JOURNAL OF CATALYSIS 86, 24–31 (1984)

TMA–Offretite. Relationship between Structural and Catalytic Properties

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Received April 5, 1983; revised October 4, 1983

Previous studies reported that synthetic TMA–offretite is an open large-pore (12-membered oxygen ring opening) zeolite. Closer reexamination of the odd *l* lines using high intensity X-ray diffraction and additional catalytic diagnostic studies suggest that some of the open 12-ring channels in the synthetic sample may be blocked randomly by single stacking faults, such that the only other openings are 8-membered oxygen ring openings perpendicular to the large channels. These structural characteristics could explain the observed shape selective catalytic dewaxing activity and the preponderance of straight-chain cracked products.

INTRODUCTION

Previous catalytic studies (*1*) demonstrated that subtle structural differences among members of the heulandite family of zeolites have a marked effect on catalytic properties. Catalytic reactions used in conjunction with analytical methods, such as X-ray powder diffraction, provide a unique diagnostic tool to probe structural defects, such as stacking faults and/or intergrowths in zeolites. This paper reexamines the relationship between the structure and the catalytic properties of a synthetic TMA–offretite sample reported previously (*2, 3*).

Structure of Offretite–Erionite

The mineral offretite, first described in 1890 by Gonnard, is the end member of a family of zeolites; the other end member is erionite. These two end members differ by the manner the cancrinite cages—the basic building units—are stacked between hexagonal prisms (*2*) (double six rings). The erionite and offretite frameworks are shown in Fig. 1. The major consequence of varying the stacking order, insofar as the channel openings are concerned, is that in offretite the 12-membered oxygen ring channels in the *c*-direction are open, because the cancrinite cages have the same alignment throughout the structure, while the 12-membered oxygen ring channels in erionite are blocked every 15 Å in the *c*-direction as a result of rotating successive layers of cancrinite cages by 60°.

Thus, erionite has only 8-membered oxygen ring openings in the *a*-direction while offretite has these 8-membered oxygen ring openings plus the 12-membered oxygen ring openings. If the rotation of the cancrinite cages is random, then a whole family of structures results. Such random rotation or random stacking has been detected in the erionite/offretite family of zeolites using transmission electron microscopy and the contrast line technique (*4, 5*).

Previous catalytic studies (*3*) showed that the 12-membered oxygen ring opening channels in offretite could be effectively blocked by a relatively low concentration of stacking faults. For example, samples for which the intensity of the odd *l* lines in their X-ray diffraction patterns indicated no more than 3% stacking faults were remarkably shape-selective toward *n*-hexane indicating that all the 12-membered oxygen ring openings were blocked and hence inacces-

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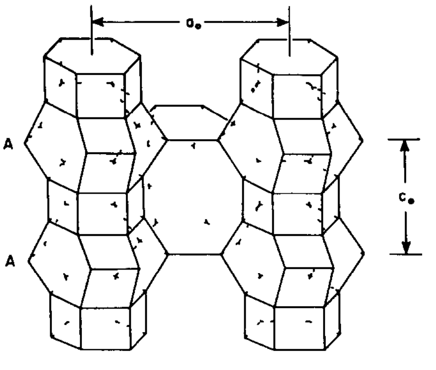
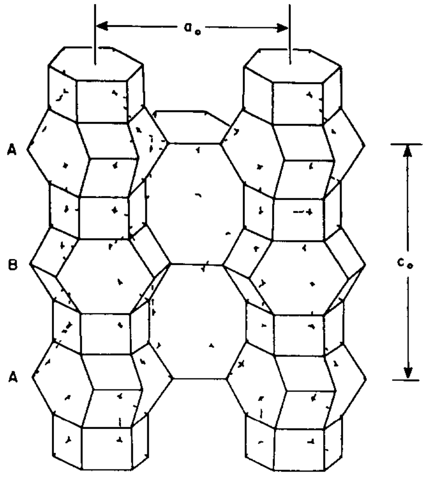


Offretite



Erionite

FIG 1 Frameworks of erionite and offretite

sible to larger hydrocarbon molecules as would be expected The first successful synthesis of an open 12-ring zeolite, TMA-offretite, was reported by Whyte *et al* (*2*) Although X-ray step scanning techniques showed the sample possessed very weak and narrow odd l lines, 7 8 wt% of cyclohexane was sorbed indicating that this trace (<1%) of "erionite" had not rendered the 12-membered oxygen ring channels inaccessible to large hydrocarbon molecules Catalytic test of the same zeolite using a mixture of n-hexane, 2-methylpentane, and benzene at 15/1 m hydrogen/hydrocarbon ratio and 15 atm total pressure showed that the TMA-offretite sample had a significant 2-methylpentane conversion (*3*) (Table 1)

TABLE 1

Result of Catalytic Test

	Conversion[a] wt%	
	n-Hexane	2-Methylpentane
Erionite	76 3	2 6
TMA-offretite	62 3	52 3

[a] Molal ratio 15/1 hydrogen/hydrocarbon, 15 atm, 4 LHSV, 370°C, Feed 1 1 2 n-hexane 2-methylpentane benzene

Published data (*6*) (Table 2) showed that the constraint index of TMA-offretite to be higher than that of large pore zeolites, such as zeolite Y, but lower than that of ZSM-5, an intermediate pore size zeolite of 10-membered oxygen ring channels (*7*) These data as well as the sorption data (*2*) are consistent with the offretite structure which has puckered 12-membered oxygen rings with a free diameter of 6 4 Å—larger than the 10-membered oxygen ring channels in ZSM-5 and smaller than the 12-membered oxygen ring openings in zeolite Y

This paper presents additional catalytic diagnostic studies and a closer reexamination of the odd l lines of the X-ray diffraction pattern of TMA-offretite These new data indicate the presence of random stacking faults These stacking faults could help explain the observation that TMA-offretite has reactant and product selectivities which are different from that of ZSM-5 or zeolite Y

EXPERIMENTAL

Materials

The TMA-offretite sample was prepared by the same methods described by Whyte *et al* (*2*) and Chen (*3*) It was synthesized from an alumina-silica gel in the presence of potassium, sodium, and tetramethylammonium hydroxides (*8*) For the catalytic experiments, the zeolite was calcined at 538°C for 16 h and exchanged four times with 0 5 N NH_4Cl solution at room temper-

TABLE 2

Constraint Indices of Various Zeolites Measured at 315°C

ZSM-5	8.3
TMA-offretite	3.7
REY	0.4

ature and then exchanged with a 0.5 *N* solution of $NH_4Cl/ZnCl_2$ at 90°C, filtered, water-washed, and air-dried. The finished catalyst had a SiO_2/Al_2O_3 ratio of 7.5 and contained 2.7 wt% residual potassium, 0.08 wt% sodium, and 2.2 wt% zinc.

The ZSM-5 sample was synthesized as described by Argauer and Landolt (*9*). It was calcined, exchanged with $NH_4Cl/ZnCl_2$ as described above. The finished catalyst had a SiO_2/Al_2O_3 ratio of 25 and contained 0.17 wt% sodium and 0.86 wt% zinc.

The zeolite Y was received in its sodium form. It was also exchanged with $NH_4Cl/ZnCl_2$ as described above. The finished catalyst had a SiO_2/Al_2O_3 ratio of 5.0 and contained 1.46 wt% sodium and 8.19 wt% zinc.

The natural erionite sample, obtained from Jersey Valley, Nevada, had the X-ray powder diffraction pattern reported by Chen and Garwood (*10*). After the treatments described above, the finished catalyst had a SiO_2/Al_2O_3 ratio of 7.8, and contained 2.42 wt% potassium, 0.07 wt% sodium, 0.14 wt% magnesium, 0.53 wt% calcium, and 1.8 wt% zinc.

X-Ray Diffraction Analysis

X-Ray powder diffraction studies were carried out on the ammonium-exchanged samples after air calcination at 538°C for 1 h with a Philips-Norelco X-Ray Diffractometer and Cu*Kα* radiation. To detect the low concentration of odd *l* lines, the intensity was increased by increasing the slit size with some loss of resolution (*11*).

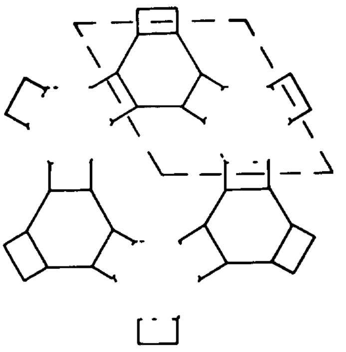
Catalytic Test

The experiments were conducted in a stainless-steel microreactor at 35 atm total pressure, feeding a 315–400°C boiling range mid-continent gas oil containing 12 wt% *n*-paraffins at 30/1 *m* hydrogen/hydrocarbon ratio. This feedstock was chosen to test the accessibility of the zeolite to high-molecular-weight, linear, and slightly branched waxy paraffinic molecules. The ability of a catalyst to selectively hydrocrack these waxy molecules is indicated by measuring the pour point of the topped liquid product according to the standard ASTM method. The feed had a pour point of 10°C. The chemical composition of the hydrocracked gas and liquid products were determined by gas chromatography.

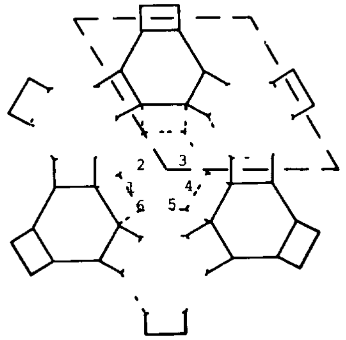
RESULTS

X-Ray Diffraction Analysis

The 001 projections of erionite and offretite are shown in Fig. 2. If the *c* parame-



Offretite
001 Projection



Erionite
001 Projection

FIG. 2. The 001 projections of erionite and offretite.

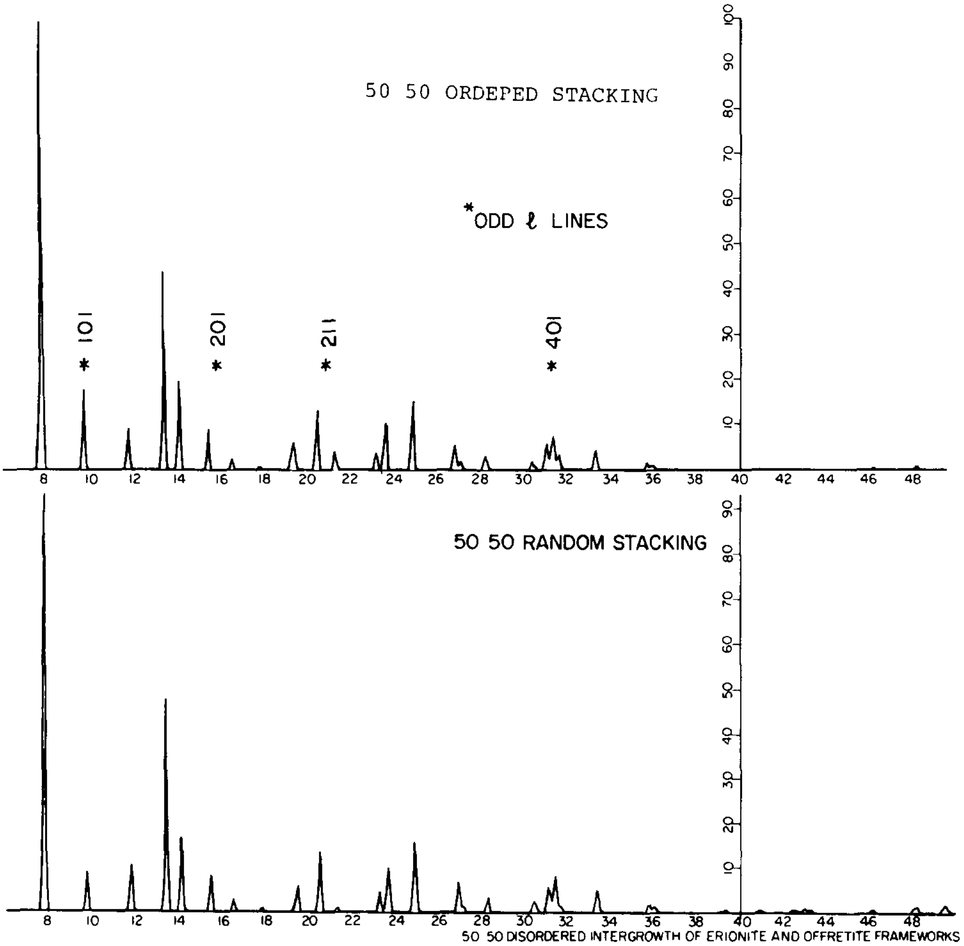


FIG 3 Simulated X-ray diffraction patterns of intergrown erionite/offretite

ter of offretite is doubled and its structure superimposed on that of erionite, all atoms are superimposed except those labeled 1 to 6 in Fig 2 If these atoms are given either ordered or random occupancy, intergrown structures having either ordered or random stacking faults would result Shown in Fig 3 are the simulated X-ray diffraction patterns of two 50% stacking-faulted structures (*12*) It is noted that the relative intensity of the odd *l* lines in these two patterns is different Specifically, the ratio of 201 line at 16 7° to the 211 line at 21 5° is greater than 1 for random stacking faults and less than 1 for ordered intergrown structures

Random stacking faults give rise to X-ray reflections corresponding to $d_{001} = \infty$ or $c^* = 0$ This causes streaking in electron diffraction patterns and broad lines in X-ray diffraction patterns

Shown in Fig 4 is the high intensity X-ray diffraction of calcined offretite Despite some loss in resolution by opening the slit, and some loss of intensity of the low angle lines, the broad lines at 16 7 and 21 5° are evident In addition, the intensity of the 201 line at 16 7° is stronger than the 211 line at 21 5° This indicates that at least some of the stacking faults are randomly distributed

As pointed out previously by Gard (*5*), even single stacking faults could have a profound effect on sorption and catalytic properties, as branched-chain hydrocar-

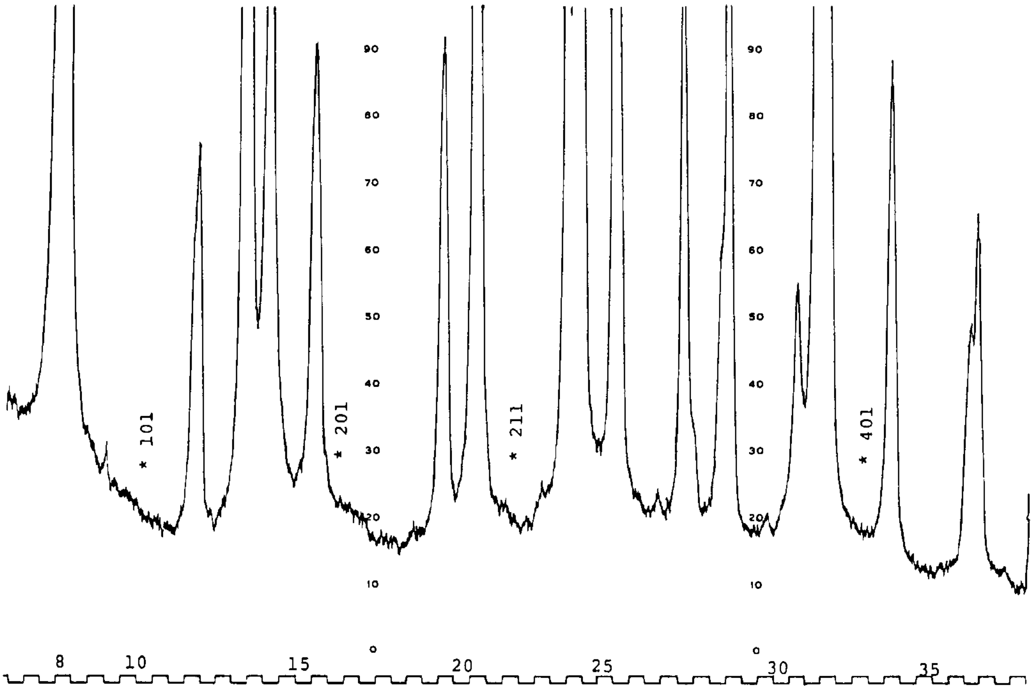


FIG 4 High-intensity X-ray diffraction pattern of calcined TMA–offretite

bons could diffuse into the 12-membered oxygen ring channels only up to the first stacking fault The blockage has the effect of closing off the exit in the *c*-direction leaving only the 8-membered oxygen ring openings accessible to the hydrocarbon molecules However, equilibrium sorption studies (*2*) showed that substantially all the intracrystalline pores available for *n*-hexane sorption are also available for cyclohexane sorption, indicating that most of the large pore channels in the *c*-direction are available for sorption, i e , they are open at least on one end A conceptual description of such a pore system is shown in Fig 5 Thus, the large 12-ring channels, each of which may be blocked by a stacking fault, are interconnected through the 8-ring channels

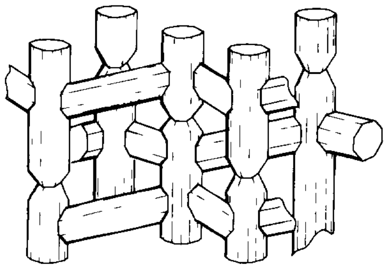


FIG 5 Pore sorption in TMA–offretite

Catalytic Selectivity of Zeolites for Pour Point Reduction

Shown in Fig 6 are the experimental results relating pour point of the dewaxed 315°C$^+$ product to the weight percentage of feed converted to 315°C$^-$ product for four zeolites an erionite which has 8-membered oxygen ring openings, a zeolite Y which has 12-membered oxygen ring openings, a ZSM-5 which has 10-membered oxygen ring openings, and the offretite in question Also shown in Fig 6 is an experimental point (△) obtained by extracting the feedstock with zeolite A, which adsorbs only *n*-paraffinic molecules (*13*) Experimental points lying to the right of this point are the result of hydrocracking of non-normal par-

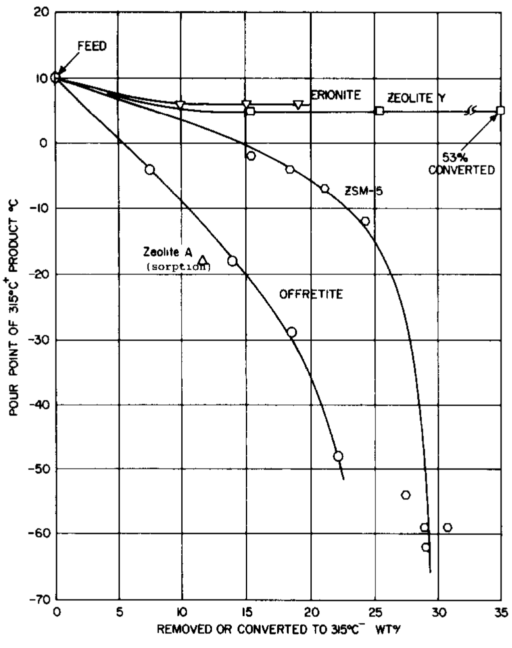


FIG 6 Selectivity of zeolites for pour point reduction

affins It is noted that preferential removal of *n*-paraffins can, at best, lower the pour point to about −18°C Therefore, it is necessary to selectively remove both *n*-paraffins and some of the high melting point nonnormals, such as mono-methyl paraffins in order to lower the pour point to below −18°C Among the four zeolites tested, only offretite and ZSM-5 lowered the pour point to below −45°C, while zeolite Y and erionite showed no dewaxing activity at all

DISCUSSION

While chemical reactivity of a paraffinic molecule increases with its degree of branching and its chain length, its melting point decreases with increased branching and shorter chain length (Fig 7) Thus, an effective dewaxing catalyst must have the ability to overcome the handicap imposed by the chemical reactivity of the molecules and preferentially attack long-chain molecules with little or no branching Earlier studies showed that although erionite admits straight-chain molecules (*10*), it is ineffective in cracking long-chain *n*-paraffins because of diffusional constraints Hence its inability to dewax gas oils is expected Zeolite Y's inability to dewax demonstrates that large planar 12-membered oxygen ring openings cannot discriminate between molecules with different degrees of branching

ZSM-5 pore structure is characterized by intermediate-sized 10-membered oxygen ring openings, which admit slightly branched waxy molecules but exclude low-melting-point highly branched molecules This is the major reason for its effectiveness as a dewaxing catalyst (*14*)

Offretite's effectiveness as a dewaxing catalyst is most interesting The data in Fig 6 show that the offretite line lies to the left of the ZSM-5 line, indicating that offretite is more selective toward straight-chain molecules and, therefore, needs to convert a smaller fraction of the gas oil to reach the same pour point than ZSM-5 does This unexpected dewaxing selectivity appears inconsistent with the offretite structure or with earlier cracking and sorption data which suggest that offretite should be more

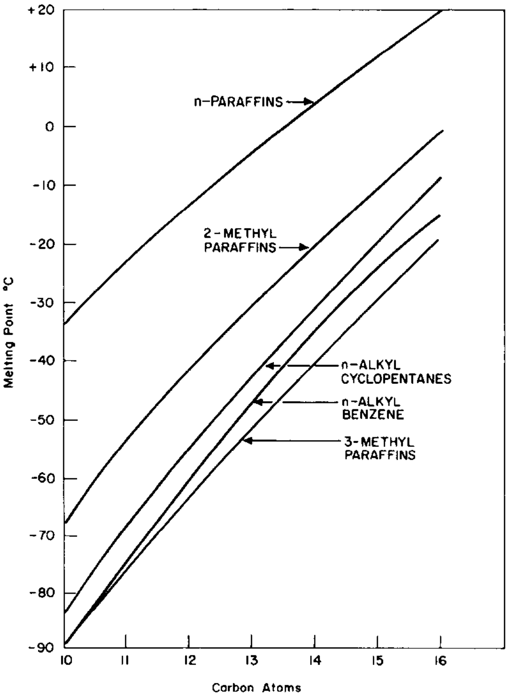


FIG 7 Melting point of pure hydrocarbons

TABLE 3

Distribution of Cracked Products

	Offretite		ZSM-5	
	wt%	n%	wt%	n%
C_1	1	—	<1	—
C_2	3	—	1	—
C_3	23	—	8	—
C_4	39	70	22	50
C_5	31	84	39	55
C_6	3	—	20	—
C_7^+	0	—	10	—
	100		100	

open and, therefore, less selective than ZSM-5

The nature of the cracked products from the dewaxing experiment also appears to be inconsistent with the open offretite structure As shown in Table 3, TMA–offretite makes more, low-molecular-weight products than ZSM-5 The products from TMA–offretite are high in normal-to-iso ratios

The observed reactant and product selectivities could, however, be attributed to the presence of a low concentration of randomly distributed stacking faults in the synthetic offretite sample Without the blockage, little discrimination among paraffinic molecules would be expected, and selectivity should approach that of zeolite Y With the blockage, only *n*-paraffins would diffuse through the entire pore structure while branched paraffins could only diffuse in and out through one end of the same channel The difference in accessibility does not appear to affect the cracking of low-molecular-weight branched paraffins such as the 2-methylpentane used in the earlier diagnostic tests The result led to the conclusion that TMA–offretite is more open and less selective than ZSM-5 With high-molecular-weight feedstocks, such as the gas oil used in the dewaxing experiments, it is evident that *n*-paraffins are preferentially cracked in TMA–offretite The interconnecting 8-membered oxygen ring openings also could increase mobility of the straight-chain cracked fragments accounting for more secondary cracking reactions and more straight-chain cracked products

CONCLUSIONS

1 Comparison of simulated X-ray diffraction patterns of ordered and randomly stacking-faulted structures with high-intensity X-ray diffraction analysis of a calcined TMA–offretite indicates the presence of a low concentration of randomly distributed stacking faults in the synthetic sample

2 While the synthetic offretite sample has open, large 12-membered oxygen ring channels which can adsorb both straight-chain and branched-chain molecules, the stacking faults block the exit port of some of the channels, so that the only openings are 8-membered oxygen ring openings perpendicular to the large channels

3 These structural characteristics are reflected in the catalytic properties of synthetic offretite Unlike a large-pore zeolite, synthetic offretite preferentially converts *n*-paraffins and gives cracked products high in straight-chain isomers

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