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Effects of Pressure on the Chemical Properties of the Solid Surface. III. The Catalytic Activity and the Structure of the Compressed Tungstic Acid

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In order to investigate the surface properties of tungstic acid samples which had been compressed at pressures of 640—3840 kg./cm^2, experimental studies concerning the catalytic activity for the vapor-phase hydration of propylene, the specific surface area, the pore structures, the surface acidities and the crystal structures were carried out. According to the experimental results, both the catalytic activity and the surface acidity became higher as the compressing pressure of the sample was increased, whereas the specific surface area remained practically constant. Further, a relation between the surface acidity and the crystal structure was deduced from X-ray diffraction studies. Namely, the crystal structure of the reduced sample approached the structure of $H_{0.1}WO_3$ from a WO_3-like structure as the compressing pressure was increased. In other words, samples with higher compressing pressures had crystal structures of a higher proton content. In addition to the above results, the total pore volume, the mean pore radius, the apparent activation energy, and the frequency factor became smaller as the compressing pressure was increased. On the basis of these experimental results, it was deduced that the catalytic activities of the compressed samples are affected by intra-particle diffusion.

The previous works$^{1,2)}$ in this series have shown the special effects of pressures on the surface acidity of several metal sulfates. Further, by the use of potassium bisulfate as a sample it has been revealed that both acid strength distributions and catalytic acitvities varied with the degree of compression. These findings seem to suggest that the surface properties of other substances might be altered by manipulating the compression; this might then be a useful procedure for improving catalytic activities.

In the present research, tungstic acid was used as the sample material in order to test the surface property and the structure in the compressed state. In testing the catalytic activity, the yields of isopropanol from water and propylene were measured. The surface acidity was measured by a conventional indicator method. Information about pore structures and crystal structures in the compressed state was also obtained. This paper will present the detailed results of the present work; these results will demonstrate the actual occurrence of the anitcipated effect.

Experimental

The Preparation of the Sample.—Powders of commercial tungstic acid were packed into the sample space of the apparatus shown in Fig. 1. Then the apparatus was sandwiched between the stationary bed and the moving bed of an oil press, by which means a desired amount of load was applied on the piston head for 10 min. period. Thus cylindrical pellets of 4×4 mm. were prepared. The compacting pressures,

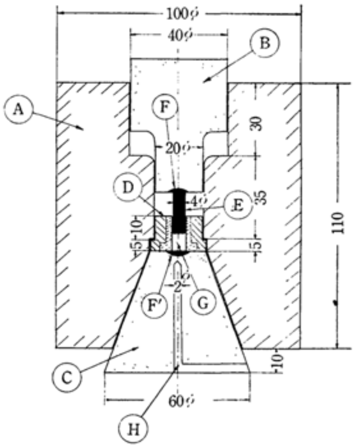

Fig. 1. The apparatus for the preparation of the sample pellet.
A: Body (stainless steel), B: The larger piston (stainless steel), C: Bottom cover (stainless steel), D: Cylinder (the inner part made from Cr-Mo steel was shrinkaged into the outer part made from Cr steel), E: The smaller piston (stellite), F, F′: Mounted stellite, G: Sample room, H: Thermo-couple well

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

2) Y. Ogino, T. Kawakami and K. Tsurumi, ibid., to be published.

which were estimated by a conventional means of calculation,1) were 640, 1280, 1920, 2560, 3200 and 3840 kg./cm^2.

Catalytic Activity.—The vapor-phase hydration of propylene over 5 ml. of sample pellets was carried out with the apparatus shown in Fig. 2. Prior to the activity test, catalyst pellets were reduced during a 0.5 hr. period with a mixed vapor of water and propylene ($H_2O/C_3H_6=2.0$, S.V.$=4.8\times10^3$ hr^{-1}) at 200°C and 1 atm. After the reduction, the temperature of the catalyst bed was adjusted to a desired value, and, after the stationary state had been reached, liquid products were collected. Except for the temperature, the reaction conditions were the same as those of the reduction. The isopropanol content in the liquid products was determined by the gas chromatographic analysis.

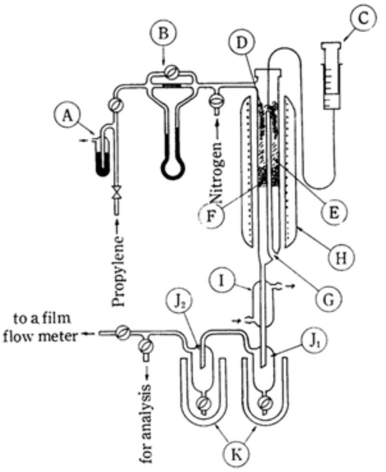

Fig. 2. The apparatus for the activity test.
A: Buffer, B: Flow meter, C: Water injector, D: Glass wool, E: Copper granules, F: Catalysts, G: Thermo-couple well, H: Electric furnace, I: Condenser, J_1, J_2: Separators, K: Ice bath

The conversion (x%) of propylene to isopropanol was evaluated from simple material-balance considerations based on the assumptions that no side reaction occurs and that the vapors of water and isopropanol are completely condensed in the separator.

After the activity test, the residual propylene was purged from the catalyst bed by the water vapor; then dry nitrogen was passed through the bed untill the reactor was cooled to room tmperature. The catalyst pellets which were taken out from the reactor were stored in an evacuated ampule.*

Surface Area, Pore Volume, Pore Radius and Particle Diameter.—The specific surface area (S, m^2./g.) was measured by means of a B. E. T. adsorption isotherm with n-butane at 0°C. The mercury displacement valume (V_{Hg}, ml./g.), as well as the water displacement volume (V_w, ml./g.), were also measured by a simple pycnometric method.3) The difference between these volumes, $V_{Hg}-V_w$, was defined as the total pore volume (V_g, ml./g.) of the sample pellet.

The mean pore radius, $\bar{r}$, was evaluated by Eq. 14)

$$\bar{r}=2V_g/S \tag{1}$$

while the mean particle diameter, $\bar{d}$, was evaluated by Eq. 2

$$\bar{d}=6V_w/S \tag{2}$$

All the experiments described in this section were carried out with the reduced sample.

Surface Acidity.—Pellets of the reduced sample were pulverized and dried for 6 hr. in a desiccator; immediately after the drying, the surface acidity of the powder was measured. Essentially the same method as that of Benesi5) was adopted in this measurement. Since the blue color of the sample powder masks that of the indicator adsorbed on the sample surface, a given weight (W, g.) of silica-alumina powder of a known acidity (A_0, mmol./g.) was mixed with the sample, and the total quantity of n-butylamine (A, mmol.) needed to neutralize the acid on the mixture was determined. Then, the surface acidity (A_s, mmol./g.) of the sample powder was evaluated by Eq. 3

$$A_s=(A-A_0W)/W_s \tag{3}$$

where W_s is the weight of the sample powder.

In the present work, three indicators, i. e., p-dimethylaminoazobenzene (pK_a =3.3), benzeneazodiphenylamine (pK_a = 1.5) and dicinnamalacetone (pK_a = −3.0), were used.

Crystal Structure.—Powder X-ray diffraction patterns of the reduced sample as well as of the unreduced sample were obtained with an X-ray diffractometer. The Cu$K\alpha$ radiation (Ni filter) at 30 kV. and at 15 mamp. was adopted.

Results

Catalytic Activity.—The relations between the conversion of propylene to isopropanol per unit weight of the catalyst pellet and the reaction temperature are given in Fig. 3. As may be seen in this figure, the conversion increases with the compacting pressure of the catalyst.

Surface Area, Pore Structure.—The values of the specific surface area of the compressed samples (reduced samples) are given in Table I. In the table, no systematic dependency of the surface area upon the compacting pressure can be seen, and the surface area seems to be roughly constant.

TABLE I. SPECIFIC SURFACE AREAS OF COMPRESSED SAMPLES

Compacting psess., kg./cm^2	640	1920	3200	3840
Surface area, m^2/g.	21.5	23.7	21.8	22.6

In Fig. 4, the total pore volume, the mean pore radius and the mean particle diameter are given as functions of the compacting pressure. It may be seen that the pore volume and the pore radius decrease with the compacting pressure, while the mean particle diameter stays at a constant

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* In this paper, samples which were treated in this manner will be called reduced samples.

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

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

5) H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

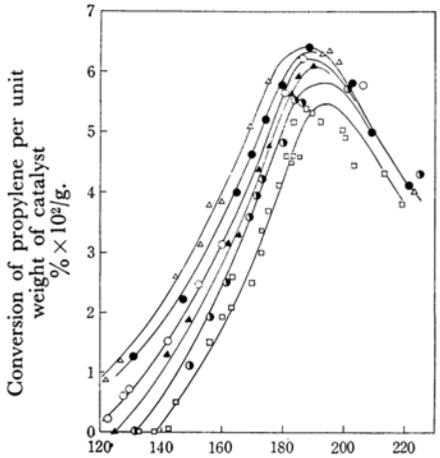

Fig. 3. Catalytic activities of the catalysts compressed at 640 (□), 1280 (◑), 1920 (▲), 2560(○), 3200 (●), 3840 kg./cm² (△).

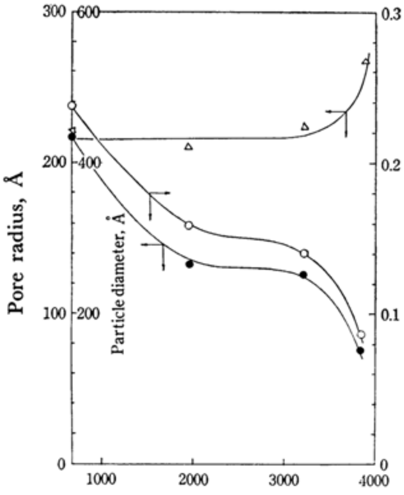

Fig. 4. Variations of the mean pore radius (●), the total pore volume (○) and the mean particle diameter (△) on compression.

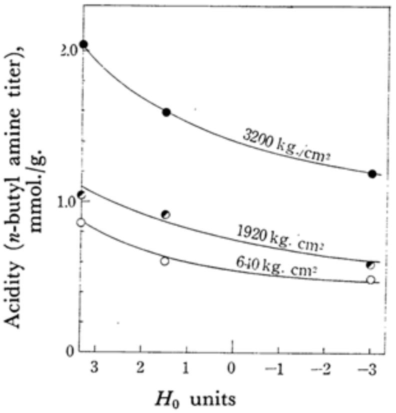

Fig. 5. Variations of the surface acidity on compression.

level.

Surface Acidity.—The relations between the compacting pressure and the surface acidity at various H_0 values⁶⁾ are given in Fig. 5. As may be seen in this figure, the surface acidity increases with the compacting pressure.

Crystal Structure.—The powder X-ray diffraction patterns of reduced samples compressed at different pressures are given in Fig. 6(a)—(c). These patterns are supplemented by Miller's notations of WO_3 and $H_{0.1}WO_3$.⁷⁾ They show that, at the lower compacting pressure, the crystal structure of the sample closely approximates the structure of WO_3, while at the higher compacting pressure it approximates the structure of $H_{0.1}WO_3$.

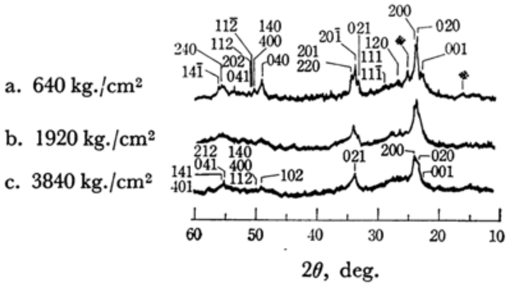

Fig. 6. X-ray diffraction patterns of reduced samples, together with Miller's notations for WO_3 (a) and $H_{0.1}WO_3$ (c).
The symbol * in (a) indicates residual peaks of H_2WO_4.

On the contrary, few changes due to the compression were observed in the X-ray diffraction patterns of unreduced samples.

Discussion

Catalytic Activity and Surface Acidity.—One of the most important results obtained in the present work may be the fact that the catalytic activity of tungstic acid can be increased by the compression of the catalyst (cf. Fig. 3). From this fact, it may be said that the effect of compression suggested in the previous paper has actually appeared.

The activity increase on compression might be due to the increase in the surface acidity. It is well known⁸⁾ that the hydration of propylene is catalyzed by acidic solids, and that increases

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6) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

7) O. Glemser and C. Naumann, *Z. anorg. u. allgem. Chem.*, **265**, 287 (1951).

8) N. M. Chirkov, M. I. Vinnik, S. G. Entelis and V. I. Tsvetkova, *Intern. Chem. Eng.*, **3**, 112 (1963).

in the surface acidity make the catalyst more active. Therefore, from Fig. 5, which shows the acidity increase on compression, the increase in the catalytic activity can be understood.

Further effects of the compression on the catalytic activity were revealed by analyzing the conversion-temperature relationship with a rate equation which had been derived by one of the present authors⁹⁾ under the assumption that the rate-controlling step is a surface reaction on a sparsely-covered surface. The results of the analysis are given in Fig. 7 and Table II. These results show that both the frequency factor of the rate constant and the apparent activation energy were decreased by the compression. In other words, the so-called compensation effect holds among the activities of catalysts compressed at different pressures. This shows that the effect of compression on the catalytic activity is not a simple one.

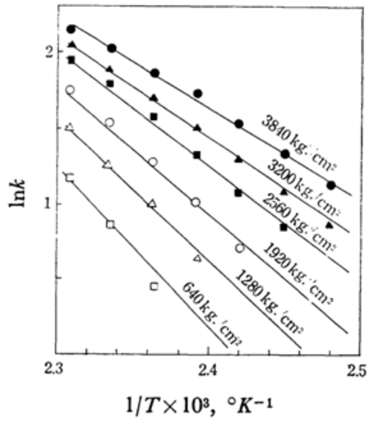

Fig. 7. Arrhenius plots.

TABLE II. FREQUENCY FACTORS AND APPARENT ACTIVATION ENERGIES FOR VARIOUS CATALYSTS COMPRESSED AT DIFFERENT PRESSURES

Compacting pressure kg./cm²	Frequency factor* ml./hr.g.-cat.	Activation energy kcal./mol.
640	1.39×10^{11}	21.2
1280	1.22×10^{10}	18.6
2560	2.88×10^{8}	15.1
3200	4.14×10^{7}	13.3
3840	1.02×10^{7}	12.1

* The rate constant whose frequency factor is given in this table was defined by the following equation

$$k=(273\boldsymbol{R}C_mP^2/1\ \text{atm.})\{(m)/(1+n+m)^2\}k_0$$

where R is gas constant, C_m is the mean compressibility factor of the mixed vapor at the standard state (N. T. P.), $m=C_3H_6/H_2O$ (mole ratio), $n=$inert gas/H_2O (mole ratio) and k_0 is the rate constant defined by the following rate equation

$$r(\text{rate of reaction, mol./hr. g.-cat.})$$
$$=k_0p_{H_2O}p_{C_3H_6}-k_*p_{C_3H_7OH}$$

where k_* is the rate constant of the reverse reaction.

At first sight, it seems possible to explain the compensation effect on the basis of the theory¹⁰⁾ of the inhomogeneity in active centers. Since the experimental results indicated in Fig. 5 showed the existence of acid centers of different strength, if it is assumed that all acid centers are effective as active centers, the theory might be applicable. However, it has previously been shown⁹⁾ that the rate of the hydration of propylene is nearly proportional to the acidity of a limited strength. Therefore, the application of the theory upon the basis of the present data is inadequate.

The Catalytic Activity and Pore Structure.—The interferences of the intra-particle diffusion of reactants and products with the intrinsic activity, which is considered to be dependent purely on the surface acidity, seem to be a cause of the compensation effect. Generally, the interference becomes more evident when the intrinsic activity is higher and when the pore radius is smaller. The experimental results show the higher surface acidity and the smaller pore radius at the higher compacting pressure. Therefore, when a highly-compressed catalyst is used for the activity test, retardations due to the diffusion process should be serious in the over-all reaction process. Further, the size of the catalyst pellet used in the present work was quite large, i. e., 4×4 mm. This would enhance the retardation. Thus, the low activation energy and the low frequency factor, both of which were found when a highly-compressed catalyst was used, might be attributed to the low activation energy of the diffusion process and to the retardation due to the diffusion respectively.

According to the explanation presented above of the compensation effect, it is necessary to consider that both the surface reaction and the intra-particle diffusion control the rate of the over-all reaction. Usually, in such cases, the experimental rate constant, $k_{\exp}$, is regarded as a product of the true rate constant, k_t, and the effectiveness factor, E_f. Although details of the pore structure of the sample are not yet clear and although a rigorous evaluation of E_f is not possible, a rough estimation under suitable assumptions showed that the E_f value for the catalyst compressed at 3840 kg./cm² is about 0.8* at 435°K. This shows that the effect of the intra-particle diffusion on the over-all reaction is considerable. Further, if it is assumed that, at the lowest reaction temperature, the reaction is purely kinetic, the activation energy for the catalyst compressed at 3840 kg./cm² is corrected to 16 kcal./mol. Although this

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9) Y. Ogino, *J. Catalysis Soc. Japan* (Shokubai), **4**, 73 (1962).

10) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Process," McGraw-Hill Book Company, New York and London (1941) p. 394.

value of activation energy is yet lower than the value for the catalyst compressed at a lower pressure, e. g., 640 kg./cm^2, the simple consideration described above seems sufficient to show that, if the pore structure of the compressed sample is clarified and the effect of intra-particle diffusion is correctly taken into account, the observed compensation effect might be explained.

Crystal Structure. — Among many works concerning the crystal structure of the reduced tungsten oxide, the work of Glemser[11] seems to contain much information relevant to the present work. Glemser observed that the reduction of WO_3 with atomic hydrogen resulted in a systematic change in the crystal structure. Namely, the crystal structure of H_xWO_3, which is the formula employed to express the composition of the reduced tungsten oxide, was varied by the reduction from the skewed structure of WO_3 (monoclinic) to the symmetrical structure of $H_{0.5}WO_3$ (cubic) by way of $H_{0.1}WO_3$ (orthorhombic) and $H_{0.33}WO_3$ (tetragonal). These results were explained by him as follows. Namely, hydrogen atoms in the crystal of H_xWO_3 are protonized; the contrapolarization effect of these protons then releases repulsions among oxygen ions in the crystal, and, as a consequence of this release, a closer packing of oxygen ions in the crystal becomes possible.

The experimental results obtained in the present work seem to be consistent with the results of Glemser. The acidity increase, which was thought to be the main cause of the activity increase on compression, seems to be related to the change in the crystal structure of the reduced tungstic acid. In the present work, it was found that the crystal structure of the reduced sample was transformed from a WO_3-like structure to a $H_{0.1}WO_3$-like structure by the compression. Therefore, the sample would contain many more protons in the highly-compressed state than in the less-compressed one. Further, the surface-area measurement showed that, irrespective of the compacting pressure, the surface area remained constant. Therefore, the probability of the appearance of protons on the surface of the sample might be higher in the highly-compressed state than in the less-compressed state. Thus, the acidity increase on compression can be understood.

The observed effect of the compression on the crystal structure might be attributed mainly to pressures.* According to high-pressure chemistry,[12] some orderings resulting from compression can be expected in microscopic structures of substances. By applying this principle to the present case, it might be expected that pressures would make some contributions to the progress of the following reactions:

$$H_2WO_4 \rightarrow WO_3 + H_2O \qquad \text{(I)}$$

$$WO_3 \xrightarrow{+H} H_{0.1}WO_3 \xrightarrow{+H} H_{0.33}WO_3 \xrightarrow{+H} H_{0.5}WO_3 \qquad \text{(II)}$$

(A loose packing of oxygen ions→ A closer packing of oxygen ions)

Indications showing the occurrence of some of these reactions have appeared in X-ray diffraction patterns of reduced samples, while they have not appeared in the patterns of unreduced samples.

These results seem to show that, in addition to the compression, the subsequent reduction of the sample was a necessary condition for the occurrence of those reactions. This is reasonable, because the progress of the reaction II may be assumed to require some proton donors. Further, the incomplete progress of the reaction II, i. e., the occurrence of the reaction $WO_3 \rightarrow H_{0.1}WO_3$ only, may be attributed mainly to the existence of water in the reducing vapor (propylene and water). According to the work of Glemser et al.,[7] highly-reduced oxides of tungsten, e. g., $H_{0.5}WO_3$ are oxidized very easily by water.

Summary

It has been established that the compression of tungstic acid is effective in increasing the catalytic activity in the vapor-phase hydration of propylene. The activity increase on compression is thought to be dependent upon the acidity increase resulting from the compression. The increase in the surface acidity has been attributed to the change in the crystal structure. Namely, it is thought that the compression and the subsequent reduction of the catalyst force the crystal structure to transform from a WO_3-like structure to a $H_{0.1}WO_3$-like structure, which is capable of containing many protons and so giving the high surface acidity.

On the other hand, the increase in the compacting pressure resulted in a considerable decrease in the pore radius of the catalyst. This fact supports the explanation that the observed compensation effect among catalytic activities of compressed catalysts is due to the interference of the intra-particle diffusion with the intrinsic activity.

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* The estimation was carried out by the method of Kubota et al. (*Chem. Eng., Japan* (Kagaku Kōgaku), **23**, 284 (1959).) under the following assumptions:

1. Since the conversion is low, reverse reaction can be neglected, and the concentration of the reactant approximates to the inlet value.
2. The diffusion coefficient of the reactant is approximated by the value of the Knudsen diffusion coefficient of propylene at 435°K.
3. The mean pore radius, $\bar{r}$, is 80 Å, and the porosity, θ, is 0.3.
4. The labyrinth factor, χ, for the uncompressed catalyst is 0.1, but by the compression of 3840 kg./cm^2 the value of χ is reduced to 0.01. (This assumption is based on the experimental result of D. van Zoonen et al. (*J. Inst. Petrol.*, **49**, 383 (1963)), who showed that, by the pelleting pressure, the diffusivity of the Co-Mo-Al_2O_3 is reduced to about 1/10 of the initial value.)

[11] O. Glemser, *Angew. Chem.*, **73**, 785 (1961).

* The increase in temperature due to the compression was less than 5°C, which might have little influences on the surface property of the sample. In this measurement, a thermocouple was inserted directly into the sample.

[12] S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London (1957), p. 4.