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The Acid Activity of 2:1 Layer Silicates

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The acid catalytically active centers in 2:1 expansible layer silicates were identified from determinations of the ion exchange capacity, surface area and the rate of catalytic decomposition of *tert*-butyl alcohol to isobutylene and water.

In these naturally occurring clay minerals the acid catalytic activity is proportional to the surface concentration of the tetrahedrally coordinated aluminum. The *total* cation exchange capacity does not determine the acid catalytic activity.

INTRODUCTION

In industry, clay minerals have been widely employed as catalysts, catalyst supports and starting materials in catalyst manufacture. In nature, these materials are an important vector in soil genesis and they form an integral part of the dynamic conditions in soil profiles where organic matter is continuously undergoing change. Also, acidity of clays are reasoned to have had their role in petroleum genesis (*1*).

Naturally occurring 2:1 layer silicates characteristically possess ion exchange properties. Unlike zeolites and amorphous silica–alumina, where tetrahedrally coordinated alumina can be equated with ion exchange, layer silicates also possess cation exchange sites that are seated in octahedral layers of these minerals. The total cation exchange site density is therefore a composite of substitutional defects of Al^{3+} for Si^{4+} in tetrahedral coordination and Mg^{2+} (Fe^{2+}) for Al^{3+} in octahedral coordination.

One may expect the acid character of these two sites to differ with possible practical applications. Because of the abundance of naturally occurring 2:1 layer silicates, it would also be useful to establish a rational correlation between composition and structure of layer silicates and their catalytic activity. For this purpose five naturally occurring standard reference clays were prepared in the H^+ form and tested for low temperature acid activity. The catalytic test was the dehydration of *tert*-butyl alcohol to isobutylene and water. Although water does compete with alcohol for active sites, it did not influence activity in the range of this investigation, and was therefore well suited for a detailed study of clay mineral structure and composition on acid activity.

METHOD

The method and apparatus for the dehydration experiment was patterned after that employed by Frilette *et al.* (*2*). The clay minerals prepared as described below were added to refluxing *tert*-butyl alcohol. The rate of isobutylene production from this dehydration reaction was followed for 20 to 60 min. The temperature remained constant at 80 ± 0.5°C throughout the duration of these tests. In each case the refluxing vessel was charged with 25 ml of dry *tert*-butyl alcohol, brought to reflux temperature and 100 mg of catalyst were added.

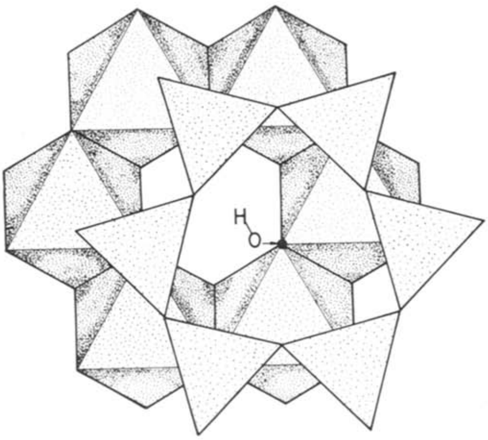

FIG. 1. The first two layers of a 2:1 neutral dioctahedral layer silicate.

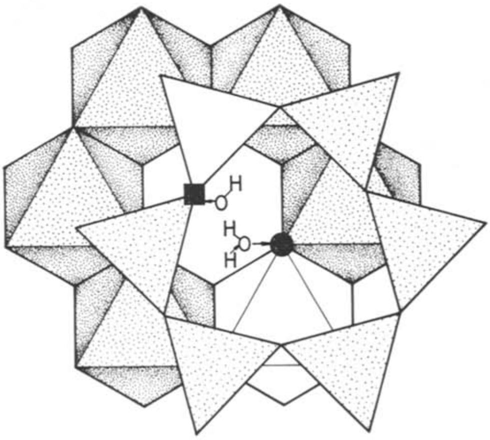

FIG. 2. Protons associated with cation exchange sites in the tetrahedral and octahedral layers of a dioctahedral layer silicate with isomorphous substitution in both layers.

The five 2:1 expanding layer silicates (smectites) selected for this investigation were fractionated and the less than 0.2 μm particle size was NH_4^+-exchanged. This material was subsequently electrodialyzed to produce the hydronium form. Immediately after electrodialysis these samples were freeze-dried, heated to 105°C for several hours and stored in the dehydrated form to prevent hydrolysis to an Al^{x+} form (*3*). Total ion exchange capacities were obtained by NH_4^+ saturation of the exchange complex and titrating the thermally evolved NH_3 (*4*). From the mineralogical composition in Table 2 tetrahedral substitution was equated with tetrahedral charge. The milliequivalents of Al^{IV} were calculated per unit molecular weight of the respective clay minerals. From this the milliequivalents of tetrahedral charge per unit weight of smectite were obtained. The "octahedral cation exchange capacities (CEC)" was taken to be the difference between "total CEC" and the calculated "tetrahedral CEC." Surface areas were determined by N_2 adsorption.

RESULTS AND DISCUSSION

When dioctahedral layer silicates have all the octahedral sites occupied by Al^{3+} and all the tetrahedral sites by Si^{4+} then the result is an electrostatically neutral framework (Fig. 1). When isomorphous substitution occurs, however, the clay mineral develops an anionic charge, provided the replacing framework cation has a lower charge to the one being replaced. There are two distinctly different positions

TABLE 1

Mineralogical Composition of Selected Clays

Clay mineral	Mineralogical composition
22	$(Al_{1.4}{}^{3+}Fe_{0.32}{}^{2+}Mg_{0.31}{}^{2+})(Si_{3.88}{}^{4+}Al_{0.12}{}^{3+})O_{10}(OH)_2$
25	$(Al_{1.53}{}^{3+}Fe_{0.15}{}^{3+}Fe_{0.01}{}^{2+}Mg_{0.33}{}^{2+})(Si_{3.91}{}^{4+}Al_{0.09}{}^{3+})O_{10}(OH)_2$
21	$(Al_{1.41}{}^{3+}Fe_{0.13}{}^{3+}Fe_{0.01}{}^{2+}Mg_{0.45}{}^{2+})(Si_{3.93}{}^{4+}Al_{0.07}{}^{3+})O_{10}(OH)_2$
24	$(Al_{1.35}{}^{3+}Fe_{0.05}{}^{3+}Mg_{0.60}{}^{2+})(Si_{3.98}{}^{4+}Al_{0.02}{}^{3+})O_{10}(OH)_2$
31	$(Al_{1.46}{}^{3+}Fe_{0.06}{}^{3+}Fe_{0.01}{}^{2+}Mg_{0.47}{}^{2+})(Si_{4.0}{}^{4+})O_{10}(OH)_2$

TABLE 2

Acid Activity and Surface Properties of Layer Silicates

Sample	Acid activity (ml/s·g)	Specific surface (m^2/g)	CEC (meq/g)			Surface charge density (10^{-6} meq/cm^2)		
			Total	Octahedral	Tetrahedral	Total	Octahedral	Tetrahedral
22	4.88	83.5	0.60	0.29	0.31	0.72	0.35	0.37
24	0.17	86.0	0.98	0.92	0.06	1.14	1.07	0.07
25	9.50	31.4	0.96	0.72	0.24	3.06	2.30	0.76
31	0.22	33.6	0.56	0.52	0.00	1.55	1.55	0.00
21	0.57	108.7	0.72	0.53	0.19	0.66	0.49	0.18

the replacing framework cation can occupy (Fig. 2):

1. Al^{3+} can proxy for Si^{4+} in tetrahedral coordination (in the "tetrahedral layer").
2. Mg^{2+} and Fe^{2+} can proxy for Al^{3+} in octahedral coordination (in the "octahedral layer").

The resulting anionic charge in the rigid framework is balanced by an exchangeable cation, which is coordinated by at least one of the oxygens associated with the proxying cation.

From Fig. 2 it can be seen that if the exchanging ion is a proton, it will be associated with two entirely different oxygens, depending upon whether isomorphous replacement occurs in the octahedral or tetrahedral layers. Prior to isomorphous replacement—i.e., in a neutral framework with no ion exchange capacity—an oxygen associated with the octahedral layer already is coordinated by a proton while those associated with the tetrahedral layer are not. When isomorphous replacement takes place two protons are associated with an oxygen in the octahedral layer and one with an oxygen in the tetrahedral layer. The ques-

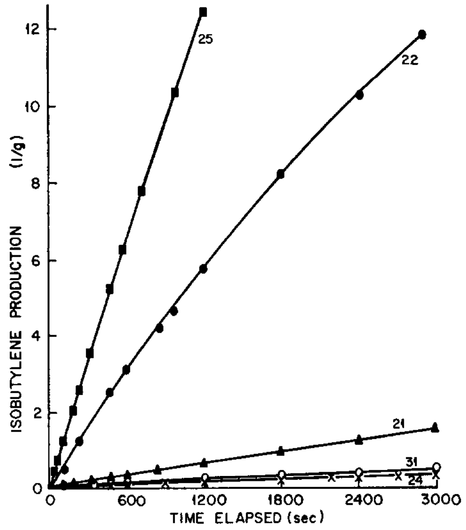

FIG. 3. Isobutylene production originating in acid activity of the 2:1 layer silicates.

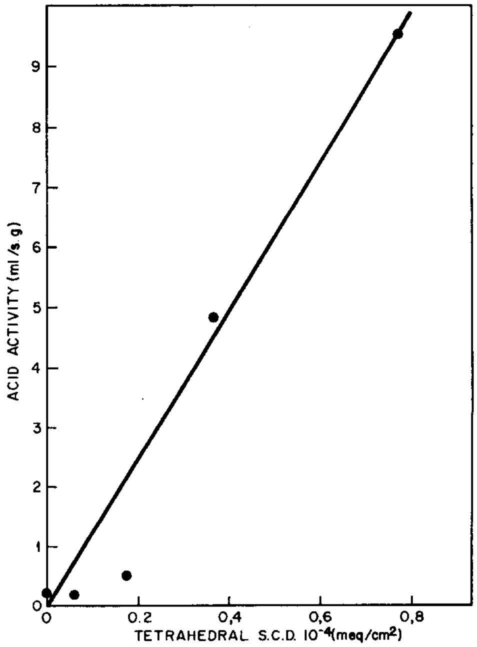

FIG. 4. Acid activity proportional to the tetrahedral surface charge density in 2:1 layer silicates.

tion that now arises is whether the "acid activity" of these two sites differ.

The mineralogical composition of the clays studied are listed in Table 1 (*5*). In Table 2, relative contributions of ion exchange capacity from octahedral, and tetrahedral layers are listed. The total ion exchange capacity is the sum of these two capacities.

From measured surface areas, total, octahedral and tetrahedral cation exchange capacities, the respective total, octahedral and tetrahedral, exchangeable cation site densities were calculated. In Table 2 measured acid activities are also listed. Either differential or integral conversion could be obtained since reaction velocity was essentially constant for the first 20 min of reaction time (Fig. 3). In this range the specific activity per gram of catalyst was obtained.

When acid activity is plotted against surface area, octahedral site density, total site density, total exchange capacity or octahedral exchange capacity, then either no correlation or very poor correlations are found. When acid activity per gram of catalyst, however, is plotted against the tetrahedral exchange site density, viz, tetrahedral exchange capacity per unit surface area of the particular layer silicate, then a proportional relation is found for the various clays (Fig. 4). Only sample No. 21 deviates somewhat, but this is probably due to diffusional restrictions on the reaction rate in this catalyst which has a very high surface area and consequently relatively narrow channels.

An early indicator to the dominant role of tetrahedrally coordinated alumina can be found in the work by Mortland and Raman (*6*) on the protonation of ammonia in 2:1 layer silicates; results obtained by the author and R. M. Lago at the Mobil Oil Central Research Laboratories on catalytic conversion tied in with this view. The work reported here shows *quantitatively* that the catalytic acid activity associated with H^+-exchanged 2:1 layer silicates finds its origin in the tetrahedral layer.

The catalytic inactivity of octahedral sites may be attributable either to shielding of the protons associated with these sites from reactant molecules or to a loss of acid character of these protons. In regard to the latter, we have indications that during thermal decomposition of NH_4^+-exchanged dioctahedral layer silicates, having octahedral isomorphous replacement alone, a corresponding dehydroxylation of the octahedral layer occurs when NH_3 is evolved. This would indicate that two protons associated with an oxygen from the octahedral layer is an unstable configuration and that these acid sites are permanently lost during deamination.

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