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Effects of Pressure on the Chemical Properties of the Solid Surface. II. The Surface Acidity and the Catalytic Activity of Compressed Potassium Bisulfate

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Experimental studies of the chemical properties of the surface of potassium bisulfate samples which had been subjected to compressions of 0—3750 kg./cm^2 at room temperature were carried out. Namely, on the compressed sample, the surface acidity at room temperature was measured by the indicator method, while the catalytic activity for the conversion of acetaldehyde to metaldehyde was measured at the temperature of a dry ice - methanol mixture by the bulk polymerization technique. Experimental results showed that the compression of the bisulfate resulted in an increase in the surface acidity at $H_0 = 1.5$ and in a reduction of the acidity at $H_0 = 4.0$. Further, it was found that the increase in the compressing pressure resulted in an increase in the catalytic activity of the sample. Thus, the existence of a close relation between the catalytic activity and the surface acidity at $H_0 = 1.5$, and the effectiveness of the pressure in the improvement of the catalytic activity through changing the acid strength distribution on the sample surface were experimentally demonstrated.

Little attention has been directed to the effect of compacting pressure on the chemical properties of solid surfaces. In view of this, the present authors started to study the surface properties of compressed solids; they have found[1] that the surface acidity of various metal sulfates can be varied by varying the compression. The present research is an extension of the finding to the field of surface catalysis.

According to the current theory[2] of catalysis, the surface acidity of a solid has a close relation to the catalytic properties of the solid; thus, an increase in the surface acidity is a useful way to improve the catalytic activity. A common way to increase the surface acidity is to heat the solid at a suitable temperature.[3] The compression of the solid has not yet been attempted.

In the present research, potassium bisulfate was chosen as the sample material, and the effects of compacting pressure on the surface acidity and the catalytic activity of the bisulfate in the conversion of acetaldehyde to metaldehyde were studied. The experimental results showed that the compression was effective in improving the catalytic activity. Further, the acid strength distribution, which is related to the catalytic activity, was found to vary upon compression.

Experimental

Sample.—About 0.5 g. of potassium bisulfate was compressed by essentially the same apparatus as that described in a previous paper.[1] Samples compressed at 0, 1250, 2500 and 3750 kg./cm^2 were prepared. The pelleted material was ground and pulverized in an agate mortar and stored for 6 hr. in a desiccator containing granules of freshly-dried silica gel. Immediately after the drying, the acidity measurement or the activity test was carried out.

Surface Acidity.—The acidity was determined by Benesi's method[4] with the following four indicators; phenylazonaphthylamine (pK_a = 4.0), *p*-dimethylaminoazobenzene (pK_a = 3.3), benzeneazodiphenylamine (pK_a=1.5), and dicinnamalacetone (pK_a= −3.0).

Catalytic Activity.—As a measure of the catalytic activity of the sample material, the conversion of acetaldehyde to metaldehyde was measured with the apparatus indicated in Fig. 1.

After the purified acetaldehyde (containing only traces of water) had been distilled in vacuo from Tube

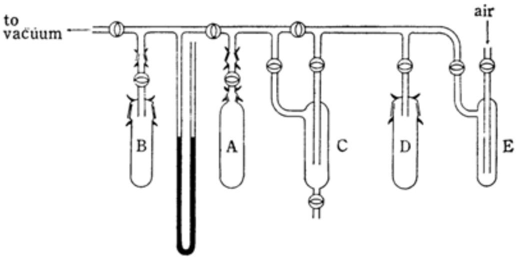

Fig. 1. The apparatus for activity tests.

A : An acetaldehyde container
B : The reaction tube (purified aldehyde)
C : A trap used for the distillation of acetaldehyde
D : An acetaldehyde container (crude aldehyde)
E : A trap containing granules of silica gel

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[1] Y. Ogino and T. Kawakami, This Bulletin, **38**, 972 (1965).

[2] N. M. Chirkov, M. I. Vinnik, S. G. Entelis and V. I. Tsvetkov, *Intern. Chem. Eng.*, **3**, 112 (1963).

[3] K. Tanabe and R. Ohnishi, *J. Research Inst. Catalysis, Hokkaido University*, Vol. X, 229 (1962).

[4] H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

D into Tube A, which was kept at −76°C, Tube A was weighed and the temperature was brought to 0°C. Then the aldehyde was distilled again in vacuo, at the rate of 10 g./hr., into the reaction tube, B, which was kept at −76°C and which contained 0.2 g. of catalyst powder. Finally, Tube A, containing residual aldehyde, was reweighed. This enabled us to evaluate the quantity of aldehyde monomers charged in the reaction tube. Usually the ratio of the monomer to the catalyst (by weight) was adjusted to 80.

The reaction was started by shaking the reaction tube; it was interrupted after 30 hr. by adding 20 ml. of a 1% solution of β-naphthylamine in acetone into the reaction tube. After the interruption of the reaction, the mixture in the reaction tube was filtered by suction. The solid product obtained on the filter paper was thoroughly washed with distilled water and, after it had been dried in vacuo, weighed. The conversion was estimated from the ratio of the weight of the product to that of the initial charge of the acetaldehyde monomer.

The solid product was identified by means of an infrared spectrometer and an X-ray diffractometer.

Results

Surface Acidity.—The relation between the surface acidity of potassium bisulfate and the compacting pressure is given in Fig. 2. As may be seen in this figure, the acidity at H_0*[1]$=4.0$ diminishes on compression, while the acidity at $H_0=1.5$ increases on compression. On the other hand, the acidity at $H_0=3.3$ varied in an irregular manner, and the acidity at $H_0=-3.0$ was essentially zero.

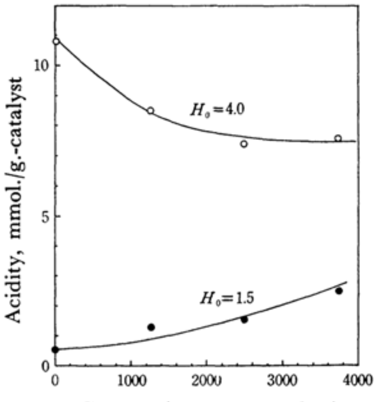

Fig. 2. Relations between the compacting pressure and the surface acidity.

Catalytic Activity.—The conversion of acetaldehyde to the solid product is given in Fig. 3 as a function of the compacting pressure. The figure shows that the catalytic activity of potassium bisulfate increases almost linearly with the compacting pressure.

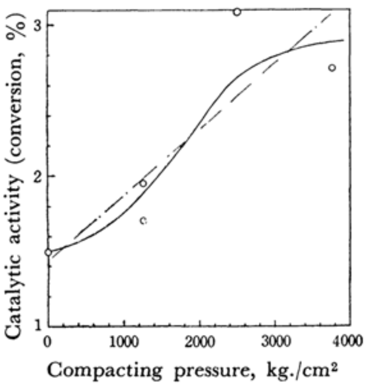

Fig. 3. The relation between the compacting pressure and the catalytic activity.

The reaction product was a white, non-tacky solid. This solid was found to decompose at 110—120°C, and it was insoluble in ordinary organic solvents. From the infrared absorption spectra given in Fig. 4 and the powder X-ray diffraction patterns given in Fig. 5, the reaction product was identified as metaldehyde. The other products, such as paraldehyde or high polymers, were found to be negligible.*[2]

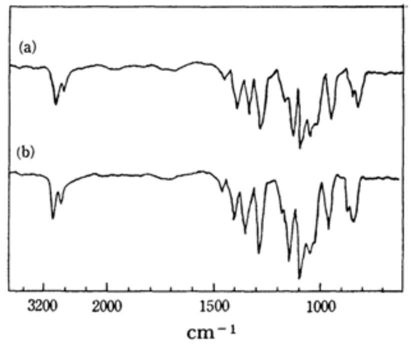

Fig. 4. Infrared absorption spectra of the solid product (a) and metaldehyde (b).

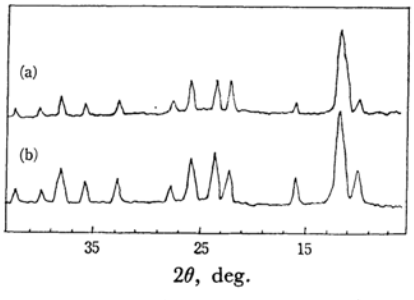

Fig. 5. X-Ray diffraction patterns of the solid product (a) and pure metaldehyde (b).

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*[1] H_0 means Hammett's acidity function (*J. Am. Chem. Soc.*, **54**, 2721 (1932)).

*[2] By adopting some different methods of reaction, an amorphous high polymer of acetaldehyde could be formed using potassium bisulfate as a catalyst.

Discussion

One of the most important facts which were established in the present research is that the distribution of acid strength on the surface of potassium bisulfate varied upon compression. Calculations based on the experimental results indicated in Fig. 2 show that the total acidity, as defined by the acidity at $H_0=4.0$, was diminished to about 70% of the original value by the compression at 3750 kg./cm^2. On the other hand, the percentage of the acidity at $H_0=1.5$ against the total acidity was increased from 5% (original value) to 32% by the compression at 3750 kg./cm^2. These results show that the quantity of weak acid on the surface was reduced by the compression, while the quantity of the strong acid, which has a H_0 value between 1.5 and -3.0, was increased by the compression.

Although the detailed mechanisms of the change in the acid strength distribution have not yet been clarified, some important roles played by the crystal imperfections formed through the dehydration[1] of potassium bisulfate to potassium pyrosulfate may be supposed. According to high-pressure chemistry,[5] dehydration due to compression can occur. However, the same sort of dehydration may also occur when the sample is heated. In fact, Tanabe and his cowerkers[6] considered that the surface acidity of nickel sulfate is due to the crystal imperfection contained in an unstable phase produced by heating the sulfate. Thus, it must be suspected that the compression of the sample might cause a rise in the temperature of the sample.

According to a preliminary experiment[*3] in the present work, the temperature of the sample was raised only 3°C by the compression at about 3000 kg./cm^2. Therefore, increases in the temperature on compression might not be the cause of the acidity change; the main cause of the change might be the formation of the crystal imperfection due to the compression.

As may be seen in Fig. 3, the catalytic activity of potassium bisulfate was increased by the compression. This experimental fact may be explained in terms of the acidity change on compression. The relations between the catalytic activity and the surface acidity at $H_0=4.0$ and at $H_0=1.5$ are given in Fig. 6. The figure reveals that the increase in the surface acidity at $H_0=4.0$ results in the reduction of the catalytic activity, whereas the increase in the surface acidity at $H_0=1.5$ makes the surface more active for the reaction. In the previous paragraph it was shown that the compression of potassium bisulfate was effective in increasing the surface acidity at $H_0=1.5$. Accordingly, it can be understood that the compression makes the surface richer in strong acids, whereby the surface of the bisulfate is brought to a more active state.

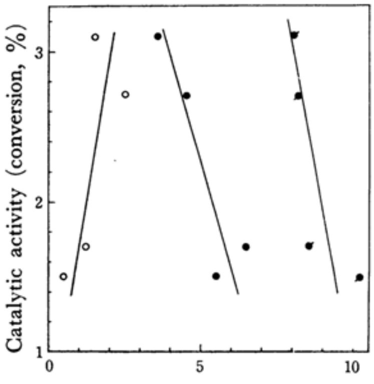

Fig. 6. Relations between the catalytic activity and the surface acidities at $H_0=4.0$ (◕), $H_0=3.3$ (●), and $H_0=1.5$ (○).

It is an important fact that the compression is effective in improving the catalytic activity through changing the acid strength distribution. Although the possibility of cases where the catalytic activity is independent of the total acidity can not be completely denied, many experimental results which support an intimate relation between the catalytic activity and the surface acidity at a given H_0 value can be seen in the literature. For instance, Takida and Noro[7] described how the catalytic activity of metal sulfates in the polymerization of acetaldehyde to an amorphous high polymer was dependent on the surface acidity at $H_0=3.3$. Thus, in order to improve the catalytic activity of acidic solids, some suitable procedures which can adjust the acid strength distribution on the solid surface are required. The experiments in the present research were confined to the case of potassium bisulfate, but it seems that the knowledge obtained here can make some contribution toward this requirement.

Summary

The acidic nature of the potassium bisulfate surface varied with the compression. Namely,

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[5] S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London (1957), p. 208.

[6] T. Takeshita, R. Ohnishi, T. Matsui and K. Tanabe, *J. Catalysts Soc. Japan (Shokubai)*, **6**, 270 (1964).

[*3] The temperature of the compressed sample was measured in the following way. The same apparatus as that described in the previous paper was used. A small hole, 3 mm. in diameter, was drilled at the center of the bottom cover of the apparatus. The inside opening of the hole was covered with a copper disk which was sufficiently thick to create an internal pressure of below 3000 kg./cm^2. Then the sample material was packed into the sample room of the apparatus, and it was compressed to about 3000 kg./cm^2. Thus, the disk was broken. At the instant of the breaking, the temperature of the sample which was flowing out from a hole opened in the disk was measured with a thermocouple.

[7] H. Takida and K. Noro, *Chemistry of High Polymers (Kobunshi Kagaku)*, **21**, 23 (1964).

the total acidity, as defined by the acidity at $H_0=4.0$, is reduced, while the acidity at $H_0=1.5$ is increased by the compression. These facts have been considered to show that the acid strength distribution on the surface of potassium bisulfate can be adjusted by the compression.

The catalytic activity of the bisulfate in the reaction of acetaldehyde to metaldehyde is increased by compressing the material. This increase in the catalytic activity can be related to the increase of acidity at $H_0=1.5$. On the basis of the experimental results, it has been suggested that the compression might be effective in improving the catalytic activity of acidic solids.