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| Title | ACID PROPERTY AND CATALYTIC ACTIVITY OF SILICA GEL TREATED WITH AMMONIUM SALTS |
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| Citation | JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 19(1), 29-34 |
| Issue Date | 1971-04 |
| Doc URL | http://hdl.handle.net/2115/24918 |
| Type | bulletin (article) |
| File Information | 19(1)_P29-34.pdf |

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# ACID PROPERTY AND CATALYTIC ACTIVITY OF SILICA GEL TREATED WITH AMMONIUM SALTS

By

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(Received December 22, 1970)

## Abstract

The effect of the treatment with ammonium salts on acid property of two commercial and a laboratory prepared silica gels was studied. It was found that strong acid sites of $H_0 \leq -3$ are formed by the treatment with ammonium carbonate in the case of the commercial gels, but not in the case of a laboratory prepared pure gel. The pure gel, however, was found to show high acid strength of $H_0 \leq -3$ when treated with ammonium sulfate. The formation of the strong acid sites by ammonium salt treatment was attributed to the formation of ammonium bisulfate, an acidic substance, from ammonium sulfate. The ammoium sulfate is formed by the reaction of sodium sulfate residue in commernial gels with ammonium carbonate, but not in pure gel containing no sulfate. It has been also shown that the treated gels of high acid strength are catalytically active for the depolymerization of paraldehyde and the first order rate constant increases with increase of the acid amount at $H_0 \leq -3$ of the gel catalysts.

## Introduction

Silica gel has been extensively used as a catalyst carrier and as an adsorbing agent and is known to have weak acid sites as $H_0 \simeq +3.3$. In the course of a study on acid property of silica gels, we noticed that a commercial silica gel becomes to show strong acid sites as low as $H_0 \simeq -3$ by treating with aqueous ammonium carbonate solution. In the present work, the effect of added ammonium carbonate or sulfate on acid property of two commercial and a laboratory prepared silica gels was studied in detail. The catalytic activity of the treated and untreated silica gels for the depolymerization of paraldehyde was also studied in connection with the acid property.

## Experimental

Commercial silica gels were obtained from Davison Chemicals Co. and

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Dokai Chemicals Co., the specifications of the properties being given in Table 1.

TABLE 1. Properties of Commercial Silica Gels

|  | Davison MS–1D | Dokai S–50 A |
|---|---|---|
| Surface area (m²/g) | 350 | 650 |
| Average pore diameter (Å) | 206 | 43 |
| SiO$_2$ (wt. % dry base) | 99.5 |  |
| Fe | 0.02 |  |
| Na$_2$O | 0.09 |  |
| Al$_2$O$_3$ | — |  |

Pure silica gel was prepared from ethyl silicate as follows. Aqueous solution of ammonia was poured under vigorous stirring into the mixture of ethyl silicate, oxalic acid and aqueous ethanol solution. The formed precipitate was separated and washed thoroughly with aqueous ethanol to remove undecomposed ethyl silicate and ammonium oxalate and then dried at 100°C. The dried gel was calcined in air at 500°C for 3 hrs.

Two commercial and a pure silica gel were treated with ammonium carbonate as described below. About 10 g of silica gel (100 mesh) ground in an agate mortar was suspended in 1000 mℓ of 2 wt. % aqueous ammonium carbonate solution and stirred for 1 hr. After filtering, the gel was dried in an air oven and calcined at 400°C for 3 hrs. The treatment of pure silica gel with ammonium sulfate was made by impregnating about 0.1 mmol of ammonium sulfate from aqueous solution to 1 g of the gel and by calcining at 400°C for 3 hrs. The acidity was measured by $n$-butylamine titration method using Hammett indicators.[1] The indicators used are benzalacetophenone (pK$_a$ = −5.6), dicinnamalacetone (−3), benzeneazodiphenylamine (1.5), dimethyl yellow (3.3) and methyl red (4.8).

The depolymerization of paraldehyde was carried out as follows. 50 mℓ of benzene solution of paraldehyde (0.411 mol/ℓ) was put in a 100 mℓ stoppered flask and about 2 g of silica gel (100 mesh powder) was added, the accurate weight of the added gel being obtained by measuring the weight of the flask before and after the addition of the gel. The mixture was stirred by a magnetic stirrer in a thermostat maintained at 26°C. Since the rate of the heterogeneous reaction depends on the efficiency of stirring if the rate is controlled by diffusion, the experiments were carried out under the condition where the efficiency is constant. After a recorded time, a small por-

tion of the solution was withdrawn and the concentration of paraldehyde was analyzed by gas chromatography.

Benzene and paraldehyde of reagent grade were dried by the calcined Linde molecular sieve 3 A. Ethyl silicate, ammonium carbonate and sulfate were of reagent grade and used without further purification.

## Results and Discussions

The acid strength of three kinds of silica gels treated with ammonium carbonate is shown in Table 2. All untreated gels have only weak acid

TABLE 2. Acid Strengte of Silica Gels

| Silica gels | | Acid Strength (pK$_a$) | | | | |
|---|---|---|---|---|---|---|
| | | −5.6 | −3.0 | +1.5 | +3.3 | +4.8 |
| Davison MS-1 D | A | − | − | − | + | + |
| | B | − | + | + | + | + |
| Dokai S-50 A | A | − | − | − | + | + |
| | B | − | + | + | + | + |
| Pure gel | A | − | − | − | + | + |
| | B | − | − | − | + | + |

A: untreated, B: treated with ammonium carbonate.
+ : adsorbed indicator showed its acidic color.
− : adsorbed indicator showed its basic color.

sites, but both Davison and Dokai gels show high acid strength of pK$_a$ = − 3.0 when treated with ammonium carbonate, though the acid strength of pure silica gel is not changed by the treatment. Fig. 1 shows the acidity distribution of Davison gel with and without ammonium carbonate treatment. The acid amount of the untreated gel is zero at $H_0 \leq +1.5$, whereas that of the treated gel is 0.076 mmol/g at $H_0 \leq -3$.

Since ordinary commercial silica gels are produced from sodium silicate and sulfuric acid, they contain usually a small amount of sodium sulfate residue. In fact, the presence of sulfur in both Davison and Dokai gels was confirmed by fluorescence X-ray analysis. However, no sulfur was detected in pure silica gel prepared from ethyl silicate. It thus appears that sodium sulfate is the origin of strong acid sites. In the presence of ammonium carbonate, sodium sulfate gives ammonium sulfate.
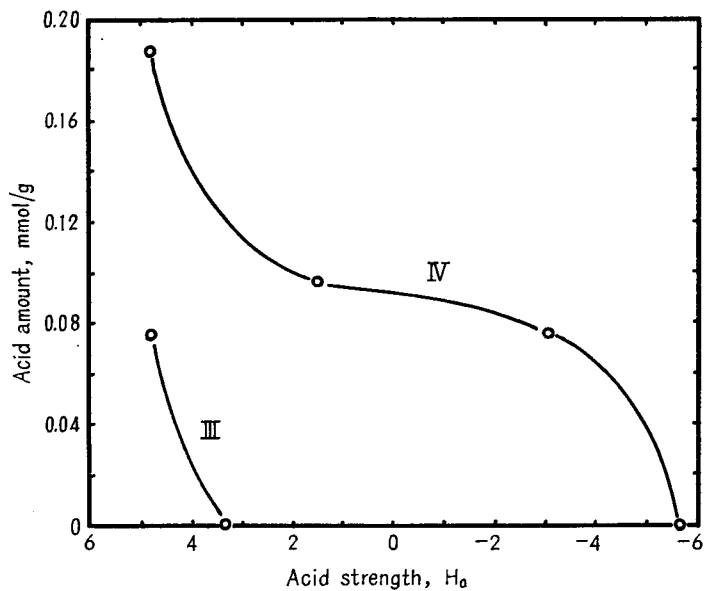
$$(NH_4)_2CO_3 + Na_2SO_4 \longrightarrow (NH_4)_2SO_4 + Na_2CO_3 \qquad (1)$$

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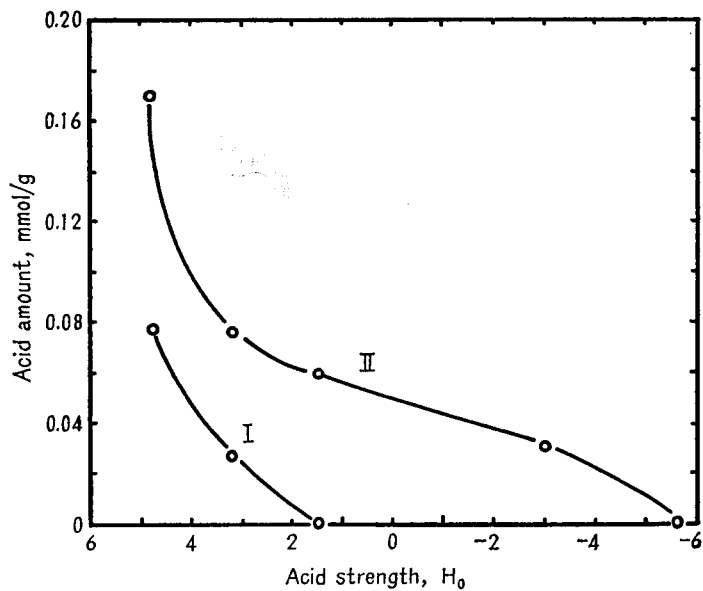


**Fig. 1.** Acid property of Davison silica gel.
I : calcined at 400°C for 3 hrs.
II : treated with ammonium carbonate and calcined at 400°C for 3 hrs.



**Fig. 2.** Acid property of pure silica gel
III : pure silica gel prepared from ethyl silicate and calcined at 400°C.
IV : pure silica gel (III) treated with ammonium sulfate and calcined
at 400°C.

The free energy change of reaction (1) is about 1 Kcal/mol and thus the equilibrium constant is estimated to be the order of $10^{-1}$. Therefore, reaction (1) is not necessarily favorable, but a part of sodium sulfate may change to ammonium sulfate. By calcination at 350–400°C, ammonium sulfate decomposes to form ammonium bisulfate,[*] which exhibits fairly strong acidic property. In the case of pure silica gel which contains no sulfate, any ammonium sulfate is not formed by the ammonium carbonate treatment and, accordingly, no acidic ammonium bisulfate is formed. However, the pure gel becomes a strong acid when treated directly with ammonium sulfate and calcined at 400°C for 3 hrs. In Fig. 2 is shown the acicity distribution of treated and untreated pure gel. It is clearly seen that the gel becomes to show large acid amont and high acid strength by the treatment with ammonium sulfate.

The catalytic activity of the Davison gel treated with ammonium carbonate and the pure gel treated with ammonium sulfate for the depolymerization of paraldehyde is shown in Fig. 3, where $a$ is the initial concentration of paraldehyde and $a$-$x$ the concentration at time $t$. The reaction is known
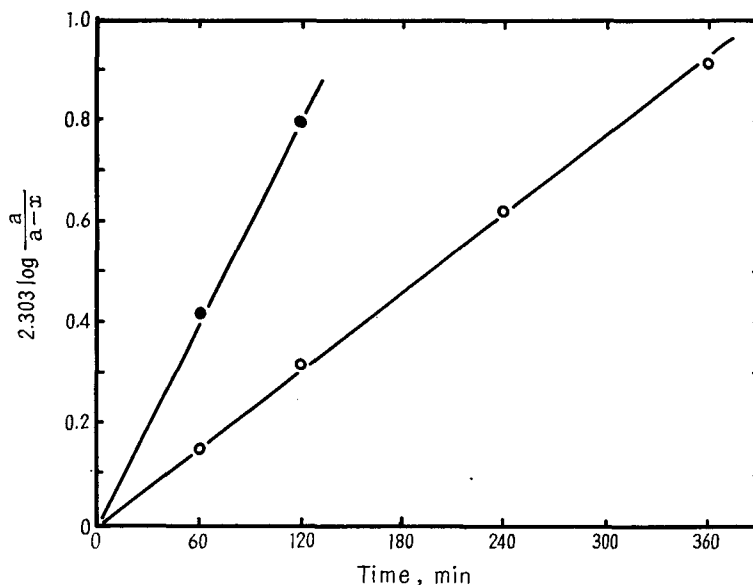


**Fig. 3.** Depolymerization of paraldehyde catalyzed by silica gels.
  ○ : Davison silica gel treated with ammonium carbonate (2.2 g).
  ● : Pure silica gel treated with ammonium sulfate (2.0 g)

[*] The decomposition of ammonium sulfate at 350–400°C was clearly shown by DTA and TGA.

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to be first order in paraldehyde concentration in the cases of homogeneous acid catalysis[2] and heterogeneous acid (metal sulfates) catalysis[3] and is also first order in this case. The rate constants obtained from the slopes of the straight lines were $k_1 = 1.2 \times 10^{-3}\,\text{min}^{-1}.\text{g}^{-1}$ for the treated Davison gel and $k_2 = 3.1 \times 10^{-3}\,\text{min}^{-1}.\text{g}^{-1}$ for the treated pure gel. However, all the untreated gels and a pure gel treated with ammonium carbonate showed no catalytic activity at all. It has been shown by Tanabe et al.[4] that the active sites for the depolymerization of paraldehyde are strong acid sites of $H_0 \leqq -3$. It is, therefore, understandable that the silica gels having no acid sites of $H_0 \leqq -3$ are catalytically inactive, while the Davison gel treated with ammonium carbonate and the pure gel treated with ammonium sulfate which have strong acid sites of $H_0 \leqq -3$ are active. Thus, the ratio of $k_2/k_1 = 2.6$ is in good agreement with the ratio (2.5) of the acid amount at $H_0 \leqq -3$ of the respective catalysts (see II in Fig. 1 and IV in Fig. 2)

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