CATALYTIC AND PHYSICOCHEMICAL PROPERTIES OF ACID-LEACHED OFFRETITES

F. HERNANDEZ, R. IBARRA, F. FAJULA, F. FIGUERAS

Laboratoire de Chimie Organique et Cinétique Chimique Appliquées - U.A. C.N.R.S. 418 - E.N.S.C.M., 8 rue de l'Ecole Normale - 34075 Montpellier Cedex France.

ABSTRACT

Two series of acid-leached offretites have been prepared by treating synthetic HK and NaK offretites with dilute HCl solution. The solids were characterized by elemental analysis, X-ray diffraction and surface area measurements. Their catalytic activity has been evaluated in the cracking of cyclohexane and the hydration of butenes. Acid treatment induces a simultaneous dealumination and decationization of the parent zeolites and structural modifications. The lattice of HK offretite is progressively destroyed by the acid whereas acid-leached NaK offretites contain mesopores and crystalline zones enriched in silica. For both zeolites the acid strength is enhanced by dealumination. The main conclusion of the study is that acid leached offretites exhibit a catalytic behaviour very similar to that of ZSM-5.

INTRODUCTION

Offretite is a hexagonal zeolite whose structure consists in parallel arrangements of cancrinite cages (cage ϵ) linked by hexagonal prisms (double six rings) in the c-direction. These ensembles delimit a system of 12-membered oxygen ring channels (free diameter 6.4 Å) along the c-axis intercommunicating through gmelinite cages (openings 3.6 x 5.2 Å) in the a-direction [1].

The porous network of offretite, available for sorbents, is virtually one-dimensional, with free apertures intermediate between those of the pentasil zeolites such as ZSM-5 (5.8 Å) and of the mordenites (6.7 Å), two zeolites types of great commercial importance in the field of catalysis.

In a large majority of cases, the lower the aluminium and residual cation content are of the zeolites, the higher their catalytic activity. With ZSM-5 and mordenite high degrees of decationization (> 95%) are readily achieved by standard low temperature ion-exchange. This is not the case for offretite. Each unit cell contains a non-exchangeable cation located in a cage ϵ [2, 3]. This cation cannot be substituted by sodium in the synthesis [4, 5] and its extraction at high temperature causes severe disruption of the framework.

On the other hand Si/Al ratios in synthetic offretites rarely exced values of 4. Steam and acid treatments must therefore be performed very cautiously in order to avoid crystal collapse.

Although the litterature dealing with the catalytic properties of offretites is very scarce, recent reports point out the potential of this zeolite for the dewaxing of gas-oils [6]

the cracking of naphtenes [7] and the hydration of olefins [8, 9]. In the above studies, data refer to offretites prepared by standard ion-exchange.

The objective of our study has been to investigate the properties of offretites activated with mineral acids.

In this paper we report our initial results obtained on a series of solids prepared by treating NaK and HK forms of synthetic offretites with dilute solutions of HCl. Some physical properties of the modified offretites are described and their catalytic properties for the cracking of cyclohexane and the hydration of n-butenes are presented and compared to that of other zeolites.

EXPERIMENTAL

Materials. Two samples of synthetic offretite were obtained from Grace Davison :
- a NaK form, of oxide composition : $[0.79$ K, 0.26 Na$]_2$O, Al_2O_3, 6.54 SiO_2, 3.28 H_2O. Its surface area $(180$ $m^2.g^{-1}$, Table 1) and cation/aluminium ratio, greater than one, suggested that this sample contained some extra-lattice material.
- a HK form, oxide composition $[0.23$ K, 0.02 Na, 0.75 H$]_2$O, Al_2O_3, 6.78 SiO_2, 3.9 H_2O, 2.5 wt % residual potassium, 0.1 wt% sodium. Its surface area was 531 $m^2.g^{-1}$. Its constraint index at $450°C$, LHSV $= 1.9$ h^{-1} was constant with time on stream and equal to 3.2. For both samples, zeolite crystals had a prismatic shape with 1 to 1.5 μm length and 0.3 to 0.6 μm width.

Procedures. Acid leaching was achieved by dispersing first one gram of zeolite in 250 ml of deionised water. The HCl solution (50 ml) chosen so that the amount of acid (expressed in meq) per gram of zeolite ranged from 0.1 to 20, was then added dropwise. After five hours at room temperature the equilibrium pH of the suspension was recorded. The solid was recovered by filtration, washed, oven dried and finally calcined in flowing air for 5 h.

The zeolites used in the comparative catalytic studies were a mordenite from the Société Chimique de la Grande Paroisse, a H-ZSM-5 from the Institut Français du Pétrole and a Y-zeolite from Linde. Their characteristics are given in refs 7 and 9.

Characterization studies. The chemical compositions of the samples were determined by atomic absorption after dissolution. Some samples were also analyzed by X-ray fluorescence. X-ray powder diffraction studies were carried out with a CGR theta 60 instrument using CuKα radiation. The crystallinity of the solids was determined as described previously [10, 11] by comparing the sum of the intensities of selected diffraction peaks to that of the area under the background. Nitrogen BET surface areas were measured in a static volumetric device equiped with an integral Barocel pressure transducer.

Catalytic tests. The conversion of cyclohexane was conducted at $450°C$ in a flow apparatus at atmospheric pressure using 100 mg of catalyst. This reaction was chosen as a test for two reasons. Firstly, the critical dimension of the cyclohexane molecule ($\simeq 6$ Å) is very close to that of the offretite pores. The reaction will therefore be very sensitive to the alterations of the zeolite porosity. Actually, offretites with stacking faults lead

o inactive catalysts [7]. Secondly, the selectivity towards cracking or isomerization is closely related to the acidity of the zeolite [7].

Hydration of n-butenes was studied at 250°C and 65 atm of pressure with a water to olefin ratio of 4.5 in a batch reactor. It was previously shown [9] that the hydration activity of zeolites is a direct function of the acid strength of the protons attached to their framework, regardless of their structure.

RESULTS AND DISCUSSION

The chemical compositions of the acid leached HK and NaK offretites, expressed as their unit cell contents, are given in Tables 1 and 2 respectively. Treatment of both zeolites with dilute HCl resulted in a parallel dealumination and decationization of the parent material. The mechanism of aluminium extraction by strong mineral acids generally supposes [12] a two step process of hydrogen ion exchange followed by the replacement of an AlO_4 tetrahedron by four OH groups. The fact that with HK offretite the two processes occur simultaneously (Table 1) can be attributed to the difficulty of removal of the potassium cations trapped in the cancrinite cages. By increasing the severity of the acid

Table 1

Unit cell content, XRD crystallinity and surface area of the samples obtained

by acid treatment of KH offretites

Sample	Equilibrium pH	Unit cell content	% crystallinity XRD	Surface area $m^2.g^{-1}$
Starting	material	$K_{0.94}Na_{0.08}H_{3.07}[Al_{4.1}Si_{13.9}O_{36}]8H_2O$	100	531
1	2.2	$K_{0.65}Na_{0.03}H_{3.20}[Al_{3.9}Si_{14.1}O_{36}]6.4H_2O$	97	371
2	1.94	$K_{0.62}Na_{0.01}H_{3.07}[Al_{3.7}Si_{14.3}O_{36}]6.6H_2O$	84	-
3	1.5	$K_{0.54}Na_{0.01}H_{2.60}[Al_{3.2}Si_{14.8}O_{36}]6.2H_2O$	71	312
4	1.4	$K_{0.40}Na_{0.01}H_{2.50}[Al_3 Si_{15} O_{36}]7H_2O$	31	171

treatment the residual cation content could be reduced to 0.4 K^+ per unit cell and up to 50 % of the aluminium atoms could be extracted. However this resulted in a severe loss of crystallinity as evidenced by the XRD measurements and the surface areas determinations (last columns of the Tables). At lower pH the zeolite became totally amorphous.

The KNa offretite sample led to somewhat different results (Table 2). Aluminium extraction began before all the readily exchangeable cations had been replaced by protons. The apparent increase of the aluminium content of sample 5 is more probably due to the removal of extra-lattice silica. Even after the extraction of nearly 50 % of the aluminium atoms from the zeolite each unit cell contained one potassium cation. This shows that the acid treatment of KNa offretite did not affect the cationic sites, and consequently the aluminium tetrahedra, associated with the cages ε. Exchange of the sodium ions was, by contrast, rapidly achieved.

A second difference concerns the physical properties of the resulting solids. Although X-ray diffraction revealed a loss of crystallinity very similar to that observed with HK

Table 2

Unit cell content, XRD crystallinity and surface area of the samples obtained

by acid treatment of KNa offretite

Sample	Equilibrium pH	Unit cell content	% crystallinity XRD	Surface area m².g⁻
Starting	material	$K_{3.33}Na_{1.16}[Al_{4.21}Si_{13.78}O_{36}]6.7\,H_2O$	100	180
5	2.55	$K_{2.59}Na_{0.26}H_{1.5}[Al_{4.4}Si_{13.6}O_{36}]8.4\,H_2O$	84	377
6	2.47	$K_2\,Na_{0.12}H_2\,[Al_{4.1}Si_{13.9}O_{36}]8.6\,H_2O$	67	400
7	2.37	$K_{1.9}Na_{0.07}H_{1.5}[Al_{3.5}Si_{14.5}O_{36}]8.23\,H_2O$	60	396
8	2.32	$K_{1.2}Na_{0.08}H_{1.6}[Al_{2.9}Si_{15.1}O_{36}]10.9\,H_2O$	37	403
9	2.2	$K_1\,Na_{0.08}H_{1.5}[Al_{2.6}Si_{15.4}O_{36}]10.4\,H_2O$	30	411
10	1.8	$K_{0.9}Na_{0.07}H_{1.4}[Al_{2.4}Si_{15.6}O_{36}]11.3\,H_2O$	24	350

offretite, the surface areas of the acid leached NaK offretites remained high and unmodified within 10 % variation. Moreover while the parent zeolite exhibited a characteristic, well defined, Type I isotherm, the shape of the curves was progressively shifted to a Type IV isotherm, indicating the appearance of a mesoporosity in the range 20-100 Å. This suggests that during the attack, portions of the crystal have been destroyed producing holes. The variations of the a and c parameters of the remaining crystalline zones of samples 5-10 as a function of their aluminium content are presented in Figure 1. As the aluminium content decreased, the a-axis shrank regularly whereas the c-axis expanded first and then remained constant. Such a unit cell contraction is consistent with the formation of new Si-O-Si bonds in the lattice with silicium atoms taking positions in the vacated tetrahedral sites [12].
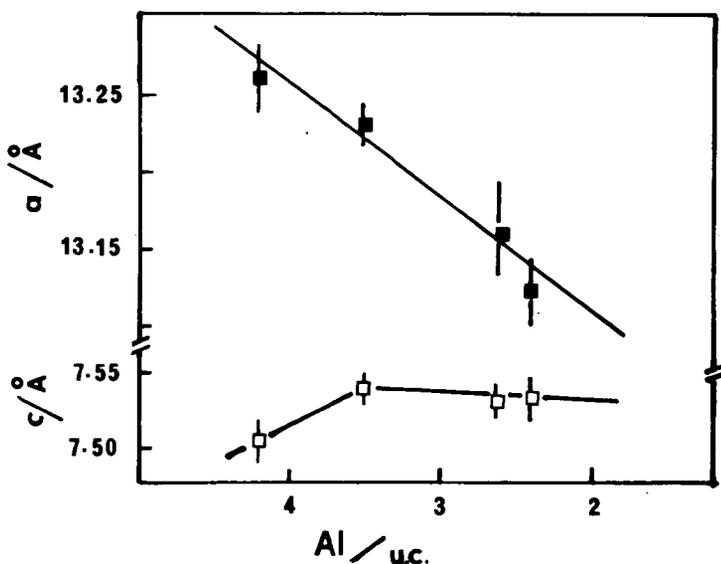

Fig. 1. Variations of the a and c parameters as a function of the aluminium content in acid leached NaK offretite.

Taking into account all these facts the texture of the acid leached NaK offretites can be represented by small crystalline zones, enriched in silica with respect to the starting zeolite, separated by holes. Recent work on the preparation of high silica faujasites by high temperature steaming and acid extraction led to similar solids [13].

There is a clear evidence that, depending on the cationic content of the parent zeolite, the treatment of offretites by dilute HCl leads to different produts.

The relationship existing between the cation content and the sieving properties of offretite have been studied by Aiello et al [14]. The presence of potassium ions in the main channels significantly reduces the penetration of guest molecules as well as the water content. During acid treatment, electrolyte invasion will thus play a dominant role. From our results it can be postulated that because of diffusion limitations, large concentration gradients exist within the crystals of NaK offretite leading to a heterogeneous acid attack.

Catalytic activity of acid leached offretites. For reactions involving all the hydroxyl groups, i.e. reactions catalyzed by the protonic sites regardless of their strength, the catalytic activity is directly correlated to the acid strength [15]. The hydration of olefins is a reaction of this type [9, 16]. The hydration of n-butene was studied on the solids prepared by acid leaching HK offretite (samples 1-4). The data of Figure 2 show that the activity per protonic site was increased by a factor of 3 when the aluminium content per unit cell
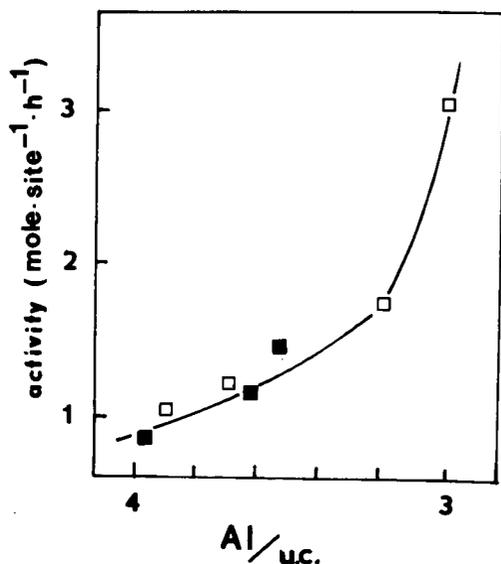

Fig. 2. Correlation between the hydration activity per protonic site and the aluminium content of offretite.

decreased from 4 to 3. On the same figure are reported (full symbols) the results obtained on offretites synthesized with various aluminium contents and then ion exchanged - up to 70 % exchange - using ammonium salts. Clearly, the activity, in other words the acid strength of the protons - is less influenced by the degree of cation exchange (at least in the region

70% - 86% exchange) than by the aluminium content. From a practical point of view, it is interesting to point out that the alcohol yields on a per gram basis increased significantly upon dealumination (Table 3). On this basis, and despite their poor crystallinity, dealuminateo offretites exhibited an activity comparable, or even higher, than that of mordenite or ZSM-5 and a selectivity which remained equal to 100 % for alcohol.

Table 3

Hydration of n-butene at 250°C, 65 atm. Activity of various acidic zeolites.

Zeolite structure	Si/Al	% exchange	Alcohol yield $mmole.g^{-1}.h^{-1}$	% eq[a]
Y	2.5	80	1.1	12
Mordenite	5	85	6.25	66
ZSM-5	49	99	5.73	61
Offretite	3.3	70	1.85	20
Offretite	4.6	83	3.48	37
Offretite	5.01	86	6.02	64

a : percentage of thermodynamic equilibrium.

A further evidence of the enhancement of the acid strength induced by acid treatment was obtained by studying the conversion of cyclohexane on samples 5-10. These solids contained similar amounts of protons (see Table 2) but the reaction rate was increased by one order of magnitude by extracting 50 % of the aluminium (Figure 3). This result also indicated that the channels of the crystalline fraction are not blocked. Moreover, the distribution of the products changed significantly (Table 4). We have shown recently [7] by comparing

Table 4

Product distributions obtained at 10 % conversion during cyclohexane cracking at 450°C.

Catalyst	Selectivity (mole %)				
	C_2-C_5	C_6-C_8 aliphatics	MCP	Benzene	C_7-C_{10} aromatics
Fresh HCeY	31	8.7	15	10.1	35.2
Used HCeY	14.4	15.8	51.3	8.3	10.3
H-ZSM-5	63.5	12.5	4.6	15	3.5
HKO-Sample 5	18.6	16	49.4	10.1	5.9
HKO-Sample 8	36	14	30.2	8.6	11.2
HKO-Sample 10	59.2	9.8	15	6	10

a series of zeolites that isomerization to methylcyclopentane (MCP) was favoured on weakly acidic solids (used HCeY, HK offretites with low Si/Al ratios) whereas cracking requiered strong acidities (Fresh HCeY, H-ZSM-5). After dealumination, the behaviour of offretite is closely related to that of ZSM-5.
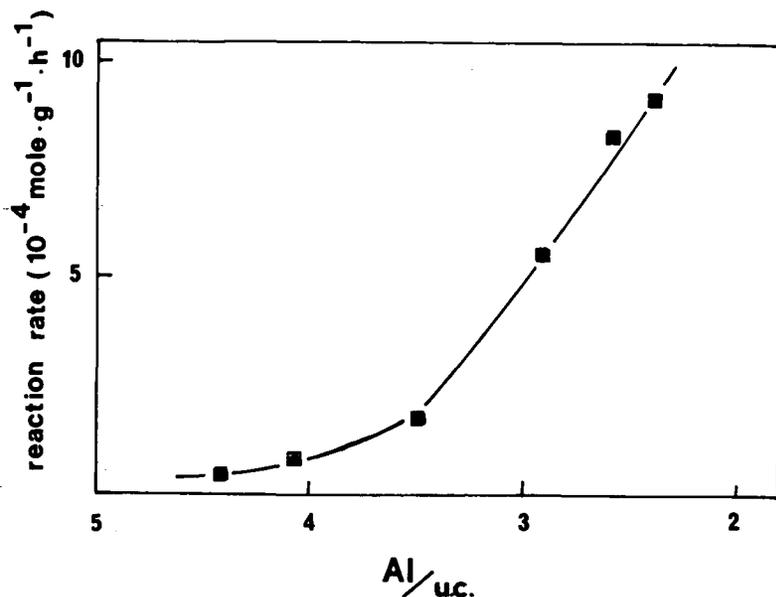
Fig. 3. Rate of cyclohexane conversion at 450°C as a function of the aluminium content in acid leached NaK offretites.

SUMMARY AND CONCLUSIONS

Treatment of synthetic offretites by dilute HCl solutions induces a simultaneous dealumination and decationization of the parent solids. In the case of HK offretite, part of the cations located in the cancrinite cages are extracted and this causes a partial destruction of the lattice. Acid attack occurs in a heterogeneous manner with NaK offretite probably because of diffusion limitations in the channels. The resulting solids contain mesopores and crystalline fractions enriched in silicium. Despite these structural modifications, the acid strength of the dealuminated offretites is greatly enhanced. The main conclusion of this study is that acid leached offretites exhibit a catalytic behaviour very similar to that of ZSM-5 for the hydration of olefins and the cracking of cyclohexane.

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