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A Novel Clay-Based Catalytic Material—Preparation and Properties

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A novel acid-leached calcined kaolin has been prepared by careful control of the calcination and acid leach conditions. A narrow calcination window gives an extremely acid-reactive calcined kaolin, which develops high surface areas at a rate much faster than that of samples calcined outside this range. This more acid active calcined kaolin also allows the use of extremely low levels of acid, which results in most of the alumina being in the solid phase during the entire leach step. Al^{27} NMR results indicate the most acid-reactive calcined clay has the lowest level of octahedral and the highest level of five-coordinate Al. Acids containing anions that do not complex with aluminum such as hydrochloric, nitric, or aluminum chloride work in this process, while acids containing anions that complex with aluminum such a sulfuric or phosphoric do not lead to the same high surface area, catalytically active products. Properly calcined and leached materials show a broad distribution of pores centered at about 40 Å. © 1991 Academic Press, Inc.

INTRODUCTION

Among the earliest solid acid catalysts were the acid activated bentonite clays (*1*). The process by which these clays were acid activated was described by Mills and Cornelius (*2*) and involves the treatment of uncalcined bentonite with 5–20% sulfuric acid at acid/clay ratios of 0.2 to 0.8 and at 93°C for times up to 16 h. With the acid treatment, alumina is removed and surface area increases substantially. Ewing (*3*) found that cracking activity increases to a maximum and then declines as severity of acid treatment increases. Ewing *et al.* (*4*) found that the maximum cracking activity occurs when 15 to 20% of the alumina plus ferric oxide is removed by this acid treatment. Mills and Cornelius (*2*) suggest that acid attack begins at the plate edges rather than by penetration of the silicon–oxygen layers.

Acid-activated kaolinite or halloysite clays have also been used to prepare cracking catalysts (*5*, *6*). Calcination of kaolin or halloysite, followed by acid activation, gives a catalyst of the same activity as acid activated montmorillonite at about one-half the fresh surface area (*1*). The acid-activated kaolinite/halloysite also have fewer acid sites than acid-treated montmorillonite, but all sites are very strongly acidic.

This work is an attempt to prepare a material which would provide large-pore matrix cracking to complement smaller-pore zeolite cracking. The leached clay product described here has a much higher catalytic activity for catalytic cracking of gas oil than earlier acid-treated clays and has a higher catalytic activity per unit surface area than other acid-treated clays or amorphous SiO_2/Al_2O_3 gels we have tested.

METHODS

^{27}Al MAS NMR were run on a Bruker AM-400 at 104.2 MHz with a 2-μs pulse width, 0.1-s relaxation delay, and about 2,000 to 10,000 scans. This is consistent with quantitative parameters reported by others (*7*). The ^{29}Si MAS NMR were run on a Bruker MSL-200 at 39.75 MHz with a 2-μs pulse width, 5-s relaxation delay and about 5,000 scans. Nitrogen pore size distribution data was collected on an Autosorb made by Quantachrome. The kaolin used here was obtained from the National Kaolin Company, Aiken, South Carolina. All acid

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leaches were done at the boiling point of the slurry and most were done under reflux at atmospheric pressure. High-temperature, pressure acid leaches were done in a zirconium autoclave. Catalytic cracking activity measurements were conducted using the microactivity test (MAT) apparatus and procedures described in ASTM No. 3907 (*8*). A typical West Texas heavy gas oil feedstock was used for cracking tests. Samples were pretreated by screening to <600 μm calcining 2 h at 538°C, and then hydrothermally deactivating by steaming for 8 h, with 100% steam at 732°C.

RESULTS

1. Effect of Calcination Conditions

The two critical steps in preparing the catalytically active acid-leached clay are the calcination conditions and the acid level. The effect of calcination temperature on the acid sensitivity of calcined clay was noted in a paper by Bremner *et al.* (*9*). They calcined various kaolin clay samples from 500 to 900°C and found little differences in alumina solubility with 26% HCl, but a 30% $AlCl_3$ solution gave the best alumina extraction with the 850°C calcined material. We have found that calcination at the optimum temperature and time produces a calcined kaolin which develops high surface area after extraction with extremely small amounts of acid.

The effect of calcination temperature and time on the rate of surface area development is summarized in Table 1. Slurries of the calcined clay, water, and HCl at $\frac{1}{6}$ the theoretical level required for complete dissolution of the alumina were boiled for 8 h under reflux. The slurry was then oven dried and calcined 2 h at 538°C prior to measuring the surface area. The results indicate that under these acid leach conditions the clays calcined from about 843 to 871°C develop high surface area. Additional data (Table 2) indicate that clays calcined up to 900°C are even slightly more reactive to acid than those calcined in the 843 to 871°C range as indicated by the faster development of surface area.

TABLE 1

Effect of Calcination Temperature, Time on Surface Area Development[a]

Calcination temperature (°C)	Time at temperature (h)	Acid-leached product surface area (m^2/g)
649	$\frac{1}{2}$	24
649	1	25
732	1	18
788	$\frac{1}{2}$	31
788	1	25
843	1	330
871	$\frac{1}{2}$	292
927	1	28

[a] All acid leaches were done at $\frac{1}{6}$ stoichiometric HCl for 8 h at reflux.

2. Effect of Acid Level

Initial results of the effect of varying the acid level on the acid leached product are summarized in Table 3. After the acid leach, the solid product was isolated by filtration and water washing. Higher levels of acid remove Al_2O_3 from the product, which produces high fresh surface areas but lower cracking activity.

In order to prepare a material which retains most of its aluminum and, accordingly,

TABLE 2

Use of $\frac{1}{24}$ Stoichiometric HCl on Kaolins Calcined at Various Temperatures

Clay calcination	Hours at reflux	Surface area (m^2/g)
$\frac{1}{2}$ h at 899°C	8	206
	12	287
	14	300
	16	338
1 h at 871°C	8	196
	10	252
	12	270
	14	278
1 h at 843°C	8	198
	12	231
	14	251
	16	251

TABLE 3

Microactivity Data on Acid-Leached Metakaolin[a] as Function of Acid Level

% Stoichiometric HCl	Time at reflux (h)	Surface area (m^2/g)	% Al_2O_3 in leached clay	Relative microactivity[a]
17	8	284	38.8	1.00
17	60	436	36.6	0.98
20	8	249	44.6	1.00
25	8	253	44.2	0.97
29	8	277	43.8	0.86
50	$\frac{1}{2}$	157	33.3	0.26
67	$\frac{1}{2}$	232	23.6	0.33
83	$\frac{1}{2}$	337	14.1	0.18
100	$\frac{1}{2}$	488	6.2	0.17

[a] Clay calcined 1 hour @ 843°C.

[b] Measured by ASTM procedure #3907 after an 8-hour, 732°C, 100% steam treatment.

has high catalytic activity, we investigated the use of very low HCl levels. Slurries were prepared of 225 g calcined clay and 675 ml of solution containing 19.2 ml of 37% HCl, which corresponds to $\frac{1}{24}$ stoichiometric HCl. The slurries were boiled under reflux for 16 h, and portions removed at various times and filtered, water washed to remove Cl^- and oven dried. The results in Table 3 indicate substantial surface area was developed even at this low acid level.

Salts, which can generate H_3O^+ via hydrolysis, can be used in place of mineral acids. Seventy-five-gram portions of kaolin calcined for $\frac{1}{2}$ hour at 899°C were added to 900 ml of solution containing varying amounts of $AlCl_3 \cdot 6H_2O$. These slurries were boiled under reflux, the pH was then adjusted to 7.0 with 14% NH_4OH and the product filtered, water washed to low Cl^-, and oven dried. Results in Table 4 indicate significant surface area development.

3. *Effect of Acid Leach Temperature*

A series of acid leaches were done at high temperatures and pressures using a zirconium autoclave. These runs were made to determine the surface properties of the product when acid leach time was reduced. These runs were made by mixing water, 37% hydrochloric acid, and calcined clay at weight ratios of 2.7/0.15/1.0, respectively, and heating this slurry over a period of about 30 to 60 min to the indicated temperature. After the proper time at temperature, the slurry was cooled to ~50°C over a 5 to 10-min period by passing cold water through the cooling coils in the autoclave. The slurry was dried, crushed, and screened to <600-μm particle size and calcined $\frac{1}{2}$ hour at 566°C prior to measuring the surface area. The results in Table 5 indicate a material of

TABLE 4

Leaching Calcined Kaolin[a] with $AlCl_3 \cdot 6H_2O$

% Stoichiometric $AlCl_3^2$	$g \cdot AlCl_3 \cdot 6H_2O$ per g clay	Reflux time (h)	Surface area (m^2/g)
$\frac{1}{2}$	1.0	$5\frac{1}{2}$	278
$\frac{1}{4}$	0.5	8	333
$\frac{1}{6}$	0.33	8	313
$\frac{1}{8}$	0.25	8	305
$\frac{1}{12}$	0.17	8	256
$\frac{1}{12}$	0.17	16	410
$\frac{1}{20}$	0.10	16	290

[a] Kaolin calcined $\frac{1}{2}$ h at 899°C.

[b] Stoichiometric is moles of Cl in $AlCl_3 \cdot 6H_2O$/mol alumina in the clay.

TABLE 5

Effect of Temperature, Time of Acid Leach on Surface Area, Pore Volume

Maximum temperature (°C)	Time at temperature	Surface area (m^2/g)	N_2 pore volume (cc/g)	Avg. pore diameter (Å)
100	16 h	198	0.18	36
115	2¼ h	158	0.14	35
130	45 min	168	0.15	36
130	75 min	167	0.16	38
150	22 min	198	0.18	36
150	33 min	203	0.19	37
170	10 min	163	0.14	34
170	20 min	185	0.15	32
200	4 min	188	0.19	40
225	5 min	275	0.32	47
240	1 min	241	0.33	55
260	1 min	193	0.21	44

similar average pore diameter is produced up to 170°C, but at higher temperatures the average pore diameter is increased.

4. *Surface Properties*

While both acid-leached montmorillonite and acid-leached halloysite or kaolinite have similar cracking activity, the surface area of the former is about 300 m^2/g, while the latter is about 160 m^2/g (*5*). We believe the higher activity per unit surface area of the acid-leached halloysite/kaolinite relative to acid-leached montmorillonite may be due to its higher alumina content (~40% versus 20%). In addition to providing a higher number of potential acid sites, the higher alumina content materials generally have better hydrothermal stability (*9*).

Pore structures of typical acid-leached montmorillonite and acid leached kaolinite were described by Milliken *et al.* (*5*). The isotherm for the acid-leached montmorillonite is consistent with its surface area of 340 m^2/g and its average pore diameter of 54 Å.

TABLE 6

N_2 Pore Size Distribution Comparison of Acid-Treated Clay Slurries with and without Filtering, Washing

Leach time (h)	2	2	4	4	8	8	16	16
Filtered, washed	Yes	No	Yes	No	Yes	No	Yes	No
BET SA. m^2/g	116	172	176	183	229	217	250	243
Avg. pore diameter (Å)	78	45	57	46	45	42	42	36
Total pore volume (cc/g)	0.227	0.193	0.250	0.209	0.260	0.229	0.265	0.221
	Surface area in pores (m^2/g)							
>600 Å	2	1	1	1	1	1	1	1
100–600 Å pores	11	4	9	4	4	3	3	3
20–100 Å pores	99	142	161	156	225	194	244	179
<20 Å	0	26	5	22	0	19	3	61

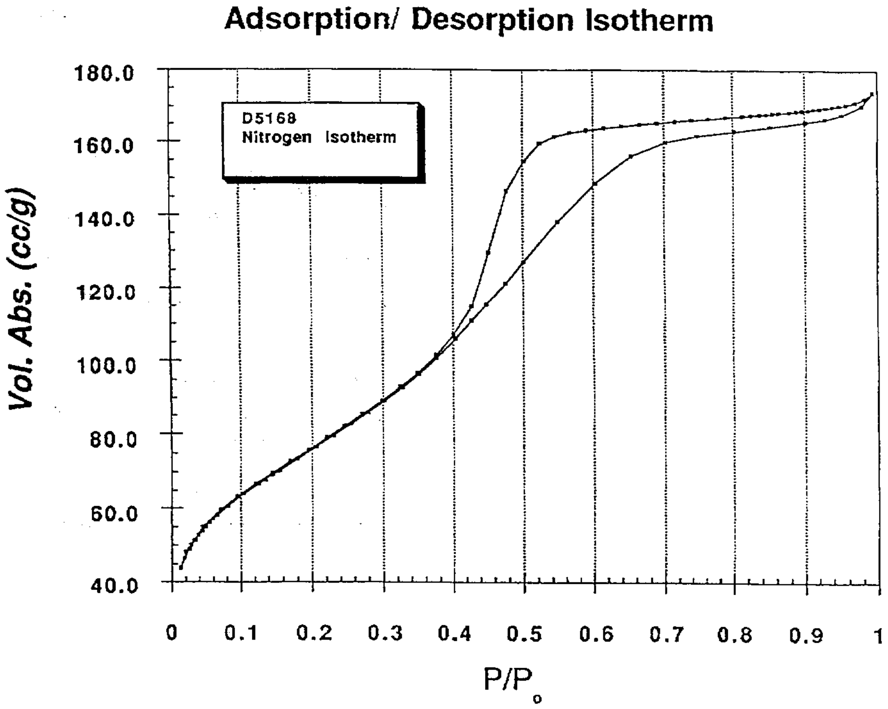


FIG. 1. Acid-treated kaolin, clay calcined $\frac{1}{2}$ h at 900°C, leached 8 h at 100°C with $\frac{1}{15}$ stoichiometric HCl at 25% solids.

The acid-leached kaolinite has a surface area of 160 m^2/g, and we have calculated, based on the data, an average pore diameter of about 48 Å (*5*).

The novel clay-based catalytic material described here has an adsorption/desorption isotherm significantly different than that of the acid-treated kaolinite described in the earlier literature (*5*). The isotherm, Fig. 1, shows a Type E hysteresis. Since the literature indicates that the most accurate pore size distribution for Type E hysteresis materials is obtained by using the adsorption curve (*11*), pore size distributions were calculated in this manner. While the average pore diameter and other surface properties do not change dramatically with either method of calculation, the pore size distribution does become much broader when calculated on the adsorption data. Typical surface properties for the material described here are given in Table 6, and a plot of $dv/d\log D$ versus log pore diameter for both the desorption and adsorption data is given in Fig. 2.

To determine the effect on the pore structure of the alumina removed as a function of hot age time, samples were boiled under reflux for 2, 4, 8, and 16 h using leach conditions as described in US Patent 4,843,052 (*12*). A portion of each sample was filtered and thoroughly washed with 65°C H_2O and then oven dried while a second portion of the same slurry was dried without filtration. A comparison of these samples is given in Tables 6 and 7 and Figs. 3 and 4, and indicates very similar pore size distributions, with the washed samples having a smaller hysteresis on the 2- and 4-h samples. The above results indicate that the characteristic average pore diameter maximum at 30–40 Å is formed very quickly on contact with acid and that most of the alumina is in the solid phase at any stage of the acid leach.

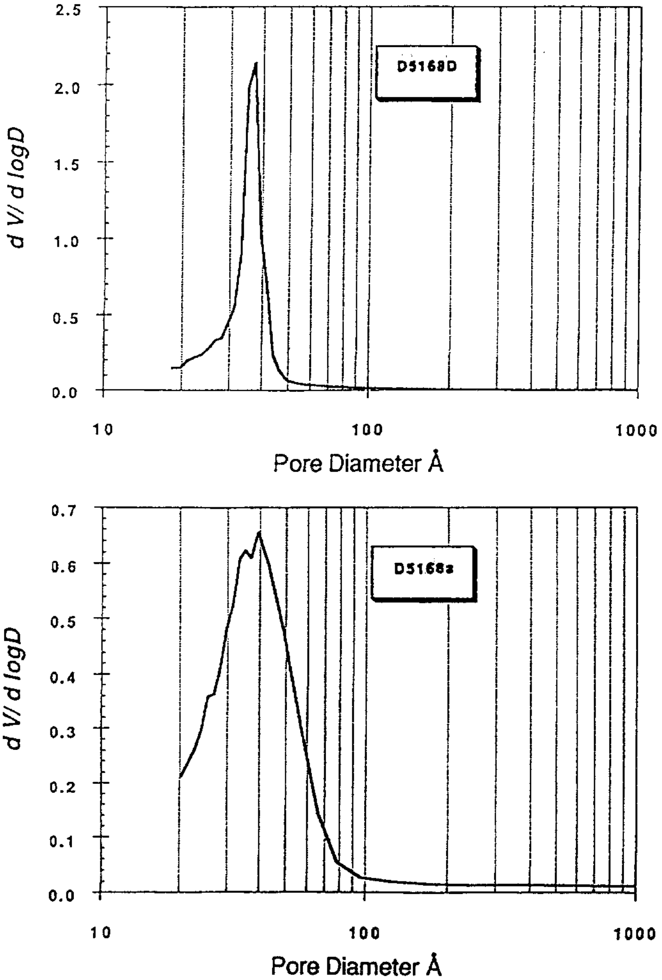


FIG. 2. Comparison of the pore size distribution calculated on the desorption or adsorption data, same sample as Fig. 1.

To determine the effect of the acid leach time on the ratio of Si/Al at the surface, samples from Table 6 which were acid leached for 4 and 16 h and then oven dried were compared to the starting calcined clay by X-ray photoelectron spectroscopy (XPS). The results, Table 8, indicate a substantial surface enrichment of Al_2O_3 during this process. The results are consistent with the filtrate data which indicates more dissolved alumina after 4 h than after 16 h. A mechanism of surface area development consistent with the above results would be where the aluminum is leached into solution, polymerizes at the relatively high pH (~3.0) and temperature and is readsorbed onto the clay surface.

5. *MAS/NMR*

Sanz *et al.* (*13*) have recently reported on Al^{27} and Si^{29} magic angle spinning nuclear magnetic resonance study of the changes occurring during the thermal transformation of kaolin to mullite. Their results show that the initial octahedral Al converts to increasing amounts of four- and five-coordinate Al as calcination temperature increases from 460 to 850°C. At 980°C, however, the mate-

TABLE 7

Comparison of Acid-Treated Clay Slurries with/without Filtration, Washing

Hours at boiling	2		4		8		16	
Treatment	Filtered and washed	Oven dried	Filtered and washed	Oven dried	Filtered and washed	Oven dried	Filtered and washed	Oven dried
			Solids Analysis					
Al_2O_3 Wt%	40.34	41.55	40.21	42.29	40.93	42.63	41.43	42.90
SiO_2	55.25	54.15	55.54	53.38	55.09	53.03	54.72	52.73
Na_2O	0.040	0.044	0.037	0.031	0.032	0.026	—	0.043
Fe_2O_3 ↓	1.442	1.439	1.363	1.456	1.314	1.466	1.308	1.478
			Filtrate (g/500 g clay)					
Al_2O_3	10.67		15.03		10.16		6.02	
Cl	10.60		12.94		9.37		6.73	
Na_2O	0.09		0.08		0.10		0.07	
Fe_2O_3	0.33		0.67		0.74		0.59	
SiO_2	0.56		0.18		0.074		0.014	

rial now has an XRD pattern attributed to γ-Al_2O_3, mullite or Al–Si spinel (*13–15*) and has a very strong octahedral peak. The sequence of Al coordination changes with calcination temperature, and our data on acid reactivity indicate that the most acid-reactive calcined clay has the lowest level of octahedral and highest level of five-coordinate Al. The γ-Al_2O_3 or Al–Si spinel phase has a high level of octahedral Al and is very unreactive to acid.

We have measured the relative populations of four-, five-, and six-coordinate Al during various stages of this process, from

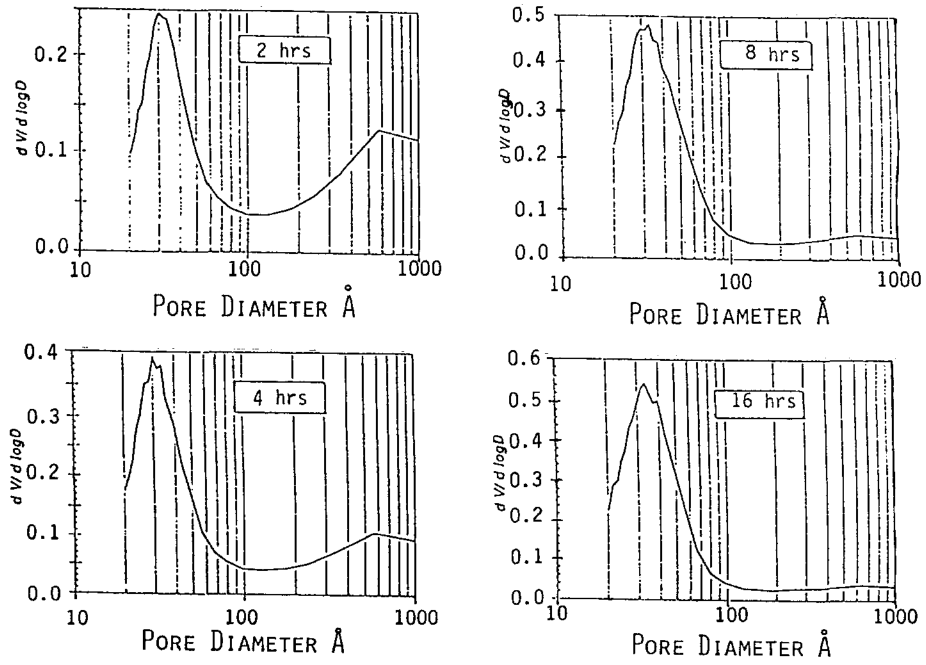


FIG. 3. N_2 pore size distribution for acid-leached clay after 2, 4, 8, and 16 h and after washing, leach conditions as given in Fig. 1.

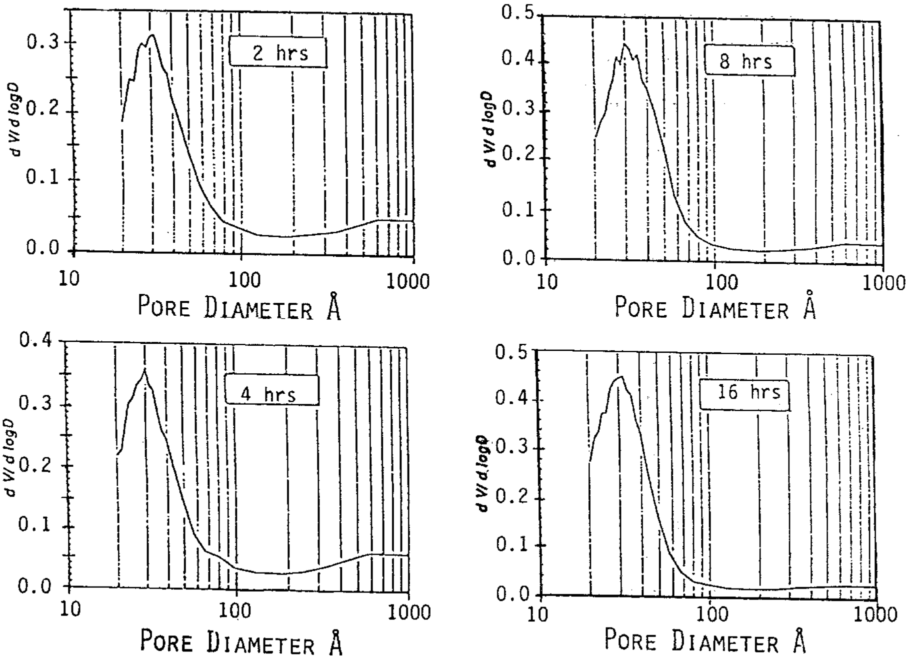


FIG. 4. N_2 pore size distribution for acid-leached clay after 2, 4, 8, and 16 h and after drying without washing, leach conditions as given in Fig. 1.

the initial clay to a hydrothermally deactivated material. The results in Table 9 and Fig. 5 indicate:

- a significant amount of amorphous Al in the calcined kaolin and the four-coordinate Al predominates over the six-coordinate Al,
- acid leaching converts essentially all the Al to six coordination, and
- calcination or steaming again converts the Al to a ratio of 1/1/0.5 of six, four, and five coordination, respectively.

TABLE 8

Si/Al Ratio at the Surface During the Acid Leach

Acid leach time (h)	% O	% Si	% Al	Si/Al
0	58.3	15.5	15.1	1.02
4	62.1	13.1	19.4	0.67
16	63.4	13.8	17.9	0.77

Note. All results are averages for two measurements on each sample using X-ray photoelectron spectroscopy and are on an atomic basis.

^{29}Si MAS NMR shows a somewhat similar pattern to the ^{27}Al MAS NMR in that the peak location for the calcined clay and the steamed acid-leached calcined clay are quite similar (Fig. 6). Raw kaolin gave a single sharp peak at −90.4 ppm (relative to TMS); however, the acid-treated sample gave broad peaks at −77.5 and −108.4 ppm. The peak at −108.4 ppm indicates the presence of $Si(OAl)_0$ species. The peak at −77.5 ppm is unusual and could represent a silicon with a high density of aluminum neighbors (i.e., $Si(OAl)_4$ or an isolated silicate moiety). Further investigation of this sample is required before an assignment can be made. Hydrothermal treatment of the acid-leached calcined clay gives a product with a broad peak at −106.7 ppm, consistent with either $Si(OAl)_0$ or $Si(OAl)_1$ species, and a shoulder at about −91 ppm. This shoulder is quite possibly due to some hydroxylation of silica in the acid-leached material. Since we have

TABLE 9

Al-27, Si-29 Signals Observed at Various Stages in the Process$_{a,b}$

Material	Percentage tetrahedral Al	Percentage octahedral Al	Percentage pentahedral Al
Kaolin	0	100	0
Calcined kaolin (½ h at 899°C)	46	30	24
Acid-treated calcined kaolin[c] (dried 121°C)	0	100	0
Acid-treated calcined kaolin (1 h at 538°C)	39	41	20
Acid-treated calcined kaolin (steamed 6 h, 760°C, SPSIG, 100% steam)	40	38	22
Filtrate after leach	0	100	0

Material	Si-29 Peak
Kaolin	−90.4
Calcined kaolin (½ h at 899°C)	−110.0
Acid-treated calcined kaolin (dried 121°C)	−77.5, −108.4
Acid-treated calcined kaolin (steamed 6 h, 760°C, SPSIG, 100% steam)	−106.7

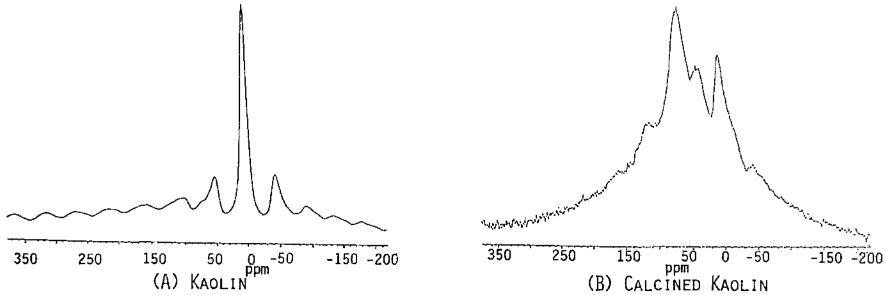
[a] Si-29 peak shifts in parts per million (ppm) relative to tetramethylsilane at 0 ppm.

[b] Relative amounts of 6, 5, and 4 coordinate Al measured at 0, 31 and 60 ppm relative to $Al(H_2O)_6^{+3}$.

[c] Acid leach at $\frac{1}{6}$ stoichiometric HCl and 25% solids for 8h at 100°C.

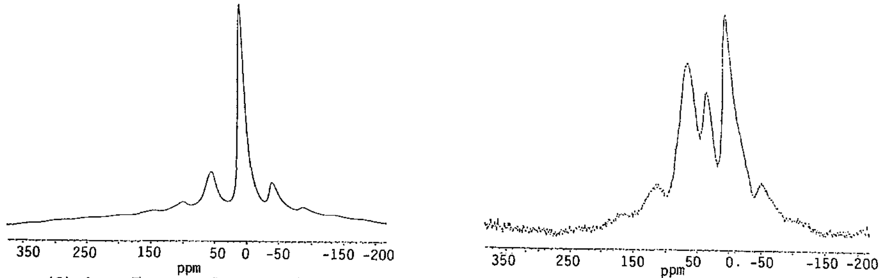
observed good catalytic activity from this material after steam treatment, the peak at −106.7 ppm is most likely due to $Si(OAl)_1$ species.

The population of octahedral Al in this material is substantially lower after calcination than in many other SiO_2–Al_2O_3 materials we have examined. For example, a SiO_2–Al_2O_3 prepared at 72% Al_2O_3–28% SiO_2 has 77% octahedral Al and 23% tetra-



(A) KAOLIN

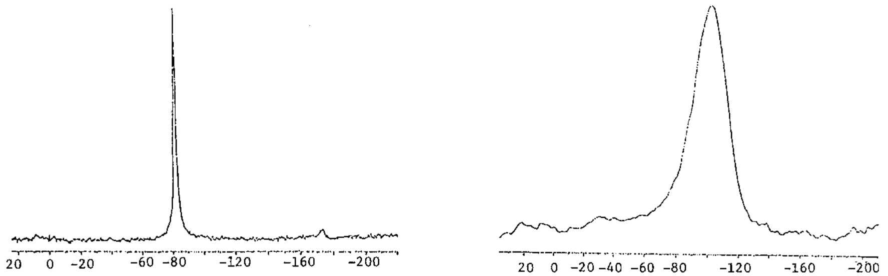
(B) CALCINED KAOLIN



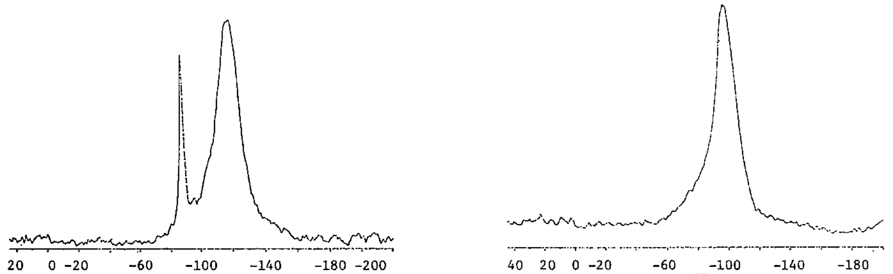
(C) ACID TREATED CALCINED KAOLIN

(D) CALCINED ACID TREATED CALCINED KAOLIN

FIG. 5. Effect of process on ^{27}Al MAS NMR, leach conditions as in Fig. 1.



(A) Kaolin (B) Calcined Kaolin



(C) Acid Treated Calcined Kaolin (D) Calcined Acid Treated Calcined Kaolin

FIG. 6. Effect of process on ^{29}Si MAS NMR, leach conditions as in Fig. 1.

hedral Al after calcination at 538°C for 2 h. We believe the relatively high fraction of Al in four and five coordination gives this material a very large number of acid sites and, accordingly, its very high cracking activity per unit surface area, which will be described in a future paper.

6. *Electron Micrographs*

Scanning transmission electron micrographs and electron diffraction were obtained at McCrone Associates, Westmont, Illinois. Electron diffraction and the transmission micrograph of the calcined clay show it has substantial residual ordering (Fig. 7), although X-ray diffraction shows no residual order. After treating the calcined clay by a relatively mild acid treatment as described earlier or as more fully described in US Patent 4,843,052 (*12*), we see no electron diffraction pattern, and the electron micrographs show only a few residual areas where aggregates containing layers connected face-to-face are present (Fig. 8). There are areas where a 14.7 ± 1.5 Å repeat distance is observed, which suggests the presence at a low level of a chlorite-type structure, but this is not the major component.

SUMMARY AND CONCLUSIONS

We have discovered that through the use of very specific calcination and acid leach conditions, a highly acidic, catalytically active surface can be produced from kaolin clay.

The major difference between the calcined-only kaolin and the acid-leached product is the great loss in ordering of layers that occurs during the acid leach. Although ordering is not completely lost, acid attack leads to a significant degree of delamination of the kaolin platelets as measured by both electron diffraction and observed in the electron micrographs. The fact that little or no Al_2O_3 is removed from the solid during leaching suggests a mechanism of polymerization and readsorption. The lack of X-ray pattern indicates that, if pillaring is occurring, it is of very short order.

The Al NMR results indicate a very high degree of four- and five-coordinate Al in the

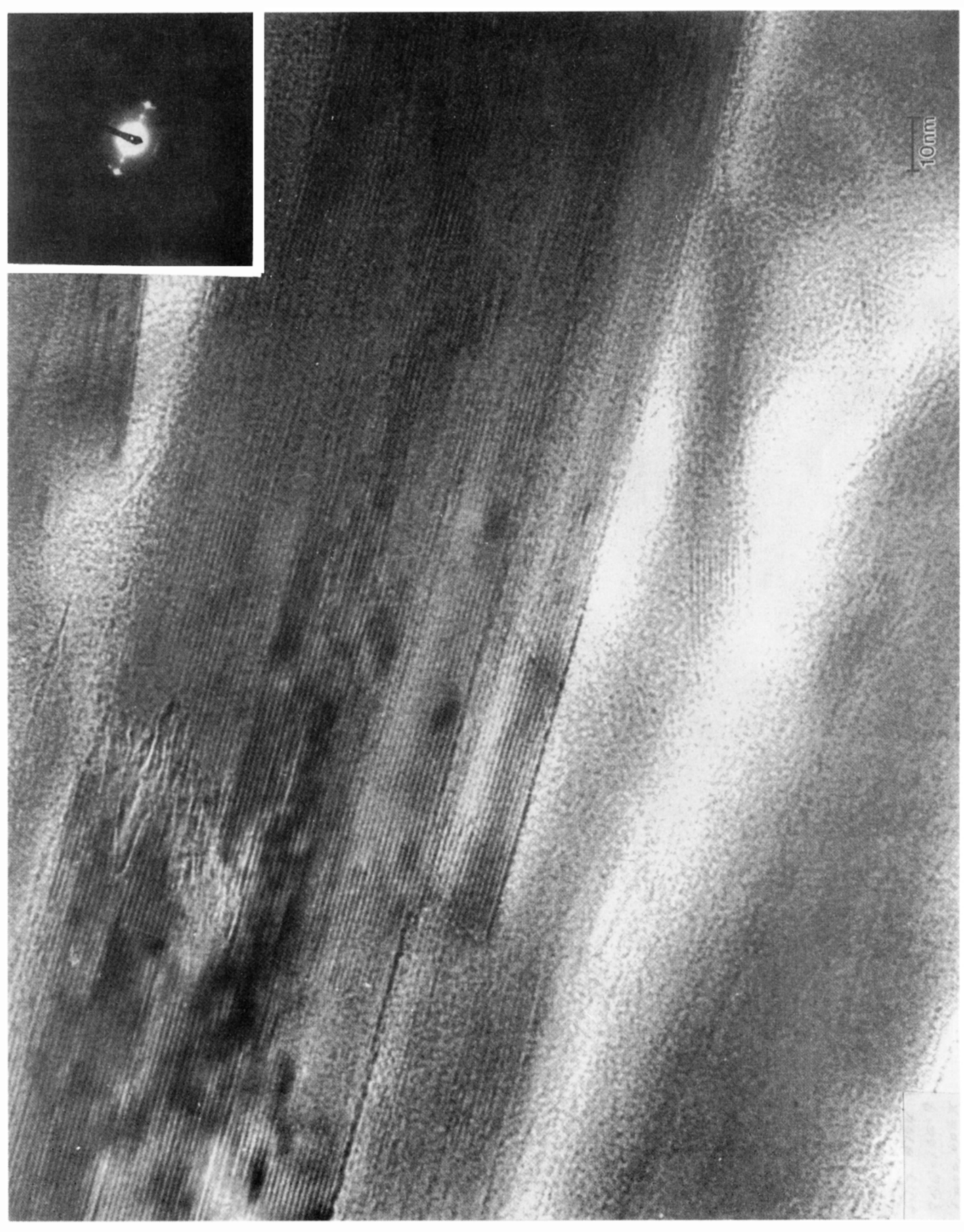


FIG. 7. Transmission electron micrograph at 1,000,000 × of kaolin calcined $\frac{1}{2}$ h at 900°C with electron diffraction pattern.

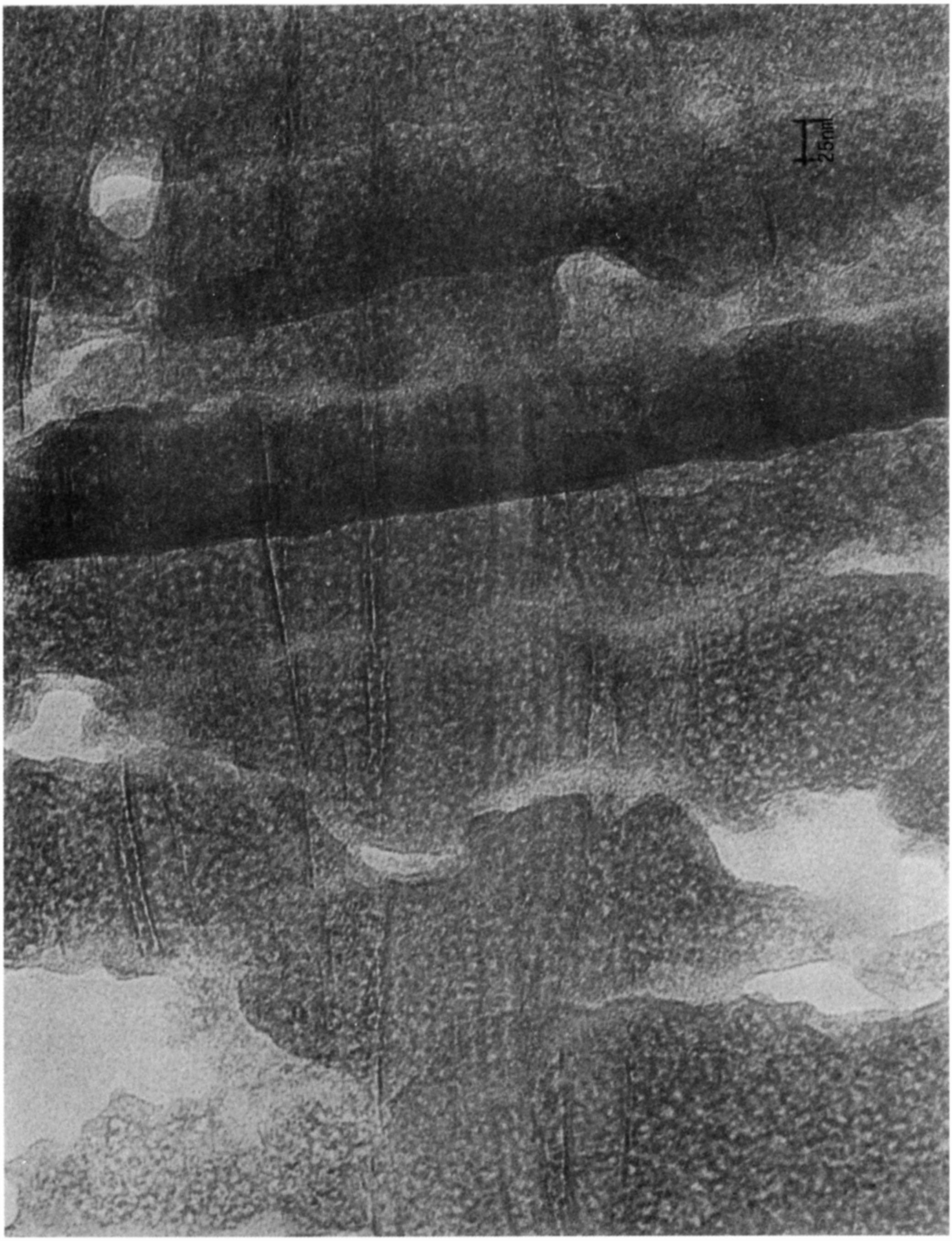


FIG. 8. Transmission electron micrograph at 300,000× after acid leaching as described in Fig. 1.

calcined acid-leached clay described here. This is consistent with our proposed mechanism of aluminum being removed from the calcined clay, polymerized, and readsorbed onto the silica-rich areas of the solid. This intimate contact between silica and alumina produces the high acid activity of the final product.

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