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The Synthesis, Characterization, and Catalytic Activity of Omega and ZSM-4 Zeolites

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The zeolites omega and ZSM-4 were both synthesized in the $[(CH_3)_4N]_2O$–Na_2O–Al_2O_3–SiO_2–H_2O system at a temperature of 95°C. Although the starting reagents and synthesis procedures are different, the omega and ZSM-4 zeolites, on the basis of X-ray diffraction, have similar aluminosilicate structures. In the omega synthesis, a faujasite → omega reconstructive transition was discovered. No such transition was found in the ZSM-4 synthesis. Adsorption measurements show that omega zeolite rapidly adsorbs cyclooctatetraene but not $(C_4F_9)_3N$. Acid catalysts derived from omega exhibit high α values for cracking of *n*-hexane. Hydrogen and lanthanum forms of omega and cocrystallized omega and faujasite show an increase in catalytic cracking activity with an increase in faujasite content. Comparative studies between omega and ZSM-4 catalysts show a slightly higher catalytic cracking activity for omega zeolite.

INTRODUCTION

In 1970, Aiello and Barrer (*1*) revealed their synthesis of the zeolite they called omega. This zeolite was crystallized in the mixed-base system, Na_2O–$[(CH_3)_4N]_2O$–Al_2O_3–SiO_2–H_2O by holding the gel at a temperature of 80°C for 7 days. The decision to synthesize the omega zeolite for catalytic evaluation was because of Flanigen's disclosure (*2*) that the omega zeolite was capable of adsorbing perfluorotributyl amine, $(C_4F_9)_3N$, which means that it has an aperture size greater than 1.1 nm. It was felt that the omega zeolite with its larger aperture size would be able to process heavier feedstocks that contained molecules too large to enter the faujasite framework but which could possibly enter the omega framework. The purpose of this paper is to give results on the synthesis, characterization, and activity measurements on catalysts based on the omega system. Additional data are also given on the zeolite, ZSM-4.

EXPERIMENTAL

The starting reagents for the omega synthesis were Ludox AS as a source of silica, sodium aluminate, and a 25 wt% solution of tetramethylammonium hydroxide in water. The starting gel composition is 3.2 $Na_2O : 0.8\,[(CH_3)_4N]_2O : Al_2O_3 : 10\,SiO_2 : 160\,H_2O$. The gels were heated in polypropylene bottles at 95°C for varying time lengths. The ZSM-4 synthesis was performed using different starting reagents than those used for the omega synthesis; the starting reagents were N-brand sodium silicate

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TABLE 1

Batch Requirements for Omega Synthesis

Starting solutions:		
1. Ludox AS	200 g	
2. $Na_2O–Al_2O_3–3H_2O$	21.8 g	in 104 ml of H_2O
NaOH	17.6 g	
3. $(CH_3)_4NOH$ (25% sol)	58.8 g	

Steps:

1. Add 3 to 2, which gives a clear solution.
2. Add 2, which gives instantaneous gelling.
3. Place gel in polypropylene bottle and heat at 95°C.

$3.2\ Na_2O:0.8\ [(CH_3)_4N]_2O:Al_2O_3:10SiO_2:106H_2O$

(8.9 wt% Na_2O, 28.7 wt% SiO_2), tetramethylammonium chloride, aluminum sulfate, and sulfuric acid. This synthesis required vigorous shaking every couple of hours to aid the crystallization. The gel composition is $0.427\ [(CH_3)_4N]_2O:8.99\ Na_2O:Al_2O_3:17.2\ SiO_2:328\ H_2O:0.128\ Cl^-:0.397\ SO_4^{2-}$. Crystallization of the gels was done at 95°C. Typical synthesis procedures for the omega and ZSM-4 zeolites are given in Tables 1 and 2, respectively.

The acid forms of both zeolites were obtained by first decomposing the tetramethylammonium ions by heating the zeolites to 500°C, followed by ammonium or lanthanum exchange for the sodium ions. The ion exchanges were done at 80°C using 1 *M* chloride solutions for a period of 4 hr. At least two 4-hr periods were used for each catalyst preparation.

Sorption capacities were measured chromatographically in 100 $cm^3/g/min$ He or H_2 carrier at about 125 kPa. Hexane, cyclohexane, benzene, and cyclooctatetraene were adsorbed at ambient temperature and 1 to 3 kPa partial pressure. Perfluorotributylamine was adsorbed at 80°C and 0.07 kPa. Pulsed and continuous flow injections of adsorbate gave essentially the same results. They were continued until at least 0.05 ml/g was passed over the zeolite and at least 99% breakthrough of the adsorbate. Consequently, adsorption rates below 10^{-5} ml/g/min (for PFTBA) or about 5×10^{-5} ml/g/min (for the hydrocarbons) were not measured. The sorption capacities reported are for rapid and largely irreversible adsorption.

Catalysts formed from the acid zeolites were tested for catalytic activity in *n*-hexane cracking using a continuous flow quartz reactor. The tests were made at atmospheric pressure in a flow of 60 $cm^3/g/min$ hydrogen to which a flow of 5.6 μl (liquid)/g/min of 99.99% *n*-hexane was added. The products were analyzed on a capillary squalane column gas chromatograph. A first sample of the effluent was taken at 5 min after the start of the hexane flow; the cracking rate constant at that point was used to calculate an α value (the rate constant relative to that of a standard silica-alumina). The sampling was continued at 15-min intervals so that a comparison of aging rates could be made. Most runs were done at 400°C with additional runs done at other temperatures to provide an indication of diffusion effects.

A modified microactivity test unit (MAT) was used to evaluate all catalysts. This unit is similar to the original MAT unit designed by Henderson and Ciapetta (*3*), except that feed is injected through a

TABLE 2

Batch Requirements for ZSM-4 Synthesis

Solutions:		
1. $Al_2(SO_4)_3–18\ H_2O$	99.9 g	
H_2SO_4 (96% sol)	25.2 g	
H_2O	195.7 g	
2. N brand sodium silicate solution[a]		540 g
NaOH (50% sol)		142 g
H_2O		268 g
$(CH_3)_4NCl$ (50% sol)		28 g

Steps:

1. Add solution 1 to solution 2 and mix resulting thick gel in Waring Blender for 1 min.
2. Place gel in polypropylene bottle and heat at 95°C.

$9Na_2O:0.43[(Ch_3)_4N]_2O:Al_2O_3:17.2SiO_2:328H_2O(0.13\ Cl^-,\ 0.4SO_4^{2-})$

[a] N brand sodium silicate solution: ratio, 3.22; Na_2O, 8.90%; SiO_2, 28.7%.

hypodermic needle permanently mounted in the reactor head and the liquid product recovery is established by weighing instead of volumetric measurements. A Kuwait gas oil with a boiling range of 260 to 427°C was used as feed. The catalyst charge was 2.5 g of 10- to 20-mesh-sized granules. All catalysts were formed identically by pressing 10 cm^3 of powder in a 1-in. die at 55 MPa (8000 psi) and then broken and sized by passing through sieves. In this manner uniformity of catalysts was ensured and skin effects were minimized. Other reaction conditions were: 482°C, 80-sec catalyst contact time, 14 WHSV, and a total feed throughput of 1 cm^3. Prior to testing but after forming, all fresh catalysts were either pretreated to simulate equilibrium catalysts or subjected to a 538°C calcination. The pretreatment consisted of a heat shock treatment at 593°C for 1 hr followed by a 10-hr steam purge at 732°C at atmospheric pressure with 100% steam. Zeolites were tested either in the pure form without dilution or after mixture with a halloysite matrix (85% by weight).

TABLE 3

Chemical Analysis of Omega and ZSM-4 Zeolite

Oxide (wt%)	Omega	ZSM-4
Al_2O_3	16.66	14.70
SiO_2	57.50	54.01
Na_2O	7.28	7.82
$[(CH_3)_4N]_2O$	5.84	6.14
H_2O	11.52	16.56
Total	98.80	99.23

RESULTS AND DISCUSSION

Preparation and Characterization

The chemical analyses of a typical omega and ZSM-4 preparation performed by Tom Garland of Gulf's analytical division are given in Table 3. The final chemical formula for the omega and ZSM-4, respectively, are:

$$\text{Omega}: 0.75\ Na_2O:0.25[(CH_3)_4N]_2O:Al_2O_3:6.01\ SiO_2:4H_2O$$

$$\text{ZSM-4}: 0.92\ Na_2O:0.28[(CH_3)_4N]_2O:Al_2O_3:6.43\ SiO_2:6.56\ H_2O$$

TABLE 4

Phase Data on Faujasite-Omega Transition

Catalyst	Time (days)	Phases present
APZ 3-97	10	Omega + (Faujasite)
APZ 3-97	0.5 hr, 400°C	Omega + (Faujasite)
APZ 3-98	10	Faujasite + Omega + (Unknown 1)
APZ 3-98	0.5 hr, 400°C	Faujasite + Omega + (Unknown 2)
APZ 3-99	4	Omega + (Faujasite)
APZ 3-99	6	Omega
APZ 3-100	4	Omega + Faujasite
APZ 3-100	6	Omega
APZ 4-6	6	Omega
APZ 4-6	8	Omega
APZ 4-13	3	Faujasite + Omega + (?)
APZ 4-14	2	Faujasite + Omega + (?)
APZ 4-15	2	Faujasite + Amorphous
APZ 4-15	3	Faujasite + Omega + (?)
APZ 4-16	3	Faujasite + Omega
APZ 4-16	6	Omega + (Faujasite)
NH 2-8 (APZ 3-100)	0.5 hr, 350°C	Omega
NH 2-8 (APZ 3-100)	0.5 hr, 500°C	Omega
NH 2-8 (APZ 3-100)	TGA to 970°C	Amorphous

TABLE 5

Omega Zeolite—Adsorption Capacities

Capacity of virgin crystals (no exchange) (ML/G)			
Calcination temperature (°C)	400	500	550
Hexane	0.004_3	0.004_6	0.005_6
Capacity after one exchange (ML/G)			
Calcination temperature (°C)	180	500	550
Hexane	0.022		
Benzene		0.036	0.049
C_8H_8			0.021
PFTBA			0.003
Cyclohexane		0.006	0.030
Capacity after two exchanges (ML/G)			
Calcination temperature (°C)	180	500	550*
Benzene			0.020
PFTBA			0.003

The excess alkali in the ZSM-4 may be due to incomplete washing of the sample. The ZSM-4 zeolite has a slightly higher silica content than the omega zeolite.

The phase data on the synthesis of omega zeolite are given in Table 4. The initial preparation crystallized over a 10-day period gave a high yield of omega zeolite with a detectable amount of a second phase. This second phase, isolated in subsequent experiments, was shown to be a faujasite-type zeolite. The phase data show that, initially, faujasite crystals separate from the gel and then slowly transform to omega-type zeolite over a period of a few days. Consideration of the crystal structure of the isostructural zeolite, mazzite, determined by Rinaldi *et al.* (*4*) shows the structure to be built from gmelinite cages. The growth of omega from the faujasite crystals has to be by the (at least) partial breakdown of the sodalite cage in faujasite containing 6- and 4-membered rings of tetrahedra to give the gmelinite cage which contains 8-, 6-, and 4-membered rings of tetrahedra. Pure omega-type zeolite can be crystallized at 95°C over a period of 6 days, which is about 2 days less than that given by Aiello and Barrer (*1*). Cocrystallized omega and faujasite are stable to at least 400°C in the sodium tetramethylammonium form. Pure omega, in the ammonium form, is stable to at least 500°C. When heated to 970°C (during thermogravimetric analysis), the pure omega zeolite in the hydrogen form decomposed to an amorphous state.

The adsorption capacities for an omega zeolite catalyst are given in Table 5. The adsorption results show that *n*-hexane is easily adsorbed after calcination to only 180°C when the zeolite is in the hydrogen form. The virgin crystals, in the Na–$(CH_3)_4N$ form, do not adsorb much *n*-hexane after calcination to much higher temperatures. The hydrogen form can adsorb benzene and a substantial increase in the benzene adsorptivity occurs after calcination in oxygen at 550°C. The omega structure, after the second ion exchange, apparently loses some crystallinity as shown by a decrease in the benzene adsorptivity. The loss of crystallinity is not detectable in the X-ray diffraction analysis, which shows the crystal structure to be stable to 550°C after the adsorption measurement. The omega structure is also able to adsorb 0.021 ml/g of cyclooctatetraene after calcination to 550°C. In no case did the omega zeolite rapidly adsorb the molecule, $(C_4F_9)_3N$ (PFTBA), which has a molecular size of about 1.1 nm. Flanigan (*2*, *8*) found considerable adsorption of PFTBA by omega zeolite at elevated temperatures in a clean vacuum system. The difference in our experiments may be due to the carrier gas

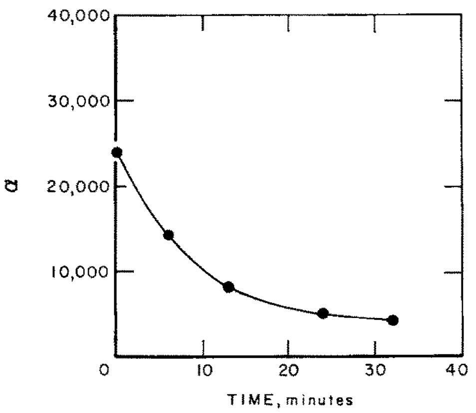

FIG. 1. Aging of H-omega zeolite during hexane cracking at 400°C.

TABLE 6

Catalytic Cracking with Omega–Faujasite System

A. Synthetic hexadecane/triethylbenzene feed

Catalyst	Conversion	
	Fresh	Steamed
H-Faujasite	100	81
H-(Faujasite + Omega)	100	62
H-Omega	54	20
H-(ZSM-4)	42	—
H, La-(ZSM-4)	44	14

	% conversion	H/B[a]	Coke	H_2
H-Omega, fresh	67	0.96	6.7%	0.16%
H-(ZSM-4) fresh	48	0.92	4.1%	0.10%

B. Kuwait gas oil feed

Catalyst, 25% in halloysite matrix	Fresh, % conversion	Steamed		
		% conversion	% gasoline	% coke
La-(Faujasite + Omega)	79	61	34	4.4
La-(Omega + Faujasite)	51	35	21	1.2
La-(Omega + Faujasite)	50	29	20	1.1
La-Omega	27			
H, La-Omega	21			

[a] Conversion ratio of hexadecane to triethylbenzene (7:3 in feed).

which was already present in the zeolite pores before injection of the PFTBA.

Activity Measurements

The α values for n-hexane cracking at 400°C in H_2 were initially about 10 times higher for H-omega zeolite than the H-faujasite prepared in the same system. They varied by about an order of magnitude depending on the degree of sodium ion exchange (below about 1% Na_2O). As shown in Fig. 1, the activity of H-omega zeolite declined rapidly with time. It could be restored by calcination in air or oxygen, so the decline was probably due to coking. The initial activity was almost as high at 300°C, indicating severe diffusional limitations.

Results of catalytic cracking tests with a 70% hexadecane–30% triethylbenzene blend and with a Kuwait gas oil are shown in Table 6. The cracking activity increased with faujasite content in the omega-faujasite system for both hydrogen and lanthanum forms of the zeolites. The aging of omega must be faster, relative to faujasite, in the absence of H_2. The ZSM-4 catalysts were slightly less active than the omega zeolite catalysts, perhaps due to a larger crystallite size. In one test where the ammonium ion-exchange conditions were kept constant, H-omega gave a higher conversion, more coke, and more H_2 from the blend than H-(ZSM-4). Neither was selective for cracking hexadecane or triethylbenzene. All of the catalysts had lower activities after steaming at 732°C. The decreases were comparable for faujasite, omega, and ZSM-4. However, only

50% of the activity was lost by lanthanum-exchanged forms dispersed in halloysite, while about 75% was lost by the hydrogen forms when they were steamed.

The lanthanum forms of omega zeolite were analyzed by X-ray fluorescence. They contained 15% La_2O_3, slightly below the 15.8% La_2O_3 expected for pure lanthanum omega. The sodium content was less than 1% Na_2O but was not known very accurately for these or any of the hydrogen forms tested.

Comparison of Ω with ZSM-4

The mole ratios of oxides in the omega and ZSM-4 synthesis for our preparations and that of Mobil (*5*) and Union Carbide (*2*) are given in Table 7. The mole ratios of oxides for the patented zeolites, omega and ZSM-4, show considerable overlap in the range of compositions covered for the growth of these zeolites. More specifically, our ZSM-4 formulation has a much higher SiO_2/Al_2O_3 ratio than the omega formulation. In addition, the total amount of base exchange ions to silica ratio is higher for ZSM-4 than for the omega synthesis. Although the total concentration of base is higher in the ZSM-4 synthesis, the concentration of tetramethylammonium oxide, with respect to Na_2O, is higher in the omega synthesis. Also, as mentioned in the experimental section, the starting reagents for sources of silica and tetramethylammonium oxide are different in each synthesis.

Even with the patent coverage and the differences in the oxide ratios, preparative procedures and catalytic differences, a striking similarity exists between the X-ray diffraction data for our omega and ZSM-4 zeolites. The diffraction patterns for our omega and ZSM-4 zeolites are given for comparison in Fig. 2. The close similarity in the 2θ values and relative intensities indicate that the aluminosilicate frameworks are quite similar although the concentration of aluminum in the tetrahedral framework sites may be different in these isomorphous zeolites. A range of SiO_2/Al_2O_3 ratios existing in similar aluminosilicate networks balanced electrically by exchangeable cations is not uncommon. Further confirmation of the close similarity in framework structure is supplied by the X-ray data in the patents on ZSM-4 and omega by Mobil (*5*) and Union Carbide (*2*), respectively. This X-ray data compilation is given in Table 8A. The X-ray data from the patent disclosures again show the close similarity in framework structure between the two zeolites.

The cell constants and the differences

TABLE 7

Mole Ratios of Oxides in Omega and ZSM-4 Synthesis

Zeolite	$\frac{Na_2O}{[(CH_3)_4N]_2O + Na_2O}$	$\frac{[(CH_3)_4N]_2O + Na_2O}{SiO_2}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{H_2O}{[(CH_3)_4N]_2O + Na_2O}$
Omega[a]	0.8	0.4	10	40
ZSM-4[a]	0.96	0.55	27.2	34.9
ZSM-4[b] (Pref.)	0.75 to 0.99	0.15 to 0.75	6 to 30	20 to 150
(Gen.)	0.31 to 1	0.05 to 0.90	3 to 60	15 to 600
Omega[c] (Pref.)	0.68 to 0.99	0.2 to 0.4	6 to 10	15 to 60
(Gen.)	0.33 to 1	0.1 to 0.6	5 to 30	10 to 125

[a] This work.

[b] E. Bowes and J. J. Wise, U. S. Patent 3,578,723 (1971)—Mobil.

[c] E. Flanigen, Netherlands Patent 6,710,729 (1968)—Union Carbide.

in port size are given in Table 8B. Supposedly the ZSM-4 structure has cubic symmetry and can adsorb cyclohexane. The omega zeolite is hexagonal and supposedly can adsorb $(C_4F_9)_3N$, which is about 1.1 nm in size. Our adsorption measurements, as indicated earlier, show that omega, like ZSM-4, can adsorb molecules such as cyclohexane and benzene but cannot rapidly adsorb $(C_4F_9)_3N$.

A significant relationship was seen in a patent by Dwyer (*6*) on a rapid production of synthetic faujasite. The relationship is quoted: "In crystallizing zeolites from the crystallization environment, synthetic faujasite is first crystallized. This is normally followed by subsequent crystallization of ZSM-4 from the same crystallization environment. The normal metamorphosis tending toward the crystallization of

TABLE 8A

X-Ray Data Compilation on Omega and ZSM-4

ZSM-4 (by Mobil)		Omega (by Union Carbide)	
d(Å)	I/I_0	d(Å)	I
16.0	20	15.95	20
9.18	100	9.09	86
7.96	20	7.87	21
6.94	30	6.86	27
6.01	33	5.94	32
5.53	7	5.47	6
5.29	7	5.25	8
4.73	31	4.70	32
3.97	11	3.97	11
3.82	69	3.91	58
3.74	28	3.71	30
3.64	26	3.62	25
3.54	54	3.52	53
3.46	14	3.45	20
3.17	48	3.13	38
3.10	23	3.074	
3.05	21	3.020	21
2.99	13	2.97	mw (Barrer)
2.93	28	2.91	36

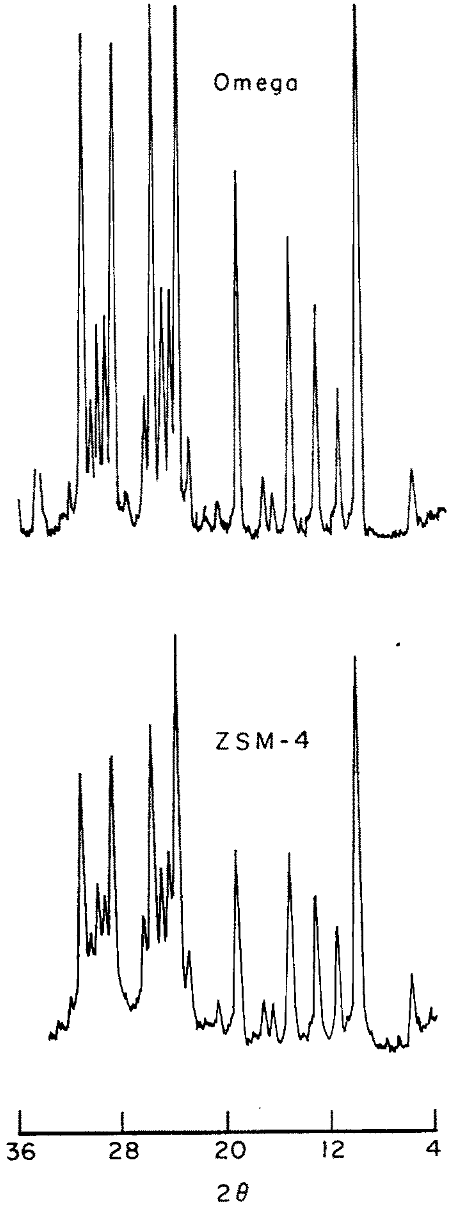

FIG. 2. X-ray diffraction patterns of omega and ZSM-4 zeolites, using Cu$K\alpha$ radiation.

TABLE 8B

Unit Cell Characteristics of Omega and ZSM-4 Zeolites

ZSM-4	Cubic	a = 22.2 A	Absorbs cyclohexane
Omega	Hexagonal	a = 18.1, c = 7.59	Large pore Size, about 11 Å Absorbs $[(C_4F_9)_3N]$
Mazzite	Hexagonal	a = 18.007 c = 7.608	

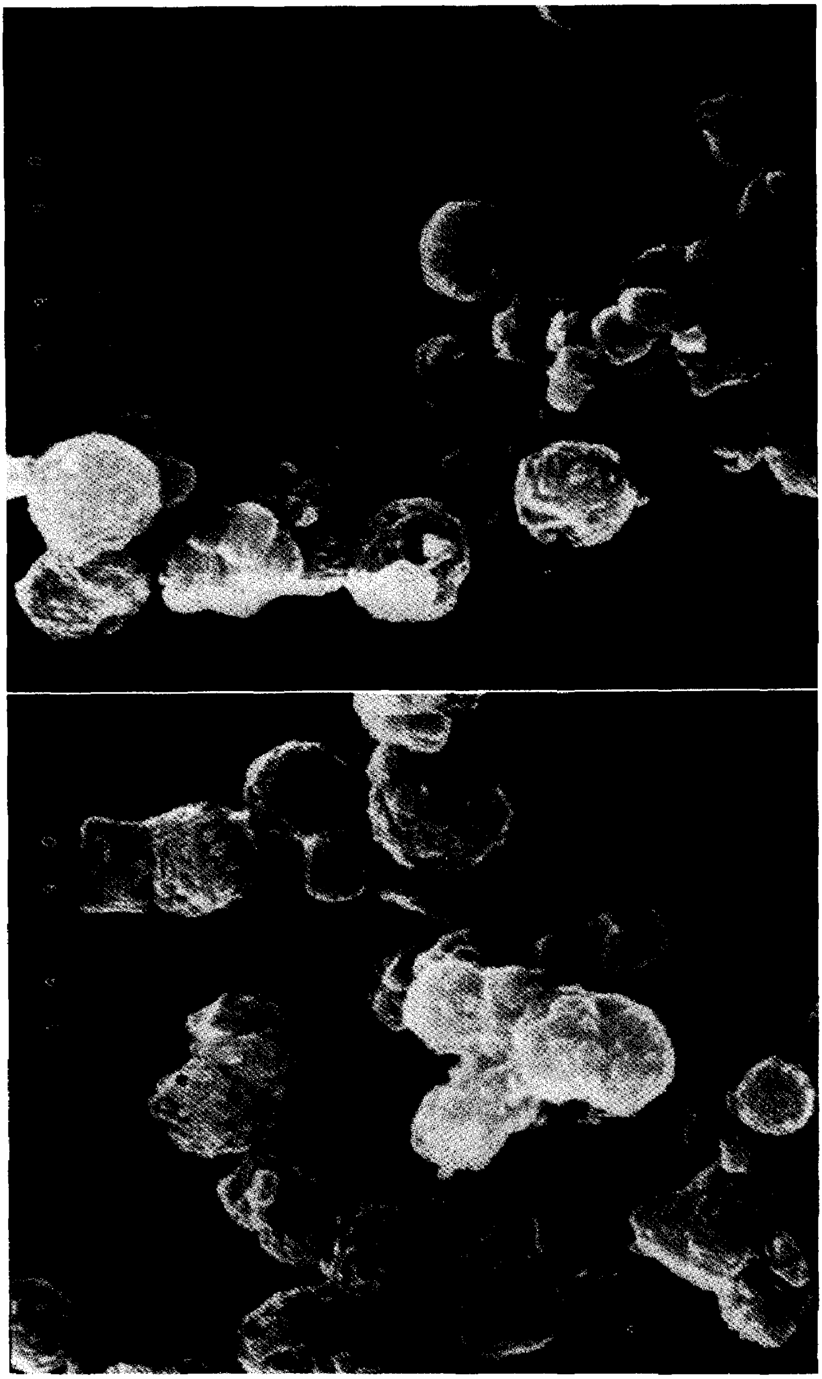

FIG. 3. Scanning electron micrographs of omega zeolites. ×6000.

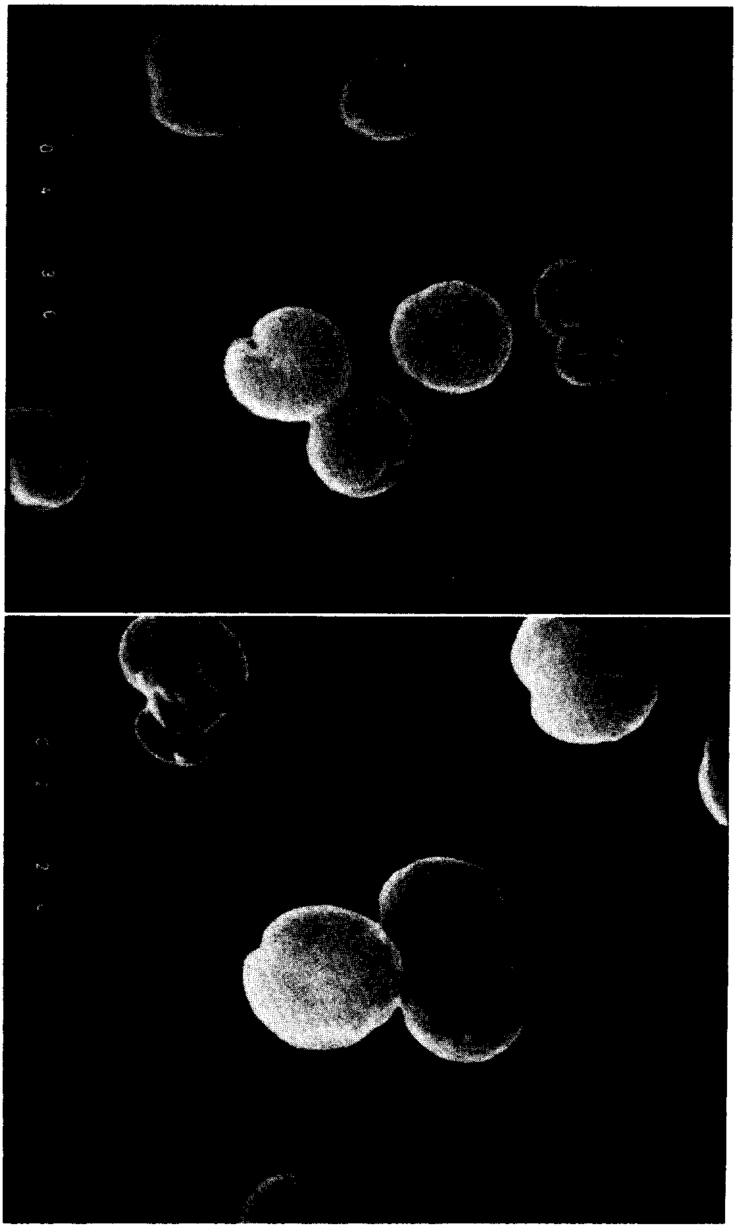

FIG. 4. Scanning electron micrographs of ZSM-4 zeolites. ×6000.

the zeolite P from faujasite is shifted." This disclosure resulted in forming the relationship between the two phase transitions:

(1) Faujasite → ZSM-4 (Mobil)

(2) Faujasite → Omega (present study)

Recognition of these transitions led to comparison of the X-ray data for both species since both syntheses required the presence of tetramethylammonium ions for crystal formation. However, it should be pointed out that the ZSM-4 synthesis (Table 2) recommended by Bowes (*7*), which is different than that of Dwyer (*6*), did not give an intermediate faujasite phase.

Scanning electron micrographs of omega and ZSM-4 zeolites are shown in Figs. 3 and 4, respectively. The micrographs of omega crystals, viewed at a magnification of ×6000, do not show well-resolved crystal faces, but rather appear as aggregates of much smaller crystals having a rough-textured appearance. The ZSM-4 particles, also viewed at the same magnification, appear to have a much smoother surface, not having the smaller fissures and rough texture characteristic of the omega zeolite. The crystals are too small to detect any differences in the crystal morphology between omega and ZSM-4 zeolite that may have occurred due to different synthesis procedures.

CONCLUSION

A reconstructive transition, faujasite → omega, occurs in the omega synthesis over a period of a few days. The omega and ZSM-4 zeolites have similar aluminosilicate frameworks. The omega zeolite can sorb benzene and cyclooctatetraene but cannot rapidly adsorb the larger molecule, perfluorotributylamine.

The hydrogen form of omega is initially more active for *n*-hexane cracking than the corresponding form of faujasite but a rapid decrease in activity with time occurs due to coking. H-omega is slightly more active than H-ZSM-4 for catalytic cracking of a synthetic blend of hexadecane and triethylbenzene, but both are less active than H-faujasite. Cocrystallized, lanthanum-exchanged omega and faujasite catalysts show an increase in catalytic cracking of gas oil as the concentration of faujasite increases.

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