USE OF CLAYS AS PETROLEUM CRACKING CATALYSTS

By T. H. Milliken,* A. G. Oblad,** and G. A. Mills ***

Introduction. The use of catalysts in the petroleum industry in recent years has undergone a remarkable expansion. The most important of these catalysts are employed in cracking processes, first introduced in 1936 (Houdry et al., 1938). As a consequence of the growth of catalytic cracking, the manufacture of cracking catalysts has in itself become a major industry with an estimated sales value of $61,000,000 in 1952. Principal emphasis has been placed on two types of catalysts both essentially composed of silica and alumina, one derived from clay and the other synthesized from aluminum and silicate solutions. A total of approximately 470 tons per day of cracking catalysts are manufactured and used to process about 2,000,000 barrels of crude daily. Clay catalysts account for about 40 percent of the total manufacture. Such a special use of clays has placed requirements on these materials significantly different than those met in other uses of clays. Moreover, the very particular physical and chemical properties required for good commercial hydrocarbon-cracking catalysts limit the economic use of clays to specific types. Until recently, only a few deposits of subbentonites were of commercial interest for catalyst manufacture.

As in certain other uses of the surface properties of clays, it is the peculiar structural features of clays which enables them to play a special role for catalyst manufacture.

At present only two clays are used for the preparation of commercial cracking catalyst: montmorillonite and halloysite. The patent literature cites many other naturally occurring materials as sources of such catalysts; kaolinite, vermiculite, and bauxite, for example. In this paper, only montmorillonite, halloysite, and kaolinite will be discussed. The general properties of cracking cata-

lysts and raw clays from which they are manufactured are shown in table 1, which presents comparative data for chemical, physical, and catalytic properties.

The catalyst is employed in the cracking of heavy petroleum fractions. In such a process, oil, more or less in the vapor state, is passed over the catalyst at 425-500°C, atmospheric pressure, and contact times of 6-20 seconds. Under the directive influence of the catalyst, a series of complicated reactions (Greensfelder, 1951) takes place with the consequent products much different from those obtained in thermal cracking. Catalytic cracking is employed in the petroleum industry because of the high quality of gasoline produced and because of the desirable distribution of products. Typically, some 6 percent of a methane to propane fraction, 10 percent butanes, 45 percent gasoline, and 40 percent recycle oil are produced. At the same time 1 to 3 percent of the charge stock is deposited on the catalyst as a nonvolatile hydrocarbonaceous residue commonly called "coke." After a 10 to 20 minute cracking period the coke is removed from the catalyst by controlled combustion. In this burning process, the temperature is limited to perhaps 600°C, although a higher local surface temperature may prevail. After such a regeneration the catalyst is ready for reuse. During use at elevated temperatures, the catalyst is exposed to various organic compounds including those containing oxygen, sulfur, nitrogen, as well as heavy metals contained in the charge stock. In addition, the catalyst must withstand water over a wide range of vapor pressures. Whereas early commercial catalytic cracking apparatuses utilized a fixed bed, present day units utilize moving beds with transfer of the catalyst from a cracking zone to a regeneration zone. (Ardern et al., 1951; Murphree, 1951). A typical process is illustrated by the flow sheet shown in figure 1. In order to maintain a "heat balance" between the endothermic vaporization and cracking of the hydrocarbons and the exothermic regeneration, a large quantity of catalyst must be circulated continuously. Depending upon re-

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Table 1. Properties of (new) cracking catalysts after calcination at 550° C.

| | Synthetic | | Clay | | | | | |
| | | | Montmorillonite | | | Halloysite | |
	SiO_2-Al_2O_3	SiO_2-MgO	Raw	Activated	Houdry type 1	Raw	Activated
Chemical							
SiO_2, Wt. percent	87.5	66.3	63.7	71.8	76.7	49.1	57.1
Al_2O_3	12.5	1.6	24.3	22.1	18.2	49.7	40.6
MgO	0	31.8	5.5	3.9	4.4	0.1	1.7
Fe_2O_3	0.1	0.2	2.5	1.5	0.1	0.6	0.4
CaO	0.0	0.2	2.0	0.3	1.0	0.2	0.0
Na_2O	0.1		2.0	0.2		0.2	0.1
Physical							
area, sq m/g	300–600	650		300	230	.	160
Catalytic							
activity index	45–50	45–50	5	40	40	12–20	35–40

Physical and catalytic properties on fresh catalysts after calcination at about 550° C.

FIGURE 1

FIGURE 2. Chemical composition of clay remaining after acid treatment (ordinate), calculated on the basis of constant $SiO_2=100$. Solid circles show Mississippi clay, open circles Nevada clay. (After Mills et al., 1950, p. 1177.)
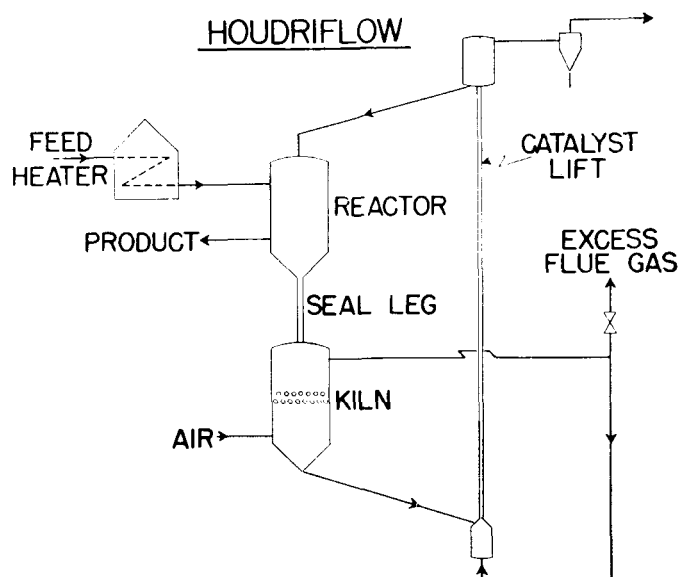
finery requirements, 0.5 to 1.5 tons of catalyst are circulated per barrel of crude charged. This tremendous circulation requires a high degree of physical stability. In short, the catalyst must maintain cracking activity when subjected to high temperatures, chemical attack from steam and contaminants in the charge, and have good resistance to abrasion.

Cracking Catalysts From Montmorillonite. There is no known chemical or physical test which will enable one to predict whether or not a particular montmorillonite clay will respond to acid treatment and produce a catalyst of high activity. Very few montmorillonite clays are known which yield satisfactory catalysts. The situation is similar to that encountered in the bleaching clay industry where it is also necessary to treat the clay sample with acid and test for decolorization activity in order to evaluate the potentialities of a particular clay.

Three deposits of montmorillonite clay suitable for the manufacture of cracking catalysts have been exploited on a commercial scale. Two are in Arizona and one in Mississippi. Recently the entire supply of such clay has come first from Chito and then from Chambers, Arizona. Some catalyst has been manufactured from clay mined at Jackson, Mississippi, but this material has proved to be less desirable than that from the Arizona deposits and its manufacture has been discontinued. Certain other American deposits have been reported by Mills, Holmes, and Cornelius (1950) to be satisfactory for the production of cracking catalysts. They found, upon examining a variety of montmorillonite clays, a wide range of susceptibility to activation and that a few clays yielded catalysts of maximum activity. These highly active catalysts proved to be comparable with synthetic silica-alumina catalysts. Suehiro (1949) has also reported on the activation of certain clays for the production of cracking catalysts.

Acid Treatment. Acid treatment of bentonites for the removal of "basic" constituents has been studied by a number of investigators. Nutting (1933; 1935; 1937;
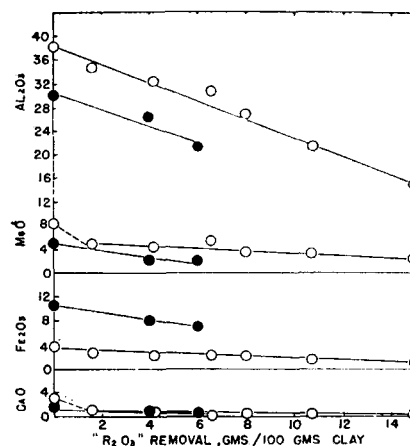
1943) has studied the changes in chemical composition believed to be related to decolorizing ability. Other authors (Burghardt, 1931; Hagner, 1939; Schroter, 1940; Hofmann, et al., 1935; Lopez-Gonzalez, et al., 1952; Escard, et al., 1950) have reported the chemical composition of many clays acid treated to give material with optimum bleaching properties. Figure 2 shows the change in composition of Ash Meadows, Nevada, clay as a function of acid treatment (Mills, et al., 1950). In this figure "R_2O_3" represents the "basic" constituents of the raw clay.

In order to simplify the discussion on the catalytic properties of the treated clays, only the initial activities
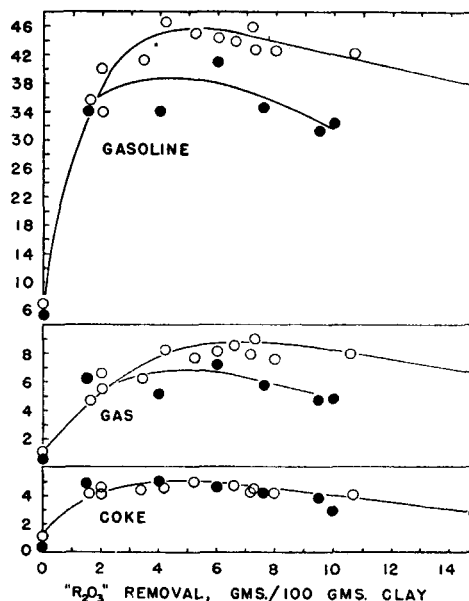

FIGURE 3. Catalytic cracking activity of acid-treated bentonite as a function of severity of acid treatment. Solid circles show Mississippi clay, open circles Nevada clay. (After Mills et al., 1950, p. 1181.)
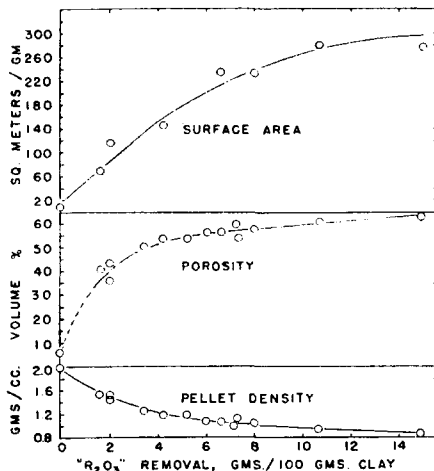
FIGURE 4. Effect of severity of acid treatment on physical properties (measured on calcined pellets) for Nevada clay. (After Mills et al., 1950, p. 1177.)

as measured by the empirical Catalytic Activity Test A (Alexander, 1947) will be used. This test, referred to as CAT-A, utilizes the conversion of a light East Texas gas oil to gasoline as a measure of activity.

In figure 3 the effect of "R_2O_3" removal on activity of two montmorillonitic clays is shown. The activity rises as the "R_2O_3" is removed until a maximum is reached. On further removal of basic constituents, the activity begins to decline. It would appear that the two clays, aside from having different activity maxima versus R_2O_3 removal, activate to different magnitudes. The activity and product distribution of these particular clay catalysts are similar to those obtained on testing active synthetic silica-alumina catalysts.

The physical changes taking place during removal of the basic constituents of the clay are of interest. The change in surface area and porosity with increasing removal of the basic components of the clay is shown in figure 4 (Mills, et al., 1950). The area increases continuously until 14 percent R_2O_3 is removed. On further acid treatment, the area decreases. Lopez-Gonzalez (1952), Escard (et al., 1950), and others have also reported variation of surface area with acid treatment.

The physical properties of acid-treated clay catalysts have also been extensively studied by Ries (1952) and by Oulton (1948). These authors reported that the gross physical form, pellet or powder, has no effect on surface area. It is further reported that a 0 to 40 micron fraction of powdered clay had the same surface area as a 40 to 100 micron fraction. This finding indicates that the fraction of the total surface area contributed by the megasurface is negligible compared with the micro-surface. A typical nitrogen adsorption isotherm may be utilized as a measure of the surface as shown in figure 5.

The pore-size distribution of clay catalysts has been reported by Oulton (1948), Ries (1952), Drake (1949), and Mills, Holmes, and Cornelius (1950). Pore size distribution reported by Oulton (1948) for a commercial clay catalyst (Filtrol) is shown in figure 6.

The great similarity between the nitrogen-adsorption isotherms of the acid-activated montmorillonite clay and
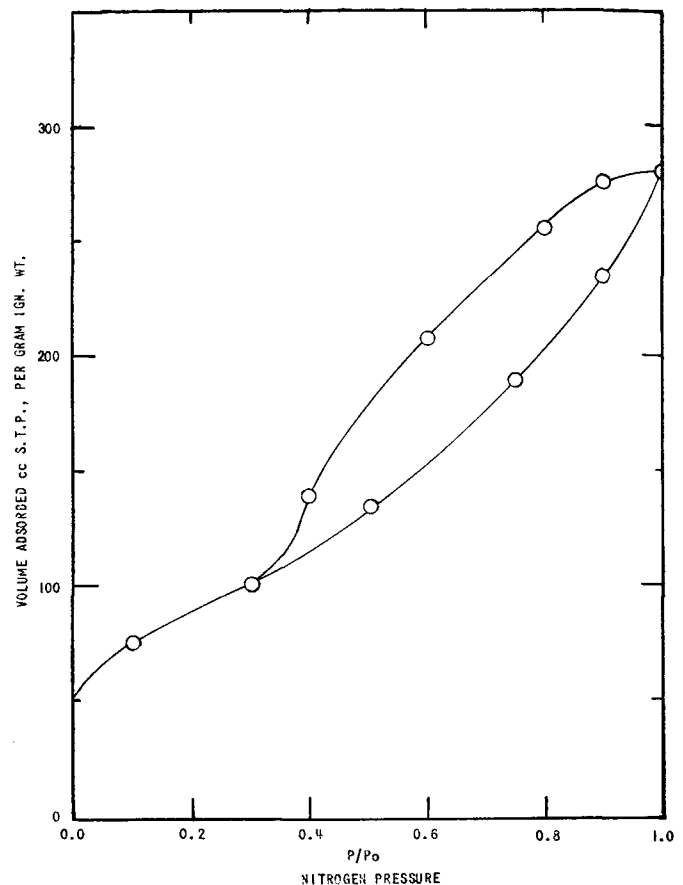

FIGURE 5. Nitrogen isotherm for acid-activated Ash Meadows, Nevada, montmorillonite. Surface area is 340 square meters per gram.
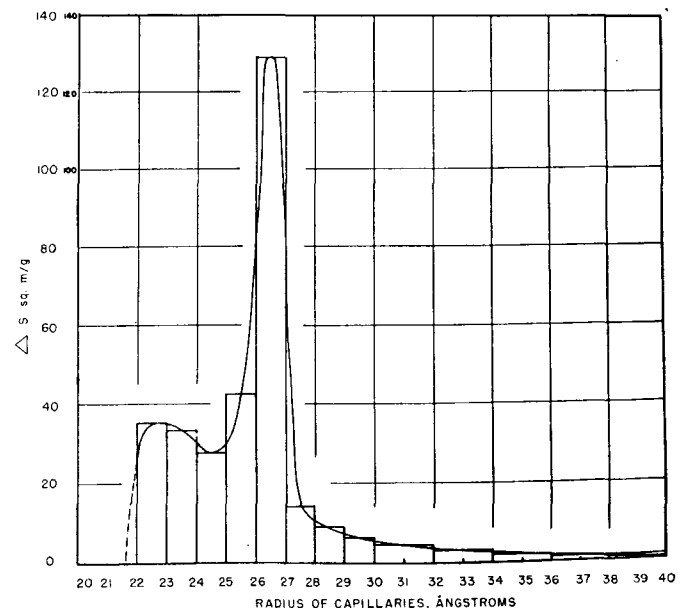

FIGURE 6. Distribution of pore size versus surface area for acid-treated montmorillonite clay.

those of synthetic silica-alumina gel-type catalysts or of silica gel itself is indicative of a common physical structure. It is logical to assume that the siliceous residue left after removal of part of the basic components is responsible in large part for this similarity.

X-Ray Diffraction. Davidson (1947), Grenall (1948; 1949), and Holmes and Mills (1951) have reported that typical montmorillonite X-ray diffraction patterns have been obtained on montmorillonites after acid treatment and calcination (550°C). The pattern is more diffuse than that of raw montmorillonite, which indicates either the presence of smaller particles or dilution with an amorphous material. A cursory inspection of the diffraction patterns shows no major shifts in crystal structure to have occurred. This would indicate, in support of the surface-area data, that a portion of the clay is destroyed by acid treatment to form an amorphous or gel-like fraction and that the remaining material is virtually unaffected by acid except for the removal of the exchangeable cations. The 9.8 Å spacing of the layers in the calcined-montmorillonite structure leaves only a 1 to 1.5 Å distance between layers. As this distance is too small for the entry of a nitrogen molecule, it seems probable that the relative surface area measured by the B.E.T. method includes only the gel surface created by the acid treatment.

Differential Thermal Analysis. Davidson (1947) has reported the results of analyses on a commercial clay catalyst (Filtrol) before and after calcination at a series of temperatures. The differential analysis curve (fig. 7) of the acid treated clay before calcination shows an endothermic peak at 120-150°C (250-350°F) and a second endothermic peak at 480-650°C (900-1200°F). The first peak is associated with the removal of reversible interlayer water contained in the clay structure. On heating the same material to 480°C (900°F) the first sharp peak disappears and is replaced by a broad band. Davidson interpreted this band to be associated with the reversible water held by the gel structure created by acid treatment and calcination. The endothermic peak occurring at 480°C (900°F) to 650°C (1200°F) and found for both materials is attributed to the loss of hydroxyl water associated with the aluminum ions of the clay
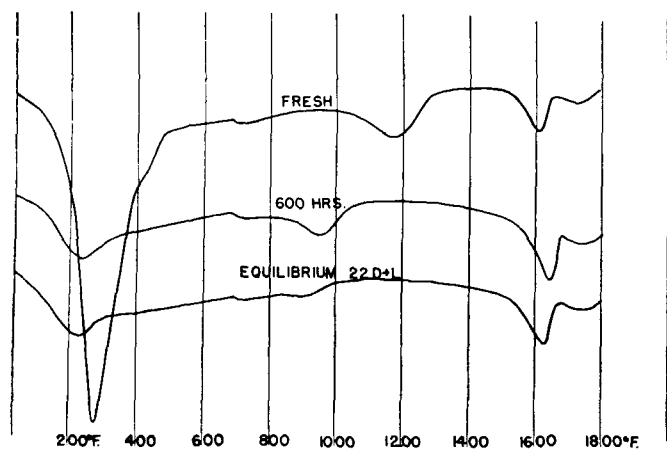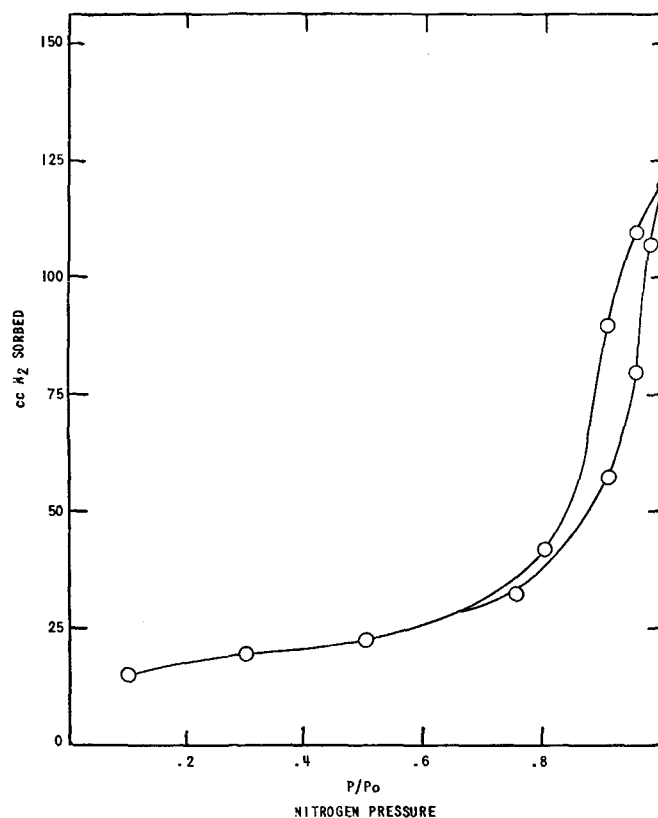

FIGURE 8.   Nitrogen isotherm for calcined and acid-leached kaolinite.

structure. Davidson states that this water content may vary from 1.5 to 2.0 percent depending on the degree of acid treatment of the clay.

Comparison of Davidson's data for acid-treated montmorillonite with that given by MacEwan (1951) for untreated montmorillonites shows a pronounced change in the position of the endothermic peak associated with the loss of hydroxyl water. For the untreated montmorillonites this peak occurs at 700-725°C. On the other hand, the acid-treated clay loses the hydroxyl water at 630°C and 500°C for "fresh" and "aged" material, respectively. The "aged" material was an acid-treated clay catalyst after 600 hours use in a commercial cracking unit.

Cracking Catalyst from Kaolins. Halloysite and kaolinite, as previously stated, may be activated by acid treatment followed by calcination. These materials so treated ordinarily give catalysts of considerably lower activity, which produce 20 to 30 percent gasoline when tested by CAT-A, compared with the best montmorillonites, which produce 40 to 45 percent. When kaolin clays are activated by calcination at 550°C followed by a mild acid treatment, a more active catalyst results (Mills, n.d.). The activity indices of a Eureka halloysite and a Georgia kaolin activated by the latter technique are 41 and 40, respectively. These CAT-A indices compare favorably with the indices of activatable montmorillonites.

The surface areas of catalysts manufactured from kaolin-type clays are lower than those generally found

FIGURE 7.   Differential thermal analysis of acid-treated montmorillonite (new and after use as a catalyst).

for activated montmorillonites (table 1). This is evident from a comparison of the nitrogen isotherm for such a catalyst, illustrated in figure 8, with a similar isotherm for a catalyst derived from montmorillonite, figure 5.

Because of the temperature range in which they are used, all cracking catalysts are, of necessity, heated to temperatures above 550°C. Kaolin, when subjected to such heat treatment, no longer produces an X-ray diffraction pattern. Thus no significant information concerning structure can be obtained by X-ray analysis of catalysts prepared from kaolins. The latest literature survey of the structure of calcined kaolins by Richardson (1951) indicates that such materials have no detectable structure as revealed by X-ray diffraction. It is pertinent that failure of active synthetic silica-alumina catalysts to give an X-ray pattern indicates they also do not possess a structure of long-range order. In a truly amorphous structure the silica and alumina should behave as chemical entities. However, the silica in a calcined kaolin is not removed with sodium carbonate (Richardson) while the alumina is readily removed by acid (Walthall, et al., 1945). This apparent discrepancy between the reactivity of the silica and that of the alumina in calcined kaolins is significant and will be discussed in more detail later.

The Chemical Composition and Crystal Structure of Clays in Relation to Their Behavior as Cracking Catalysts. While the foregoing data are informative as to the physical structure as well as the overall chemical composition of the catalysts prepared from clays, they do not describe the critically important chemical properties of the surface of the catalyst. The reversible water content of these catalysts in the range 450-650°C throws some light on the chemical character of their surfaces. The method used in the Houdry Laboratory to determine the reversible water content is similar to that used in thermal-weight-loss experiments. However, the furnace is so designed that a constant flow of air of controlled water content and larger samples can be used. The sample is dried to constant weight in the apparatus at 650°C in flowing air. The air is dried to contain not more than 10^{-5} atmospheres partial pressure of water vapor as determined by dew point. The furnace and sample are then cooled to the desired temperature and air with various water contents passed over the sample. The gain in weight of the sample is followed until not more than 1 mg is picked up in an hour. This may take

as long as 24 hours at a given set of conditions. A number of materials were investigated in this manner. All materials, except pure silica gel, show a definite reversible water content. The water content has been expressed as the gain in weight of the dried sample when exposed to one atmosphere of water vapor (100 percent steam) at 450°C. These data are tabulated in table 2.

Under the experimental conditions, pure silica gel shows little or no reversible water content. However, alumina, silica-alumina synthetic catalyst, and the clay catalysts show the presence of reversible water content in varying degree. If the following assumptions are made: one, that the water held in this fashion is present only on the alumina, and, two, that the alumina present has the same area per gram as the total material, then it is possible to calculate for the alumina the ratio of reversible water content to the surface area. This value is shown in the last column of table 2 and indicates that within limits a close relation exists between the amount of alumina present and the reversible water content, except in the case of the acid activated montmorillonite.

As pointed out by Davidson (1947), there is a reversible water content of approximately 2 percent in freshly activated montmorillonite-clay catalyst. In this case it is difficult to distinguish, at the conditions of the experiment, that part of the reversible water content associated with the residual clay structure. An inspection of the water adsorption isotherms at 510°C for the alumina and the montmorillonite-clay samples respectively (fig. 9) shows a distinct difference between the two samples.
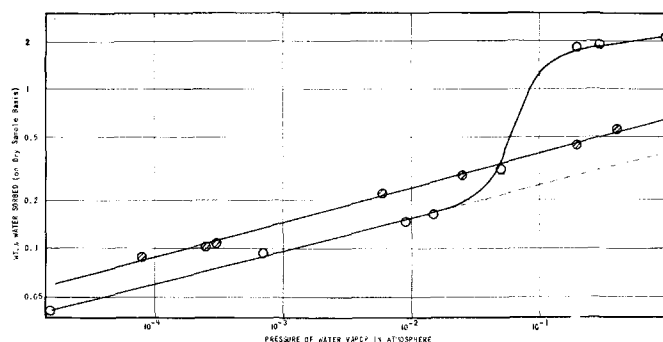

FIGURE 9. Open circles show acid-treated montmorillonite (Nevada, Ash Meadows); hachured circles show activated alumina (Harshaw Chemical Co.). Water sorption: 510°C isotherms.

For the alumina a linear relationship exists between its equilibrium water vapor pressure and its specific water adsorption when the data pertaining thereto are plotted on log-log coordinate paper. The same plot of the data for the clay parallels that for the alumina for a good portion of the curve. However, the parallelism breaks down between 10^{-2} and 10^{-1} atmospheres water pressure. Isotherms at other temperatures show the same difference between the alumina and the clay, indicating that the clay contains two types of water. If isochores are plotted, using smoothed isotherms as the source of the data, the heats of sorption can be calculated from the resulting slopes (fig. 10). It is interesting to compare the distribution of energy of water adsorption for the two materials. The graph of these relationships shows

Table 2.

Sample description	Surface area, sq m/g	Percent Al₂O₃ (calculated)	Percent reversible H₂O pick-up 450-650°C	Grams reversible H₂O per sq m of Al₂O₃
Ash Meadows, Nevada bentonite acid activated and calcined____	330	22.1 (11.5)	2.4 (0.4)	3.1×10^{-4} 1.1×10^{-4}
Silica 87.5 percent, alumina 12.5 percent, synthetic gel catalyst__	250	12.5	0.25	0.8×10^{-4}
Halloysite (Eureka), calcined and acid leached_____	164	40.6	0.8	0.9×10^{-4}
Silica gel ex ethyl orthosilicate, calcined_____	290	0.0	0.0	_____
Gamma-alumina_____	78	99.8	0.66	0.8×10^{-4}

LEGEND
---- GAMMA ALUMINA (Harshaw Chem. Co.)
——— ACID TREATED MONTMORILLONITE (Nevada Ash Meadows)
2.1 WATER CONTENT % DRY BASIS
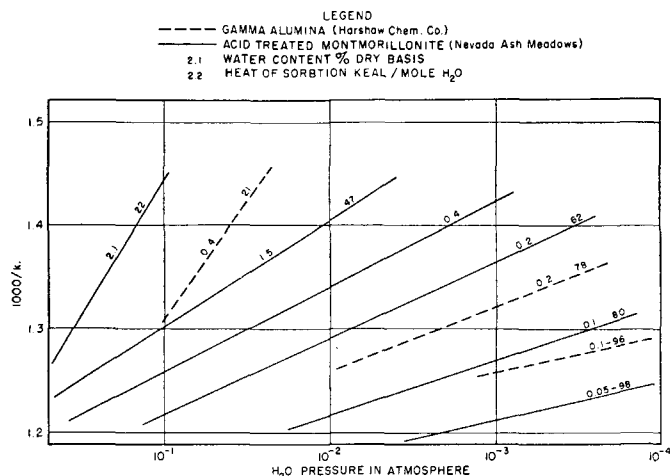2.2 HEAT OF SORBTION KCAL/MOLE H_2O

FIGURE 10. Isochore plot for alumina and activated clay.

for the clay sample a large amount of the sorbed water falls in a narrow energy range, 47-62 kilocalories per mole of water. No such narrow range exists for the alumina; the energy changes rapidly with water content in this case. Assuming that the portion of the clay isotherm parallel to the alumina isotherm represents the water held by the "free" alumina and extrapolating the linear portion of the curve (dotted line in fig. 9), the equilibrium amount of water at 1 atmosphere of water pressure is obtained. For the 450°C isotherm this value is 0.4 percent water. Since the total water sorbed at these conditions is 2.4 percent, the difference leaves 2.0 percent water that can be attributed to residual clay structure. The theoretical or calculated value for this type of water in the raw Ash Meadows sample of montmorillonite is 4.93 percent H_2O. Thus if 2.0 percent is the value for the acid-treated sample, 2.0/4.93 or 40 percent of the original clay structure is left after acid treatment. Making proper allowance for the loss of basic constituents, the alumina in the residual clay structure should be 10.6 percent by weight of the acid-treated clay. Since the total alumina content of the activated clay is 22.1 percent, the difference leaves 11.5 percent "free" alumina in a non-clay form. Using this value for the alumina, 0.4 percent for the reversible water and 330 sq. m/g. for the surface area, the value 1.1×10^{-4} grams of water per square meter of alumina is obtained. This checks the pure alumina value (0.8×10^{-4}) remarkably well considering the number of steps used to obtain it.

This method, being extremely complex, is not proposed as a means of quantitatively determining the amount of "free" alumina in any given material. However, the agreement shown by data given in column 5 of table 1 indicates qualitatively that a certain fraction of an alumina present in the clay catalysts is behaving very similarly to gamma-alumina.

On the basis of the correlation developed in the previous paragraphs and taking note of the physical data relating to active clay catalysts, the following mechanism is proposed for the acid activation of clays: 1) all or nearly all the ions held in base exchangeable positions are removed; 2) the smaller clay particles are completely destroyed, yielding essentially a mixture of silica and alumina; 3) part of the alumina set free by the acid treatment is dissolved by the acid. In step 2 the larger particles of clay are also attacked by the acid, particularly at the edges of the layers. However, in this instance the destruction of the lattice proceeds very slowly as the stability of a large particle is much greater than that of a small particle. Thus, two reactions take place: 1) there is a loss of lattice structure occurring relatively rapidly, and 2) there is a dissolving of alumina from both the "free" alumina created by the destruction of the small clay particles and the alumina still held in the lattice of the large particles. If the acid to clay-weight ratio is high, the "free" alumina created by lattice destruction is completely dissolved and the activity drops as shown in figure 3. However, the lattice destruction continues by the further removal of alumina from the large crystallites, so that more silica is released. As a result of the release of silica, the surface area increases, as illustrated in figure 4.

It is well known that after mild acid treatment the active clay catalyst still shows a strong montmorillonite pattern. This is consistent with the proposed mechanism in that 1) the particles of the raw clay in the size range 20-100 Å (the readily destroyed clay fraction) are too small to diffract X-rays; 2) the larger particles (the stable clay fraction) are responsible for the X-ray pattern in both the raw clay and the acid-activated clay. The existence of monmorillonite particles in the 20-100 Å range has been shown by Davis and coworkers (1950) and T. F. Bates (1952).

As previously shown, there is a similarity between kaolins activated by calcination followed by acid treatment and acid-activated montmorillonites. Kaolins, in distinction to montmorillonites, consist substantially of relatively large, well-formed crystallites (Davis, et al., 1950). On the basis of the mechanism proposed, these materials should be relatively stable to acid attack. Kaolinite, as previously pointed out, shows only moderate activation on acid treatment. For the raw kaolinite having large stable crystallites, the clay structure is destroyed only when and where the alumina is removed from the lattice by complete dissolution. Thus for the kaolins, in contrast to the montmorillonites, a free silica structure is believed created, but little or no "free" alumina remains.

The calcination of kaolins, however, apparently destroys the lattice structure in the case of halloysite and kaolinite. Such calcination probably creates a large number of very small particles. The mechanism of acid activation of these calcined clays is similar to that described for montmorillonite.

MacEwan (1951) has discussed the structural changes of kaolins occurring during the calcination at 550°C and has pointed out the possibility that a new structure has been created. Such a structure is not identifiable since the crystallites are so small that X-ray diffraction cannot be used to determine its presence. Even if a new structure were created, the stability of the new crystallites in the smaller than 100 Å range would be much less than that of the original clay which consists of particles in the 1,000 to 20,000 Å range. Therefore, whether a new structure or an amorphous one is induced by calcination of these clays, subsequent acid treatment would bring about the same results; namely, a rapid

destruction of the small clay crystallites and a consequent deposition of "free" alumina in either case.

That extremely small crystals are less stable than large crystals is strongly supported by many physical and chemical phenomena. One supporting piece of evidence is the variation of the endothermic peak (600°C) in the differential thermal analysis of different samples of kaolinite. This variation is known to depend on the degree of crystalline perfection. Another example is the shift in the endothermic peak to lower temperature on prolonged wet grinding of kaolinite. In another field, Dowden (1952) has pointed out that for finely divided metals the surface Tamman temperature is 0.3 of the absolute melting point, whereas it is known to be 0.5 for the bulk metal. Bevan and coworkers (1948) report a high surface electrical conductivity of oxide semiconductors compared to their bulk conductivity and ascribed the phenomenon to different energy states in the bulk and surface of a particle.

An extremely small particle, 20 to 100 Å in diameter, of clay has a large percentage of its total ions on its surface. In a crystal lattice the ions on the surface still retain the crystal pattern. However, such surface ions tend to be distorted (Cook, Oblad, and Pack, 1951) as a result of trying to accommodate the unused valences. The smaller a particle is, the larger the percentage of ions on the surface is. Consequently, the distortion or strain becomes larger and larger as the particles become smaller. If the terminal ion of the lattice is an oxygen, it will generally pick up an associated proton to satisfy its valence requirements. However, this does not relieve the distortion completely. The effect of the distortion probably extends into the lattice at least two or three ions deep, leading to differences in the coulombic forces around these outer ions, and weakening the structure in this region. Thus, in a 30 Å diameter particle the first two or three oxygen ion layers would constitute from

50 to 80 percent of the total oxygens in th crystallite, assuming it is roughly a cube or a sphere. In clays with their layer-like structure, the instability of a layer one unit cell thick (along the c axis) would be a function of the dimensions of the crystallite along the other two axes of the crystal (in the case of kaolin and montmorillonite the a and b axes). If the dimensions 20-30 Å are assumed for the a, b axes, then the oxygens at the terminal edges of the layer would constitute from 35-65 percent of the total oxygens in the particle.

The study of the decomposition of ammonium-exchanged zeolitic materials of widely varying average particle size shows a pronounced relationship between particle size and stability. Typical curves depicting loss of ammonia versus temperature are shown in figure 11. Curves are shown for an 87.5 percent silica, 12.5 percent alumina gel-type synthetic zeolite, a raw montmorillonite (Nevada Ash Meadows), and a sample of natrolite, all treated with ammonium chloride to replace the normally held ions—sodium, calcium, etc.—with ammonium ion. The first two of these zeolites represent materials occurring in the manufacture of commercial cracking catalysts. The abscissa is the percentage of the total ammonia content of the sample lost by heating to the temperature shown on the ordinate and holding at this temperature in a flowing stream of dry, oxygen-free nitrogen until the sample reaches a constant weight.

Comparison of the curves below 450°C shows that the acid-ammonium "salt" of the clay decomposes to a significant extent at considerably lower temperatures than the ammonium natrolite and higher temperatures than the synthetic zeolite. The crystallite or particle size of the natrolite sample was large (20-200 microns). The synthetic zeolite sample average particle size was 30 Å. The clay size range of 30 to 10,000 Å falls between these two extremes. The reactions are not truly reversible under the conditions of the experiment. Exposure of the samples, after loss of ammonia by heating, to an atmosphere of ammonia restores only a small part of the ammonia lost. This irreversibility proves conclusively that the structure causing the "acid" is destroyed during the dissociation of the ammonia.

The ionic structure responsible for the "acid" is essentially the same for the clay and the natrolite, in each case aluminum ions are isomorphously substituted for silicon ions in the lattice. Therefore, the clay "acid" should be equivalent in strength to the natrolite "acid" and the decomposition curves should be the same. Contrary to expectation, the two materials behave quite differently on decomposition. A likely explanation for the dissimilarity appears to lie in the very large difference in the average particle size of the different materials. This leads to a lower structural stability for at least part of the ammonium montmorillonite. Here again the smaller crystallites have lower stability. This is also supported by the fact that the synthetic zeolite with the lowest particle size decomposed at the lowest temperature.

One other point of interest in this experiment is that, of the three materials, only the synthetic zeolite had a high catalytic activity after removal of the ammonia by heating. This would indicate that a relatively gross intermixing of small particles of silica and alumina is more favorable to catalytic activity than the ordered ionic
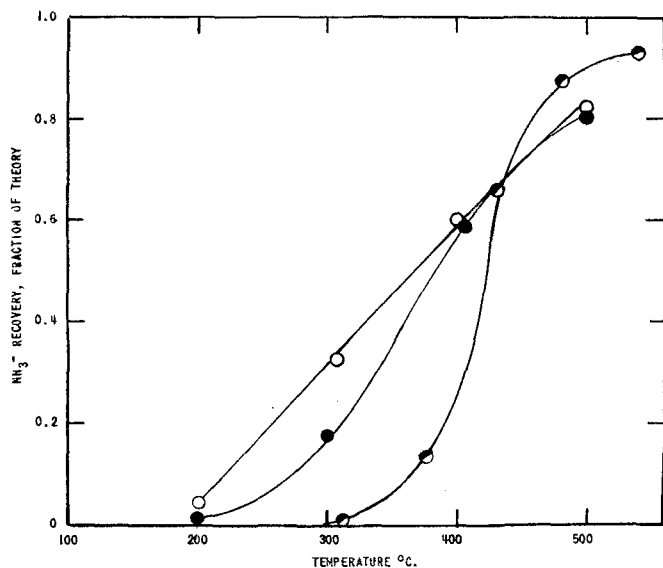

FIGURE 11. Ammonia loss versus temperature. Open circles show silica alumina gel NH₄- exchanged; solid circles show Ash Meadows, Nevada, montmorillonite NH₄- exchanged; half-filled circles show natrolite NH₄ exchanged.
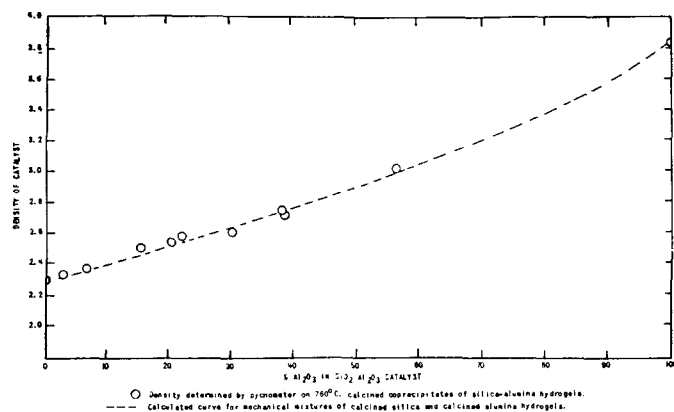
Figure 12. Density of silica alumina synthetic catalysts.

arrangement of silica and alumina found in natural zeolites and clays.

Nature of the Catalyst. In the foregoing discussion it was pointed out that clays in their natural state are not catalysts and that the process of acid treatment and calcination form a new composition, at least in part, having many characteristics of silica-alumina gel catalysts.

At this point it is pertinent to discuss some experimental work that has been done on gel catalysts and which has a bearing on the relationship between the chemical and physical properties and the structure of the material. Oblad, Milliken, and Mills (1951) have shown by various physical and chemical tests that the structure of synthetic silica-alumina gels after calcination is a mixture of extremely small silica and alumina particles. The alumina present has the specific gravity of gamma-alumina (fig. 12). The authors have proposed that aluminum and silicon share oxygens at the linear interfaces between the alumina and silica particles. The degree of oxygen sharing is enhanced by the method of preparation, wherein the hydroxides

are coprecipitated or treated after precipitation with a strong base so that all or nearly all the alumina is in the four-coordinate state or "acid" form according to Pauling (1930). If the mixed gels are put in the ammonium "zeolite" form the material may be calcined, at which time it loses all the ammonia (viz. fig. 11), and yields a material with a high surface area (200 to 300 sq m/g) and cracking activity. It retains none of its original base-exchange capacity but, nevertheless, has a base-exchange potential.

Utilizing strong inorganic or organic bases it was found that the activity of the catalyst formed by this method could be almost completely poisoned with as little as 0.06 milliequivalents of base per gram of catalyst. An accurate correlation was found between the amount of quinoline chemisorbed by a catalyst and its ability to crack hydrocarbons (fig. 13).

On the basis of these and other data it was proposed that the alumina is present as gamma-alumina, which is largely six-coordinated aluminum, and, as shown in figure 10 and table 2, contains reversible water, probably as OH^- groups. The low acidity, 0.06 me./g, is associated with the alumina at or near the silica-alumina interface, where the strain set up by the bond sharing of the two dissimilar materials causes the normally six-coordinated alumina to tend to become four-coordinated or more like silica in structure. However, the influence of silica alone was believed to be insufficient to bring about the coordination shift for the following reasons: first, zeolitically held ammonium ions are completely lost from the catalyst by heat treatment and under the experimental conditions are not reversibly adsorbed; second, under the proper conditions calcined silica-alumina catalyst can be partially reconverted to a silica-alumina "zeolite."

The calcined catalyst on treatment with solutions of ammonium acetate at various pH, said treatment being continued to approximately equilibrium by continuously
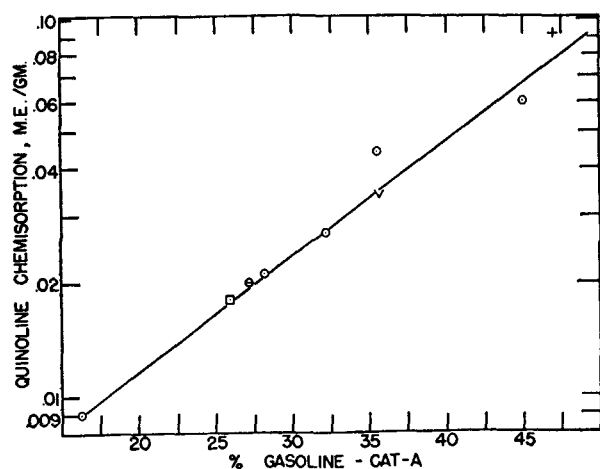

Figure 13. Quinoline chemisorption at 316°C as a function of activity for cracking light east Texas gas oil. Circle with central dot represents SiO_2—Al_2O_3 (Houdry type S); circle with dash represents SiO_2—1 percent Al_2O_3; rectangle with central dot represents clay catalyst (Filtrol); plus shows position of SiO_2—MgO; V shows SiO_2—ZrO_2
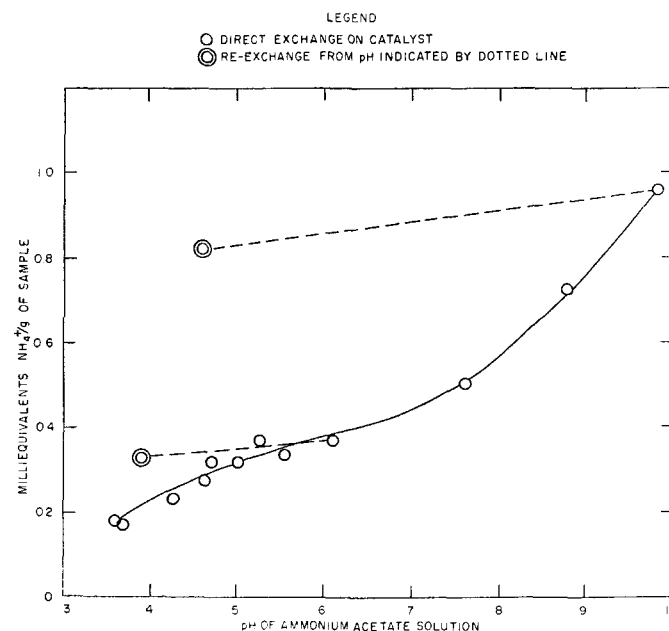

Figure 14. Base-exchange capacity of calcined synthetic silica-alumina versus pH of exchange solution.

running fresh salt solution over the sample, gives the relationship shown by the curve in figure 14. In this curve the base-exchange capacity is shown as a function of pH of the exchange solution. A sample was pretreated with ammonium acetate solution of 9.5 pH. It was found to contain 0.96 me./g of dry calcined catalyst. The squares on the graph represent the base-exchange capacity of the material measured subsequently at the indicated pH. This experiment appears to refute the concept that acids of varying strength exist in the catalyst since it indicates a new structure has been created by the pretreatment at 9.5 pH capable of holding 0.81 me. ammonium ion per gram at 4.5 pH. This is to be compared with the value of 0.25 me. NH_4^+ base-exchange capacity per gram at 4.5 pH on the original calcined material.

From these data it appears that the presence of both silica and a basic ion are necessary for the alumina to shift from six coordination to four coordination at pH lower than about 10. Further, it can be postulated that for the bulk of the alumina particle the structural change taking place during either the loss or the gain of a basic ion is not readily reversible and that the new structure is relatively stable at the experimental conditions. This bulk quality is modified the closer the aluminum ions in the particle are to the silica-alumina interface, at which point even very weak bases, such as olefins, paraffins, or other hydrocarbons, can cause the coordination shift.

Structural reversibility requires that bonds be broken and reformed in the alumina structure. In the presence of water and OH^-, as in the ammonium acetate experiment just discussed, this would occur readily. In the case of catalysts at normal cracking temperatures, 450-500°C, the shift can be presumed to occur with equal facility for the following reasons: first, the O^{--} and OH^- ions are highly mobile in the structure, particularly at 450-500°C; and, second, the hydroxyl or water content of the alumina in this range is reversible and is held with a wide range of energies (viz. fig. 10). At the temperature of 450°C the isotope O^{18} ion can be substituted for the O^{16} ions in the lattice to equilibrium in less than 30 seconds by treating a sample of the silica-alumina catalyst with a known amount of H_2O^{18}. As a base approaches the alumina-silica interface the demand for an extra oxygen or hydroxyl necessary for the shift from six to four coordination can be supplied to the site of greatest strain—i.e., those sites closest to the silica—from the lower energy sites by means of the mobility of the oxygen ions. Actually the transfer is probably effected more by small shifts of individual adjacent ions rather than the long range movement of a specific O^{--} or OH^- from a low energy site to a higher energy site.

The presence of water vapor will increase the number of low-energy sites available, make possible the formation of more acid sites, and thus change the activity of the catalyst. That such takes place has been found by Hansford (1947) for certain hydrocarbon reactions and by Mills and Hindin (1950) for deuterium-hydrogen exchange between various hydrocarbons and catalyst.

Application of the Reversibility Concept to Clay Structures. It is obvious that the catalyst structure is a very specific one and that clays must be modified by particular chemical and physical treatments to approximate the synthetic silica-alumina catalyst. Moreover, the application of some of the above concepts to certain characteristics of clays seems possible and may offer an explanation for some of the anomalies in clay behavior.

One of the least reproducible procedures used in clay investigations is the preparation of the so-called "hydrogen" or "acid" clays. Various investigators using similar or apparently similar techniques on samples of the same montmorillonite clay report widely varying results (Kelley, 1948). It is quite likely that the variations depend on the very low stability of the four coordinate aluminum ions in the "acid" state. As Kelley has pointed out, the use of electrodialysis for cation removal results in partial destruction of the clay and an appearance of free silica and alumina at the electrodes. Electrodialysis requires very long periods of time compared with the mild acid treatment usually employed in preparing a hydrogen clay. The long time allows the degradation of the clay to proceed to a point where it is obvious that destruction has occurred. Likewise on prolonged mild acid treatment the destruction of the clay is equally apparent (Gedroiz, 1924). Further evidence as to the instability of the "acid" form of the clay is the previously mentioned nonreversibility of the ammonium-clay, and the drop in temperature of the endothermic peak from 700° to 500°C. In this last instance, the acid-treated clay has a differential thermal analysis endothermic peak of 500°C while the raw montmorillonite has a 700°C peak. This drop represents a very pronounced change in the energy with which the aluminum ion layer hydroxyls are held. Since the four-coordinate aluminum ions in the silica layer are always within one oxygen distance from the hydroxyl position, any change in the structure of this aluminum would affect the energy with which the hydroxyl is held.

The three important phenomena described in the previous paragraph can be explained on the basis of structural change. An "irreversible" change takes place as a consequence of removal of the cations from the base-exchange sites. The degree to which this change takes place is a function of time and temperature and particle size. The inherent instability of extremely small particles leads to rapid breakdown of the structure with the loss of the stabilizing basic ion. The larger particles take considerably longer times or more severe treating conditions before losing the structural characteristics of the alumina.

There are a number of instances where materials containing four-coordinate aluminum ions in the "acid" state do not yield active catalysts. Thomas (et al., 1950) has reported that mildly acid-treated, calcined "hydrogen" montmorillonite is not catalytically active. It has been reported here that calcined ammonium montmorillonite and calcined ammonium natrolite are not active cracking catalysts. The surface areas of those montmorillonite samples are adequate for cracking activity. In the opinion of a number of workers in this field these materials should be catalysts, for, according to their theories, a four-coordinated aluminum with an associated proton should be present in each. The present authors think that such is far from true. They consider that an isolated four-coordinate aluminum with an associated proton is insufficient for activity. Furthermore, the exist-
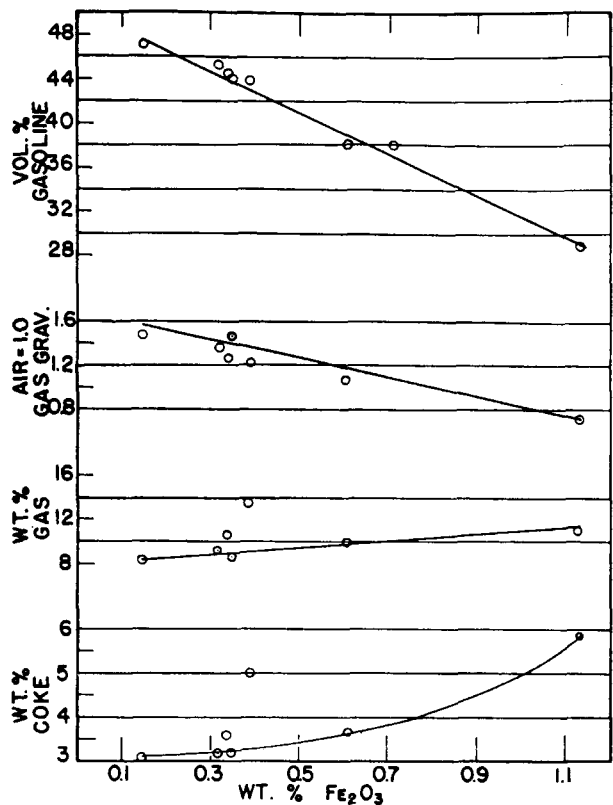
FIGURE 15.   Effect of iron on selectivity of Houdry synthetic silica-alumina; catalytic activity test-A.

Table 3.   Effect of hydrogen sulfide treatment at 550° C. on montmorillonite clay catalyst.

Mole percent H_2S in gas during calcination	Gasoline volume percentage	Coke weight percentage	Gas weight percentage	Gas gravity (air=1.0)
0	38.8	3.6	6.5	1.55
20	24.8	6.2	9.3	0.66

give the desired reversibility which, the authors predicate, is required for catalytic cracking.

The destruction of the clay lattice, already alluded to, must be sufficient to give some free alumina in order to result in an active clay catalyst. Obviously, if the foregoing hypotheses relating to the structure and action of synthetic catalysts are correct, the alumina formed from the clay must have some oxygen linkages remaining between it and the silica. In this manner the "strained" interfacial layer is created.

Effect of Oxides Other Than Silica and Alumina.   The alkali and alkaline-earth metal ions are removed to a large extent by acid treatment, and if care is taken during washing their removal is complete for all practical purposes. This removal is important since these basic ions are powerful poisons for the catalyst, acting to "neu-

ence of such a four-coordinate acid is disproved by the data cited. In each of the three cases cited the acid is irreversibly destroyed by either the acid treatment or the calcination. In the case of synthetic silica-alumina catalyst, the residual structure after calcination of the ammonium zeolite contains *gamma-alumina,* a crystal form that can shift reversibly to a limited extent. The calcined "hydrogen" montmorillonite still retains its aluminum in the clay-like structure and thus no gamma-alumina or any other meta-stable form of alumina is formed to
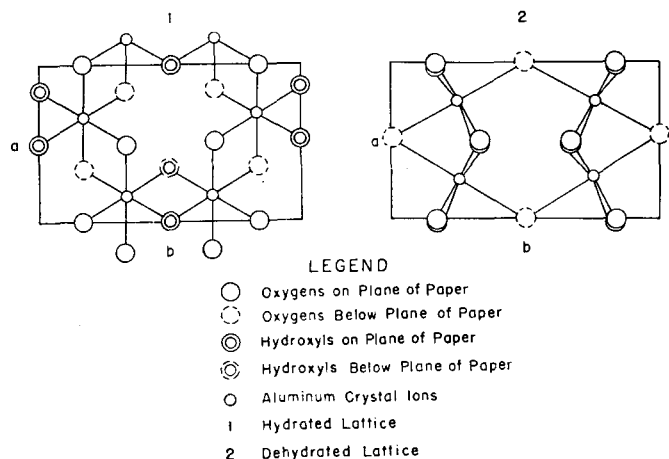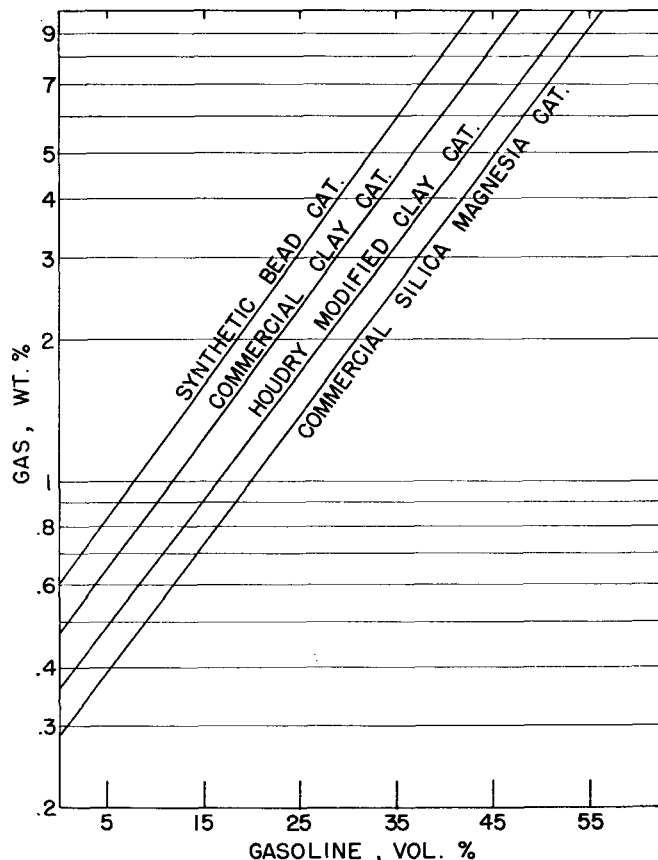

LEGEND

◯ Oxygens on Plane of Paper
◌ Oxygens Below Plane of Paper
◎ Hydroxyls on Plane of Paper
◎ Hydroxyls Below Plane of Paper
○ Aluminum Crystal Ions
1 Hydrated Lattice
2 Dehydrated Lattice

FIGURE 16.   Change in alumina layer structure on 550-750°C. Dehydration of montmorillonite (after Bradley).

CATALYST SELECTIVITY , CATALYTIC TEST – A

FIGURE 17.

tralize" the acid cracking function which is necessary for activity. The iron, and in montmorillonites the magnesia, remaining in the clay after acid treatment are generally isomorphously substituted for six-coordinate alumina in the clay lattice. The presence of free iron and magnesia materially alters the nature of the catalyst. If these ions remain in their original lattice positions, they have only minor effects on the activity of the finished clay catalyst. Free magnesia does not appear to be basic enough to act as a poison. Instead magnesia modifies the catalysts prepared from clay containing it by shifting the distribution of products, giving somewhat less gas for the same conversion than synthetic silica-alumina catalysts (see fig. 17), thus being more like synthetic silica-magnesia.

The iron in freshly prepared or "new" clay catalysts causes a slight increase in coke formation over that given by synthetic catalysts. On continued use, particularly when the catalysts is exposed to petroleum crudes possessing a high content of organic sulfur compounds, the iron tends to leave its lattice positions and as a "free" or non-isomorphously substituted iron causes large changes in the performance of the catalyst. Figure 15 illustrates the effect of small amounts of iron added to silica-alumina synthetic catalyst. Table 3 shows the effect to be similar when a clay catalyst containing iron is treated with hydrogen sulfide. In both instances the decrease in gasoline yield and the increase in coke and gas indicate the presence of "free" iron.

At present there are three expedients for avoiding or preventing the damaging effect of iron. Two are now used commercially, the third has been extensively tested on pilot plant scale. The three expedients will be described in the following paragraphs.

The first expedient is represented by Filtrol Corporation's "SR" catalyst. This catalyst is prepared from a halloysite with a fairly low iron content. The commercial results, using this catalyst with a charge stock having a high sulfur content, appear to be satisfactory insofar as resistance to the effects of sulfur is concerned (E. J. Thomas, 1950).

The second expedient used in many commercial cracking plants is specific for catalysts prepared from iron-containing montmorillonite. It was found that pretreatment of the clay catalyst with steam before it enters the cracking zone will, to a large extent, prevent the harmful activation of the iron. This phenomenon is probably related to the reversible water content of the clay in the following manner. As pointed out earlier in this paper, a large part of the reversible water content can be associated with the residual montmorillonite structure. This water, as has been postulated by Grim and Bradley (1948), comes from the hydroxyl groups on the alumina layer occurring in the hexagonal ring of silica tetrahedra. Bradley, on the strength of X-ray data, has proposed that on the loss of this OH^- group the oxygen and aluminum ions in the lattice shift to a new arrangement shown in figure 16. The new arrangement requires a slightly larger oxygen-to-oxygen distance than is normal in a closely packed oxygen structure, and results in a strain that is relieved by readsorption of water and reformation of the original lattice with the hydroxyl groups replaced. A strained

structure is more easily destroyed than an unstrained structure. The situation is similar in a way to the strain induced by the large surface to bulk ratio of extremely small particles discussed previously. Thus the reaction between the iron ions in the strained lattice and the sulfur ions in the hydrocarbons or hydrogen sulfide on the surface of the lattice is enhanced and takes place under conditions at which little or no reaction would occur with an unstrained lattice. The clay catalyst during the regeneration portion of the cracking cycle loses the clay lattice OH^- groups since the temperature in regeneration is 620°C and the partial pressure of water vapor seldom exceeds 0.05 atmospheres (fig. 10). If this material is introduced to the reactor with a high-sulfur-content crude oil without presteaming, the lattice is in a strained state and the iron reacts with the sulfur in the hydrocarbon charge. If the catalyst before reaching the cracking zone is presteamed at the proper temperature and steam pressure to insure replacement of the hydroxyl groups, the lattice is not strained and the iron-sulfur reaction proceeds more slowly or is prevented entirely.

The third means of solving the iron problem is to remove it selectively from the clay (Shabaker et al.). The treatment about to be described yields a catalyst of low iron content. This catalyst is known as Houdry Type 1. For montmorillonite the technique involves acid activation of the clay followed by treatment at 750°C with a dry inert gas, such as nitrogen, containing from 1 to 25 mole percent hydrogen sulfide. Since at these conditions the hydroxyl water is lost from the clay structure and the lattice is in the strained state described above, the iron reacts readily with the hydrogen sulfide. The color of the clay, originally light tan or off-white, turns black on sulfidation. The sulfided clay on oxidation (500°C) becomes a bright brick red, indicating the presence of free iron oxide. The clay with the iron in the sulfide form is leached with cold, dilute acid to remove the iron and minor amounts of alumina. During the course of this treatment the clay structure is destroyed to an even greater degree than in normal acid activation. However, some residual lattice structure can be seen on X-ray diffraction of samples of this material. If the clay catalyst prepared in this fashion contains magnesia in the 1.0 to 6.0 percent range, it gives a distribution of cracked products on testing different from those obtained with the original clay catalyst or synthetic silica-alumina catalyst. The relationship between the gas and gasoline yields for a number of different catalysts is shown in figure 17. The two curves for commercial clay catalyst and "modified" or iron-free Type 1 clay catalyst were obtained by testing Filtrol catalysts and Houdry Type 1 catalysts prepared from Filtrol clay. Catalysts of different activity levels were obtained by steam treatment. It can be seen that the Type 1 tends to be more like a synthetic silica-magnesia catalyst than the original clay catalyst before modification. These data indicate that the magnesia (4.9 percent) in the clay lattice remaining after acid activation has been activated by the destruction or partial destruction of the lattice during the iron removal. When montmorillonites containing little or no magnesia are activated and modified, using the procedure de-

scribed, the values obtained for the gasoline and gas yields fall on the synthetic silica-alumina catalyst curve. Thus the properties of the Type 1 catalyst can be like those of a synthetic silica-alumina or tend towards those of a silica-magnesia by selection of clays of different magnesia contents. When iron and magnesia are not present in the final catalyst prepared from montmorillonite-type clays, the cracking characteristics are very similar to synthetic silica-alumina gel-type catalyst. This finding further supports the proposal that the new form created when clay is activated is essentially a mixture of amorphous silica and alumina. The residual clay lattice of the modified clay catalyst disappears on heating to 785°C and the structure appears to be amorphous since no X-ray diffraction pattern is observed. The thermal stability of iron-free Type 1 gives it an important advantage over ordinary acid-activated clay catalyst which is deactivated at about 75°C lower temperature. Using the Type 1 technique, catalysts can be prepared from both montmorillonites and kaolins with excellent sulfur stability. In the case of montmorillonites containing magnesia, the new catalyst structure has specific cracking characteristics that are desirable in many applications.

Summary. The changes taking place in a montmorillonite-, kaolinite-, or halloysite-clay structure on acid treatment and calcination can be interpreted as involving the creation of a structure with physical and chemical characteristics and catalytic activity similar to synthetic silica-alumina gel catalyst. Such clay properties as high temperature dehydration behavior only reflect the degree to which a minor fraction of the clay structure has remained unattacked. When magnesia is absent and when iron is removed selectively by further treatment, there results a catalyst having essentially identical characteristics as synthetic silica-alumina. The original structure and chemical composition of the raw clay play a large part in determining the degree and type of destruction taking place on acid and heat treatment. In spite of the work that has been done in the field of clay catalysts, one must still resort to empirical testing of any given clay in order to establish its suitability as a raw material for catalyst manufacture.

Consideration of experimental data presented for reversible hydration at high temperatures, loss of ammonia upon heating the ammonium zeolite form, and titration experiments by base leads to a concept of reversible coordination shift from six to four of the aluminum ion. This concept has been utilized to explain behavior of clays in electrodialysis.

DISCUSSION

M. W. Tamele:

Milliken's idea of considering clay to be a reservoir of silica and alumina is interesting and may resolve some of the discrepancies noted in the past. Various ideas have been recorded in the literature as to how much R_2O_3 must be removed to achieve optimum activity, and the material in this paper reconciles the situation.

Will Milliken explain the presence of pores of 25 Å radius (fig. 6). I cannot see how such pores can be formed by the removal of the inner layer of the montmorillonite lattice, but rather it would indicate to me that another phase is being introduced.

T. H. Milliken:

The 25 to 26 Å radius pore size was calculated assuming the pores to be capillaries and essentially round. This is obviously not the case and for interlayer spacing, different methods of calculation should be used. We have no correlation of this spacing with X-ray diffraction powder spectra. Although we cannot pick up spacings of this magnitude with our instrument; second-, third-, and fourth-order reflections should show up. There is a good chance of a new phase being introduced. These longer spacings may be due to the presence of particles of silica between the originally swollen layers preventing them from coming together again. Do MacEwan's techniques show these?

D. M. C. MacEwan:

Spacings up to 120 Å have been measured in our laboratories (by K. Norrish), and I do not think there is any doubt that spacing of the reported pore size in the activated material could be observed if they exist as definite spacings. I have examined activated montmorillonite with filtered radiation and no such long spacings were seen. On the other hand there was evidence to indicate that there was some material between the layers which prevented their collapsing completely but the order of magnitude of the pores that would result would be about 10 Å. Those particular observations might have missed a spacing of about 30 Å had it been present.

Isaac Barshad:

Does not the acid treatment break up the lattice structure by removing units throughout the particle and giving it a sieve-like structure? This may explain anomalies noted in work on the total exchange capacity of activated materials.

T. H. Milliken:

The possible sieve-structure in the silica sheets might be explained on the basis of the fourfold Al positions being points of acid attack.

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