9.0.

Effects of Alumina Powder Addition on the Crystallization of Zeolite

A finely pulverized mixture of one part γ-Al_2O_3, 0.2 μm in size, and three parts α-Al_2O_3, 1 μm in size, was added as a skeletal material before crystallization. As presented in Table 2, catalyst performance

TABLE 2

The Effect of the Amount of Alumina Powder Added on the Total Amount of Each Hydrocarbons Yielded

Alumina powder added (wt%)	Product yield (mol/liter)								ΣHC (mol/liter)	BET surface area (m²/g)
	C_1	$C_{2=}$	C_3	$C_{3=}$	C_4	$C_{4=}$	$C_{5<}$	$C_2 \sim C_4$ olefins		
0	0.33	1.81	0.46	2.37	0.34	1.39	0.54	5.57	7.24	243
18	0.55	3.00	1.59	3.75	0.68	2.14	0.84	8.89	12.55	249
36	0.41	2.72	0.78	2.97	0.56	1.49	0.52	7.18	9.45	206
87.5	0.09	0.58	0.17	0.78	0.14	0.38	0.11	1.74	2.25	102

TABLE 3

Catalyst Performance for Typical Catalysts

Preparation method	Product selectivity (mol %)								ΣHC^{a} (mol/liter)	RC^{b} (mol/liter)
	$C_{2=}$	$C_{3=}$	$C_{4=}$	$C_2 \sim C_4$ olefins	C_1	C_3	C_4	$C_{5<}$		
Choline chloride 100°C, 131 day[c]	32.5	20.5	11.0	64.0	21.3	9.9	4.9	0	6.16	1.8
TMAH[d], 187°C, 2 h	27.9	31.4	15.6	74.9	7.1	7.3	5.1	5.6	5.51	2.3
TMAH, 187°C, 2 h +seed crystals[e]	23.5	34.2	23.6	81.3	7.9	1.1	1.1	8.6	11.97	3.9
TMAH, 187°C, 2 h +(γ- and α-alumina)[f]	23.9	29.9	17.1	70.9	4.4	12.7	5.4	6.7	12.55	3.6

[a] Total amount of all hydrocarbons produced up until the beginning of DME formation.

[b] Residual carbon accumulated up until deactivation.

[c] Prepared according to ZSM-34 produce.

[d] 1/15 molar ratio to alkali.

[e] 9 wt% addition.

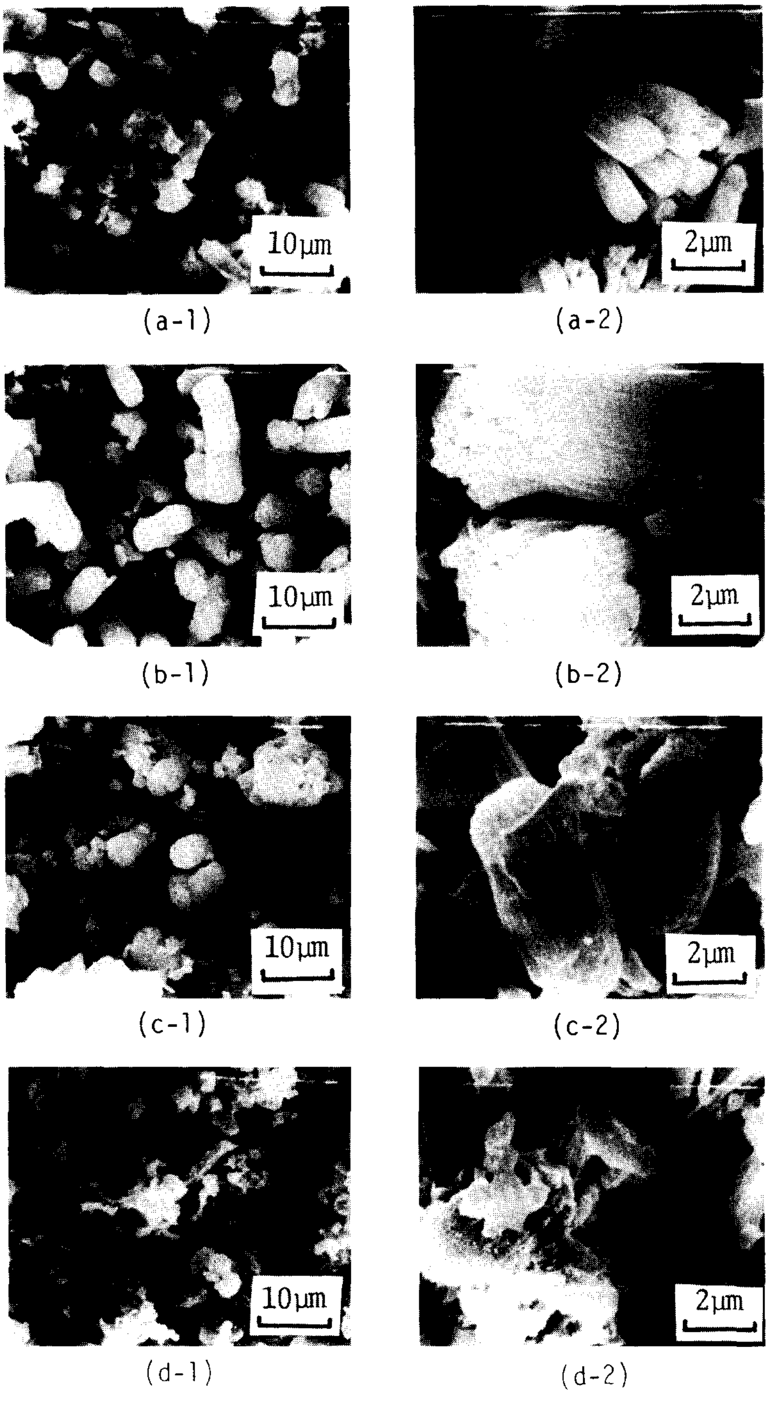
[f] 18 wt% addition.

(ΣHC) was maximized by the addition of about 18 wt% alumina to the zeolite crystallization solution. Compared with nonseeded catalysts from ESM photographs shown in Fig. 8, this catalyst had small, uniform crystals (Fig. 8); however, when larger amounts of alumina powder were added, the formed catalyst became nonuniform, and catalytic activity was greatly decreased (Table 2). BET surface areas of these catalysts were larger than that of nonseeded catalysts demonstrating good correlation between BET surface area and catalytic activity (Table 2). In Table 3, the performance of catalysts prepared with 18 wt% alumina was compared with that of catalysts prepared with 9 wt% seed crystals. Both catalysts had extended lifespans in comparison to catalysts prepared by the standard (Mobil) formula; however, catalysts prepared with 18 wt% alumina retained the high paraffin selectivity of the standard catalyst. A combination of 9 wt% alumina plus 8 wt% seed crystals in the preparation of zeolite yielded catalysts whose overall performance was no better than that of catalysts prepared with alumina alone. The addition of MgO, active carbon, MS-5A, or Amberlite IRA-400 at 8 wt% to catalyst preparations did not produce any

TABLE 4

The Effect of the Kind of Seed Material on the Total Amount of Each Hydrocarbon

Seed material	Product selectivity (mol%)								ΣHC (mol/liter)
	C_1	$C_{2=}$	C_3	$C_{3=}$	C_4	$C_{4=}$	$C_{5<}$	$C_2 \sim C_4$ olefins	
MgO	13.1	32.1	5.9	29.8	3.6	11.9	3.6	73.8	8.4
Active carbon	12.3	32.1	4.9	30.9	2.5	12.4	4.9	75.4	8.1
MS-5A	12.5	29.2	2.8	33.3	1.4	15.3	5.5	77.8	7.2
IRA-400	11.2	34.6	5.6	28.0	2.8	13.1	4.7	75.7	10.7



(a-1) (a-2)

(b-1) (b-2)

(c-1) (c-2)

(d-1) (d-2)

FIG. 8. Scanning electron micrographs of zeolites prepared by adding and nonadding alumina powder. Alumina powder added (wt%): (a) 0; (b) 18; (c) 36; (d) 88.

noticeable affects toward catalyst performance in comparison to nonseeded catalysts (Table 4).

CONCLUSION

The addition of 9 wt% seed zeolite or 18 wt% of a mixture of γ- and α-alumina powder to the standard materials for zeolite synthesis produces marked affects on the size and uniformity of the resulting zeolite crystals. The added seed zeolite or alumina appears to serve as crystallization nuclei that promote the formation of small, uniform crystals. Such zeolite catalysts show high olefin selectivity and extended effective lifespans compared with standard zeolite catalysts. These results demonstrate the significance of crystal size and uniformity on catalytic performance and provide practical and effective methods for regulating the shape of zeolite catalysts.

REFERENCES

1. Rubin, M. K., Rosinski, E. J., and Plank, C. J., U. S. *Pat.* 4,086,186 (1978).
2. Mobil Oil Co., *Japan. Pat. Appl. Disclosure* 58499 (1978).
3. Inui, T., Ishihara, T., and Takegami, Y., *J. C. S. Chem. Commun.* 936 (1981).
4. Inui, T., Ishihara, T., Morinaga, N., and Takegami, Y., *React. Kinet. Catal. Lett.* **19,** 71 (1982).
5. Inui, T., Komatsu, K., and Nagase, S., *J. Chem. Soc. Japan* 820 (1977).
6. Breck, D. W., and Acara, N. A., U.S. *Pat.* 2,950,952 (1960).
7. Kerr, G. T., and Kokotailo, G. T., *J. Amer. Chem. Soc.* **83,** 4675 (1961).
8. ICI, *Japan Pat. Appl. Disclosure* 58500 (1978).
9. ICI, *Japan Pat. Appl. Disclosure* 145399 (1977).
10. Perrotta, A. J., Kibby, C., Mitchell, B. R., and Tucci, E. R., *J. Catal.* **55,** 240 (1978).