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Nature of Active Sites of Aluminosilicate Catalysts

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The catalytic activity of aluminosilicates with respect to the hydrogen redistribution reaction is shown to be due exclusively to exchangeable ions and hydrolytic acidity. There is no important difference between the two kinds of acidity. Silica gel is found to contain active, "hydrolytic," and nonactive OH groups. Silica gel acquires ion-exchange capacity and catalytic properties exclusively as a result of substitution of aluminum for the protons in hydrolytic OH groups. There is a linear relationship between the content of hydrolytic ions of aluminum and activity. It is shown that H-aluminosilicates are unstable and spontaneously convert by inner exchange to Al-aluminosilicates. Consequently, the exchange acidity of aluminosilicates is due solely to the presence of exchangeable ions of aluminum on their surface. The exchangeable aluminum is a strong Lewis acid. The ability of aluminosilicates to acquire catalytic activity only in the presence of traces of moisture is assumed to be a result of complex formation of the exchangeable aluminum with water. The ionization of this complex leads apparently to the appearance of acid sites of the Brönsted type. Evidentally, the active site is the exchangeable aluminum ion in combination with one water molecule. In catalytic conversion experiments aluminum ions prove to be equal in activity, even though they differ in their ability for exchange in an aqueous medium. The active sites are completely accounted for by the value of hydrolytic acidity. The true value of this acidity may be obtained by the carbonate method. Those methods of titration in anhydrous media by butylamine or ethyl acetate fail to take into account just that part of aprotonic acidity that is responsible for the activity of the catalyst.

INTRODUCTION

The catalytic properties of aluminosilicates are usually attributed to the presence on the surface of acid sites of either the Brönsted (*1–9*) or Lewis (*8–15*) type. But in spite of the great number of works dedicated to investigations in the field of catalysis on aluminosilicates, discussion of this problem continues.

This paper presents data which enable the two viewpoints to be reconciled.

EXPERIMENTAL

The materials used were co-gelled commercial synthetic aluminosilicate of the Houdry type containing 30% Al_2O_3, 70% SiO_2 (surface area, calculated from adsorption isotherms of methyl alcohol vapor $S = 222$ m²/g, average pore radius $r = 27$ Å); samples of fine-pore (S from 665 to 732 m²/g, $r = 8$–10 Å) and large-pore (S from 230 to 424 m²/g, r from 38 to 72 Å) silica gels; and activated bentonite (commercial pelleted catalyst obtained by activation of natural clay by acid).

The silica gel was cleaned by boiling in a concentrated solution of HCl, washing with water, drying and calcining at 500°C. (The aluminosilica gel was prepared by treating fine-pore silica gel for several days with a solution of aluminum chloride, one-fourth neutralized with 1 N NaOH solution.)

The exchange acidity and the hydrolytic acidity were determined by treatment with normal sodium chloride and sodium acetate solution. Treatment of aluminosilicate by the neutral salt solution was followed by sorption of salt cations and displacement into the solution of the equivalent amount of H^+ or Al^{3+} ions. But treatment by the sodium acetate solution results in reaction of H^+ or Al^{3+} with the alkali formed as the result of sodium acetate hydrolysis. The solution thus contains the equivalent quantity of acetic acid. Five-gram batches of pulverized samples of particle size 0.25–0.5 mm were calcined at 500°C and then repeatedly treated by shaking with fresh portions of the sodium salt solutions for 2 days. The solutions were decanted into 500-ml flasks and the acidity of the salt extract was determined by titration with 0.03*N* NaOH solution in the presence of phenolphthalein as indicator.

The aluminum content in the NaCl extract was determined from the difference between the total acidity of the solution and the content of free acid. The content of free acid was determined by an alkali titration after the aluminum was bonded into a Na_3AlF_6 complex by adding an excess of sodium fluoride solution. In this, the Sokolov method (*16*), the complex possesses no acid properties and is not titrated by alkali. The amount of basic forms of aluminum in the solution in terms of $Al(OH)_3$ was calculated from the difference between the total aluminum content and the content of trivalent ions. The total aluminum content was determined by the Sokolov method after all the basic forms of aluminum were converted to $AlCl_3$ by adding a small excess of hydrochloric acid.

The aluminum content in aluminosilica gel samples was determined by the method already described (*17*) by repeated treatment of the sample with a normal solution of hydrochloric acid at room temperature for 2 hr, in the case of uncalcined samples, and by boiling for 1 hr in the case of calcined samples. The 25-ml hydrochloric acid extract was saturated with NaCl, and 2 ml of 1*N* CH_3COOH and 27 ml of 96% C_2H_5OH were introduced, together with one drop of fresh saturated $FeSO_4$ solution. A strong CO_2 flow was passed through the solution for 5 min, and under continuous CO_2 flow the potentiometric titration by 0.1*N* NaF solution was done with the smooth platinum electrode (*18, 19*). In some samples aluminum was determined by the Sokolov method (in a weak acid solution extract).

The content of sodium ions was found by washing dried samples with a weak standardized solution of hydrochloric acid. Portions of the solution obtained in this way were titrated with standard sodium hydroxide solution (*20*).

The content of chemically bound pyridine in the samples was found by the method previously described (*21*), that is to say, the aluminosilicate was destroyed by boiling with a 40% alkali solution, while the isolated pyridine was trapped with ice water and titrated with hydrochloric acid. Bromphenol blue was used as indicator.

Sample activity was determined by the hydrogen redistribution reactions and was characterized by the degree of cyclohexene conversion, by determining the percent of saturated hydrocarbons in the monomeric fraction. For this purpose cyclohexene was obtained by the dehydration of cyclohexanol over active aluminum oxide at 350°C. After distillation and drying, the product obtained had a boiling point of 83°C, n_D^{20} 1.4469, and an iodine number of 308.7. The reaction was followed by formation of methylcyclopentane and polymerization products. The product obtained was distilled and the monomeric fraction was collected. The iodine number of this fraction was determined by Kaufmann's method (*22*).

Catalytic conversion experiments were carried out in a flow system using conventional apparatus employed in studying catalytic processes. Samples of 30-ml volume were placed in the glass reactor and were blown for 30 min with CO_2 at 320°C. Under these conditions cyclohexene passed through the reactor at a volume liquid flow rate of 2 hr^{-1}.

RESULTS

Exchange adsorption of aluminum on silica gel. Samples of fine-pore and large-pore silica gel were treated for 24 hr with aluminum nitrate solutions of different concentrations, and solutions with an increased content of basic forms of aluminum. Then the excess of salt was washed out.

Some samples were prepared by impregnation with a concentrated $Al(NO_3)_3$ solution. The samples were dried and then calcined at 450–500°C. The exchange and hydrolytic acidity and aluminum content of the prepared samples were determined. The results are given in Tables 1 and 4.

TABLE 1
Exchange and Hydrolytic Acidity of Aluminum Oxide, Original Silica Gel, and Aluminosilica Gels

Sample	Acidity (meq/100 g)	
	Exchange	Hydrolytic
Aluminum oxide	0	0
Original silica gel	0.6	27.6
Silica gel		
Treated with $Al(NO_3)_3$ solution		
0.1 *N*	1.8	27.6
0.2 *N*	3.0	27.6
1.0 *N*	3.5	27.6
Impregnated with $Al(NO_3)_3$ solution, Al_2O_3 applied		
1%	4.6	29.4
3%	9.6	33.6
Treated with 1 *N* $AlCl_3$ $\frac{1}{4}$ neutralized with 1 *N* NaOH for		
1 day	9.6	34.2
3 days	13.0	35.9
7 days	18.0	39.6

The data show that appreciable increase of hydrolytic acidity began only after the amount of aluminum adsorbed became higher than the hydrolytic acidity of the original silica gel. Exchange acidity increased continually with an increase in the aluminum content. The most intensive adsorption of aluminum was observed with $AlCl_3$ solutions partly neutralized with a NaOH solution.

When treatment with these solutions was carried out for 2 weeks, changing the solutions periodically, the exchange acidity of the aluminosilica gels formed approached the hydrolytic acidity of the initial samples (*23*), as may be seen from the data of Table 2.

TABLE 2
Exchange and Hydrolytic Acidity of Silica Gels Treated with a Solution with High Content of Basic Forms of Aluminum

Silica gel sample	Hydrolytic acidity of original silica gels (meq/100 g)	Acidity of Al-silica gels (meq/100 g)	
		Exchange	Hydrolytic
Fine-pore			
No. 1	28.8	27.4	62.4
No. 2	28.2	24.0	61.2
No. 3	25.2	24.0	52.8
Course-pore			
No. 1	13.8	12.6	55.2
No. 2	9.9	9.6	41.4

Poisoning of synthetic aluminosilicate with sodium ions. Synthetic aluminosilicate was treated with NaCl and CH_3COONa solutions of different concentrations and with an excess alkali solution. It was also impregnated with solutions containing a known amount of NaOH.

The degree of conversion of cyclohexene on the samples poisoned with sodium ions is shown in Table 3 and in Fig. 1. It will be seen that there was an inverse linear relationship between the degree of conversion of cyclohexene and the number of sodium ions adsorbed by the aluminosilicate. This was true regardless of whether the salt solution treatment was used or if the aluminosilicate was impregnated with alkali solutions. The only difference produced by these two pretreatments was that in the first case a particular degree of conversion of cyclohexene was obtained at a lower sodium ion content (*24*).

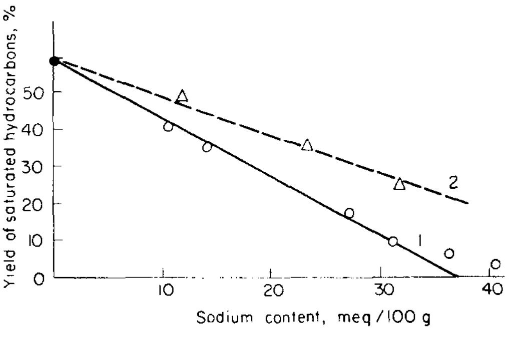


Fig. 1. Degree of conversion of cyclohexene on synthetic aluminosilicated poisoned with sodium ions: (1) relationship for samples treated with solutions of sodium salts; (2) same for samples impregnated with alkali solutions.

TABLE 3

DEGREE OF CYCLOHEXENE CONVERSION ON SYNTHETIC ALUMINOSILICATE POISONED WITH SODIUM IONS

Treating solution	Adsorbed sodium ions (meq/100 g)	Degree of cyclohexene conversion (% of saturated hydrocarbons)
Water	0	59.9
NaCl solution		
0.5 *N*	10.5	41.5
1.0 *N*	14.0	35.5
CH_3COONa solution		
0.25 *N*	27.1	17.0
0.5 *N*	31.2	10.2
1.0 *N*	36.1	6.1
1.0 *N*	40.6	3.0
Solution containing known amount of NaOH	11.9	48.1
	23.2	35.8
	31.9	25.8
Solution containing excess NaOH	151.0	0.1

Catalytic activity and acidity of silica gel treated with aluminum salt solutions. Aluminosilica gel samples were obtained by activating fine-pore silica gel with aluminum by the following methods: (1) treatment with solutions of nitrate salts of different concentrations with subsequent washing out of the NO_3^{-1} ion; (2) impregnation with a definite amount of a concentrated $Al(NO_3)_3$ solutions; (3) treatment with a normal $AlCl_3$ solution one-fourth neutralized with 1 *N* NaOH solution, and washing out of the Cl^- ion; (4) treatment with a $BaCO_3$ suspension in a normal sodium chloride solution with subsequent substitution of aluminum ions for the adsorbed sodium ions by treatment with an $Al(NO_3)_3$ solution, and washing out of the salt with water. The duration of treatment and volumes of aluminum salt solutions were also varied.

Table 4 contains data on the degree of

TABLE 4

DEGREE OF CONVERSION OF CYCLOHEXENE ON ALUMINOSILICA GEL WITH DIFFERENT ALUMINUM CONTENT

Method of activation	Aluminum content (meq/100 g)	Degree of conversion (% of saturated hydrocarbons)
Original silica gel	0	1.4
Treated with $Al(NO_3)_3$ solution		
0.1 *N*	6.5	16.8
0.2 *N*	8.9	20.8
1.0 *N*	12.4	28.2
Treated with $BaCO_3$ suspension in 1 *N* NaCl and then 1 *N* $Al(NO_3)_3$ for		
2 days	17.2	37.6
5 days	27.2	48.3
Impregnated with $Al(NO_3)_3$ solution, Al_2O_3 applied		
1%	58.5	39.1
3%	176.4	47.9
Treated with 1 *N* $AlCl_3$ solution $\frac{1}{4}$ neutralized with 1 *N* NaOH for		
1 day	64.2	48.7
7 days	84.5	55.7

conversion of cyclohexene on the original silica gel and on the samples with different aluminum content. The part of the data that refers to the samples prepared by the first and fourth methods (above) is plotted on the graph (Fig. 2), from which it follows that the relationship between the aluminum content in these samples and the degree of conversion of cyclohexene is nearly linear (*25*).

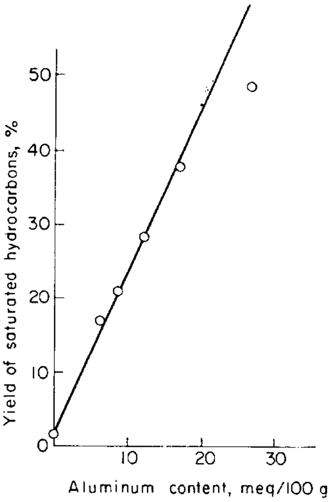


Fig. 2. Relationship between degree of conversion of cyclohexene and content of hydrolytic ions of aluminum.

Exchange acidity of aluminosilicates and aluminosilica gel after repeated treatment with hydrochloric acid solution, and aluminum content in NaCl extracts. Equal sample batches were repeatedly treated with a hydrochloric acid solution until acid soluble aluminum was almost all removed from them, after which the acid was removed by rapid washing and the samples were treated simultaneously with a normal NaCl solution and with a weak HCl solution, the concentration of which was close to the total acidity of the NaCl extract of the particular sample.

Treatment with the salt solution and the weak acid solution was carried out immediately after the acid had been removed by washing, and also at different time intervals, as well as after drying and calcination. After this treatment, the total acidity and aluminum content of the solutions were determined by the Sokolov method. The experimental results are presented in Table 5.

The data obtained show that the treatment with both solutions, when carried out immediately after removal of the HCl by washing, was accompanied by practically no aluminum released into the acid solution and, for the activated bentonite, also into the sodium chloride solution. The amount of aluminum released into the NaCl solution was, for this sample, only 0.14 meq/100 g, the resultant total acidity of the solution being 9.22 meq/100 g. Thus it is seen that the acidity of this sample was due almost entirely to the hydrogen ions. The amount of aluminum released into the sodium chloride solution was somewhat higher for the other samples, but it was still many times below the total acidity of the solution.

Treatment with an NaCl solution of samples which had been standing with water for some time was attended by the release of greater amounts of aluminum into the solution. For activated bentonite this amount was 2 meq/100 g after 2 hr, with the total acidity of the solution remaining unchanged. After 24 hr, it was found that 6.05 meq/100 g of aluminum had been released into the solution, and after 3 days 7.63 meq/100 g. Treatment of the same samples with a weak acid solution was not accompanied by any release of aluminum into the solution (*26*).

Table 6 shows data on the variation of the exchange acidity of the samples and of the aluminum content of the salt extracts which took place as a result of their repeated treatment with a normal hydrochloric acid solution, drying, and calcination. For active bentonite the amount of aluminum that has passed into the hydrochloric acid solution in each treatment cycle has also been determined. The experimental results show that in aluminosilica gel the exchange acidity continuously decreases after each treatment cycle, whereas in activated bentonite it remained unchanged. But in synthetic aluminosilicate this decrease practically ceased after the third cycle. The aluminum content of the salt extract varied similarly (*27*).

Adsorption of hydrogen and aluminum

TABLE 5

TREATMENT WITH 1 N NaCl AND WEAK HCl SOLUTIONS OF ALUMINOSILICATES FROM WHICH ACID-SOLUBLE ALUMINUM WAS REMOVED[a]

Aluminosilicate	When treated with solution	Treatment with weak HCl solution		Treatment with NaCl solution	
		Total acidity of solution after treatment	Amount of aluminum appeared	Total acidity of solution after treatment	Amount of aluminum appeared
Activated bentonite	Directly after washing off acid	8.78	0.14	9.22	0.14
	After 2 hr	8.78	0.07	9.36	2.02
	After 3 hr	8.78	0.07	9.43	2.09
	After 1 day	8.57	0.00	9.36	6.05
	After 3 days	8.21	0.14	9.22	7.63
	After drying	7.78	0.22	8.06	5.04
	After calcination	7.13	1.22	9.36	8.21
Synthetic aluminosilicate	Directly after washing off acid	8.49	0.14	5.11	0.65
	After 3 hr	8.55	0.07	5.18	2.16
	After 2 days	8.35	1.15	6.19	5.4
	After drying	8.35	3.82	6.19	5.62
	After calcination	8.28	3.17	6.41	5.83
Aluminosilica gel	Directly after washing out acid	7.63	0.00	4.32	0.29
	After 1 day	7.63	0.07	4.39	2.59
	After 3 days	7.63	0.43	4.32	3.60

[a] Almost all acid-soluble aluminum was previously removed by 1 N HCl. 5 g of ground sample was shaken with 60 ml of solution for 15 min. Results expressed in meq/100 g.

ions by aluminosilicates and silica gel. Aluminosilicates converted to the H form by repeated treatment with a hydrochloric acid solution, Na-aluminosilicates obtained by treating H-aluminosilicates with a NaCl solution, and Na-silica gel obtained by treating fine-pore silica gel with a sodium acetate solution were treated with solutions containing definite amounts of $AlCl_3$ and HCl.

TABLE 6

VARIATION IN THE VALUE OF EXCHANGE ACIDITY OF ALUMINOSILICATES AND ALUMINUM CONTENT IN SALT EXTRACT AS A RESULT OF ALTERNATE TREATMENT WITH 1 N SOLUTION OF HYDROCHLORIC ACID AND CALCINATION[a]

Sample	Characteristics	Initial	Treatment cycle 1	2	3	4	5
Activated bentonite	Exchange acidity	8.4	10.8	10.8	10.8	10.8	11.4
	Aluminum content in NaCl extract	8.4	10.8	10.8	10.8	10.3	10.8
	Amount of aluminum passing into hydrochloric acid solution	—	68.4	46.4	30.8	33	29
Aluminosilica gel	Exchange acidity	8.8	4.9	3.7	3.7	2.7	2.1
	Aluminum content in NaCl extract	8.8	4.3	2.2	1.9	1.2	0.9
Synthetic aluminosilicate	Exchange acidity	17.0	14.4	10.8	7.8	8.2	7.6
	Aluminum content in NaCl extract	17.0	14.4	10.2	7.2	7.6	6.4

[a] In meq/100 g.

TABLE 7

ADSORPTION BY Na-ALUMINOSILICATES AND Na-SILICA GEL OF H^+ IONS AND Al^{3+} IONS WHEN BOTH ARE PRESENT IN SOLUTION[a]

	Na form						H form			
	Content in solution				Amount which disappeared as a result of treatment		Content in solution			
	Initial		After treatment				Initial		After treatment	
Sample	Free acid	Aluminum	Free acid	Aluminum	Free acid	Aluminum	Free acid	Aluminum	Free acid	Aluminum
Activated bentonite	15.8	17.8	13.0	7.4	2.8	10.4	15.8	17.8	24.7	8.9
Synthetic aluminosilicate	15.8	17.8	14.2	12.0	1.6	5.8	15.8	17.8	21.1	12.5
Silica gel	13.9	16.1	0.5	11.5	13.4	4.6	—	—	—	—
	50.4	55.2	33.6	55.2	16.8	0	—	—	—	—

[a] Values expressed in meq/100 g.

Table 7 shows that in aluminosilicates sodium ions were chiefly displaced by aluminum ions. With the contents of aluminum and hydrogen ions in the solution being approximately equivalent, the amount of adsorbed aluminum exceeded by almost fourfold the number of adsorbed hydrogen ions. If H-aluminosilicates were subjected to treatment as above, aluminum ions displaced the exchange hydrogen ions from the aluminosilicate surface in spite of the fact that their concentration in the solution was low, and that the solution contained about the same amount of free acid.

Treatment of Na-silica gel with a solution containing approximately equivalent amounts of H^+ and Al^{3+} resulted in the displacement of sodium ions exclusively by hydrogen ions. But if the amount of acid in solution was below the content of sodium ions in the sample, the displacement of the latter by aluminum ions began only after complete consumption of the acid (*28*).

Poisoning of synthetic aluminosilicates with pyridine. Equal batches of aluminosilicate were impregnated with aqueous and ether solutions containing a definite amount of pyridine. Some samples were obtained by treatment with excess aqueous solution of pyridine for 24 hr. The samples were dried at 110°C, then the physically adsorbed pyridine was removed by a stream of CO_2 at 320°C for 3 hr.

Data on the degree of conversion of cyclohexene shown by the samples, so obtained, are given in Table 8 and Fig. 3. Straight lines are drawn through the points corresponding to the activity of the samples in the second and third series of experiments.

When pyridine was applied from ether solutions 5.2–5.6 meq/100 g of pyridine was required for complete poisoning of the catalyst. When impregnation was from an aqueous solution followed by drying directly after the treatment, the amount of pyridine found by extrapolation to zero activity was 11.9 meq/100 g. For samples treated with excess aqueous solution of pyridine, equal degrees of poisoning were caused by different amounts of pyridine (*29*).

Relationship between determined values of exchange and hydrolytic acidity and treatment time and the total volume of salt solution. The results of these experiments are presented in Table 9. With sufficient treatment time and total volume

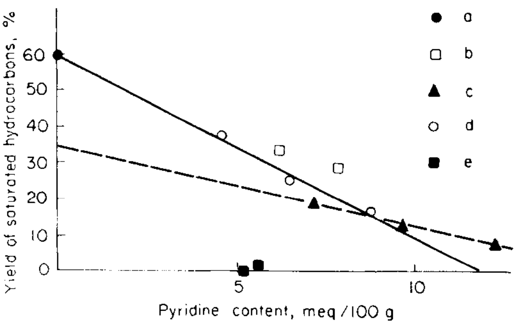


FIG. 3. Degree of converion of cyclohexene on: synthetic aluminosilicate poisoned with pyridine (a) original; (b) 1st series of experiments; (c) 2nd series of experiments; (d) 3rd series; (e) 4th series.

TABLE 8

Degree of Conversion of Cyclohexene on Synthetic Aluminosilicate Poisoned with Pyridine

Solution used for treatment of aluminosilicate, and treatment conditions	Pyridine found in sample after experiment (meq/100 g)	Degree of conversion (% of saturated hydrocarbons)
Water-treated	0	59.9
Treated with excess aqueous solutions of pyridine of different concentration		
1st series of experiments	6.23	32.9
	7.96	29.3
2nd series of experiments	7.2	19.8
	9.7	12.7
	12.3	7.9
Impregnated with aqueous solutions of pyridine and dried directly after impregnation (3rd series of experiments)	4.75	38.0
	6.53	26.6
	8.84	16.6
Impregnated with ether solution of pyridine (4th series of experiments)		
Dried after 24 hr	5.2	0.6
Dried directly after impregnation	5.6	2.0

of solution, constant values of exchange acidity were obtained for all samples. This was not true with the hydrolytic acidity in aluminosilica gel, and synthetic aluminosilicate, the values for which increased continuously with the total volume of the solution and treatment time (*27*).

Table 10 shows the values of exchange and hydrolytic acidity of the samples studied, and also the acidity as determined by the carbonate method. The carbonate method will be described briefly here.

Sample batches of 2.5 g each were treated for 24 hr with 100 ml of fine $BaCO_3$ suspension in a 1N NaCl solution with periodic shaking. The barium carbonate was then removed in a suspended state by shaking the sample with a 1N NaCl solution and by subsequent decantation of the solution. Then the samples were washed rapidly twice with CO_2-free water, to remove most of the NaCl and thereby avoid the salt error in titrating filtrates with alkali, and after the sample was dried the content of sodium ions was determined by treatment with a weak standardized hydrochloric acid solution. The treatment of Na-bentonite with hydrochloric acid solution was accompanied not only by the neutralization of the acid but also by its physical adsorption. The amount of the adsorbed acid was taken into account by simultaneous treatment of the initial sample of activated bentonite with the acid solution.

It will be seen that for the activated bentonite the acetate and carbonate methods yield equal results, while for the synthetic aluminosilicate higher values are obtained by the first method (*20*).

Discussion

The appearance of acid sites of the Brönsted type on the surface of aluminosilicate catalysts is attributed by Thomas (*4*) and other investigators (*6*, *12*) to the replacement of Si^{4+} in SiO tetrahedra by Al^{3+}. The negative charge appearing is balanced by the proton, which may be exchanged for other cations. According to X-ray investigations of Hoffman, Endell, and Wilm (*30*) the lattice of the natural aluminosilicate montmorillonite consists of two layers of SiO tetrahedra and a layer of hydroargillite that gives aluminum atoms octahedrally surrounded by O and OH. These authors assume that the exchangeable cations in montmorillonite are on the boundary of the layer SiO tetrahedra, that is to say, where no Si–O–Si bonds are formed.

In natural aluminosilicates the exchangeable sites may appear in both ways but in the synthetic aluminosilicates the theory of

TABLE 9

EFFECT OF DURATION OF TREATMENT WITH NORMAL SOLUTIONS OF NaCl AND CH_3COONa AND OF TOTAL VOLUME OF SOLUTION ON EXCHANGE AND HYDROLYTIC ACIDITY

Sample:	Synthetic aluminosilicate					Activated bentonite			Aluminosilica gel					Fine-pore silica gel				
Total volume (ml):	250	500			1000	500		1000	250		500			250		500		
Treatment time (days):	2	1	2	3	2 (weeks)	1	2	2 (weeks)	1	2	1	2	3	1	2	1	2	3
Acidity (meq/100 g) when treated with																		
NaCl solution	16.6	17.0	18.0	18.0	18.0	8.4	9.6	9.6	17.1	19.5	20.4	24.0	24.0	—	—	—	—	—
CH_3COONa solution	44.0	46.2	51.0	54.0	61.2	28.2	28.8	28.8	46.5	49.2	51.0	52.8	53.4	19.8	19.8	25.2	25.2	25.2

TABLE 10
ADSORPTION OF SODIUM IONS BY ALUMINOSILICATES FROM $BaCO_3$ SUSPENSION IN 1 *N* NaCl SOLUTION[a]

Aluminosilicate	Initial samples: Exchange acidity	Initial samples: Hydrolytic acidity (acetate method)	Initial samples: Adsorption of acid from HCl solution	After treatment with $BaCO_3$ suspension in 1 *N* NaCl: Adsorption of acid from HCl solution	After treatment with $BaCO_3$ suspension in 1 *N* NaCl: Content of sodium ions
Activated bentonite	8.4	25.8	16.3	41.7	25.4
Synthetic aluminosilicate	18.0	42.8	0	40.8	40.8

[a] In meq/100 g.

ruptured bonds is apparently more probable. For example, the appearance of the exchange acidity by activation of silica gel with aluminum cannot be explained as a replacement of Si^{4+} in SiO tetrahedra by aluminum. The reason for this is that the aluminum oxide is supported on the surface of silica gel, the structure of which is already formed.

The view of some investigators who believe that the acid hydroxylic group in aluminosilicates is located at an aluminum atom, can hardly be true. The data of Table 1 show that aluminum oxide possesses neither exchange nor hydrolytic acidity. The exchange acidity of silica gel is very low but its hydrolytic acidity is considerable. It is therefore more probable that chemical interaction between Al_2O_3 and SiO_2 leads to an increase of acid properties in silica gel but not to appearance of these properties in Al_2O_3. The lability of the hydrogen atom of the hydroxylic group that is located at the silicon atom is evidently due to the presence of the Si–O–Al bond because the inductive effect of the aluminum ion, which has an unoccupied *p*-orbital, weakens the O–H bond in this group.

The data on the exchange adsorption of aluminum on silica gel presented in this paper permit establishment of the mechanism of exchange acidity appearance, and of catalytic activity in silica gel, and also advancement of the assumption concerning the presence of two types of hydrolylic groups in silica gel. According to Carman (*31*) silica gel is represented by a three-dimensional irregular lattice formed by SiO tetrahedra (Fig. 4). To complete tetrahedral coordination the boundary atoms of silicon add one water molecule each, as a result of which two hydroxylic groups are formed on each silicon atom. Consequently, silica gel may be regarded as a dibasic acid the degree of dissociation of which in the first stage is much higher than in the second.

Attention will now be directed to Tables 1 and 4 and the explanation of the data presented therein.

Treatment of silica gel with a sodium acetate solution leads apparently to the displacement of hydrogen ions only in one of the "pair" hydroxylic groups. (Such a hydroxylic group will be referred to herein as an active or hydrolytic OH group.) The

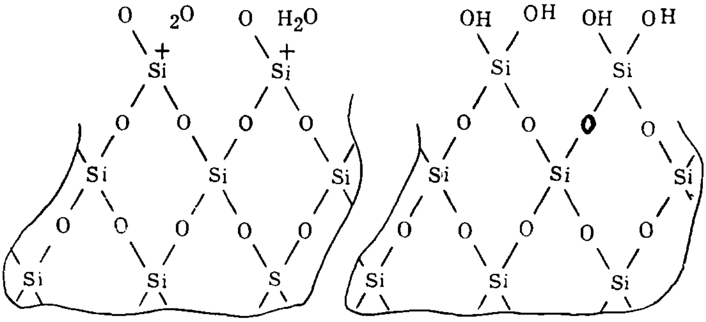


FIG. 4. Structure of silica gel lattice, after Carman (*31*).

Na-silica gel so formed is capable of exchanging sodium ions for cations of other neutral salts (*28*).

The appearance of exchangeability as a result of treatment with solutions of $Al(NO_3)_3$ is due to the displacement of protons in hydrolytic OH groups by aluminum ions. In this case the hydrolytic acidity remains unchanged since an equal number of aluminum ions are displaced into the sodium acetate solution in place of the hydrogen ions. If aluminum does not replace all hydrogen in hydrolytic OH groups, the hydrolytic acidity yields the sum of the displaced H^+ and Al^{3+} ions.

In treatment of silica gel with solutions of aluminum salts with an increased content, of basic forms of aluminum, or in impregnation by concentrated solutions of $Al(NO_3)_3$ the displacement of protons in second hydroxylic groups begins. The increase in exchange acidity occurring in this case is due exclusively to the increase in the mobility of the hydrolytic aluminum, that is to say, the aluminum which has replaced hydrogen in the active hydroxylic groups. With a sufficiently large total amount of adsorbed aluminum, all these ions become exchangeable. As a result of this the value of the exchange acidity of aluminosilica gel becomes close to the hydrolytic acidity of the original silica gel, while the aluminum ions which have replaced the protons in the second hydroxylic groups may now be displaced into the solution of sodium acetate as shown in Table 2.

The maximum number of active hydroxylic groups found in the experiments did not exceed 29 meq/100 g. At the same time, the total number of hydroxylic groups calculated from water adsorption was about 1100 meq/100 g for a fine-pore sample. It is very possible that in the formation of the silica gel lattice the major part of the boundary atoms of silicon may be bound with only one hydroxylic group each (Fig. 5). Such a lone hydroxylic group is much less active than one of the "pair" OH groups.

The adsorption of aluminum by silica gel evidently results from the interaction between the hydroxylic groups of the silica gel and the basic forms of aluminum contained in the solution. The replacement of hydrogen ions by aluminum ions is hardly probable, since the latter display less affinity for silica gel than do hydrogen ions (Table 7).

The basic forms of aluminum in the solution appear, of course, as a result of salt hydrolysis. Increasing the content of basic forms by partial neutralization with an alkali solution, or the utilization of a more readily hydrolyzable salt, increases the amount of aluminum adsorbed. This reaction may be represented by the equation:

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\mathrm{Al}{<}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{Al}{<}\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix} + \mathrm{H_2O}$$

The conversion of aluminum ions to the solid phase is accompanied by the substitution of OH groups for the remaining Cl ions as a result of hydrolysis. The OH groups in turn interact with the hydroxylic groups of silica gel. When treated with solutions having a large content of basic forms of aluminum, part of the OH groups may remain at aluminum atoms, because the adsorption of the basic forms by silica gel proceeds so vigorously that until the chlorine ions remaining at aluminum atoms are replaced by OH groups no free hydroxylic groups of silica gel will remain in the vicinity of these atoms. Such aluminum atoms are retained by silica gel less strongly than the trivalent aluminum, since their bond with the surface is effected by only one or two valencies. It is highly probable that for this reason these aluminum ions may be displaced into the sodium acetate solution even when the hydrogen in the lone hydroxylic group is replaced by aluminum. (The hydrolytic acidity of aluminosilica gels in Table 2 exceeded more than twofold the hydrolytic acidity of the original silica gels.)

Co-gellation apparently leads to the formation of two types of compounds—the aluminosilica gel type and the montmorillonite type. The probable structure of the aluminosilica gel type was considered above.

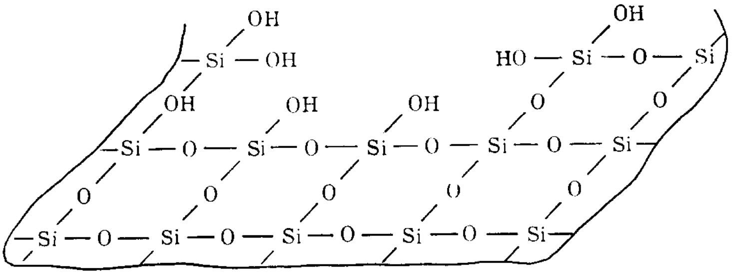
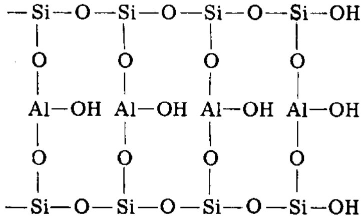
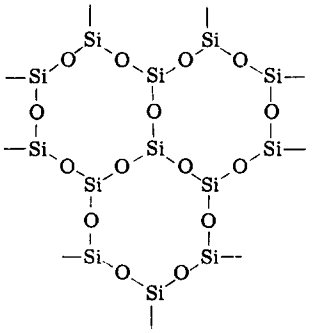


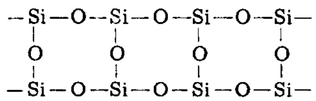
Fig. 5. Probable structure of silica gel lattice.

The structure of the montmorillonite type may be represented as follows (*32*):



The fourth valency of the silicon atom is linked through the oxygen bridge with the silicon atom located in a plane perpendicular to the drawing. In the vertical projection of this lattice there may be either six-membered rings similar to those of montmorillonite, or parallel chains.





The less the association of rings, or the shorter the chains, the more boundary atoms of silicon (per unit weight) are formed, and hence the higher the exchangeability. Since in the montmorillonite type each aluminum atom is bound with two silicon atoms, and the exchangeability of aluminosilicate is due to the presence of the Si–O–Al bond, maximum acidity should take place when the aluminum-silicon ratio is equal to 1:2.

The presence in synthetic aluminosilicate of both structural types may be judged from the nature of variation in the exchangeability of different samples, as a result of their treatment with a hydrochloric acid solution (Table 6). The continuous decrease in the exchange acidity of aluminosilica gel after each treatment cycle was due to the fact that in aluminosilica gel the Si–O–Al bond is located on its surface, and easily ruptured by the acid (*17*).

Calcination of the sample is attended by the interaction of the aluminum oxide remaining free with the OH groups of silica gel formed as a result of the rupture of the Si–O–Al bonds. The experiments show that this leads to a slight increase in exchange acidity because of the substitution of aluminum ions for hydrogen ions. Replacing the hydrogen ion in the hydroxylic group of the silica gel, the aluminum of the oxide acquires the ability of separating out in the subsequent treatment with acid. Thus, as a result of alternate calcination and treatment of aluminosilica gel with acid, most aluminum was removed from the sample after the fifth cycle of treatment, and the value of exchange acidity became insignificant.

In activated bentonite, treatment with

acid did not decrease its exchange acidity, because the montmorillonite structure makes the Si–O–Al bond invulnerable to acid and the lattice destruction takes place only on its edges. Besides, as lattice size diminishes, the number of exchangeable sites per unit of sample weight conversely increases (*33*).

Synthetic aluminosilicate occupies an intermediate position between the activated bentonite and aluminosilica gel with respect to the variation in the value of exchange acidity. After the fifth treatment cycle its exchangeability was halved. The acid extracted from the synthetic aluminosilicate almost all the aluminum which had been bonded with the silica gel structure, and the remaining exchange acidity of the sample was due mainly to the structure of the montmorillonite type. The decrease in the exchange acidity of the synthetic aluminosilicate practically ceased beginning with the third treatment cycle. This indicated that nearly complete removal of the free aluminum oxide was achieved during the first two treatment cycles, and the sample lost its ability to reduce that part of the exchange acidity which was due to its silica gel structure.

We turn now to consideration of the catalytic activity shown by samples discussed above with respect to the reaction of hydrogen redistribution. Silica gel displays little catalytic activity in this respect. It does however acquire catalytic properties together with exchange properties after activation with aluminum oxide, as shown in Tables 1 and 4. Considering this fact, and also the linear decrease in the catalytic activity with increasing content of sodium ions adsorbed from NaCl solutions (Fig. 1), it may be concluded that exchangeable sites act simultaneously as catalytically active sites.

Free alkali is evidently capable of interacting also with nonexchangeable sites. The second linear relationship in Fig. 1 should, therefore, be attributed to the fact that the poisoning of active sites is proportional to the amount of alkali introduced. Since the points corresponding to the activity of the samples treated with NaCl and CH_3COONa solutions lie on the same straight line, it is obvious that, in aluminosilicates, treatment with solutions of both salts is concerned with one and the same type of acidity, that is to say, there is no important difference between the two kinds of acidity. Exchange acidity comprises just a part of hydrolytic acidity. A slight deviation is observed only for samples treated with a normal solution of sodium acetate, with which nonexchangeable sites of aluminosilica gel entering into the composition of the aluminosilicate are capable of interacting as well. In this manner, the catalytic activity of aluminosilicates may be said to be due solely to the ions, causing their exchange and hydrolytic acidity.

These ions differ in their exchangeability in an aqueous medium. Not all of them are replaced equally easily by the cations of a neutral or alkali acetate salt. But they do prove to be equal in catalytic conversion experiments as shown by straight line 1 on Fig. 1. For this reason the strength of the acid sites of aluminosilicate catalysts determined in aqueous or anhydrous media at ambient temperatures may not be compared with their catalytic activity. Treatment of silica gel by the first and fourth methods (see under Results: Catalytic activity and acidity of silica gel treated with aluminum salt solutions) results in the displacement of protons only in the hydrolytic OH groups. The linear relationship between the aluminum content in such samples and the degree of cyclohexene conversion, and the fact that a sample in which the content of hydrolytic ions of aluminum is equal to the hydrolytic acidity of the original silica gel, exhibits an activity which is close to maximal, proves that only those ions of aluminum are active that have replaced protons in hydrolytic OH groups. Thus the activity of aluminosilica gel is determined by the value of the hydrolytic acidity of the original silica gel.

Many investigators believe that the exchangeable hydrogen ions take part in the catalytic reactions on the aluminosilicate. But the data of the present investigation permit the suggestion that no exchangeable hydrogen ions are present on the aluminosilicate surface.

It is difficult to determine the nature of the aluminosilicate acidity. No matter whether H^+ or Al^{3+} ions are adsorbed on the surface, aluminum ions in the neutral salt solution and hydrogen ions in the alkali acetate solution will be present only. Aluminum in the neutral salt solution can appear as a result of a secondary chemical reaction between the acid replaced into the solution and the aluminosilicate. The absence of aluminum ions in alkali acetate solution is explained by the fact that the basic forms of aluminum which appear as a result of aluminum acetate hydrolysis are very strongly adsorbed by aluminosilicates, and the acetic acid remains in the equilibrium solution (*19*).

The data of Table 5 show that treatment of the samples with a NaCl solution immediately after the removal of all the acid-soluble aluminum from them is attended by a direct exchange of H ions for Na ions. The appearance of, and increase in the content of, aluminum in NaCl extracts during treatment with a salt solution at different time intervals may only be attributed to the fact that H-aluminosilicates formed as a result of treatment with hydrochloric acid solution are unstable and spontaneously change to Al-aluminosilicates with time. This occurs at the expense of the aluminum contained in the aluminosilicate itself. Elevated temperatures accelerate this process.

In activated bentonite this conversion occurs at the expense of the aluminum of the hydroargillite layer. It may be seen from Table 6 that, beginning with the third treatment cycle, the amount of aluminum passing into the hydrochloric acid extract becomes approximately equal to the hydrolytic acidity of this sample. That is to say, practically only the exchange aluminum passes into the solution. The aluminum that was additionally released into the acid solution during the first two treatment cycles evidently represented a product of partial destruction of the montmorillonite lattice in industrial activation of natural clay with a hot solution of the acid.

In aluminosilica gel the H form changes to the Al form at the expense of the free aluminum oxide. In synthetic aluminosilicate this change occurs at both the expense of the aluminum oxide and the aluminum contained in the structure of the montmorillonite type. The instability of the H form and its spontaneous conversion to the Al form indicates that the exchange acidity of both natural and synthetic aluminosilicates is due exclusively to the aluminum ions. The exchange aluminum hypothesis for natural aluminosilicates is also supported by the fact that the adsorption power of aluminosilicates with respect to aluminum ions is much higher than in respect to hydrogen ions as shown in Table 7. Because there is no radical difference between the exchange and hydrolytic acidities of aluminosilicates, the conclusion made above is also valid as far as the nature of the hydrolytic acidity of aluminosilicates is concerned.

The exchangeable ion of aluminum represents a strong Lewis acid because it is located at the silicon atom possessing an O–H bond (in silica gel containing only active aluminum ions) or an O–Al bond. Incorporation of a proton into the electron shell of the oxygen atom, or the inductive effect of the aluminum entering into the structure of aluminosilicate or aluminosilica gel, brings about a displacement of the electron density which leads to an increase in the positive charge on the exchange ion of aluminum. That is to say, it leads to an increase in the strength of its aprotonic acidity.

The Lewis acid as such does not catalyze reactions proceeding according to the cationic mechanism. It acquires catalytic properties only when traces of moisture are present. Therefore, it should be assumed that the exchangeable aluminum and the water molecule form an ionized complex (Fig. 6), perhaps something like the analogous hypothetical complex $[AlCl_3OH]^-H^+$ (*32*). With increasing moisture content the degree of ionization of the complex diminishes. It is quite obvious that no such complex can exist in an aqueous medium. The Lewis acidity of the free aluminum oxide, and of the nonexchangeable aluminum, is not strong enough to form a complex with water capable of ionization.

Formation of the catalytic complex of exchangeable aluminum with water explains

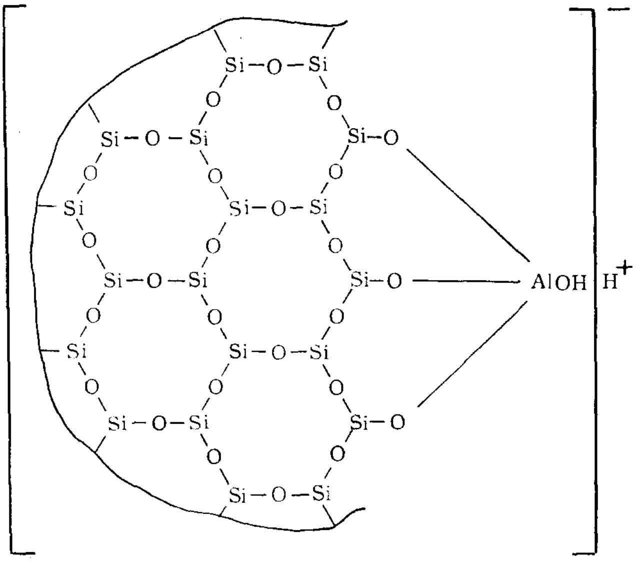
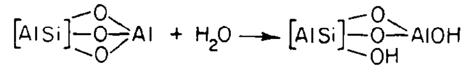


Fig. 6. Assumed structure of complex of exchange aluminum with water.

the effect of insignificant amounts of moisture on the activity of aluminosilicate catalyst (*2, 34-36*). Thus, the active site is a single exchange ion of aluminum which, complexing with one water molecule, forms an acid site of the Brönsted type. This is also confirmed by the results of experiments described above, according to which the acquisition of catalytic properties by silica gel is due exclusively to the substitution of Al^{3+} for H^+ in the active hydroxylic groups.

Since one atom of aluminum binds three exchangeable sites simultaneously, owing to its trivalency, the number of active sites is one-third that of the exchangeable sites. Thus the minimum amount of water (in terms of millimoles) that is necessary to impart to the catalyst a maximum activity should be equal to the true value of hydrolytic acidity expressed in milliatoms of aluminum.

The foregoing point of view agrees with the results of experiments on poisoning synthetic aluminosilicate with pyridine as shown in Table 8 and Fig. 3. Complete poisoning of synthetic aluminosilicate by impregnation with aqueous solutions requires twice as much pyridine as when the poison is applied from ether solutions. This may be attributed to the fact that in the first case a complex of pyridine with exchange aluminum in the ratio of 1:1 is formed, whereas as in the second case the ratio is 2:1. The literature contains indications (*37, 38*) that the formation of complexes of pyridine with $AlCl_3$ and $AlBr_3$ of different compositions is possible. In treatment with excess aqueous solution of pyridine there evidently occurs a partial hydrolysis of the aluminum salt of aluminosilicate, the first stage of which can be represented by the equation



$$[\mathrm{AlSi}]\begin{matrix}-\mathrm{O}-\\-\mathrm{O}-\\-\mathrm{O}-\end{matrix}\mathrm{Al} + \mathrm{H_2O} \longrightarrow [\mathrm{AlSi}]\begin{matrix}-\mathrm{O}-\\-\mathrm{O}-\\-\mathrm{OH}\end{matrix}\mathrm{AlOH}$$

where [AlSi] is the aluminosilicate complex. Exchange ions of hydrogen which appear as a result of hydrolysis are bound into a complex with pyridine in the ratio of 1:1. Changes in the conditions of treatment with aqueous solutions of pyridine may cause variations in the degree of hydrolysis of the sample.

The principal argument in favor of the theory connecting the activity of aluminosilicates with the presence on their surfaces of acid sites of the Brönsted type are the regularities established in the poisoning of catalysts with ions of alkali metals. Previous investigators were unable to establish a direct relationship between the activity and the value of aprotonic acidity.

This is evidently due to the facts that, firstly, a considerable part of aprotonic acidity is accounted for by the free aluminum oxide and the nonactive aluminum (the aluminum replacing the hydrogen in the second hydroxyl of the pair group and in lone hydroxylic groups of silica gel). And secondly, the existing methods for the determination of aprotonic acidity do not allow taking into account just that part of acidity which is caused by exchange aluminum. For instance, in the work of Trambouze *et al.* acidity which was determined by titrating with butylamine in an anhydrous medium by the Tamele method (*10*), remained unchanged after treatment with solutions of sodium salts, although with that treatment the exchangeable ions of aluminum are removed from the surface of the aluminosilicate. Consequently these ions are not titrated by butylamine. The reason for this is probably because butylamine is incapable of destroying the complex of exchange aluminum with water.

The same refers to Trambouze's method of thermometric titration (*39*). The work performed by Topchieva and Moskovskaya (*40*) shows that poisoning of an aluminosilicate catalyst with lithium ions only slightly reduces the value of acidity after Trambouze. The heat of adsorption of ethyl acetate is evidently offset by the heat of decomposition of the complex of exchange aluminum with water and the heat of desorption of the water. According to Kiselev (*41*), the heat of adsorption of water by aluminosilicates is considerable.

The number of exchangeable ions of aluminum is fully taken into account by the hydrolytic acidity of aluminosilicates. However, in the case of synthetic aluminosilicate and aluminosilica gel, treatment with sodium acetate solution yields excessive results. It follows from the data of Table 9 that an increase in the treatment time and in the total volume of the solution of this salt is attended, for the above samples, by a continuous increase in the acidity of the salt extract. This may only be explained by the fact that, besides the exchangeable ions, the aluminum ions bound with the nonexchangeable sites are displaced into the sodium acetate solution. This must be true because no similar phenomena are observed for activated bentonite and silica gel. For this reason, the carbonate method (*20*) should be adopted for the determination of the hydrolytic acidity of synthetic aluminosilicates.

In treatment of aluminosilicates with a solution of a neutral salt a complete displacement of the ions of hydrolytic acidity is not achieved. The reason for this is that the treatment with the solution of the neutral salt is terminated when the pH of the equilibrium solution becomes practically equal to that of the original solution. But exchange does not end there and insignificant amounts of acid continue to appear in the solution. The more complete the replacement of the ions causing the exchange acidity of the aluminosilicates, by the cation of the neutral salt, the smaller is the amount of acid appearing in the solution needed to prevent any further exchange. However, if the acid appearing in the solution of the neutral salt is neutralized by the addition of barium or calcium carbonate, the exchange will then proceed to completion.

The results obtained and the principle of the carbonate method itself suggest that this method can be used to determine the true value of the base-exchange capacity of aluminosilicates as shown in Table 10. For synthetic aluminosilicate, the value of hydrolytic acidity found by the carbonate method was 40.8 meq/100 g.

The acidity value that characterizes the activity of aluminosilicate may also be determined by extrapolating the line expressing the relationship between the degree of conversion of cyclohexene and the number of sodium ions adsorbed from the salt solution, to zero activity (*24*). For the aluminosilicate under study, this value was 38 meq/100 g. The lower acidity value obtained in this case as compared with the data of the carbonate method is due to the fact that, owing to their large size, the sodium ions block part of the active surface.

A still more considerable blocking of the surface evidently occurs in the case of poisoning of the catalyst with pyridine. The average amount of pyridine that completely deprived the sample of its activity was 5.4 mmoles/100 g when applied from an ether solution, and 11.9 mmoles/100 g, from an aqueous solution which, in terms of acidity expressed in meq/100 g, corresponds to 32.4 (ratio Py:Al = 1:2) in the first case and 35.7 (ratio Py:Al = 1:1) in the second.

Treatment of silica gel with a $BaCO_3$ suspension in a sodium chloride solution also results in the substitution of sodium ions for protons in hydrolytic OH groups (*28*).

The possibility of taking into account the hydrolytic acidity of silica gel by the carbonate method, as well as the fact that the only and sufficient condition for the appearance of catalytic properties in silica gel is the substitution of aluminum for protons in hydrolytic OH groups, gives us grounds to assume that active hydroxylic groups of silica gel are also true exchangeable sites.

Inasmuch as natural clays may contain minerals of the silica group in which part of the adsorbed and exchangeable cations may not belong to the true exchange sites, it is more nearly correct to estimate the base-exchange capacity of clays from the value of hydrolytic acidity which clay acquires after a weak acid solution irreversibly removes all cations which do not belong to the true exchange sites. Thus, the activity of aluminosilicate catalysts is due to the presence on their surface of only those aprotonic sites which are due to exchangeable ions of aluminum. Acid sites of the Brönsted type on the surface of aluminosilicates arise only in the presence of moisture traces as a result of the formation of an ionized complex of exchange aluminum with water. The maximum number of these sites is one-third that of the exchange sites. The latter are taken into account by the value of hydrolytic acidity, the true value of which is yielded by the carbonate method.

The optimum moisture content in terms of millimoles should be equal to the value of hydrolytic acidity expressed in milliatoms of aluminum. An increase in the moisture content decreases the number of protonic sites. In an aqueous medium, no protonic sites are present.

The number of active sites may be calculated from the formula $n = (HN \times 10^{-9})/3S$, where n is the number of active sites per sq cm; H is the true value of hydrolytic acidity in meq/100 g; N is Avogadro's number; and S is surface area in m^2/g. For the synthetic aluminosilicate sample under study, n was 3.7×10^{13}.

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