dence it can be concluded that: (1) without the presence of oxygen no decomposition of formic acid nor monomer polymerization occurs at room temperature; (2) when oxygen is present in not too large amounts decomposition occurs and polymerization sets in. An induction period is present, and increases with increasing amount of oxygen in the solution; (3) in the presence of large excess of oxygen the decomposition reaction occurs but no ready polymerization can be detected. Therefore, there must be an optimum concentration of oxygen, which gives rise to polymerization with the shortest induction period. This can be explained in the following way. At constant formic acid and monomer concentration the velocity of the initiation step is dependent on the amount of oxygen present on the surface

$$v_i = k_i' [O_2]_{\text{surface}} \qquad (3)$$

Under similar conditions the velocity of saturation of polymer radicals by molecular oxygen is

$$v_t = k_t' C^* [O_2]_{\text{liquid phase}} \qquad (4)$$

Using steady state approximation the velocity of propagation of polymer chains is

$$v_p = k_p \frac{k_i'}{k_t'} [M] \frac{[O_2]_{\text{surface}}}{[O_2]_{\text{liquid phase}}} \qquad (5)$$

From equation (5) it can be seen that, for low values of $[O_2]_{\text{liquid phase}}$, the metal surface not being saturated with oxygen, polymerization can occur at a measurable rate. As $[O_2]_{\text{liquid phase}}$ increases, the surface saturation is reached, $[O_2]_{\text{surface}}$ becomes constant. The increased concentration of oxygen in the solution leads however to values of v_p which are too low to be measured.

Acknowledgment.—I wish to express my sincere thanks to Professor H. S. Taylor for his help, advice and criticism during the course of this investigation. E. I. du Pont de Nemours and Company assisted this work through a grant-in-aid to Princeton University, for which assistance best thanks are also extended.

Summary

1. The decomposition of formic acid solutions at the surface of platinum sol in the presence of oxygen and of methyl methacrylate initiates polymerization of the monomer.

2. Acrylonitrile is not polymerized under the same conditions since it poisons the surface for formic acid decomposition.

3. The rate of polymerization is proportional to the amount of platinum employed and to formic acid and monomer concentrations.

4. The average degree of polymerization is directly proportional to monomer concentration, inversely proportional to formic acid concentration and independent of the amount of platinum employed.

5. Kinetic mechanisms to interpret the data have been derived.

6. Only a very small fraction of the decomposed formic acid initiates chain polymerization of the monomer.

7. The effect of oxygen on both formic acid decomposition and polymerization is discussed.

PRINCETON, NEW JERSEY RECEIVED JUNE 22, 1950

[CONTRIBUTION FROM HOUDRY PROCESS CORPORATION, MARCUS HOOK, PA.]

Chemical Characterization of Catalysts. II. Oxygen Exchange between Water and Cracking Catalysts

BY G. A. MILLS AND S. G. HINDIN

Introduction

The reactions occurring between water and oxides used in petroleum cracking catalysts are of special importance because (1) water is the medium from which oxide catalysts are prepared in hydrogel form, (2) water is normally responsible for loss of activity during catalyst use, and (3) water is believed to be fundamental to the mechanism of the cracking process.[1,2]

The reactions between water and the surfaces of cracking catalysts were investigated by tracing the reaction with isotopic oxygen. These exchange data have been correlated with ignition loss and surface area determinations, and the results interpreted in terms of the atomic structures of the surfaces involved.

While the bulk structure of many solids are known in detail, little experimental evidence is available to establish the surface structure. The measurement of physical properties, although giving valuable information, does not define the chemical nature of the surface, nor does it allow conclusions concerning reactions that may be occurring there. These highly specific surface chemical properties have been widely recognized in colloidal phenomena and particularly in heterogeneous catalysis, and the first paper of this series[3] has discussed a chemical characterization of petroleum cracking catalysts through their reaction with basic substances.

Although isotopic tracer methods have been used to elucidate the mechanisms of catalyzed hydrocarbon reactions, most investigators have been concerned with atomic rearrangements in

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[1] Hansford, *Ind. Eng. Chem.*, **39**, 849 (1947).

[2] Milliken, Mills and Oblad, *Trans. Far. Soc.*, Symposium on Heterogeneous Catalysis, 1950.

[3] Mills, Boedeker and Oblad, THIS JOURNAL, **72**, 1554 (1950).

the hydrocarbon molecules; few have investigated the catalyst itself. In the case of oxide catalysts, it is possible to measure critical catalyst properties by following the transference of oxygen between catalyst and reactant molecules. Titani, Morita and their co-workers have made an extensive study of the exchange between metal oxides and molecular oxygen, and current publications indicate new interest in this exchange.[4,5,6] Oxygen exchange between inorganic oxygen-containing substances and water has also been investigated to some extent and, for soluble inorganic oxy-anions, exchange was shown to proceed, in general, through reversible anhydride formation.[7,8,9] Exchange between water and metallic oxides has also been measured by Morita and Titani. This work has been reviewed by Geib.[10]

Experimental Procedure

Samples of the oxides were calcined at different temperatures, cooled, and then allowed to react with water enriched in the heavy isotope of oxygen (H_2O^{18}) for various periods of time (fifteen minutes to one month) at 100° or 105°. In some experiments the H_2O^{18} was made acid or alkaline with hydrochloric acid or sodium hydroxide. A few exchange experiments were also made at 565°. After reaction, the water was separated and the reduction in isotopic concentration of the H_2O^{18} was determined, using the mass spectrometer. From this and the weights of materials used, the extent of oxygen exchange was calculated for the reaction

$$M_xO_y^{16} + H_2O^{18} \rightleftarrows M_xO_y^{18} + H_2O^{16}$$

where $M = Si$ or Al. A few experiments were also made using D_2O, and the hydrogen content of the oxide calculated from the H–D exchange.

Preparation of the Oxides

1. **Silica.**—Two silica preparations were used: (a) The first sample, SiO_2-1, was prepared from Philadelphia Quartz Company N-Brand sodium silicate and sulfuric acid. The resulting hydrogel was washed sulfate-free with water and dried at 70°. The dry material was calcined for six hours at 760° in dry air. Before use in exchange experiments, it was recalcined one hour at 540° under vacuum.

(b) The second sample, SiO_2-2, was prepared by treating N-Brand sodium silicate with ammonium sulfate. The hydrogel was washed with 10% ammonium sulfate solution, and then water-washed sulfate-free. Two separate portions of the hydrogel were dried at temperatures of 100° and 450° at about 1 mm. pressure.

2. **Alumina.**—The alumina was prepared according to Heard.[11] Aluminum was amalgamated with mercury, treated with acetic acid, and precipitated with ammonium hydroxide. The hydrogel was water-washed, though not to complete removal of ammonium and acetate ions (to prevent peptization) and filtered. The ammonium and acetate ion contents of the materials were not determined. Two separate portions of the hydrogel were dried at 100° and 450° at about 1 mm. pressure.

3. **Silica-Alumina.**—This material was standard Houdry Type S catalyst (12.5 wt. % alumina, 87.5 wt. % silica) which had been dried at 730° for twelve hours in the presence of air containing 8% steam. Before use in exchange experiments it was recalcined for one hour at 540° under vacuum.

4. **Clays.**—(a) The kaolin clay, from Florida, is known commercially as Edgar Company plastic kaolin. It was mixed with water, extruded and dried. Before use it was dried for four hours at 100° under vacuum.

(b) The bentonite clay is a fairly pure montmorillonite from Ash Meadows, Nevada. It was mixed with water, extruded and dried. Before use it was dried for four hours at 100° under vacuum.

(c) Samples of activated bentonite-1 (Filtrol TCC) and -2 (Ash Meadows): Both clays were sulfuric acid-activated bentonites, water-washed free of sulfate ion and dried at 105°. They were then calcined at 565° for two hours in dry air. Before use they were redried for one hour at 450° under vacuum.

Physical Properties.—The moisture content was obtained by blast lamp ignition in platinum to constant weight. Complete nitrogen adsorption isotherms were measured, the surface areas calculated by the method of Brunauer, Emmett and Teller and the pore size distribution estimated by use of the Kelvin equation.[12] Powdered samples were also examined for their X-ray diffraction patterns using a Norelco machine with a copper target and a nickel filter.

Exchange Procedure.—A weighed amount (*ca.* 0.3 g.) of water enriched with H_2O^{18} was added to a weighed sample (*ca.* 0.6 g.) of the oxide in a Pyrex tube. The mixture was frozen to liquid nitrogen temperature, the air pumped off, and the tube sealed while under vacuum. The tube was shaken vigorously and was then held at 100° or 105° for a chosen time. For exchange reaction times up to eight hours, the tube was placed in a vigorously boiling water-bath; for longer reaction times, the tube was kept in a drying oven at 105 ± 2°.

After the exchange period the tube was broken open and the water distilled over into a receiver, under vacuum, using liquid nitrogen as coolant. Approximately one-half cc. of carbon dioxide was added and the water–carbon dioxide mixture equilibrated for forty-eight hours at room temperature (about 27°). The carbon dioxide was then taken off and its O^{18}/O^{16} ratio determined by mass spectrometric analysis.

The silica–alumina cracking catalyst and the silica dried at 760° were also exchanged at 100° for periods up to eight hours with H_2O^{18} solutions, tenth-normal with respect to hydrochloric acid or to sodium hydroxide.

Blank determinations were made on the water enriched with H_2O^{18} sealed in Pyrex and maintained at 105 ± 2° for periods up to four days, and on the 0.1 *N* alkaline solution for periods of time up to eight hours at 100°. In neither case did measurable exchange with oxygen from the glass surface occur.

The major source of error involved in this procedure arises from the incomplete removal of all sorbed water from the oxide surface after reaction, prior to equilibration with carbon dioxide and, as a result, the exchange values shown here are believed minimal. With the same oxide preparation, precision is limited primarily by the accuracy of the mass spectrometric analysis, and is of the order of ±3% absolute. With different preparations of some oxides, variations are of much greater magnitude.

The exchange data are calculated in terms of the fraction of the oxygen in the oxide sample which has equilibrated with the water. This value is obtained from the relationship: $M_3/M_2 \times 100 = \%$ of oxygen which has equilibrated, where: $M_3(0.20) + M_1(1.53) = \alpha(M_1 + M_3)$ and M_1, M_2 and M_3 are, respectively, the weights of oxygen in the added water, in the oxide sample, and in the oxide sample which has equilibrated; α is the atom per cent. O^{18} in the water after exchange (1.53 atom %

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(4) Allen and Lauder, *Nature,* **164,** 142 (1949).

(5) Houghton and Winter, *ibid.*, **164,** 1130 (1949).

(6) Karpacheva and Rozen, *Doklady Akad. Nauk, S. S. S. R.*, **68,** 1057 (1949).

(7) Titani and Goto, *Bull. Chem. Soc. Japan*, **14,** 77 (1939).

(8) Mills, This Journal, **62,** 2833 (1940).

(9) Winter and Briscoe, *J. Chem. Soc.*, 631 (1942).

(10) Geib, "Handbuch der Katalyse," edited by G. M. Schwab, Vol. 6, Springer Verlag, Vienna, 1943, pp. 86 *et seq.*

(11) Heard, U. S. P. 2,274,634 (1942).

(12) Holmes and Emmett, *J. Phys. Colloid Chem.*, **51,** 1280 (1947).

originally). This calculation is believed to give a truer picture of the exchange than that of the approach to equilibrium of the entire mixture.

Data and Discussion

The results of the exchange experiments at 100° are shown in Table I and the physical properties of the oxides before and after reaction with water in Table II and in Fig. 1. It is evident that there are reactions occurring which are so extensive that, in some instances, there is almost complete equilibration of all oxygen of the oxide with the added water. At the same time, there has been a marked change in the physical structure of the oxides.

For clarity, the data relating to silica gel will be considered in detail first. Referring to Table I, exchange is seen to occur in two distinct stages. Initially, there is a rapid exchange involving 10–20% of all the silica oxygen, while the second stage is a continuing, slow exchange involving a further 30–50% of the silica oxygen. After one month some 40–70% of all the oxide oxygen has equilibrated with oxygen in the added water. The rate and extent of exchange are alike for the samples dried at 450 and 760°.

TABLE I

PER CENT. OF OXYGEN IN EQUILIBRIUM WITH H_2O^{18} AT 100–105°

Oxide	Max. drying temp., °C.	Reaction time, hours 0.25	0.50	1.0	3.0	8.0	96	168	720
SiO_2-2	100								
Sample 1		20	21	22	..	30	..	61	71
Sample 2		..	..	18	18	23	42	..	..
SiO_2-2	450	8	10	9	..	..	..	25	41
SiO_2-1	760								
Sample 1		7	10	9	..	15	..	31	41
Sample 2		..	..	7	9	13	26	..	..
Al_2O_3	100								
Sample 1		26	29	24	..	37	..	74	87
Sample 2		..	..	33	37	46	76	..	..
Al_2O_3	450								
Sample 1		24	24	27	..	37	..	57	72
Sample 2		..	..	49	53	63	60	..	..
SiO_2-Al_2O_3	730								
Sample 1		15	15	12	..	18	..	36	44
Sample 2		..	..	11	..	17	31	..	..
Kaolin clay	100	..	..	0[a]	..	0	..	0	0
Bentonite clay	100	..	..	0[a]	..	0	..	0	0
Bentonite clay, acid-activated-1 (Filtrol TCC)	565	11	..	12	..	8	..	13	21
Bentonite clay, acid-activated-2	565	9	..	11	..	13	..	20	27

[a] No reaction with experimental error—*ca.* ±0.03 atom % O^{18}.

The surface areas of the silica samples have decreased considerably during one month contact with water at 105°, as illustrated by a comparison of the fifth and sixth columns of Table II. This change in surface area is accompanied by far-reaching changes in pore structure toward larger average pore diameter as indicated by the change in the nitrogen adsorption isotherms, shown in Fig. 1.

TABLE II

PHYSICAL AND CATALYTIC PROPERTIES OF THE OXIDES

Oxide	Maximum drying temp., °C.	Ignition loss at 1000°[a]	*p*H of oxide-H_2O slurry at 280°	Surface area, sq. m./g. Before reaction	After reaction for 1 month	Cat. activity, wt. % conversion[b]
SiO_2-2	100	7.0, 4.8	5.0 ± 0.5	267	148	~7
SiO_2-2	450	2.6	5.0	276	222	~7
SiO_2-1	760	0.93	4.8	330	157	~7
Al_2O_3	100	42.6, 43.9	4.8	350	217	11
Al_2O_3	450	4.5, 5.3	6.3	372	366	11
SiO_2–Al_2O_3	730	0.77	5.5	312	208	53
Kaolin	100	13.2	7.7	29	26	20
Bentonite	100	8.0	9.1	76	70	8
Activated bentonite-1	565	2.2	5.0	256	247	45
Activated bentonite-2	565	1.9	5.3	240	230	48

[a] Where two values are shown, they are for samples 1 and 2. [b] Alexander, *Proc. Am. Petroleum Inst.*, **27** (III), 51, Nov. (1947).

From X-ray examination: 1. Silica–no crystal pattern was observed.

2. Alumina—the sample dried at 100° showed poorly defined lines of Boehmite, γ-$Al_2O_3 \cdot H_2O$. After one month reaction, the Boehmite pattern became much stronger. The alumina dried at 450° showed a few lines of γ-alumina. After one month reaction, a strong Boehmite pattern was seen; a few weak unidentified lines were also present—they may be γ-alumina.

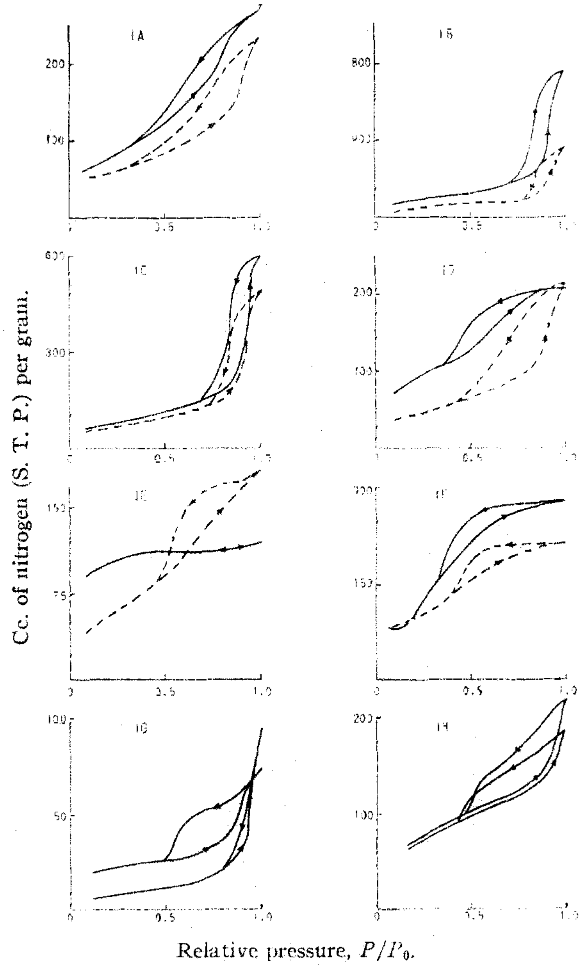
3. Silica–alumina—no crystal pattern was observed.

4. Kaolin—no change in the kaolinite pattern was seen after one month's reaction.

5. Montmorillonite—for the natural and acid-activated bentonites, the montmorillonite pattern was obtained before and after one month's reaction, with the lines somewhat weak after reaction.

These data are interpreted in the following manner: The initial, rapid exchange involves oxygen of the oxide present both in hydroxyl form as [SiOH] and HOH and in an electronically strained configuration which results from the dehydration process. The slow, continuing exchange involves the remainder of the surface oxygen, linked to silicon through both valence bonds. Coincident with the slow exchange, migration of the surface occurs, exposing fresh oxygen, previously in the body of the oxide which becomes available for exchange. This involves an hydrolysis: [SiOSi] + H_2O → [2SiOH], and exchange then occurs through hydration, as previously established for inorganic oxy anions.[8] This explanation is borne out by calculations involving the ignition loss and surface area values, as will be shown.

The oxide oxygen present as hydroxyl can be calculated from the ignition loss. For the samples dried at 450 and 760°, the loss of water on ignition arises from the reaction [2SiOH] → [SiOSi] + H_2O; for silica dried at 100°, physically bound water is lost also. Therefore, the ignition loss may be used to calculate the total hydroxyl oxygen content of the oxide, whether present as



In Figs. 1A–1F, the solid curves are the adsorption–desorption isotherms of the samples before reaction with water; the dotted curves are the isotherms after reaction with water at 105° for one month. For the samples shown in Figs. 1G and 1H, the isotherms, after reaction, were identical with those before reaction. 1A, (silica–alumina); 1B, (silica)-2 dried at 100°; 1C, (silica)-2 dried at 450°; 1D, (silica)-1 dried at 760°; 1E, (alumina) dried at 100°; 1F, (alumina) dried at 450°; 1G, upper isotherm (kaolin), lower isotherm (bentonite); 1H, upper isotherm (acid activated bentonite)-1, lower isotherm (acid activated bentonite)-2.

[SiOH] or as HOH. Results of these calculations are seen in column 3 of Table III.

TABLE III

PER CENT. OF OXYGEN IN OXIDE PRESENT IN HYDROXYL FORM

Oxide	Present in hydroxyl calculated form, % From surface area	From ignition loss	Undergoing rapid exchange experimental
SiO_2-2 (100°)	6	23	21 ± 1
SiO_2-2 (450°)	6	9	10 ± 1
SiO_2-1 (760°)	8	3	8 ± 2

To determine the hydrogen contents of the oxide samples, a series of exchange reactions was run using D_2O. These reactions were studied at two temperatures: (1) in sealed ampules at room temperature, and (2) in sealed ampules at 565°. The data are shown in Table IV and are in general agreement with those obtained by ignition loss measurements.

TABLE IV

H–D EXCHANGE BETWEEN D_2O AND H-CONTAINING OXIDES

Pretreatment: (a) sample dried for three hours at 760° with evacuation at $< 10^{-3}$ mm. (b) sample dried for three hours at 930° with evacuation at $< 10^{-3}$ mm.

Oxide	Exchange conditions	"H_2O" content of oxide, wt. %, calculated
SiO_2 (a)	2 hr.—565°	0.30
Al_2O_3 (a)	2 hr.—565°	0.29
SiO_2-Al_2O_3 (a)	2 hr.—565°	1.05
SiO_2-Al_2O_3 (a)	6 days—room temp. (*ca.* 27°)	0.70
SiO_2-Al_2O_3 (b)	6 days—room temp.	0.06

As indicated, the observed exchange data do relate to the oxide structure, where the latter is estimated from its surface area and density. Thus, assume the silica present as a cylindrical fiber. Though the assumption of such regular structure is an over-simplification, nonetheless the general conclusions are still valid, and for a sample of 267 sq. m./g. area and a density of 2.25 g./ml. a fiber diameter of 67 Å. is obtained.

Figure 2 is a schematic representation approximately to scale of the cross-section of such a fiber having the cristobalite structure. The solid circles represent silicon atoms, the whole circles oxygen atoms, the dotted circles oxygen atoms above and below the plane of the cross-section. With the known atomic dimensions of the unit cell it is possible to draw a cross-section of *ca.* 67 Å. in di-

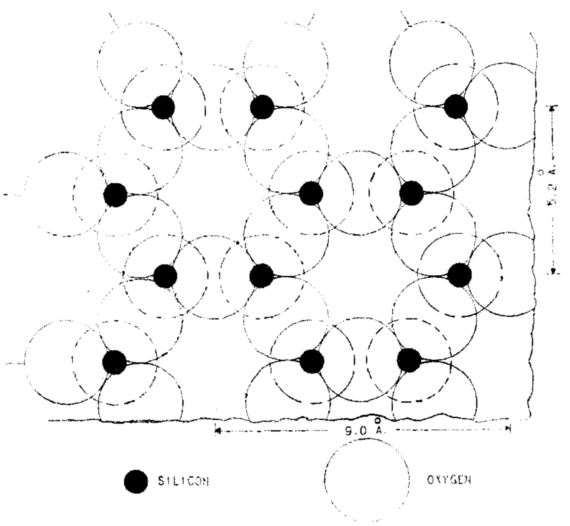


Fig. 2.—Schematic representation of the cristobalite structure.

ameter (for the SiO_2-2 dried at 100°) and to count the number of oxygen atoms in the cross-section. Those on the surface as [Si–OH] and [Si–O–Si] may then be counted and differentiated from those in the body of the structure. The fractions of oxygen present as [Si–OH] and as surface [Si–O–Si] for the other silicas from their areas determined in this manner are shown in Tables III and V. Also shown are the experimentally determined values for the initial rapid exchange and the exchange after a one-month reaction time.

TABLE V

PER CENT. OF OXYGEN IN OXIDE PRESENT ON THE SURFACE

Oxide	Present on surface, % *i. e.*, Si–OH + Si–O–Si calculated from surface area	Undergoing exchange in one month—experimental, %
SiO_2-2 (100°)	6 + 18 = 24	71
SiO_2-2 (450°)	6 + 18 = 24	41
SiO_2-1 (760°)	8 + 22 = 30	41

It is evident that, as water continues to split out with increasing time and temperature of calcination, there is insufficient hydroxyl left to satisfy the normal valency of those silicon atoms present at the surface. Thus, splitting out of water must leave a portion of the surface in a state of strain, *i. e.*, a highly reactive condition. This may be seen in the data of Table III for the silica-1 dried at 760°. The ignition loss shows that there can be only 3% of the oxygen in hydroxyl form, whereas the experimentally determined rapid exchange value is 8 ± 2%. It thus appears that there may be oxygen on the surface, possibly present as ions, held in an unusual fashion between two or more silicon atoms. Since in this form there would be a distortion of the normal unit cell, such oxygen should be quite reactive.[13]

Oxides other than silica will now be considered. Referring to Tables I and II and Fig. 1, the data show oxide behavior similar to that seen with the silica samples except in the case of untreated kaolin or bentonite which, within experimental error, show no exchange and no change in pore structure.

Table I shows that the rate and extent of exchange varies with the oxide composition. Morita and Titani[14] found that exchange between water and silica occurred only above 650°. However, their samples had been subjected to high temperatures and had undoubtedly sintered, and it is obvious a highly-developed surface is required to provide sufficient oxygen for the exchange reaction to become measurable. Referring again to Table I, in the case of the one sample of silica-alumina catalyst examined, the exchange values fall between those of silica and alumina with about the proper weighting considering its composition (12.5% Al_2O_3, 87.5% SiO_2). This is further evidence that silica–alumina is primarily a mixture of silica and γ-alumina.

The exchange values obtained with the two alumina samples are of interest. Though the ignition loss varied from 42.6% to 4.5% with increase in calcination temperature from 100 to 450°, no difference was observed in the rapid exchange values. Even after a reaction period of one month the exchange values were 87 and 72%, respectively. From this it appears that with material calcined at 100° the ignition loss must, in large part, arise from water or hydroxyl not on the surface but in the body of the structure. The similarity in the rapid exchange values for these two samples is seen as fortuitous. The surface ions of the material calcined at 450° must be very reactive toward water, a fact substantiated by an observed temperature rise on wetting. The ability of alumina to change from γ-alumina to Boehmite[15] would provide a means for exchange which is not possible for silica. A further unusual effect is seen with the alumina samples. Though the surface area of the alumina dried at 100° dropped very markedly after a reaction time of one month, that for the alumina dried at 450° remained constant. This may mean that in the latter case there is not much actual structural change in going from γ-alumina to Boehmite.

The lack of any measurable exchange with the raw clays even after a one-month reaction period may be ascribed at least in part to their relatively low surface areas. Also important may be the inherent stability of these crystalline materials toward water. With these clays, however, the loss of water upon ignition indicates that marked exchange should occur. That it does not must mean that the [OH] groups that give rise to the ignition loss lie in the body of the material and are not open to attack by water at 100°; *i. e.*, under these experimental conditions the planes are not cleaved. After acid activation and relatively high temperature calcination, with marked increase in surface area, exchange does occur. The surface, however, seems to be far more stable than that of the synthetic oxides in that no change in surface area is found after reaction with H_2O for one month at 105°.

The relationship between water and the cracking catalyst is of major importance. The water molecule supplies both a proton and an hydroxyl group and can be regarded as a co-catalyst in the same fashion that HCl acts with $AlCl_3$.[2] The water acting with a Lewis base makes possible the change of coördination of aluminum in the catalyst from six to four.[2] This concept of changing coördination as a basis of catalytic action requires a labile surface and the data presented here supply the proof of this lability.

Low Temperature (100°) Exchange with H_2O^{18} 0.1 *N* in Sodium Hydroxide and Hydrochloric

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(13) W. A. Weyl, Research (May, 1950) and in a paper, "The Role of Ionic Deformation in Surface Chemistry," New York Academy of Science, May, 1950, recently has presented independent evidence and proposed a structure for a silica surface from which water has been removed to the point where one of the rules governing the crystal structure of silica must have been violated.

(14) Morita and Titani, *Bull. Chem. Soc. Japan*, **13**, 601 (1938).

(15) Laubengayer and Weisz, THIS JOURNAL, **65**, 247 (1943).

Acid.—The silica dried at 760° and the silica–alumina cracking catalyst reacted at 100° with both 0.1 *N* sodium hydroxide and hydrochloric acid, *ca.* 1.40 atom % O^{18}. With acid, the exchange rate was identical with that in neutral solution. With alkali, the silica showed a marked increase in rate of exchange, the silica–alumina showed no change compared with exchange in neutral solution. The data are shown in Tables VI and VII.

Table VI

Per Cent. of Oxygen in Oxide that Exchanges with H_2O^{18} 0.1 Normal in Hydrochloric Acid and in Neutral Solution

Oxide	Reaction time, hours 0.25	1.0	8.0
SiO_2–Al_2O_3 (730°) with HCl	9	13	18
without	(15)[a]	(12)	(18)
SiO_2-1 (760°) with HCl	6	6	7
without	(7)	(8)	(14)

[a] Values in parentheses are for exchange with (neutral) H_2O^{18}.

Table VII

Per Cent. of Oxygen in Oxide that Exchanges with H_2O^{18} 0.1 Normal in Sodium Hydroxide and in Neutral Solution

SiO_2–Al_2O_3 (730°) with NaOH	8	11	20
without	(15)	(12)	(18)
SiO_2-1 (760°) with NaOH	19	20	34
without	(7)	(8)	(14)

The most probable explanation of the difference between the effect of alkaline solution on silica–alumina as contrasted with silica gel is this: with the silica–alumina no effect on rate of exchange is observed since the Na^+ present did not effectively exceed the base exchange capacity of the oxide. Thus, the acid catalyst neutralized the added base. With the silica, however, there is no base exchange capacity and a constant solution and redeposition of the surface occurs, for hydroxyl ions facilitate the rupture of [Si–O–Si] bonds.

High Temperature (565°) Exchange between Oxide and Water.—Several exchange reactions were studied at a higher temperature, 565°. These experiments were of two types: (1) water was passed over the oxide maintained at 565° by being alternately condensed into traps at opposite ends of the reaction vessel, and (2) the water–oxide mixture was sealed in quartz ampules and maintained at temperature, 565°, for two hours. In the first series the contact time is not known, but it is probably of the order of seconds. The data are shown in Table VIII.

The high temperature exchange data of Table VIII are similar to the results at lower temperature. Even though it is not possible to relate directly the exchange conditions, since the times and temperatures of the two groups of exchange reactions were different, nonetheless some 11–14% of the oxygen atoms in silica-alumina exchange in a short time at 565° (compared with the value 11–15% from Table I at 100°). Here, too, with longer reaction times, a further slow exchange reaction is also seen.

Table VIII

Oxygen Exchange between Water Vapor and Silica or Silica–Alumina at 565°

Oxide[a]	Exchange conditions	Oxygen in oxide in equilibrium with water, exp., %
SiO_2–Al_2O_3	Water passed over oxide 10 times	14
	Water passed over oxide 20 times	11
SiO_2–Al_2O_3	2 hr., sealed in quartz ampule	25
SiO_2	2 hr., sealed in quartz ampule	41

[a] Oxides all pretreated by calcination at 760° for three hours with evacuation (at 10^{-3} mm.).

Acknowledgments.—The interpretation of data has been aided greatly by discussions with other members of this Laboratory. Acknowledgment is also made to A. V. Grosse for some results not reported here. Permission by the Houdry Process Corporation to publish these results is appreciated.

Summary

1. The exchange of oxygen between water and silica gel, alumina gel, active silica–alumina cracking catalyst, kaolin clay, bentonite clay, and acid-activated bentonite clay was measured at 100°, and in a few instances at 565°.

2. The high surface area materials undergo exchange in two stages, first a rapid exchange involving 10–25% of all the oxide oxygens and then a further slow exchange which, in a period of one month at 105°, involves a further 10–60% of the oxide oxygens. In contrast, natural kaolin or bentonite undergoes no apparent exchange. This may be due to their relatively low surface area (< 80 sq. m./g.) but may also depend on the low reactivity toward water of such crystalline substances.

3. Physical measurements showed substantial changes occurred to the oxides (other than clay) during contact with water for one month at 105°.

4. Oxygen exchange is postulated as occurring through surface oxygens; oxygen present either as hydroxyl or in a strained condition resulting from dehydration exchanges rapidly, that present in metal–oxygen–metal linkages exchanges at a slower rate. With time, surface migration occurs, exposing new oxygen ions previously in the body of the structure and these then become available for exchange. Material which has been calcined at high temperatures has some oxygen ions in a state of strain so that such linkages hydrate rapidly.

5. The mobility of the catalyst surface is believed to play an integral part to its ability to act as a catalyst.

Marcus Hook, Penna. Received April 1, 1950