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## 🌱 The Adsorption of Fatty Acids from Vegetable Oils with Zeolites and Bleaching Clay/Zeolite Blends

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### ABSTRACT

The adsorption of model fatty acids (heptanoic, oleic), using spiked vegetable oils, was studied using different kinds of zeolites (A-zeolite, X, Y-zeolites, mordenite), Y-zeolite exchanged with different cations (alkali, alkaline earth, transition metal ions), and with bleaching clay/zeolite blends. The adsorption process was shown to be governed by the molecular sieving properties of the zeolites involved as well as the electrostatic field strengths of the exchange cations. Facile interparticle diffusion of cations between clay and zeolite particles in the blends was verified by electron microprobe analysis and shown to cause unexpected results with respect to bleaching and fatty acid removal.

### INTRODUCTION

Fatty acids are a natural component of vegetable oils and animal fats and are also generated during contact of these oils with high activity bleaching clays (1). Normally, other than the loss in oil they represent, they are not a problem because they can be removed during deodorization. However, in those cases where bleaching is to be conducted without subsequent deodorization, or where there are other constraints on removing the fatty acids by distillation, there will then be a problem of removing the entrained acids from the product oil. As one part of a program to develop a specialty bleaching clay formulation for such applications, we examined the use of zeolites to accomplish this objective. This work is reported here.

The generation of free fatty acids during bleaching with acid-activated clays is a fairly complex process that can involve any number of contributing factors including moisture content of the oil, soap content, atmosphere present, temperature and time of contact (1). Acid-activated bleaching clays possess some very strong Brønsted acid sites on their surfaces (2,3,4) and the acid-catalyzed hydrolysis (5) of the glyceride ester linkage by these surface acid sites is presumably a major source of free fatty acids generated during the bleaching operation. Soap decomposition to yield free fatty acid as a consequence of sodium ion adsorption by the clay has been suggested (6) as another mechanism for fatty acid generation during bleaching. Whatever the detailed mechanism(s) responsible for free fatty acid rise during bleaching operations, the role of high-activity clays in generating these acids is clearly implicated since neutral or only slightly acid clays often reduce fatty acids somewhat through preferential adsorption (1).

Besides the surface Brønsted or "intrinsic" surface acidity mentioned above, the acid-activated montmorillonites used as bleaching clays will also contain a certain amount of unwashed acid salts which impart an additional acidity component termed "residual" acidity. This type of acidity is related directly to free fatty acid rise in the bleaching of oils (7). Both residual and intrinsic acidity can be reduced, the former by improved washing, the latter by ion-exchange with alkali or alkaline earth cations. However, the result, in both cases, is usually reduced bleaching efficiency. It has been shown (8), for instance, that acid-activated bleaching clay subsequently exchanged with sodium cations exhibits only 1/5 the adsorptive capacity for  $\beta$ -carotene as it does in its fully activated form.

An alternative approach, given the seemingly irrevocable nature of the correlation between clay acidity and bleaching efficiency (and its consequences with respect to the tradeoffs between free fatty acid generation and color reduction), was needed. We chose to concentrate on trying to adsorb fatty acids selectively from the oil, simultaneously as they were formed. In particular, we were interested in studying zeolites for this role since claims (9) had already been made that X-zeolite could be used for the closely related process of removing fatty acids from used cooking oils (color reduction was not studied).

That such a selectivity for fatty acids over the parent triglyceride molecule should exist might be expected from a consideration of the known molecular sieving properties of zeolites and the large size differences between fatty acid vs triglyceride molecules. In addition, a study by workers in Spain (10) had already shown a very low adsorption of triglyceride molecules on X-zeolite as compared to the fatty acids.

Keeping in mind that zeolites are crystalline aluminosilicates exhibiting a broad range of chemical and physical properties depending on their uniquely specific array of structural atoms and exchangeable (mobile) cations (11), we wanted to know how such differences might affect the selectivity and capacity for adsorbing fatty acid molecules from vegetable oils. Specifically, we wanted to know how internal structure (type of zeolite), type of exchangeable cation present, and silica/alumina ratio would affect fatty acid adsorption. These factors are known (12,13) to influence adsorption of hydrocarbons by zeolites.

During the course of our work employing clay/zeolite blends, we discovered evidence of a surprisingly facile cross-

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exchange between cations present in the zeolite and those present in the clay, even though the 2 substances were mixed as nominally dry powders.

## EXPERIMENTAL

## Materials and Methods of Preparation

Typical samples of refined safflower and soya oil were obtained from refiners in the USA. Heptanoic acid was obtained from Celanese Chem. Co., and oleic acid (Lowtiter, Emersol 221) was obtained from Emery Industries. Amberlite IRA-400 ion-exchange resin was obtained from Rohm & Haas. Acid-activated clay used in these experiments was commercial Filtrol Gr 105.

Hydrogen mordenite was obtained from the Norton Company and converted to its sodium form by exchange with 20% sodium chloride solution. Calcium A-zeolite and sodium Y-zeolite were obtained from Union Carbide (Linde Div.); partially exchanged hydrogen Y-zeolite was prepared by exchanging sodium Y-zeolite 5 times with dilute sulfuric acid (pH 3.5) followed by washing and drying. Sodium A-zeolite was synthesized in the laboratory. The sodium

zeolites were, in all cases, verified by comparison of their X-ray diffraction powder patterns against known standards. Table I lists relevant analytical data on the zeolites used in these studies.

A series of cation-exchanged Y-zeolites were prepared using the following procedure. The sodium Y-zeolite was dispersed in an aqueous solution of a nitrate, sulfate or chloride salt of the exchange cation in distilled water. The exchanges were each performed in multiple contacting treatments, where the pH of the exchange solutions was maintained above 4.5 to minimize any zeolite degradation. The exchange treatments were performed at ambient temperature. For the potassium exchange, potassium chloride was used initially, followed by potassium hydroxide.

After this contacting, the resultant slurry was filtered, and the filtered solids were washed with distilled water until free of soluble nitrate, sulfate or chloride. The filtered and washed solids were sampled and analyzed for silica, alumina, sodium and exchanged-cation contents. The composition of each of the exchanged Y-zeolites is set forth in Table II. Because significant surface area and pore volume losses were observed for the iron-exchanged Y-zeolite, no attempt was made to include it in this study.

TABLE I

Analytical Data—Study Zeolites

Zeolite	Crystallinity <sup>a</sup>	Particle size <sup>b</sup> ( $\mu\text{m}$ , diam)	SA( $\text{m}^2/\text{g}$ )	Formula <sup>c</sup> (based on chemical analysis)
Na-A	100	5.75	5.5 <sup>d</sup>	1.0 Na <sub>2</sub> O:2SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
Na-A (milled)	100	3.28	16 <sup>d</sup>	1.0 Na <sub>2</sub> O:2SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
Ca-A	100	4.98	491	0.26 Na <sub>2</sub> O:0.55 CaO:1.9 SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
Na-Mordenite	100	5.80	293	1.0 Na <sub>2</sub> O:12.6 SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
H-Mordenite	100	7.80	392	0.07 Na <sub>2</sub> O:1.86(H <sub>3</sub> O <sup>+</sup> ):14.6 SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
Na-X	~80	3.31	443	1.0 Na <sub>2</sub> O:2.93 SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
Na-Y <sub>1</sub>	100	1.04	667	1.1 Na <sub>2</sub> O:3.7 SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
Na-Y <sub>2</sub>	97	2.25	661	0.9 Na <sub>2</sub> O:4.4 SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
Na-Y <sub>3</sub>	100	5.24		1.1 Na <sub>2</sub> O:4.8 SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
NaH-Y <sub>3</sub>	80	2.17	552	0.25 Na <sub>2</sub> O:1.50(H <sub>3</sub> O <sup>+</sup> ):4.7 SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>

<sup>a</sup>Based on X-ray diffraction powder pattern comparison with standard.

<sup>b</sup>Average particle size, expressed as equivalent spherical diameter ( $\mu\text{m}$ ).

<sup>c</sup>Proton content of hydrogen zeolites determined by difference needed to achieve electronic neutrality; all formulae reported on volatile free basis.

<sup>d</sup>Na-A zeolite does not adsorb N<sub>2</sub> at liquid nitrogen temperatures hence only external surface area of zeolite particles is measured.

TABLE II

Chemical and Physical Analysis of Cation-Exchanged Y-Zeolites

Zeolite	Chemical analysis (wt %)				% Na <sup>+</sup> Exch'd.	SA <sup>b</sup> ( $\text{m}^2/\text{g}$ )	PV <sup>b</sup> (cc/g)
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	$\frac{\text{M}_2\text{O}^{\text{a}}}{n}$			
Na-Y	62.9	24.3	12.8	—	100	658	.34
NH <sub>4</sub> Na-Y	66.8	20.3	3.5	9.3	76	—	—
K Na-Y	62.8	20.6	0.3	16.3	97	559	.30
Li Na-Y	68.8	23.8	3.4	4.0	71	570	.29
Ba Na-Y	56.4	19.1	2.7	21.8	77	522	.28
Ca Na-Y	64.1	23.6	3.8	8.5	71	614	.33
Mg Na-Y	67.2	22.8	3.9	6.2	71	645	.33
Mn Na-Y	60.5	23.9	3.5	12.2	75	614	.32
Fe Na-Y	64.0	22.9	3.3	9.8	72	440	.23
Co Na-Y	62.3	25.2	3.1	9.4	72	577	.30
Ni Na-Y	64.3	21.2	3.5	11.0	72	600	.31
Zn Na-Y	61.3	22.2	3.1	13.4	77	588	.33

<sup>a</sup>Wt % exchange cation expressed as corresponding oxide and n = valency of cation.

<sup>b</sup>BET N<sub>2</sub> adsorptions at liquid N<sub>2</sub> temperatures using Quantachrome Quantasorb Surface Area Analyzer. Zeolites were outgassed for 1/2 hr at 250 C prior to nitrogen adsorption measurements.

Blends of the dried zeolite (1.5-2.5 wt % free moisture) and Filtrol Gr 105 bleaching clay (10-15 wt % free moisture) were thoroughly mixed in powder form for 1-3 hours in a motor-driven V-blender. Blends were made to contain 10 wt % zeolite and 90 wt % Gr 105 (volatile free basis).

#### Adsorbent/Oil Contact Conditions

Contacts between vegetable oils and adsorbent solids were conducted by rapidly heating open vessels containing a stirred slurry of oil and adsorbent to 120 C and holding at that temperature for a period of 5 min according to a procedure analogous to that of AOCS Official Method Cc 8a-52. For those studies involving contacts with unblended (pure) zeolites, the zeolites were dried at 120 C/16 hr. Oil/adsorbent ratio was 10:1 (wt/wt basis). In those cases where vegetable oils were spiked with a known amount of fatty acid, the oil was first contacted with Amberlite IRA-400 ion-exchange resin prepared according to the method of Hornstein (14) et al., to reduce the free fatty acids to a level below 0.03 wt %.

#### Analytical Methods

Percentage free fatty acid in the oil was determined by titration of the oil in isopropanol according to the AOCS Official Method Ca 5a-40. Color of the oil was determined on a Lovibond Automatic Tintometer (Model 01-0100, Tintometer USA) according to the AOCS Official Method Cc 13b-45. X-ray diffraction patterns were obtained using a Phillips-Norelco X-ray Diffractometer. Unless otherwise noted, surface areas were obtained using Micromeritics instruments (either Model 2200 Surface Area Analyzer or Model 2500 Automatic Multi-gas Surface Area and Pore Volume Analyzer); particle size analyses were obtained using the Micromeritics Sedigraph (Model 5000-D).

#### Electron Microprobe Analysis

Conventional microanalysis of cation exchange within dry zeolite/clay blends is limited due to difficulties involved in preparing suitably flat surfaces. The inherent porosity and thermal instability of these materials during analysis also make microprobe analysis less reproducible.

These limitations were minimized by pressing at 3000 psi a mixture of 5 wt % K<sup>+</sup> A-zeolite and clay into thin 1½ in. diameter disks. The disks were given a 200 Å carbon coating to make them conductive.

The surfaces were imaged and analyzed for potassium at 15 kV with a 50 nanoamp beam in a JEOL JXA-733 electron microprobe. Two wavelength dispersive spectrom-

eters, at nearly 90° to each other, and energy dispersive spectroscopy were used to assure insensitivity to X-ray adsorption due to surface irregularities.

## RESULTS AND DISCUSSION

### The Study Zeolites

At present, there are over 100 different natural and synthetic zeolites known; however, the present study restricts itself to only 3 of the synthetic sodium zeolites chosen so as to span essentially the range of variables (exchange capacity, pore volume, pore size and framework silica/alumina ratio) exhibited by all the zeolites. Some typical properties for the 3 (A-zeolite, mordenite and X- and Y-zeolite) are listed in Table III. These particular species have been singled out as study zeolites primarily because they (with the exception of A-zeolite) have pore openings large enough to permit entrance by hydrocarbon molecules to the interior of their structures. In addition, they are well characterized and, as synthetic zeolites, they can be obtained in high purity.

Zeolites are crystalline aluminosilicates with specific 3-dimensional structures; Figure 1 shows structures of the study zeolites. In these representations, either a tetrahedral aluminum atom or tetrahedral silicon atom occupies each vertex shown, and an oxygen atom is located at the midpoint along the lines connecting these vertices.

As shown, the A-zeolite is characterized by a cubic array of β-cages linked together by 4-membered rings. In its sodium form, A-zeolite has a pore opening of 4.0 Å and hence should not be expected to adsorb hydrocarbons whose kinetic diameter, measured perpendicular to the axis of its chain, is usually stated to be 4.3 Å (15).

Y-zeolite is also composed of interconnecting β-cages, but now the linkage is through the 6-membered rings with the result that a much more open structure is generated with generously large pore opening of ca. 7.4 Å.

X-zeolite has the exact same structure as Y-zeolite with the exception that more of the tetrahedral framework positions are occupied with aluminum atoms. Both have a system of large, interconnecting cavities whose internal dimensions measure about 13 Å across.

Mordenite is, as shown, composed of a system of both small and large parallel channels. The large channels can easily adsorb a benzene molecule, and, indeed, the adsorption of this molecule is commonly used to verify the presence of the large-port variety (such as used in these studies). Although the large-port mordenite will adsorb large molecules, one can easily visualize from its structure that access

TABLE III  
Some Typical Physiochemical Properties of Study Zeolites<sup>a</sup>

Zeolite	Structure type <sup>b</sup>	Na <sub>2</sub> O:SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub> Mol ratio <sup>c</sup>	Framework Si/Al ratio <sup>d</sup>	Exch. cap. <sup>e</sup> (meq/g)	Pore volume (cc/g)	Pores <sup>f</sup> (Å, diam)
A	—	1:2:1	1	7.0	0.30	4
Mordenite <sup>g</sup>	Mordenite	1:10:1	5	2.6	0.20	7
X	Faujasite	1:3:1	1-1.5	7.0-5.8	0.36	7.4
Y	Faujasite	1:4.5:1	1.5-3	5.8-3.8	0.34	7.4

<sup>a</sup>D. W. Breck, Zeolite Molecular Sieves, John Wiley & Son, NY (1973).

<sup>b</sup>Name of structurally-related mineral.

<sup>c</sup>Typical mol ratio of metal oxides in zeolite (volatile free basis).

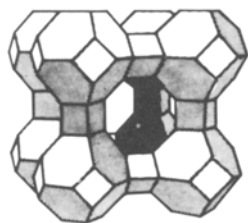
<sup>d</sup>Range encountered for Si/Al framework atoms.

<sup>e</sup>Exchange capacity expressed as meq Na<sup>+</sup> cation/gm of zeolite (volatile free).

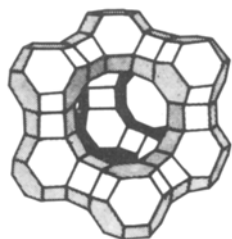
<sup>f</sup>Diameter (Å) of largest pore openings for given zeolite.

<sup>g</sup>Large port variety.

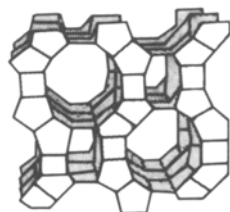
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**A-ZEOLITE**

- Cubic array of  $\beta$ -Cages linked by D4R units
- Largest pore opening 4.0 Å diam.
- Interior cavity 11.4 Å diam.

**Y-ZEOLITE**

- $\beta$ -Cages linked tetrahedrally through D6R units (diamond structure)
- Largest pore opening 7.4 Å diam.
- Interior cavity— 13 Å diam.

**MORDENITE**

- Complex chains of 5-rings crosslinked by 4-rings
- Largest pore opening— 6.7 x 7.0 Å diam.
- Parallel, cylindrical channels

FIG. 1. Structure and pore openings for study zeolites.

into and out of this zeolite will be more restricted since a molecule migrating through its interior is constrained to a one-dimensional system of noninterconnecting parallel channels (actually, the large parallel channels are interconnected by small channels, but only very small molecules, of 2 or 3 atoms, can pass through these smaller channels). This is in contrast to the 3-dimensional system of interconnecting pores and cavities afforded by the faujasite (X, Y-zeolite) structure (16).

### Adsorption Studies with Pure (Unblended) Zeolites: Effect of Zeolite Type

Figure 2 summarizes the data obtained when safflower oil spiked to different levels with heptanoic acid was contacted with samples of the pure zeolites.

As shown, the order of increasing efficiency for removing (adsorbing) heptanoic acid is sodium Y-zeolite > sodium mordenite > sodium A-zeolite. In all cases, the sodium form of a given zeolite is more effective than its counterpart exchanged with other cations (i.e., compare NaY vs NaHY; Na-mord. vs H-mord.; and NaA vs CaA).

Reference to the data in Table IV, as well as consideration of the results summarized in Figure 2, indicates quite clearly that access to zeolite large-cage pore volume is of primary importance as far as fatty acid adsorption from vegetable oil is concerned. Sodium Y-zeolite (which is essentially identical to sodium X-zeolite) possesses large pore openings and considerable large-cage pore volume. In accord with these properties, it is observed that sodium Y-zeolite is also the most efficient of the zeolites studied for adsorbing fatty acid. Sodium A-zeolite is less efficient than sodium mordenite (even though it actually has greater large-cage pore volume than the mordenite) because its pore

TABLE IV

Apparent Pore Size and Void Volume of Large Cavities for Some Representative Zeolites

Zeolite	Apparent pore size (Å) <sup>a</sup>	Volume (large cage) <sup>b</sup>
Na Mord	6.7 × 7.0	0.151 cc/g
H Mord	—	0.176 cc/g
Na A	3.6 - 4.0	0.213 cc/g
Ca A	4.2 - 4.4	0.242 cc/g
Na X	7.4	0.31 cc/g

<sup>a</sup>D. W. Breck, *Zeolite Molecular Sieves*, John Wiley & Sons, 1974, pp. 634-644.

<sup>b</sup>Based on O<sub>2</sub> adsorptions at -183 C; D. W. Breck and R. W. Grose, *Molecular Sieves*, Adv. in Chem. Series 121:319 (1978).

openings are so small that fatty acid molecules simply cannot pass through them. Sodium mordenite, which has reasonably large pore openings, but ca. ½ the internal pore volume of Y-zeolite is, as expected, less efficient than Y-zeolite. The rather rapid dropoff in adsorptive capacity for sodium mordenite with increased fatty acid content in the oil suggests, furthermore, that the noninterconnecting parallel channels of this structure are more sensitive to blockage than is the case for the Y-zeolite with its 3-dimensional array of interconnecting large cavities.

A more surprising result apparent in the data from Figure 2 is that cation exchanges conducted in an effort to increase accessibility by opening up the zeolite pores did not, in fact, lead to increased fatty acid adsorption. It is known that the hydrogen forms of Y-zeolite and mordenite, as well as the calcium form of A-zeolite, generally exhibit increased adsorptive capacity (12,16) for neutral hydrocarbons; however, in all cases studied here, it can be seen that fatty acid uptake decreased with these exchanges. Although it might be argued that the pore opening for the calcium A-zeolite is still not large enough to accommodate access by large fatty acid molecules, it is, nevertheless, difficult to understand the drop in adsorptive capacity for the 2 large pore zeolites when they are converted to their hydrogen forms. Quite obviously, there are specific cation-sorbate interactions in this system which exert considerable

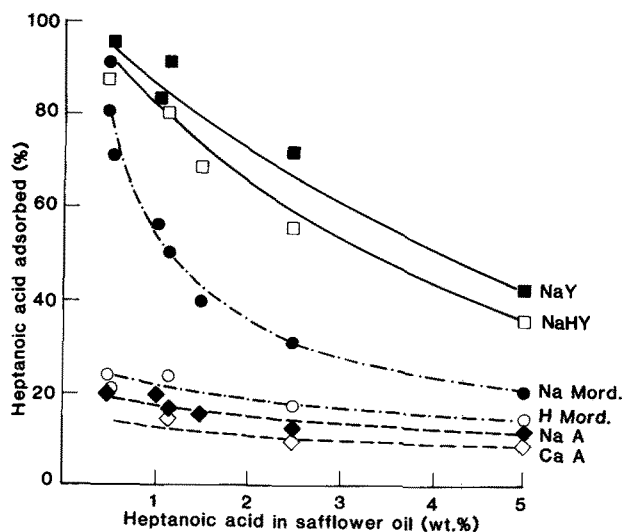


FIG. 2. Plot of percentage heptanoic acid adsorbed from spiked safflower oil as a function of concentration for different zeolites: ■ sodium Y-zeolite, □ partially exchanged hydrogen Y-zeolite (1.5% residual sodium cation), ● sodium mordenite, ○ hydrogen mordenite, ◆ sodium A-zeolite, ◇ calcium A-zeolite.

selectivity control over the adsorption process. Previous workers (17,18) have noted an enhanced ability for Ca X-zeolite to adsorb organic acids as compared to Na X-zeolite. However, the operative mechanism for this selectivity was not presented and will be a subject dealt with at length in a later section of this paper.

Figure 3 shows that heptanoic acid is adsorbed to a greater extent than oleic acid. This result may be taken as further evidence that fatty acid adsorption from oils is also governed by the known molecular sieving properties of zeolites where size effects such as chain length affect the adsorption process (12,16,17,18).

### The Effect of Zeolite Silica/Alumina Ratios

The silica/alumina framework ratios in sodium X, Y-zeolites can be varied over a considerable range with a concomitant inverse variation in cation (sodium) content; other properties (structure, unit cell dimensions) are only affected minimally. This property of X, Y-zeolites provides a means to judge the relative importance exerted by cation site density as a factor in the adsorptive process. In order to study the effect of this parameter on the fatty acid adsorption process, we contacted a series of sodium X- and Y-zeolites with safflower oil spiked with 0.52 wt % heptanoic and a refined soya oil containing 0.041 wt % free fatty acids. The zeolites had silica/alumina ratios spanning the range 3.0-4.7. Duplicate contacts were made in all cases and the data analyzed by linear regression methods. Although there was a very slight upward slope in the adsorption levels with decreasing silica/alumina ratio (i.e., increasing number of cation sites), the coefficient of determination is quite low and reduces the significance of the data considerably. It appears that the adsorption is only influenced slightly by silica/alumina ratio (cation site density), at least over the range studied here.

### The Effect of Zeolite Exchange Cation

Having established that X, Y-zeolites are preferred over mordenite and A-zeolite for the adsorption of fatty acids from vegetable oil, we wished to examine in detail the question of selectivity control as exerted by the zeolite

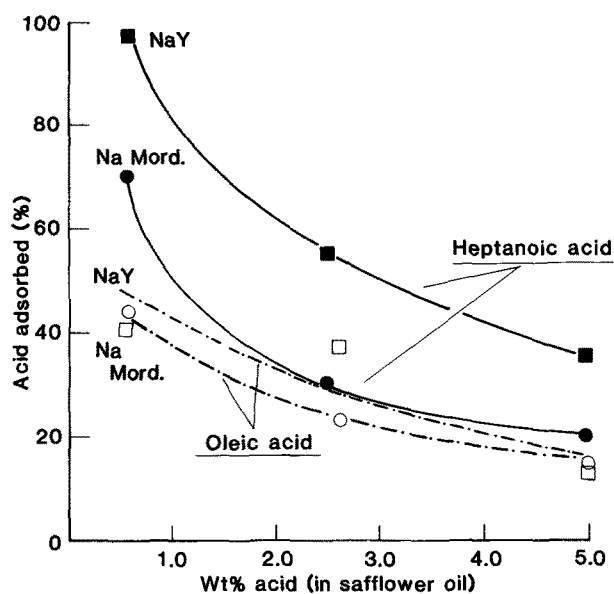


FIG. 3. Effect of fatty acid chain length versus percentage of adsorption as a function of acid concentration and type zeolite used: ■ sodium Y-zeolite/heptanoic acid (solid line), □ sodium Y-zeolite/oleic acid (dash-dot line), ● sodium mordenite/heptanoic acid (solid line), ○ sodium mordenite/oleic acid (dash-dot line).

exchange cation. To do so, we took a sodium Y-zeolite and exchanged it with a broad range of alkali, alkaline earth and first-period transition metal ions and then subjected the resultant exchanged zeolites (with 71-97% of sodium replaced) to adsorption studies as in previous sections of this study.

In a general sense, zeolite cations are well known to exert control over both adsorptive (12,13) as well as catalytic (19) properties of zeolites, but the specific selectivities and their underlying causes are often surprising and quite unpredictable. We were primarily interested in determining whether surface acidity, pore volume, or electrostatic field effects as a function of the cation present in the zeolite correlated in any meaningful way with the observed behavior for the adsorption of fatty acids. Figure 4, patterned after a drawing by Lechert (20), presents a 3-dimensional representation of the Y-zeolite (faujasite) framework and shows, in particular, how the large supercage contains numerous cations near its inner surfaces and around the mouth of its pore openings. It is these cations which will play a key role in fatty acid adsorption since only the supercages are penetrated by fatty acids during the adsorption process.

Table V summarizes the experimental data obtained when refined soy oil spiked with oleic acid was contacted with Y-zeolite exchanged with various cations. As can be seen, the fatty acid adsorption characteristics of the various zeolites vary rather widely as a function of cation present. By examination, one can discern quickly that the divalent alkaline earth cations function somewhat better than the divalent transition metal ions and considerably better than the monovalent alkali metal cations; the ammonium cation is especially poor with respect to fatty acid adsorption. The adsorption data do not seem to correlate in any meaningful way with supercage pore volumes (as measured by  $N_2$  adsorption [21]). Similarly, it was concluded that neither surface acidity (as measured by titration with a Hammett indicator [22,23]) nor aqueous pH (as measured by pH meter on a stirred slurry of the zeolite in water) correlate. If surface acidity were the deciding factor in fatty acid adsorption, then one would expect the Ba-exchanged homolog to be appreciably lower and the  $NH_4$ -exchanged homolog to be appreciably higher in adsorptive capacity than is actually observed. Notice that Mg-exchanged homolog, with a surface acidity of 72.3 meq of base/100 g zeolite is the best fatty acid adsorber whereas the  $NH_4$ -exchanged homolog, with only slightly less surface acidity, is actually the poorest fatty acid adsorber. If basicity (aqueous pH) were related to adsorptivity, then one might expect the Na-exchanged homolog to be the best. It is, in fact, somewhat intermediate in terms of fatty acid adsorptive character.

There is, however, a good fit between the adsorptivity

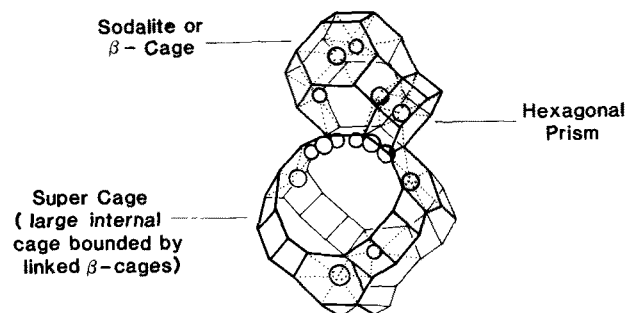


FIG. 4. Idealized structure of faujasite framework showing univalent cation positions.

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TABLE V

## Adsorption of Oleic Acid in Soya Oil Onto Cation-Exchanged Zeolites

Periodic group	Exch. ion	Oleic acid adsorbed (%) <sup>a</sup>	(Meq/100g) <sup>b</sup>	Supercage pore volume (cc/g) <sup>c</sup>	Electrostatic field (V/Å) <sup>d</sup>	Pauling ionic radius (Å)	Chrg. radius ratio (e/Å)	Surface acidity <sup>e</sup> (Meq/100g)	Aqueous pH <sup>f</sup>
Alkaline Earth Ions	Mg	83	33.3	.333	4.9	0.65	3.16	72.3	6.9
	Ca	68	28.4	.333	3.8	0.99	2.01	68.5	6.0
	Ba	68	27.7	.280	2.8	1.35	1.48	5.9	6.2
Transition Metal Ions	Mn	67	27.0	.324	4.8	0.80	2.50	n/a	6.6
	Zn	65	26.2	.328	5.1	0.74	2.70	56.1	7.6
	Co	60	24.1	.298	4.9	0.78	2.56	n/a	n/a
	Ni	46	19.1	.309	4.9	0.78	2.56	24.5	6.6
Alkali Metal Ions	Li	58	24.1	.291	2.1	0.60	1.67	26.3	7.1
	Na	51	21.3	.340	1.3	0.95	1.05	4.1	9.1
	K	36	14.9	.298	1.0	1.33	0.75	4.0	7.7
	NH <sub>4</sub>	20	8.5	—	0.94 <sup>g</sup>	1.48 <sup>g</sup>	0.68	70.9	6.1

<sup>a</sup>Wt % oleic acid adsorbed from refined soya oil spiked 0.57-0.59 wt % with oleic acid (contact conditions: 10/1 oil/zeolite wt. ratio, heated to 120 C in 5 min, held at 120 C/5 min).

<sup>b</sup>Milliequivalents oleic acid adsorbed onto 100g zeolite (volatile free basis).

<sup>c</sup>Pore volume measurements based on adsorption of N<sub>2</sub> after outgassing zeolite for 1½ hr at 250 C.

<sup>d</sup>J. W. Ward, J. Cat. 10:34 (1968); *Ibid.*, J. Cat. 22:237 (1971).

<sup>e</sup>Surface acidity measurements in meq. n-butylamine required to titrate adsorbed 4-(p-ethoxyphenylazo)-m-phenylenediamine (pKa + 5.0, Hammett indicator). Zeolites were dried at 120 C/24 hr prior to titration.

<sup>f</sup>pH of 10% slurry of zeolite in distilled water; measured at 25 C with stirring using Corning model 125 pH meter.

<sup>g</sup>Extrapolated from a plot of monovalent charge/radius ratio data vs monovalent electrostatic field data for Li, Na, K; ionic radius for NH<sub>4</sub><sup>+</sup> cation taken from E. R. Nightingale, J. Phys. Chem. 63:1381 (1959).

data and the charge/radius ratio data, or the electrostatic field data (19) for the various cations studied as indicated by an examination of Figure 5. As shown, there is a smooth and generally well behaved trend toward increasing fatty acid adsorption with increasing charge/radius ratio or increasing cation electrostatic field. The most noticeable deviations from the curves are exhibited by the transition metal cations, and, in particular, by the cobalt and nickel ions. The most probable explanation for this behavior is that these ions reside in more shielded environments (i.e.,

in the interior of  $\beta$ -cages or hexagonal prisms) and hence are less able to interact with the fatty acid molecules which can only enter the large supercages. The tendency for transition metal ions to enter small-cage sites, especially on heating, has been well documented for transition metal exchanged Y-zeolite (24,25,26) and studied in detail for the case of the Ni-cation (27).

The basic conclusion we draw from these results is that the adsorption of fatty acid molecules from an oil (triglyceride) medium by Y-zeolite involves the diffusion of the fatty acid molecule into the interior of the zeolite where the degree of interaction (adsorption) is controlled to a large extent by the field strengths of the cations present in the zeolite supercages. When the cation field strengths are low (e.g., alkali cations) or when access to the zeolite interior is restricted (e.g., A-zeolite, mordenite), then fatty acid adsorption will also be low.

Assuming each unit cell of Y-zeolite contains about 8 large supercages, and  $0.45 \times 10^{20}$  unit cells/g of Y-zeolite (21), it is possible to calculate the occupancy of supercages by oleic acid molecules as a function of exchange cation. The results of performing this calculation indicate that about one in 2 of the supercages are occupied in the case of the magnesium exchanged Y-zeolite. This value drops to one in 3 for the sodium-exchanged material, one in 4 for the potassium-exchanged material, and as low as one in 7 for the ammonium-exchanged material.

One apparent anomaly regarding the results of the surface acidity data presented in Table V deserves further comment. Previous workers have generally reported a good correlation between electrostatic field and surface acidity (22,24) in contrast to the much poorer correlation reported here. However, their pretreatments were always done at higher temperatures (>400 C) where hydration spheres around the cations are largely stripped away. Here, the pretreatments were done at 120 C, the same temperature at which the zeolite was to be brought into contact with the hot oil. Brønsted surface acidity titrations are very much affected by the pretreatment temperature (24). It is perhaps to be expected that surface acidity titrations conducted on zeolites pretreated at lower temperatures (where

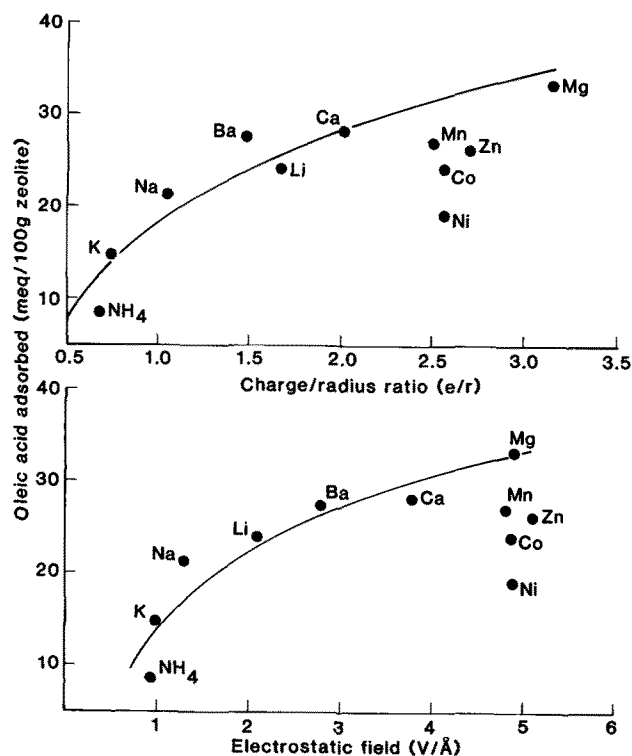


FIG. 5. Plot of oleic acid adsorbed vs charge/radius ratio and electrostatic field (in zeolite) for exchange cations.

differences in degree of cation hydration and site preferences will be most pronounced) would show poorer correlation with electrostatic field data. Whether zeolite surface acidity is actually changing under contact conditions through a dehydration process and therefore not accurately reflecting the results of the Hammett titrations done on zeolite dried at 120 C, is a concern that was not resolved by the current experiments.

#### Adsorption Studies with Blends of Zeolite and Bleaching Clay

Having identified the Mg-exchanged Y-zeolite as a more efficient sorbent compared to the Na-exchanged form (ca. 1½ times more efficient), it was desired to demonstrate the same magnitude and direction of selectivity with blends of these 2 zeolites in bleaching clay. To accomplish this goal, the 2 zeolites were blended (10 wt %, volatile free basis) with Filtrol Gr 105 bleaching clay. The blends were made using air dried powders, and thorough mixing was assured by tumbling the mixture in a V-mixer for 1-3 hr before any testing was conducted. Once the blends were made, they were allowed to stand in contact for a period of 3 weeks. During that time they were sampled on a weekly basis to check stability and analyzed for their ability at bleaching and adsorbing fatty acids from a refined soya oil spiked with oleic acid.

Our expectation, based on the preceding results with pure zeolites, was that the Mg-exchanged Y-zeolite/clay blend would prove to be a superior adsorber of fatty acid as compared to the Na-exchanged Y-zeolite/clay blend. Although we had no *a priori* notions regarding the relative bleaching efficiencies of the 2 blends, we did not expect large differences since the blends only contained 10% zeolite. The remainder was the exact same bleaching clay in each case. Any differences in bleaching efficiencies for the 2 blends would have to be ascribed to the different zeolites used, and zeolites are known (28) to be inefficient sorbents for carotenoids as compared to bleaching clays at any rate.

In direct contradiction to expectation, the results plotted in Figure 6 were obtained. As shown essentially no difference exists between the 2 blends in terms of fatty acid adsorption, but there is a significant difference in terms of decolorizing (bleaching) efficiency. For all practical purposes, the blends are acting as if they were made with the same (cation-exchanged) zeolite, but different (cation-exchanged) bleaching clays.

Since bleaching clays exchanged with different cations have been shown to exhibit (8) different adsorption capacities for  $\beta$ -carotene, it seemed probable that the results obtained could be explained if it were assumed that intercrystalline diffusion of cations between zeolite and clay particles was occurring. According to this hypothesis, the zeolite would give up its exchange cations to the clay particles while in return receiving balancing cations from the clay. The net result would be to exchange acidic cations on the clay for less efficient sodium or magnesium cations (thereby changing decolorization efficiency) while simultaneously driving the zeolite particles toward a state of identity (and thereby rendering them equal in terms of fatty acid adsorption). The clay in the Mg Y-zeolite/clay blend would be less reduced in decolorizing efficiency because it would receive fewer sodium ions and more magnesium ions than for the Na Y-zeolite/clay blend.

Although it is easy to understand cross-exchange of cations between clay and zeolite particles in the aqueous state, and we were aware of studies (29) in which the exchange of potassium and calcium ions had been demonstrated for thick pastes of these 2 minerals, we were at first hesitant to ascribe this type of process to the present case

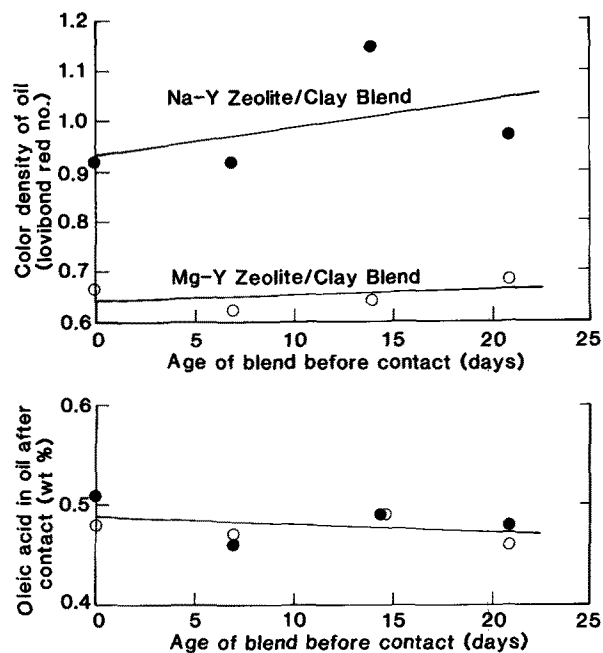


FIG. 6. Plot of decolorizing efficiency and free fatty acid reduction efficiency for 10% zeolite/clay blends vs zeolite exchange ion (std. contact using refined soya spiked with .59 wt % oleic).

since the 2 minerals were actually being mixed as dry powders. Nevertheless, a similar process has been described in detail for the case of mixture of dry zeolites (30) exchanged with different cations. To provide some evidence that intercrystalline diffusion of cations is occurring, a microprobe analysis of potassium-exchanged Linde 3A zeolite mixed with Filtrol Gr 105 bleaching clay was performed. As shown by the micrographs in Figure 7, there is clear evidence of potassium migration from the zeolite particles onto the clay particles with time.

The cubic morphologies of the zeolite particles and submicron particle size distribution of the clay, as mixed and after 26 days, are shown in the figure. High dot densities within the potassium distribution maps taken on "as mixed" samples clearly show a correspondence between high potassium areas and zeolite particles. Potassium maps taken of a similar area in the same sample after 26 days show uniform concentrations of potassium and no such correspondence. This result is entirely consistent with the idea that interparticle diffusion of cations does occur between clay and zeolite crystallites, even though mixed as nominally dry powders. We conclude, then, that an inherent problem with trying to control component specific adsorptions based on cation-derived selectivities when mixing minerals (or adsorbents) containing unlike, but nonetheless exchangeable cations, is that interparticle cation diffusion may well occur with concomitant loss in desired adsorptive selectivity.

In spite of any such problems which may exist for the zeolite/clay system, we believe more work of this general nature will yield the new bleaching clay formulations of the future. Given the increasing demands being put on oil refiners to obtain maximum yields of processed edible oils, it is axiomatic that increased selectivity for removing troublesome components be built deliberately into the bleaching clay. This will undoubtedly require an enhanced understanding of the nature of specific sorbate interactions at the molecular level. For purely technical reasons, we plan to study in more detail the phenomenon of interparticle cation diffusion between clay and zeolite minerals in their dry states.

## FATTY ACID ADSORPTION BY ZEOLITES

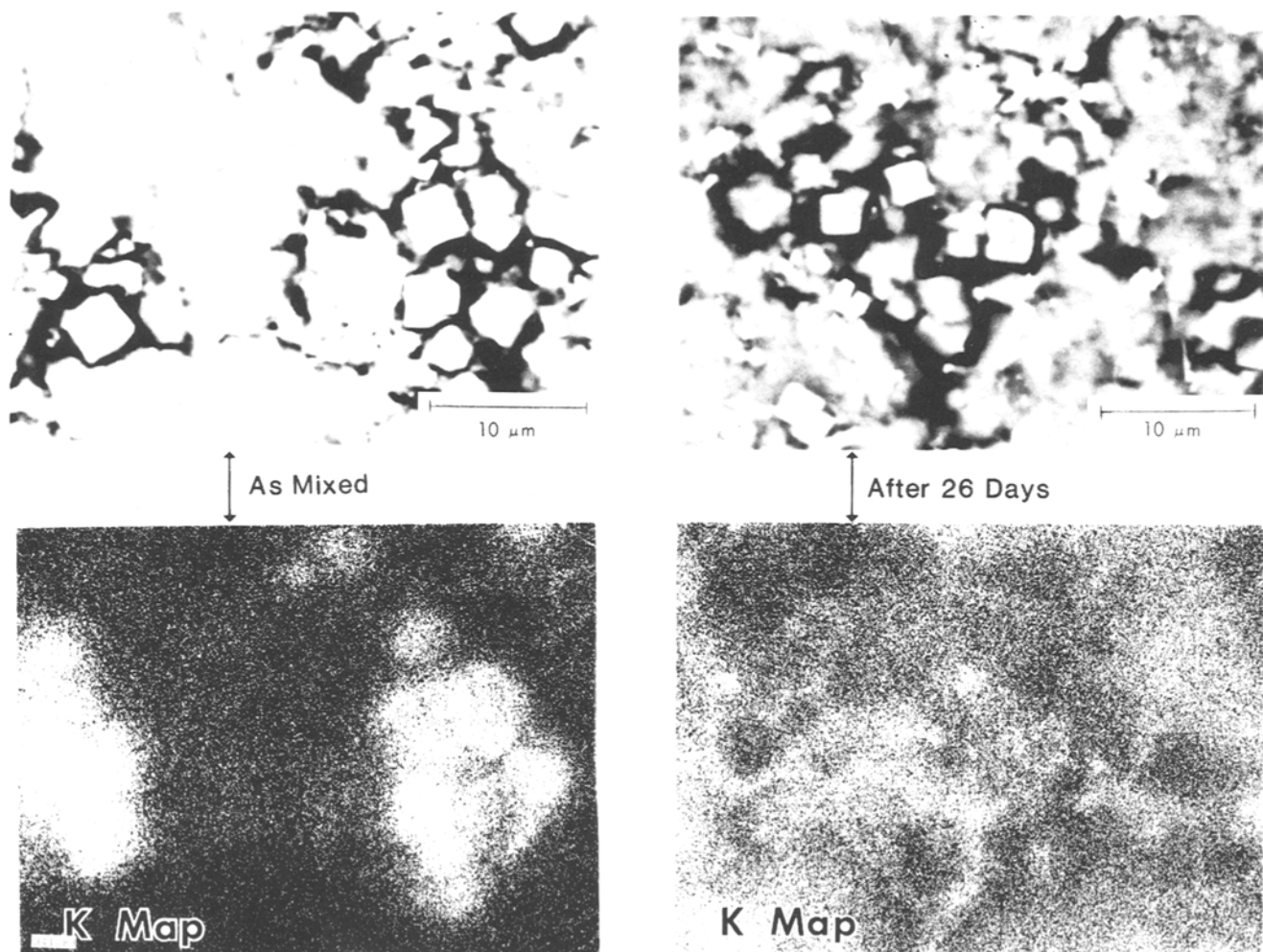


FIG. 7. Electron micrographs and potassium maps of zeolite/clay mixtures as mixed and after 26 days.

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