Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Selective Removal off Nitrogenous-Type Compounds from Fuels by Using Zeolites

G. Jean[a]; S. M. Ahmed[a]; H. Sawatzky[a]
[a] Hydrocarbon Processing Research Laboratory Energy Research Laboratories, Ottawa, Canada

To cite this Article Jean, G. , Ahmed, S. M. and Sawatzky, H.(1985) 'The Selective Removal off Nitrogenous-Type Compounds from Fuels by Using Zeolites', Separation Science and Technology, 20: 7, 555 — 564
To link to this Article: DOI: 10.1080/01496398508068237
URL: http://dx.doi.org/10.1080/01496398508068237

SEPARATION SCIENCE AND TECHNOLOGY, 20(7 & 8), pp. 555-564, 1985

The Selective Removal of Nitrogenous-Type Compounds from Fuels by Using Zeolites

G. JEAN, S. M. AHMED, and H. SAWATZKY

HYDROCARBON PROCESSING RESEARCH LABORATORY
ENERGY RESEARCH LABORATORIES
CANMET
ENERGY, MINES AND RESOURCES CANADA
OTTAWA, K1A 0G1, ONTARIO, CANADA

Abstract

Several zeolites were tested for the selective removal of nitrogenous compounds from an organic solution. A model compound study showed that the extent of sorption from a complex mixture is a function of the nature of the nitrogenous compounds. A correlation between the extent of sorption and the size of a compound suggests that diffusion is the controlling parameter. A capacity of 10 wt% was obtained for the model compound study. The zeolites were also tested for the removal of nitrogenous compounds from a coker naphtha and from a hydroprocessed naphtha. The low capacities relative to the model compound study of $\simeq 1$ wt% and $\simeq 3$ wt% obtained for the coker and the hydroprocessed naphthas, respectively, suggest the sorption of nonnitrogenous compounds.

INTRODUCTION

The production of fuels requires hydrotreating of the feedstock in the early stages of upgrading in order to remove the nitrogenous and sulfurous compounds which can poison the catalysts (*1*, *2*) and promote gum formation in the final product (*3–5*). Nitrogenous compounds are more resistant to hydrotreating than sulfurous compounds, and for synthetic crudes dictate the process severity. Thus, nitrogenous compounds are more troublesome than sulfurous compounds.

Hydrotreating is a very expensive process because of the severity required. Under these conditions a fraction of the starting material is lost

0149-6395/85/2007-0555$3.50/0

through extensive cracking which produces unwanted gases. This problem is compounded by the fact that the whole feed is hydrotreated even though only a small fraction of the feed contains nitrogen.

In certain cases it may be more economical to remove the nitrogenous compounds selectively. Separation by sorption is a possible alternative to the expensive hydrotreating process.

Various sorbents have been used for the analytical separation of nitrogenous compounds from petroleum fractions. Supported ferric chloride (*6*), macroreticular ion-exchange resins (*7–9*), basic and neutral alumina (*10*), and acid-modified silica (*11*) can selectively remove the nitrogenous compounds. The separations mentioned above were designed for small scale.

A preliminary study using brominated ilmenite as a sorbent demonstrated the possibility of using sorption for the large-scale removal of nitrogenous compounds (*17*). A high degree of selectivity in favor of basic nitrogenous compounds, low adsorption capacity, and sorbent instability was observed.

This paper describes the selective removal of nitrogenous compounds using zeolites. Zeolites are stable sorbents and are known to separate on size effect as well as on physical and chemical interaction with the sorbate.

The study determines the selectivity of sorption for compounds of various natures as a function of the degree of saturation. The removal of nitrogenous compounds from naphtha fractions was also investigated.

EXPERIMENTAL

Model Compound Studies

A standard feed containing 18 nitrogenous compounds was prepared using toluene as the solvent. The composition of this standard feed is given in Table 1.

A typical experiment involved pumping the feed continuously at 0.5 mL/min into a 30-cm long × 0.4 cm i.d. stainless steel column packed with zeolite. A fraction collector was used to collect 5-mL samples which were subsequently analyzed using a Varian 6000 gas chromatograph equipped with a 12.5 m long SE-30 capillary column. All studies were performed at room temperature.

The zeolites used in this study were obtained from BDH Chemicals Ltd. and were untreated. Zeolite 13X is in the sodium form, 10X is in the calcium form, and zeolite 5A is in the calcium form.

TABLE 1
Composition of Standard Solution

Compound	ppm N
Aniline	30.12
1,2,5-Trimethylpyrrole	28.20
Benzylamine	39.79
n-Octylamine	32.62
Quinoline	32.02
n-Decylamine	27.08
Indole	29.37
3-Methylindole	26.74
2,2′-Dipyridyl	55.58
2-Phenylpyridine	24.26
1-Phenethylpiperidine	22.88
Dibenzylamine	26.48
Tetrahydrocarbazole	27.70
Carbazole	25.24
2-Methylacridine	19.40
3,4-Benzacridine	7.85
2-Aminochrysene	13.90
Phenothiazine	29.60
Total N concentration	518.21

Studies with Naphtha Samples

A naphtha obtained from hydroprocessing experiments and a coker naphtha obtained from Gulf Canada Ltd. were used in this study. The physical properties of the two naphthas are given in Table 2.

The experimental procedure was similar to that previously described. The column effluent was collected every 5 mL and was subsequently analyzed for total nitrogen using a Dohrman total nitrogen analyzer using chemiluminescence detection.

Calculation

For the model compound study the fraction of each compound present in a given sample of the effluent was calculated by comparing the corresponding peak area of the gas chromatogram for that sample with the area obtained for the original feed solution.

TABLE 2
Properties of Naphthas

	Hydroprocessed	Coker
Specific gravity (60/60°F):	0.745	0.753
Sulfur (wt%)	0.18	0.18
Carbon (wt%)	85.98	85.25
Hydrogen (wt%)	13.45	13.88
Nitrogen (wt%)	0.05	0.002
Bromine No.	24.	74
Refractive index (20°C)	1.4220	1.4242
Aniline point (°F)	139.6	105.8
Compound type:		
Paraffins (wt%)	55	24.61
Olefins (wt%)	15	61.79
Naphthenes (wt%)	19	0
Aromatics (wt%)	10	13.60

$$\text{Fraction species } i = \frac{\text{area of peak } i \text{ in sample}}{\text{area of peak } i \text{ in original feed}}$$

$$\text{Fraction total nitrogen} = \frac{\Sigma \text{ area of peaks in sample}}{\Sigma \text{ area of peaks in original feed}}$$

The results are presented in graph form to show the fraction in the effluent versus volume of feed pumped into the column. This type of curve is referred to as a "breakthrough curve."

For the naphthas, a "total nitrogen versus volume" curve is presented which is referred to as a "total nitrogen breakthrough curve."

RESULTS

The model compound study was designed to give detailed information on the fate of each compound present in a complex mixture during the sorption process. The 18 compounds were chosen to represent a broad range of basicity, molecular structure and size, boiling point, aromaticity, and saturation.

The results of the sorption of the model compounds by zeolite 13X are shown in Fig. 1. These results clearly show that the selectivity strongly

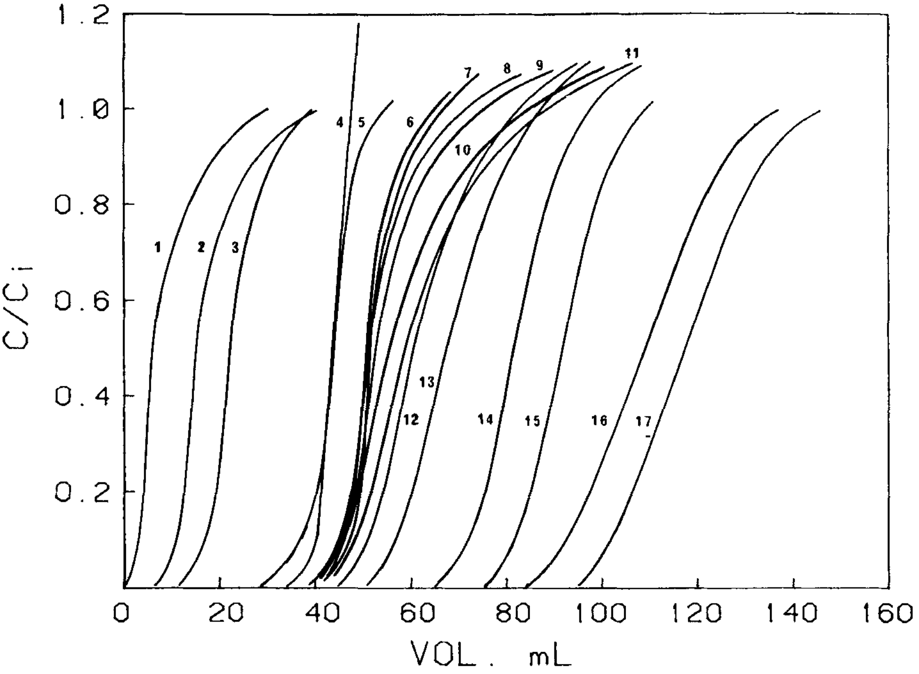

FIG. 1. Selectivity of sorption of zeolite 13X for a standard mixture. 1) Benzacridine, 2) 1,2,5-trimethylpyrrole, 3) tetrahydrocarbazole, 4) *n*-decylamine, 5) 2-methylacridine, 6) aminochrysene, 7) carbazole, 8) *n*-octylamine, 9) 1-phenethylpiperidine, 10) phenothiazine, 11) 2-phenylpyridine, 12) 3-methylindole, 13) dibenzylamine, 14) indole, 15) quinoline, 16) aniline, 17) 2,2'-dipyridyl. Benzylamine did not elute after 150 mL, 3.0 g zeolite, was used.

depends on the nature of the compound. Indeed, the extent of sorption varies for each compound. Compounds such as benzacridine and tetrahydrocarbazole are not extensively retained and appear in the effluent after only 20 mL has been collected. Compounds such as aniline and benzylamine are still being selectively removed after 100 mL. The maximum loadings for each compound can be calculated from the area over the breakthrough curve of Fig. 1 and its initial concentration in the mixture (Table 3). Since sorption is a molecular phenomenon, the number of moles sorbed is the best representation of the sorption capacity. The fact that the amount sorbed varies for each compound indicates the importance of subtle variations in the nature of the sorbate.

The results presented in Table 3 show an inverse correlation between

TABLE 3
Total Loading on Zeolite 13X for Model Compounds

Compound	Concentration (mol/L)	Total loading		% Retained
		mmol	mg	
1. Benzacridine	0.496×10^{-3}	0.004	0.966	6.14
2. Trimethylpyrrole	1.75×10^{-3}	0.032	3.49	13.00
3. Tetrahydrocarbazole	1.72×10^{-3}	0.041	1.09	17.17
4. Aminochrysene	0.86×10^{-3}	0.044	10.65	36.66
5. 2-Methylacridine	1.21×10^{-3}	0.054	10.36	31.72
6. 1-Phenethylpiperidine	1.42×10^{-3}	0.078	14.79	39.37
7. Carbazole	1.56×10^{-3}	0.082	13.78	37.50
8. 2-Phenylpyridine	1.51×10^{-3}	0.093	14.36	43.78
9. *n*-Decylamine	2.13×10^{-3}	0.093	14.64	31.18
10. 3-Methylindole	1.66×10^{-3}	0.104	13.69	44.81
11. *n*-Octylamine	2.03×10^{-3}	0.108	13.96	38.02
12. Dibenzylamine	1.65×10^{-3}	0.113	22.32	49.00
13. Phenothiazine	2.48×10^{-3}	0.145	26.22	41.71
14. Indole	1.82×10^{-3}	0.149	17.41	58.11
15. Quinoline	1.99×10^{-3}	0.183	23.11	65.76
16. Aniline	1.87×10^{-3}	0.205	19.14	78.43
17. 2,2'-Dipyridyl	1.92×10^{-3}	0.226	35.28	84.00
18. Benzylamine	2.48×10^{-3}	0.346	37.14	100.00
Total		2.1	298.4	

the amount sorbed and the molecular size of a compound. Indeed the amount of three- and four-ring compounds sorbed is generally lower than the amount of two- and one-ring compounds. The relation between separation and molecular size is well documented: zeolites are known as shape-selective sorbents because of their uniform pore size (*12, 13*). To study the effect of the pore size, two zeolites of smaller pore size were used. Zeolite 13X has a pore diameter of ≃ 10 Å; zeolite 10X, ≃ 8 Å; and zeolite 5A, ≃ 5 Å. The efficiency of separation was found to be proportional to pore size, as shown in Fig. 2.

Zeolite 13X was therefore tested for the removal of the nitrogenous compounds from a naphtha. Figure 3 shows the fraction N found in the effluent as a function of the effluent volume for both naphthas. As expected, the coker naphtha, which has the lowest nitrogen content, took longer to saturate the bed. Using the area over the total breakthrough curve and the initial nitrogen concentration, the sorption capacity was calculated at 4.61 mg N (1.36 mg N/g zeolite) for the coker naphtha and

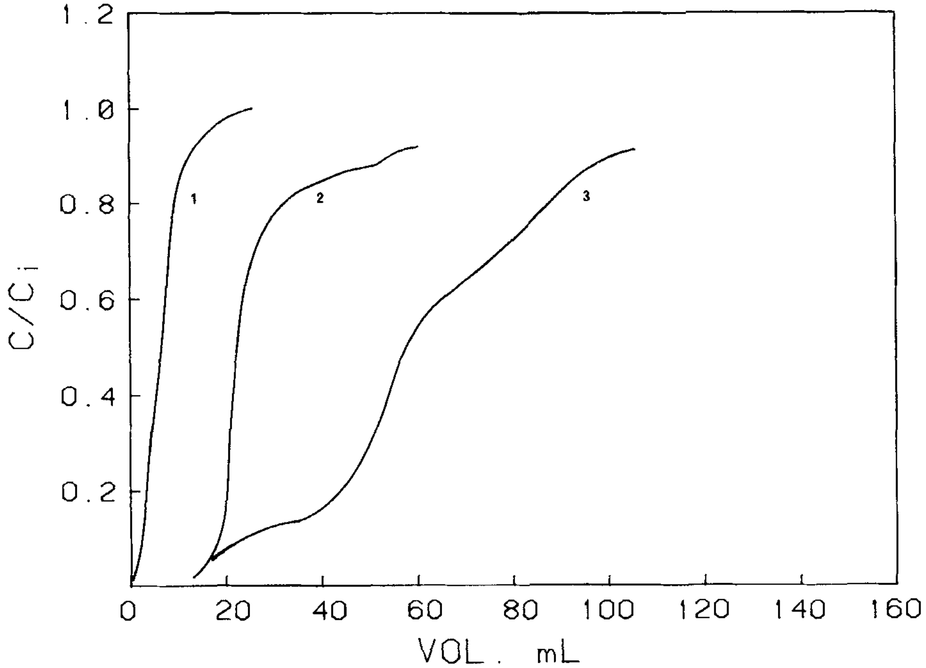

FIG. 2. Total nitrogen breakthrough curves for three zeolites. The standard feed was used. 1) Zeolite 5A = 3.2 g, 2) zeolite 10X = 3.0 g, 3) zeolite 13X = 3.0 g.

14.24 mg N (4.3 mg N/g zeolite) for the hydroprocessed naphtha. Assuming only one nitrogen atom per molecule, the quantities sorbed are 0.10 mmol/g zeolite for the coker naphtha and 0.31 mmol/q zeolite for the hydroprocessed naphtha, which is significantly lower than 0.7 mmol/g zeolite obtained for the model compounds (Table 3).

The effect of pore size was also tested using the coker naphtha. The extent of nitrogen removal was much lower for zeolite 5A (Curve 1, Fig. 3) compared to zeolite 13X (Curve 2, Fig. 3). This is consistent with the results obtained with model compounds.

DISCUSSION

The success of a separation method such as the one proposed in this study depends on the ability to remove all the nitrogenous compounds indiscriminately. One classic example of such a process is the separation

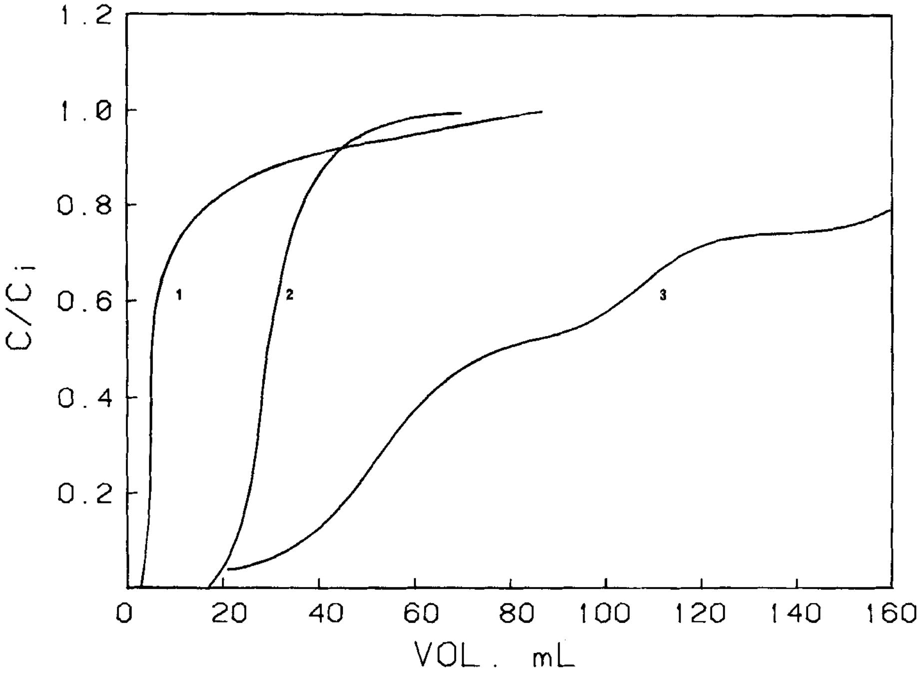

FIG. 3. Total nitrogen breakthrough curves for a coker naphtha sorbed on zeolite 5A (Curve 1), hydroprocessed naphtha sorbed on zeolite 13X (Curve 2), and coker naphtha sorbed on zeolite 13X (Curve 3). Conditions were 6.2 g of zeolite 5A, 0.4 cm i.d. × 60 cm long column; 3.4 g zeolite 13X for coker naphtha study and 0.4 cm i.d. × 30 cm long column; 3.3 g zeolite 13X for hydroprocessed naphtha, 0.4 cm i.d. × 30 cm long column.

of normal paraffins from isoparaffins in a naphtha fraction using zeolite 5A (*14–16*). This process removes 98% of the normal paraffins and the selectivity is the same for all the normal paraffins.

The results obtained in the present study show that the extent of sorption of nitrogenous compounds on zeolite 13X depends on the nature of the compounds. The extent of sorption is inversely related to molecular size. This suggests that sorption is diffusion controlled. Since diffusion processes are dependent on temperature, the extent of sorption should increase with increasing temperatures. Diffusion parameters may also depend on such intrinsic properties of the zeolite as surface acidity and the nature of the cation. It may be possible to control these variables in order to design sorbents that will remove all nitrogenous compounds indiscriminately. These aspects are presently under investigation.

Previous results suggest that zeolites will probably be most effective to denitrogenate naphtha fractions. Indeed, the nitrogenous compounds contained in naphthas are substituted pyridines and quinolines, and according to the model compound study, these nitrogenous compounds should be extensively removed. The naphtha study confirmed this.

The breakthrough curve for the hydroprocessed naphtha is very sharp, indicating that all the nitrogenous compounds are removed indiscriminately. In the case of the coker naphtha the breakthrough curve resembles that of the model compound study, suggesting discrimination toward certain types of nitrogenous compounds. No attempt was made at identifying the nitrogenous compounds not sorbed. It is worthwhile noting that the basis of discrimination is not necessarily size but could also be based on acid/base character as was observed in the case of treated ilmenite (*17*). Zeolites are known to be very acidic, having a large number of both Lewis and Bronsted acid sites (*18*). Nitrogenous bases such as pyridine, *n*-tributylamine, and trimethylamine have been shown to adsorb on Lewis and Bronsted acid sites, and have actually been used extensively to measure the surface acidity of various solids (*19, 20*). The nature of the nitrogenous compounds contained in these two naphthas is likely to be different and could explain the observed differences.

The sorption capacity of the zeolite can easily be calculated from the breakthrough curves. The sorption capacity for model compounds was 0.1 g/g sorbent, which is comparable to the capacities obtained for vapor-phase sorption of hydrocarbons and nitrogen bases. Breck and Flanigen showed that 0.227 g of tributylamine per gram of zeolite could be sorbed on zeolite X at room temperature (*21*). In a liquid-phase experiment, $C_8F_{18}O$ was separated from $(C_4F_9)_3N$ by sorption on a zeolite 13X: the $C_8F_{18}O$ loading at breakthrough was 0.3 g/g of zeolite (*22*). The capacity of 0.1 g/g of zeolite obtained in this study without any optimization of the process certainly demonstrates the feasibility of large-scale removal of nitrogenous compounds using zeolites.

The sorption capacities for naphthas were found to be 0.10 mmol/g for the coker naphtha and 0.31 mmol/g for the hydroprocessed naphtha, significantly lower than the 0.7 mmol/g obtained for the model compounds. The lower sorption capacities could be due to the differences between the nature of the nitrogenous compounds contained in the naphthas and in the model compound solution. For instance, larger nitrogenous compounds or long-chain substitution could explain the lower capacities observed. It could also be due to the sorption of nonnitrogenous compounds. The sorbent may not be totally selective for nitrogenous compounds.

The selectivity showed by a sorbent toward a sorbate is determined by several types of interaction energies such as dispersion, repulsion, polarization, and dipole/quadrupole interaction. These interactions are functions of the properties of the sorbates and sorbent. For a given feed the selectivity will be a function of such variables as the nature of the cation in the zeolite, the surface acidity, and the sorbent pretreatment. For instance, large pore size zeolites such as 13X exhibit selectivity for the aromatic components of a mixture of aromatics and paraffins. The selectivity is reversed when the polarizing cation is replaced by protons (*23*). In the case of naphtha it may be possible to increase the selectivity for nitrogenous compounds at the expense of olefins and aromatics. A detailed investigation has been undertaken to assess and control the selectivity of sorption of olefins, aromatics, naphthenes, paraffins, and nitrogenous compounds.

REFERENCES

1. A. A. Oswald and F. J. Noel, *J. Chem. Eng. Data, 6*, 294 (1961).
2. R. K. Artzmark and J. B. Gilbert, *Hydrocarbon Process., 46*, 163 (1967).
3. M. W. Schrepfer, R. J. Arnold, and C. A. Stansky, *Oil Gas J.*, p. 79 (January 16, 1984).
4. J. W. Frankenfeld and W. F. Taylor, *Ind. Eng. Chem., Prod. Res. Dev., 22*, 608 (1983).
5. J. W. Frankenfeld and W. F. Taylor, *Ibid., 22*, 615 (1983).
6. D. M. Jewell and R. E. Snyder, *J. Chromatogr., 38*, 351 (1968).
7. D. M. Jewell, J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham, *Anal. Chem., 44*, 1391 (1972).
8. D. E. Hirsh, R. L. Hopkins, H. J. Coleman, F. O. Cotton, and C. J. Thompson, *Ibid., 44*, 915 (1972).
9. H. Sawatzky, A. E. George, G. T. Smiley, and D. S. Montgomery, *Fuel, 55*, 16 (1976).
10. C. D. Ford, S. A. Homes, L. F. Thompson, and D. R. Latham, *Anal. Chem., 53*, 831 (1981).
11. J. M. Schmitter, I. Ignatiadis, P. Arpino, and G. Guiochon, *Ibid., 55*, 1685 (1983).
12. D. W. Breck *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, Wiley, London, 1974.
13. W. M. Meier and S. B. Uytterhoeven (eds.), "Molecular Sieves," *Adv. Chem. Ser., 121* (1973).
14. M. F. Symoniak and A. C. Frost, *Oil & Gas*, p. 16 (March 15, 1971).
15. G. J. Griesmer, W. F. Avery, and M. N. Y. Lee, *Hydrocarbon Process. Pet. Refiner, 44*, 147 (1965).
16. M. J. Sterba, *Ibid., 44*, 151 (1965).
17. G. Jean, M. Poirier, and H. Sawatzky, *Sep. Sci. Technol., 20*, 541 (1985).
18. K. Tanabe, *Solid Acids and Bases*, Academic, New York, 1970.
19. L. Forbi, *Catal. Rev., 8*, 65 (1973).
20. W. Pohle and P. Brauer, *J. Catal., 77*, 511 (1982).
21. D. W. Breck and E. W. Flanigen, *Molecular Sieves*, Society of Chemical Industry, London, 1968, p. 47.
22. B. J. Mair and M. Shamaiengen, *Anal. Chem., 30*, 276 (1958).
23. P. E. Eberly, *Ind. Eng. Chem., Prod. Res. Dev., 10*, 433 (1971).

Received by editor January 15, 1985