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Effects of Pressure on the Chemical Properties of the Solid Surface. IV. Dehydrogenation of Isopropanol on the Compressed $CuO-Cr_2O_3$ System

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In order to examine the idea that the chemical properties of a solid surface would vary on compressions, the catalytic activities of $CuO-Cr_2O_3$ samples compressed at 340—5120 kg/cm^2 were measured at 100—200°C and under 1 atm pressure. In addition, some experimental studies of the structure of the samples were carried out. The activity of the sample compressed before the reduction decreased monotonously with the compression. It was considered that the retardation of the reaction due to an intra-particle diffusion might be the cause of this activity change. On the other hand, in the case of the sample compressed after the reduction, an unexpected rise in the catalytic activity was found to result from the compression of 3000—4000 kg/cm^2. The cause of this phenomenon was thought to be an increase in the surface area resulting from a disintegration of the sample particles. Further, the activation energy was found to decrease on compression. From the results of electron-diffraction studies, it seems that the decrease in the lattice distances of surface copper may be thought to be the cause of this activation-energy change.

Few investigations concerning the effects of compacting pressure on the surface properties of solids have been made. Considering this situation, the authors have started a series of systematic investigations of this problem, in the course of these studies, it has been found that the surface acid-ities of some solids vary on compression.[1,2] In addition, changes in the catalytic activities have been found to occur as a consequence of the acidity change.[3] These findings have encouraged the view that the chemical properties of solid surfaces would also vary on compressions, and from the extension of this view, the necessity to investigate the pressure effects on surface properties of other nonacidic solids has been recognized.

First, the authors conducted a study of the pressure effects on the surface properties of mixed oxide systems, the $CuO-Cr_2O_3$ system was chosen as the sample material. For this system, the dehydrogenation of isopropanol has been chosen as a test reaction. The experimental results have revealed that the compacting pressure affects the catalytic activity in an interesting manner. Further, it has been found that the compression affects not only the surface area and the pore structure of the sample, but also the crystal structure of active species existing on the sample surface. In this paper, the experimental results will be described and discussed.

Experimental

Samples. The sample powders used for compression were prepared by means of a co-precipitation method. At room temperature, from two separate flasks, containing an aqueous solution of ammonium hydroxide and a mixed solution of copper nitrate and chromium nitrate, the solutions were dropped simultaneously, with vigorous stirring, into a vessel containing 10 *l* of distilled water. After several decantations, a co-precipitated mixture of hydroxides of copper and chromium was separated from the solution by filtration. The resultant voluminous paste was dried at

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

[2] Y. Ogino, T. Kawakami and K. Tsurumi, *ibid.*, **39**, 639 (1966).

[3] Y. Ogino, T. Kawakami and T. Matsuoka, *ibid.*, **39**, 859 (1966).

115°C for 24 hr to reduce the volume. Then, the product was washed repeatedly with 100 l of distilled water until no nitrate ions were detected in the filtrate. Finally, the solid product was dried in an oven at about 120°C for 6 hr. The resultant powder showed a greenish-blue color. In the present research, the sample which was made by compressing this powder was called the sample A.

Next, the above-mentioned greenish-blue powder was reduced with isopropanol vapor. That is, at room temperature nitrogen was passed through a vessel containing isopropanol, and the gas saturated with the alcohol was led into a reducing tube containing about 20 g of the original powder. During the reduction, the temperature and the space velocity of nitrogen were kept at 200°C and 300 hr^{-1} respectively. Then, the reduced powder was compressed to make the B sample.

The compression of the sample powder was carried out using a piston-cylinder device described in a previous paper.³⁾ By applying a desired value of pressure on the powder for 10 min, several kinds of samples with different compacting pressures (340—5120 $\mathrm{kg/cm^2}$) were prepared. The dimensions of the final cylindrical tablet were 1—2 mm in length and 4 mm in diameter.

Activity Tests. Under 1 atm pressure and at various temperatures (ranging from 100 to 200°C), the catalytic activities of the samples in response to the dehydrogenation of isopropanol were measured with a conventional flow-type reactor.³⁾ In carrying out this test, the cylindrical sample was crushed and sieved to a 1—2 mm size and 1 ml of the resultant granules was packed into the reactor to serve as a catalyst. Then, isopropanol was fed into the reactor at a constant rate of 0.2 ml/min, then the temperature was raised to 230°C. This condition was maintained for 3 hr in order to stabilize the catalytic activity. Then, the reaction temperature was adjusted to the desired value. In order to avoid such side reaction as the formation of methyl isobutyl keton, a reaction temperature below 200°C was chosen.

Surface Areas and Pore Structures. Granulse of the sample which had been used for the activity test served for measurements of the surface area, the mercury-dead space and the water-dead space. The surface area, Σ ($\mathrm{m^2/g}$), was evaluated by applying the B.E.T. theory to the adsorption data of *n*-butane at 0°C. The mercury-dead space and the water-dead space were measured by conventional pycnometric methods.⁴⁾ The former gives the bulk density, ρ_b (g/ml), of the sample, while the latter gives the true density ρ_t (g/ml) of the sample. The total pore volume, V_g (ml/g), the mean pore radius, $\bar{r}$ (Å), and the mean particle radius, $\bar{R}$ (Å), of the sample were evaluated by a conventional method⁵⁾ with the values of Σ, ρ_b and ρ_t.

X-Ray Diffraction and Electton-Diffractions. Powder X-ray diffraction patterns of the samples were obtained with an X-ray diffractometer. The Cu$K\alpha$ radiation (Ni filter) at 30 kV and 15 mA was used. Photographs of the Debye-Scherrer rings of the sample were obtained from electron-diffraction studies.

Results

Catalytic Activities. As is shown in Fig. 1, the catalytic activity of the A sample decreased monotonously with the increase in the compacting pressure. On the other hand, the activity of B sample varied in a complex manner. Namely, at lower pressures the activity decreased on compression, but it tended to increase at about 3000 $\mathrm{kg/cm^2}$, reached a maximum value at about 4000 $\mathrm{kg/cm^2}$, and decreased on further compression.

Surface Areas. As Fig. 2 shows, the specific surface area of the A sample reached a maximum at about 1200 $\mathrm{kg/cm^2}$; at higher compacting pressures the surface area decreased monotonously. On the other hand, the specific surface area of the B sample varied in a manner somewhat analogous to the change in the catalytic activity of this sample. Namely the surface area decreased with the pressure up to 1500 $\mathrm{kg/cm^2}$, but it tended to increase at

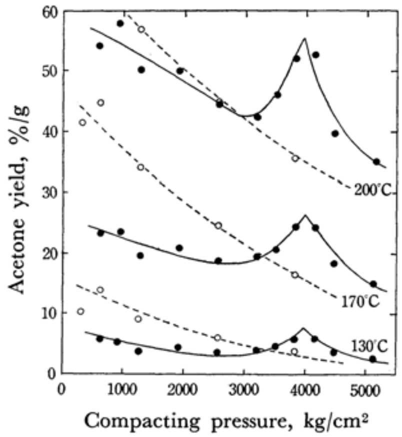

Fig. 1. Relations between the catalytic activity and the compacting pressure.
--○-- A —●— B

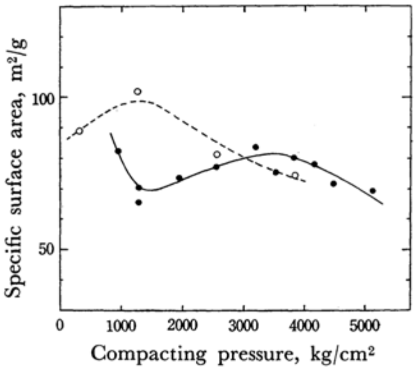

Fig. 2. Relations between the specific surface area and the compacting pressure.
--○-- A —●— B

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4) A. J. Juhola and E. O. Wiig, *J. Am. Chem. Soc.*, **71**, 2078 (1949).

5) A. Wheeler, "Catalysis," Vol. II, ed. by P. H. Emmett, Reinhold Publishing Corporation, New York (1955), p. 105.

about 2000 kg/cm^2 and reached a maximum value at about 3500 kg/cm^2.

Pore Volumes. It can be seen in Fig. 3 that the total pore volume of the A sample decreased monotonously on compression, while the total pore volume of the B sample varied in a somewhat complex manner. A maximum can be seen on the curve which represent the relation between the total pore volume of the B sample and the compacting pressure.

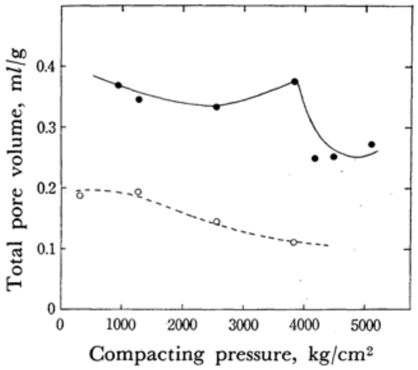

Fig. 3. Relations between the total pore volume and the compacting pressure.
--○-- A —●— B

The Mean Pore Radius. The relations between the mean pore radius and the compacting pressure are given in Fig. 4. The figure shows that the value of $\bar{r}$ for the A sample decreased on compression. On the other hand, in the case of the B sample, some irregularities can be seen at about 4000 kg/cm^2, though there seems to be general tendency for $\bar{r}$ to decrease as the compacting pressure increases.

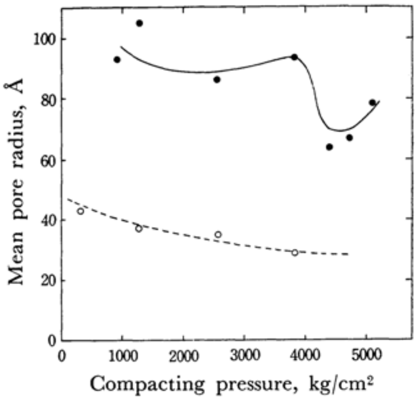

Fig. 4. Relations between the mean pore radius and the compacting pressure.
--○-- A —●— B

The Mean Particle Radius. The relations between the mean particle radius and the compacting pressure are given in Fig. 5. As can be seen in this figure, the $\overline{R}$ value for the A sample increased on compresions, whereas the $\overline{R}$ value for the B sample decreased on compression below 3500

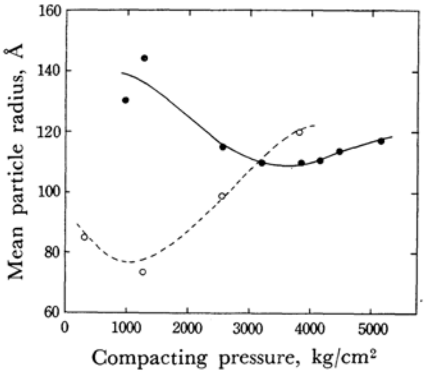

Fig. 5. Relations between the mean particle radius and the compacting pressure.
--○-- A —●— B

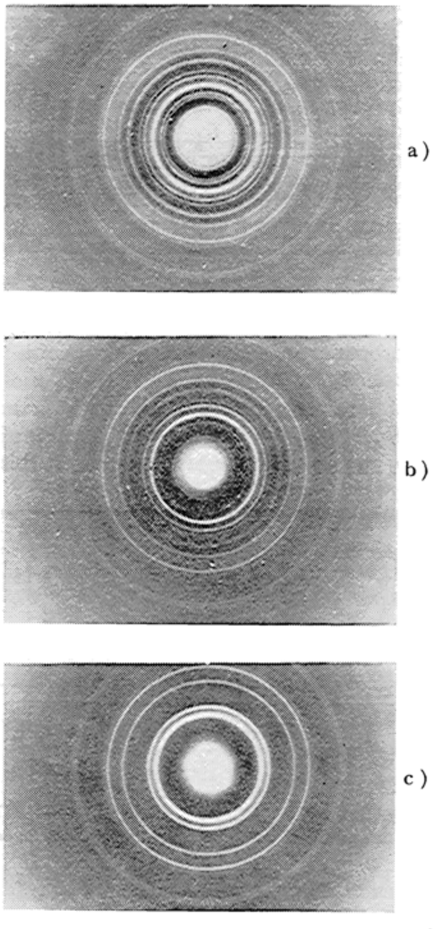

Fig. 6. Examples of Debye-Scherrer rings obtained by electron diffraction studies:
a) B compressed at 0 kg/cm^2
b) A compressed at 2560 kg/cm^2
c) B compressed at 640 kg/cm^2

kg/cm², while above this pressure it increased slightly.

X-Ray Diffraction and Electron-Diffractions. In the X-ray diffraction pattern of the A sample and the B sample, only a small peak, which could be attributed to Cu(111), was seen; no other peaks weer observed.

Some photographs of Debye-Scherrer rings obtained from the electron-diffraction studies are illustrated in Fig. 6. The clear rings in this figure were found to be attributed to copper crystals. In addition, faint rings which could be attributed to Cr_2O_3 were seen in the original photographs. The results of electron-diffraction studies of all the samples which had been used for the activity tests showed analogous results.

Discussion

The A Sample. Since the curve representing the surface area had a maximum (Fig. 2), while the curve for the catalytic activity had no maximum (Fig. 1), the main cause of the observed activity change due to the compression of the A sample can not be the change in the surface area. To demonstrate this more quantitatively, the catalytic activity should be expressed by a rate constant. According to Neish,⁶⁾ the dehydrogenation of isopropanol obeys a first-order kinetics. Hence, the rate constant, k (ml/hr/ml-cat), is given by:

$$k = (SV)\left\{2\left(\ln\frac{z+1}{z} - \frac{1}{z+1}\right) - 0.386\right\} \qquad (1)$$

where SV (hr^{-1}) is the space velocity of the feed vapor, and z (mole fraction) is the concentration of isopropanol in exit vapors. Arrhenius plots of k obtained by applying Eq. (1) to the experimental data are given in Fig. 7. The values of k_s (ml/hr/m²), *i. e.*, the rate constant per unit of surface area of the sample, are also plotted on this figure.

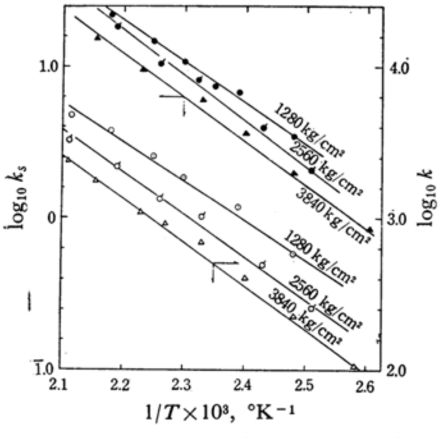

Fig. 7. Arrhenius plots for k and k_s of the sample A.

As can be seen in this figure, k_s varies on compression. If k is proportional to $\sum$, k_s should be constant at a given temperature, irrespective of the compacting pressures.

In order to explain the activity change due to compression, it seems necessary to take the change in pore structures into consideration. As has been pointed out in the "Experimental" section, the total pore volume and the mean pore radius of the A sample decreased on compression. Analogous results have been reported by Rivarola,⁷⁾ Wade,⁸⁾ and van Zoonen and Douwes.⁹⁾ van Zoonen and Douwes have considered that a reduction in the pore size would make the resistance to intraparticle diffusion serious and the apparent reaction rates would decrease. Generally speaking, the pore radius of the A sample was small (30—40Å). Therefore, retardations of the reaction rate due to the intra-particle diffusion might be expected, and the reduction in the pore size would result in reduction of the reaction rate.

Usually, the effects of intra-particle diffusion on the reaction rate are expressed by an effectiveness factor E_f. In the present research, the effectiveness factor for the A sample was evaluated by a conventional procedure¹⁰⁾ on the assumption that the labyrinth factor, χ, was 0.1 irrespective of the compacting pressure. The results are given in Fig. 8. This figure shows that, as expected, the retardations of the reaction rate due to the intraparticle diffusion are considerable. Further, the effectiveness factor at 200°C seems to show that it becomes smaller as the compacting pressure increases. This result suggests that the apparent

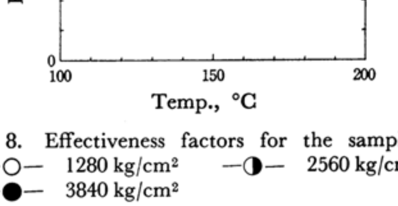

Fig. 8. Effectiveness factors for the sample A.
—○— 1280 kg/cm² —◑— 2560 kg/cm²
—●— 3840 kg/cm²

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6) A. C. Neish, *Can. J. Res.*, **23**, 49 (1945).

7) J. B. Rivarola and J. M. Smith, *Ind. Eng. Chem. (Fundamentals)*, **3**, 308 (1964).

8) W. H. Wade, *J. Phys. Chem.*, **68**, 1029 (1964).

9) D. van Zoonen and C. Th. Douwes, *J. Inst. Petrol.*, **49**, 383 (1963).

10) C. N. Satterfield and T. Sherwood, "The Role of Diffusion in Catalysis," Addison-Wesley Publishing Company, Reading, Massachusetts. Palo Alto. London (1963), p. 65.

catalytic activity would decrease when the catalyst is compressed.

It should be noted that the treatments described above were based on the assumption that $\chi=0.1$ irrespective of the compacting pressures. This is, however, only an approximation, probably the value of χ would decrease on compression.[9)] Thus the actual activity decreases due to the compression would be more marked than that predicted by the approximation.

In the discussions described above, it was implicitly assumed that the intrinsic activity of the A sample does not vary on compression. According to electron-diffraction studies, the sample was found to be composed of copper and chromium oxide. Both copper and chromium oxide are active in the dehydrogenation of isopropanol. However, according to Sabatier[11)] the activity of copper is much higher than that of chromium oxide. Therefore, the observed catalytic activity might be attributed mainly to copper existing on the sample surface. Figure 9 shows the relations between the lattice distances of copper crystal and the compacting pressure. It may be seen in this figure that, in the case of the A sample, the lattice distances were not affected by compression. Thus, there seems to be no reason to expect any variations in the intrinsic activity of the A sample provided that the surface concentration of the copper does not vary on compression.

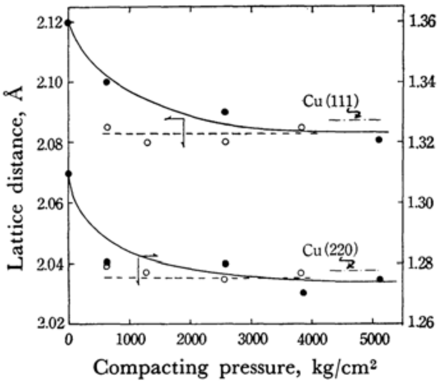

Fig. 9. Relations between lattice distances of surface copper and the compacting pressure.
--○-- A —●— B

The B Sample. In the present research, it was found that the catalytic activity of the B sample had a maximum value at the compacting pressure of about 4000 kg/cm^2. This fact demonstrates that, sometimes, the compression of catalysts results in unexpected changes in the catalytic activity.

In connection with the activity change, the specific surface area of the B sample behaved interestingly. As has been pointed out previously, a maximum appeared at 3500—4000 kg/cm^2 on the surface-area *vs.* pressure curve. From this fact, it was suspected that the change in the catalytic activity was caused by the change in the surface area. In fact, Fig. 10, where, in place of values of k, values of k_s are plotted against the reciprocal absolute temperature, shows that the differences in the catalytic activities per unit of surface area are less significant than the differences in the apparent catalytic activities, *i, e.*, the rate constant, k (Fig. 11). From this result, it may be said that in the case of the B sample the change in the surface area contributes greatly to the activity change due to compression.

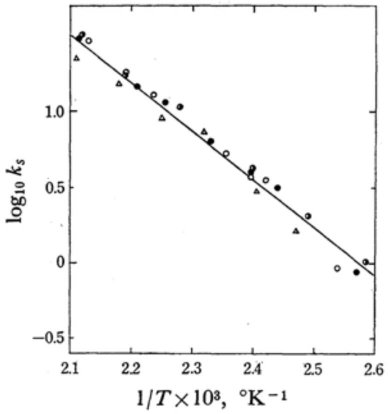

Fig. 10. Arrhenius plots for k_s of the sample B.
—◑— 640 kg/cm^2 —○— 1280 kg/cm^2
—●— 3840 kg/cm^2 —△— 5120 kg/cm^2

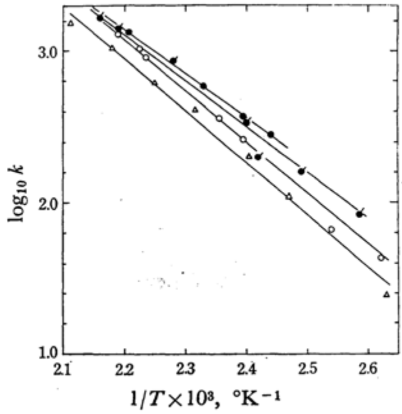

Fig. 11. Arrhenius plots for k of the sample B.
—◐— 640 kg/cm^2 —○— 1280 kg/cm^2
—●— 3840 kg/cm^2 —△— 5120 kg/cm^2

From the fact that increases in the surface area have resulted from the compression of the pressure range of 2000—3500 kg/cm^2, it may be supposed that some drastic changes, *e. g.*, the disintegration of elementary particles or their aggregating state, have occurred on compression. The maximum

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11) P. H. Emmett and P. Sabatier, "Catalysis Then and Now," Franklin Publishing Company, Englewood, N. J. (1965), pp. 650—678.

appearing at about 4000 kg/cm^2 on the curve which represents the total pore volume (Fig. 3) and the irregular change in the mean pore radius (Fig. 4) seem to support the supposition. Further, the observed decrease in the particle radius below 3500 kg/cm^2 (Fig. 5) makes the supposition more realistic.

Speculatively, it might be possible to consider that a fresh surface with a higher catalytic activity would appear when the particles or their aggregating state disintegrate. According to this speculation, in addition to the contribution from the increase in the surface area, a further increase in the catalytic activity might be expected. However, no available experimental data to support this are now at hand. Therefore, it is safe to say that the disintegration due to the compression contributes to the catalytic activity mainly through an increase in the surface area.

To explain the activity change in the B sample, some other factors in addition to the change in the surface area must be taken into consideration. Namely, the experimental results given in Fig. 12 shows that the activation energy of the reaction varies on compression. This fact can hardly be explained in terms of the change in the surface area.

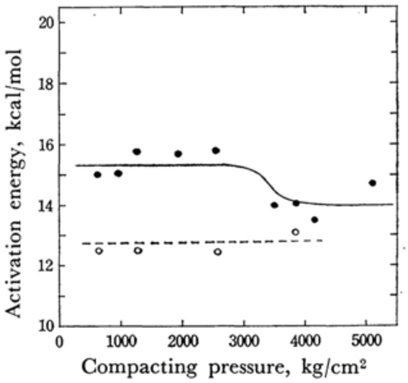

Fig. 12. Relations between the apparent activation energy and the compacting pressure.
--○-- A —●— B

The first factor to be considered may be the effect of the intra-particle diffusions. However, unlike the A smaple, the mean pore radius of the B sample was not very small, and it was possible to show that the effectiveness factor of this sample is 0.9—0.95 under the experimental conditions. Therefore, the retardation of the reaction rate due to the intraparticle diffusion would be small and negligible.

The second factor which seems to affect the activation energy is the change in the crystal structure of this sample. Similar to the case of the A sample, electron-diffration studies showed copper crystals as well as chromium oxide crystals on this sample. Thus, for the same reason as has been described in the case of the A sample, it can be considered that the catalytic activity of the B sample is also due to the activity of the surface copper. Accordingly, it might be said that any change in the crystal structure of the copper would result in the activity change. As Fig. 9 shows, analyses of the results of the electron-diffraction studies revealed that the lattice distances of the copper crystals on the B sample varied on compression. Namely, the lattice distances decreased with an increase in the compacting pressure. By combining this fact with Balandin's findings(12) that the activities of metal catalysts in the dehydrogenation of isopropanol are a function of the distance between atoms of the metal, and that the activition energy decreases with a decrease in the distance, the following conclusion could be derived: the decrease in the lattice distances of the surface copper is the cause of the decrease in the activation energy for the B sample.

At first sight, it seems surprising that the compressions of the order of 10^3 kg/cm^2 could reduce the lattice distance of a solid, *i. e.*, copper. Usually, changes in the lattice distances of solids due to compressions occur at pressures of 10^4 kg/cm^2 or above.(13)

However, it must be noted that the copper crystals on the noncompressed sample had larger lattice distances than those of the regular copper crystal, and on compression they approached regular values (Fig. 9). Thus, strictly speaking, the phenomena found in the present research are different from the usual ones, *i, e.*, the reductions in regular lattice distances to lower values. Hence, the findings in the present study are natural. A recent report(14) which described the surface of a solid as being more sensitive to compression than the bulk phase also supports the consideration described above. At any rate, it is remarkable that the compression had direct effects upon the active species on the solid surface and resulted in the activity change.

The authors wish to express their thanks to Professor Masanobu Wada and Mr. Tadashi Koda, Research Institute of Electrical Communication, Tohoku Universty, for their kind help in the electron-diffraction studies.

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13) For instance, G. K. Lewis, Jr., and H. G. Drickamer, *J. Chem. Phys.*, **45**, 225 (1966).

14) W. B. Daniels and A. I. Skoultchi, *J. Phys. Chem. Solids*, **27**, 1247 (1966).

12) A. A. Balandin, *Uspekhi Khimii*, **31**, 1265 (1962); translated into Japanese by E. Takai, *J. Catalysis Soc. Japan* (*Shokubai*), **5**, 342 (1963).