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Studies on the Copper Chromite Catalyst

III. Increase in the Activity of the Copper Chromite Catalyst by the Water-Gas Reaction

B. MIYA, F. HOSHINO, AND I. IWASA

From the Kao Research Laboratory, Wakayamashi, Japan

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The copper chromite catalyst is used in the reduction of fatty esters into higher alcohols. In this reaction the copper chromite catalyst, $CuO/CuCr_2O_4$*, is reduced to Cu/Cr_2O_3* by hydrogen. In this reduction a part of the water formed is adsorbed onto the catalyst and gives $Cu/Cr_2O_3 \cdot (H_2O)_{ad}$. The other part of the catalyst remains as Cu/Cr_2O_3, which is at least one form of the true active catalyst. If carbon monoxide is added to this system, the water-gas reaction takes place, and results in $Cu/Cr_2O_3 \cdot (CO_2)_{ad}$. By evacuation this becomes Cu/Cr_2O_3, the activity of which is larger than that of the originally formed Cu/Cr_2O_3. Externally added water behaves similarly with that formed by the reduction of the catalyst.

Reduction of $CuO/CuCr_2O_4$ by carbon monoxide also gives Cu/Cr_2O_3, but the treatment of the reduced catalyst with CO and water does not increase the activity of the catalyst.

INTRODUCTION

The copper chromite catalyst has been widely used in the production of higher alcohols from fatty acid esters by high-pressure hydrogen reduction since the catalyst was first reported by Adkins *et al.* (*1*) in 1931. During this period of time many papers (*2–4*) have been presented on the reactions in which this catalyst participated. Relatively few papers (*5–9*), however, have been presented on the properties of the catalyst itself.

In a previous paper (*10*) the authors have reported the following experiments. The activity of the copper chromite catalyst was increased when a small amount of methanol was added to the reaction system, followed by the removal of this methanol under vacuum at the reaction temperature, 275°C. The activity increase was proportional to the amount of methanol added. The rate of the ester reduction reaction was first order in hydrogen pressure, first order in ester concentration, and directly proportional to the amount of catalyst. Thus, the rate was first order in the ester concentration if the amount of catalyst and the hydrogen pressure during the reaction were kept constant. Though the rate was affected by the amount of ester in the autoclave, by a proper selection of conditions the rate could be determined reproducibly. Thus, if the reaction was carried out in a 500-ml autoclave with 150 g of ester and 4.5 g of the catalyst, at the initial hydrogen pressure of 10 kg/cm², heating from room temperature to the reaction temperature 275°C in 1 hr, and at the reaction pressure of 120 kg/cm², the first order rate constant k was 0.013/min.

If, in this reaction, a small amount of methanol, say, 16 g, was added to the system and if this methanol was removed just before starting the reaction, k took a value of 0.083/min. This increase in

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* The present authors use this way of presentation, because $CuO \cdot CuCr_2O_4$ (or $Cu \cdot Cr_2O_3$) is apt to be misunderstood as meaning a molecular compound.

the catalyst activity was attributed, at least in part, to the action of carbon monoxide formed by decomposition of methanol during the heating period. In fact, the increase in the activity was observed when carbon monoxide was used instead of methanol. (Although the hydrogen pressure at the beginning of heating was 20 kg/cm^2.) But in this case k was 0.04 irrespective of the carbon monoxide pressure above about 5 kg/cm^2.

By a more detailed examination of this difference between methanol and carbon monoxide, we have been able to make clear the cause of the difference. Furthermore, we have obtained some knowledge about the properties of the copper chromite catalyst.

EXPERIMENTAL

Rapeseed fatty acid methyl ester. Rapeseed oil was subjected to methanolysis in the presence of potassium hydroxide catalyst, washed with water, and distilled. Acid number, 0.21; saponification number (S.V.), 177.1; iodine number (I.V.), 102.0; hydroxyl number, 0.81; moisture, 0.023%.

Carbon dioxide. Commercial cylinder carbon dioxide was used as such. When a mixture of 150 g of ester and 4.5 g of catalyst was subjected to the reaction at the hydrogen pressure of 120 kg/cm^2 after treating the mixture with carbon dioxide of 4 kg/cm^2 at 275°C for 30 min, followed by the substitution of the carbon dioxide by hydrogen, the reaction rate was no different from that of a reaction without carbon dioxide treatment. It is clear, therefore, that, at least, no nonvolatile catalyst poison was present in this carbon dioxide.

Water. Ion-exchanged water was used; the resistivity was larger than 500 million ohm-cm.

Other materials. These were the same as described in the previous paper; hydrogen was that obtained by electrolysis, carbon monoxide was IR-spectroscopically and gas-chromatographically pure and contained no catalyst poison.

The catalyst was prepared as follows: A solution containing 4.85 moles of NH_3 and 212 g of water was added to 1 mole of $Na_2Cr_2O_7$ dissolved in 1280 g of water. To this solution was added in 15 min 2 moles of $CuSO_4$ dissolved in 1630 g of water which was maintained at 80°C. The precipitation temperature was 50–60°C. Then the mixture was kept at 80°C for 1.5 hr. The precipitate was filtered and washed with 1 liter of water eight times. Then the cake was dried at 110°C for 20 hr, powdered, and calcined at 400 ± 20°C for 30 min. The final product weighed 290 g.

Calculation of rate constants. The hydrogen pressure was kept constant at 120 kg/cm^2 during reaction; small samples were withdrawn at 0, 10, 20, 30, and 45 min, and S.V. and I.V. were determined. The first order rate constants were calculated. When the reaction was fast, the hydrogen pressure was reduced to 60 kg/cm^2 and the rate constants obtained were multiplied by 2. (The rate is directly proportional to the pressure.)

The ester reduction reaction obeys the first order reaction up to about 70% conversion, while hydrogenation of the unsaturated bond obeys the first order reaction up to above 90% saturation.

Analysis by X-ray diffraction. The Geigerflex model D-3F of Regaku-Denki Co. was used. The conditions were as follows: Cu K_α radiation (Ni filter); 35 kV; 15 mA; time constant, 4 sec; ratemeter scale factor, 32; divergence slit, 1°; scatter slit, 1°; receiving slit, 0.4 mm.

RESULTS AND DISCUSSION

Difference in the Increase in the Catalyst Activity by Methanol and Carbon Monoxide

Sixteen grams of methanol and 4.5 g of catalyst were added to 150 g of ester. The reaction system was heated under varied initial hydrogen pressures to 275°C in 1 hr. After the system was kept under the vacuum of 400 mm Hg for 10 min, the reaction was carried out at 275°C and the hydrogen pressure of 120 kg/cm^2. The first order rate constants are shown in Fig. 1, curve 1. The abscissa is the hydrogen pressure (gauge) at the beginning of heat-

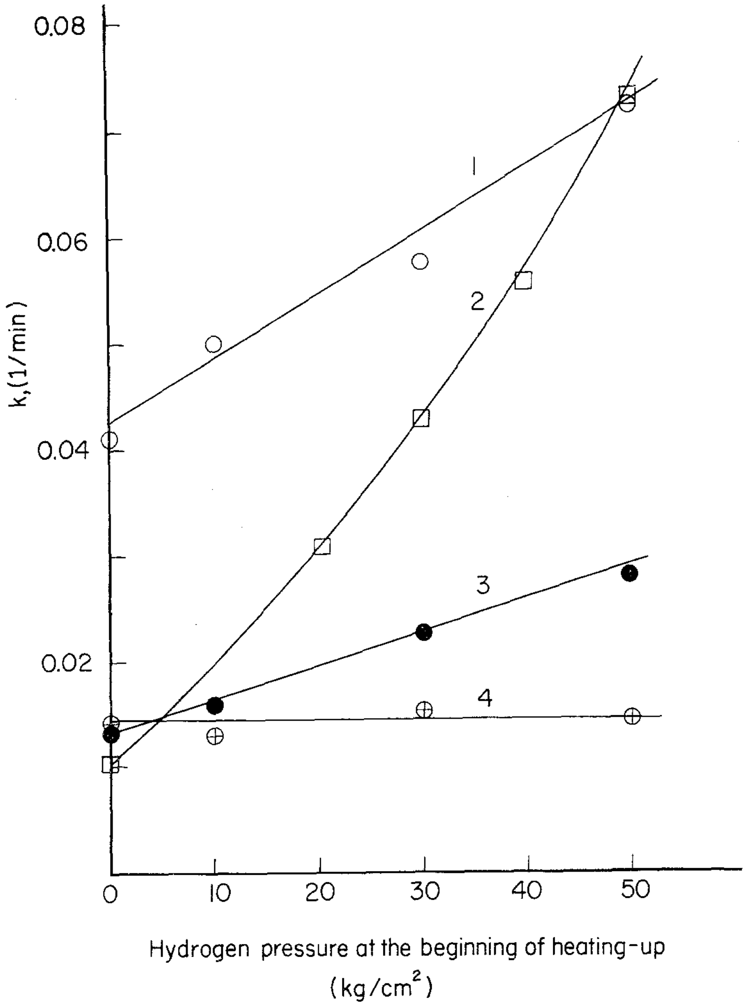

FIG. 1. Difference in the increase in the catalyst activity by methanol and carbon monoxide.

ing. Curve 3 shows results of the same experiments without adding methanol. Also, curve 4 shows results when neither methanol nor evacuation was applied.

Curve 2 is the result of the reactions carried out as follows. A mixture of 150 g of ester and 4.5 g of catalyst was heated up to 275°C under varied initial hydrogen pressures, then carbon monoxide was introduced up to 30 kg/cm^2 (at 275°C), and the system was kept at that state for 1 hr, then at 400 mm Hg for 10 min, after which the reaction was carried out at 120 kg/cm^2 and 275°C.

In both curves 1 and 2, the rate increases as the initial hydrogen pressure increases. But the two curves are different from each other in that on curve 1 the activity is high even at the hydrogen pressure of zero, whereas on curve 2 it is equal to the value of the blank (curve 4). As already described in the previous paper, carbon monoxide contributes to the phenomena of activity promotion, but the difference in curve 1 and 2 shows that hydrogen, too, has an effect. In the case of methanol hydrogen as well as carbon monoxide is formed by decomposition of added methanol even if the initial hydrogen pressure is zero (about 15 kg/cm^2, calibrated to the room temperature, when 275°C was reached), while in the case of carbon monoxide there is only a trace of hydrogen. As can be seen later, the higher the hydrogen pressure, the larger the extent to which the copper chromite catalyst, $CuO/CuCr_2O_4$ is reduced to Cu/Cr_2O_3. And as will be described later, the activity of Cu/Cr_2O_3 is increased when the water-gas reaction takes place on it. The ascension of curves 1 and 2 as the hydrogen pressure increases can be explained by the same reasons.

Reduction of $Cu/CuCr_2O_4$ *by Hydrogen*

There has been some confusion about the form of the true active catalyst of copper chromite. Adkins and co-workers (*8*) have stated that the catalysis action is due to CuO, and $CuCr_2O_4$ is a stabilizer. Brihta and others (*9*) have stated from thermodynamical consideration that the deactivation of CuO is caused by its changing into Cu_2O. On the other hand, Rabes *et al.* (*6*) have thought that fine Cu supported on Cr_2O_3 is the state of the catalyst in reactions. Stroup (*7*) has called attention to the fact that deactivation is often caused by reduction of $CuCr_2O_4$ to $Cu_2Cr_2O_4$ in a reaction with cupric oxide competing with the reduction of this oxide to metallic copper. But he stated nothing about the true catalyst.

We have studied this point and have come to the conclusion that the formula of the copper chromite catalyst is $CuO/CuCr_2O_4$ before use, in agreement with many authors, and Cu/Cr_2O_3 after use, in agreement with Rabes *et al.* (*6*). The course to these conclusions was as follows:

A new catalyst was heated in oxygen-free nitrogen at 500–550°C for 3 hr. Its X-ray diffraction pattern agreed completely with that of a mixture of CuO and $CuCr_2O_4$ (*7*). The catalyst was subjected to alkali fusion with a mixture of Na_2O_2 and K_2CO_3. Determination of Cu gave a formula of 1.08 $CuO/CuCr_2O_4$, which will hereafter be designated as $CuO/CuCr_2O_4$.

A sample of a catalyst which was used at 250 kg/cm^2 and 275°C was washed with ether and then with methanol by decantation to avoid contact with air, and then it was heated in nitrogen at 600°C for 10 hr. This sample gave an X-ray pattern completely agreeing with that of a mixture of Cu and Cr_2O_3, and there were not any peaks of CuO, Cu_2O, $CuCr_2O_4$, or $Cu_2Cr_2O_4$. In connection with this experiment, $Cu_2Cr_2O_4$, which was prepared from a new catalyst by heating it at 960°C for 5 hr and then by leaching it with concentrated hydrochloric acid, was heated at 600°C for 10 hr in nitrogen, but it showed no change into Cr_2O_3. The catalyst was repeatedly used several times for hydrogenation of ester, but it showed no change in activity.

From these experiments it is clear that the true active catalyst is Cu/Cr_2O_3, in agreement with Rábes (*6*).

It may be important to point out the following facts to avoid misunderstanding: The catalyst that Stroupe studied was a deactivated catalyst, and it had a red color, while our used catalyst was black and active. This difference seems to be a cause of an apparent disagreement between our results and those of Stroupe.

It is interesting to add that when the used catalyst, its composition being Cu/Cr_2O_3, was heated at 500–550°C for 3 hr in the air, it changed into the original form $CuO/CuCr_2O_4$. When a mixture of commercial Cu powders and Cr_2O_3 was heated at 960°C for 5 hr, the powders reacted and gave an X-ray pattern of $CuO/CuCr_2O_4$ in addition to those of Cr_2O_3 and $Cu_2Cr_2O_4$, though at 500–550°C for 3 hr, no reaction occurred. In contrast with this, Stroupe stated that when $Cu_2Cr_2O_4$ was heated at 600–700°C for several hours it also changed into $CuO + CuCr_2O_4$.

Though at least one of the forms of true active catalysts is Cu/Cr_2O_3, it cannot be denied that $CuO/CuCr_2O_4$ has any activity, because, as was mentioned previously, even when the ester hydrogenation is carried out at lower pressures, the reaction obeys first order kinetics, and if $CuO/CuCr_2O_4$ has no activity the reaction order must not be first order because of the increasing amount of Cu/Cr_2O_3 with reaction time.

Though the form of the catalyst after ordinary reactions is Cu/Cr_2O_3, the complete reduction of all $CuO/CuCr_2O_4$ into

Cu/Cr_2O_3 can be expected only under rather severe conditions (presumably above 100 kg/cm^2). When the hydrogen pressure at the beginning of heating is relatively low, as in this experiment, the rate of this reduction is relatively slow. This will be shown below.

In a 500-ml autoclave 100 g of ester and 10 g of catalyst were heated from room temperature to 275°C in 1 hr under varied initial hydrogen pressures. Immediately after the temperature reached 275°C, 2 liters (NTP) of gas from the gaseous phase was bubbled into methanol in 5 min, and the absorbed water was determined by the Karl Fischer method. The results are shown in Fig. 2, which clearly indicates that the reduction rate of the catalyst is not so rapid. (If the reduction of the catalyst is carried out in a dry state instead of a suspension in ester, the reduction proceeds very fast even with hydrogen at atmospheric pressure; about 2 moles of water are formed from 1 mole of catalyst at 80–100°C in a few minutes.)

In view of this result, it is clear that in the experiments of Fig. 1, curves 1 and 2, the catalyst reduction is not complete at the beginning of the reactions.

Synergistic Action of Water and Carbon Monoxide

As can be seen from Fig. 1, curve 2, the higher the hydrogen pressure, the more effective the promoting action of carbon monoxide. When the catalyst is reduced, water is formed. As will be described later, water is a catalyst poison, but if it coexists with carbon monoxide the activity of Cu/Cr_2O_3 is, on the contrary, increased, as shown below.

Sixty grams of $CuO/CuCr_2O_4$ was added

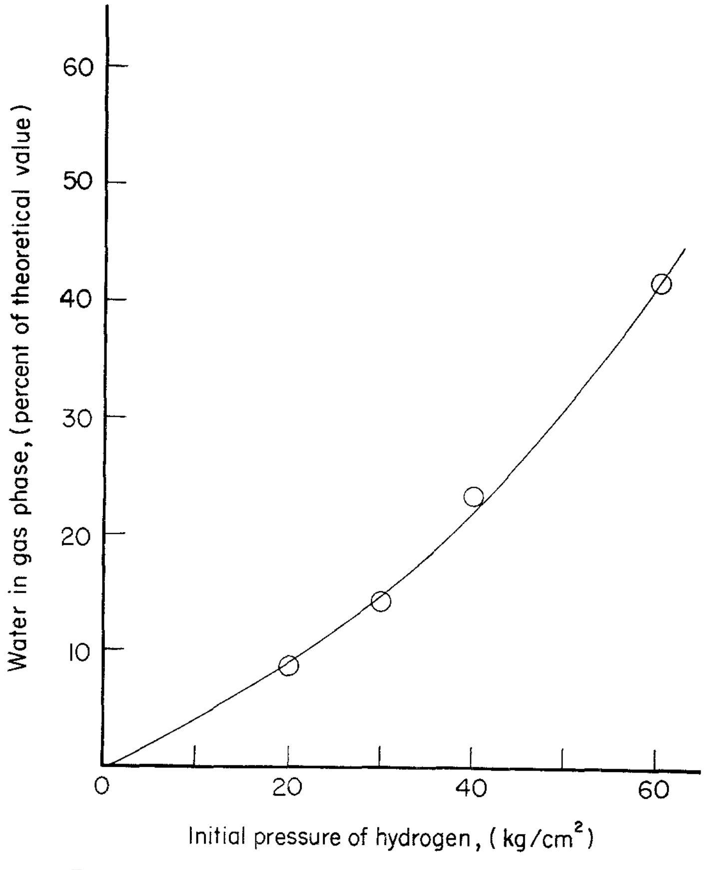

FIG. 2. Reduction of suspended catalyst by hydrogen.

to 100 g of ester and was completely reduced to Cu/Cr_2O_3 under the hydrogen pressure of 250 kg/cm^2 for 1 hr. The completeness of the reduction was checked by the conventional chemical analysis and X-ray diffraction method.

A portion of this paste equivalent to 4.5 g of $CuO/CuCr_2O_4$ was added to 150 g of ester. (The water content was not determined, because the Karl Fischer measurement is interfered with by copper.) Varied amounts of water were added to the mixture and it was heated up to 275°C in 1 hr under the initial carbon monoxide pressure of 30 kg/cm^2 and was kept at that temperature for 1 hr. After the system was kept at 400 mm Hg for 10 min, the reaction was carried out under the hydrogen pressure of 120 kg/cm^2 at 275°C. As shown in Fig. 3, k in these experiments increases with increasing amount of water added; k' is the rate constant of the hydrogenation reaction of the double bond. The reaction is first order in the concentration of double bond when the pressure and the catalyst amount are constant.

The increased activities in the experiments of Fig. 1, curves 1 and 2, are due to

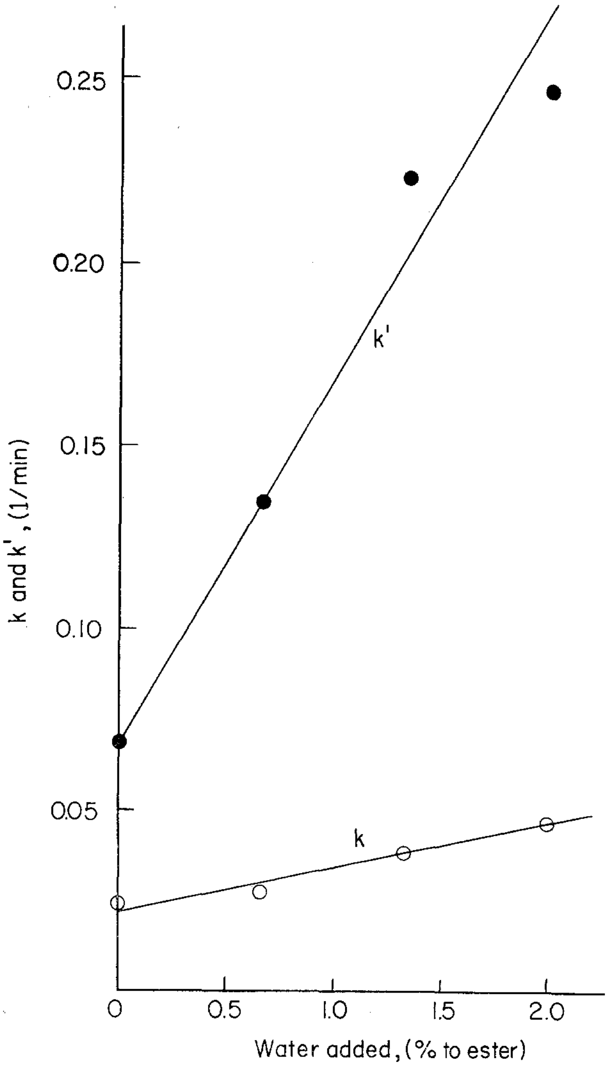

FIG. 3. Increase in activity by coexistence of water and carbon monoxide.

the synergistic action of water and carbon monoxide upon Cu/Cr_2O_3; this Cu/Cr_2O_3 ratio increases with increasing hydrogen pressure.

Poisoning Action of Water

The same experiments as in the preceding section were carried out with the hydrogen pressure of 10 kg/cm^2 instead of carbon monoxide. The results are shown in Fig. 4. It is clear that water is a catalyst poison. The fact that when no water was added *k* was 0.02, and when neither water was added nor evacuation was applied (blank—Fig. 1, curve 4) *k* was 0.013, shows that in the blank reaction the water formed by the reduction of the catalyst is adsorbed onto the catalyst to form $Cu/Cr_2O_3 \cdot (H_2O)_{ad}$ and this water can be desorbed by the evacuation. Furthermore, considering the fact that when the amount of water increases, *k* decreases, the desorption of water may be incomplete under the conditions of the present experiments. In conclusion, the adsorption of water is neither so strong nor so weak.

As shown above, water is adsorbed in equilibrium on the catalyst. In other words, a larger amount of total water results in a larger amount of water adsorbed on the catalyst. Thus in the experiments of the preceding section, as well as in those of the present section, more water has resulted in a larger amount of $Cu/Cr_2O_3 \cdot (H_2O)_{ad}$; and the addition of carbon monoxide followed by evacuation is considered to have increased the catalyst activity.

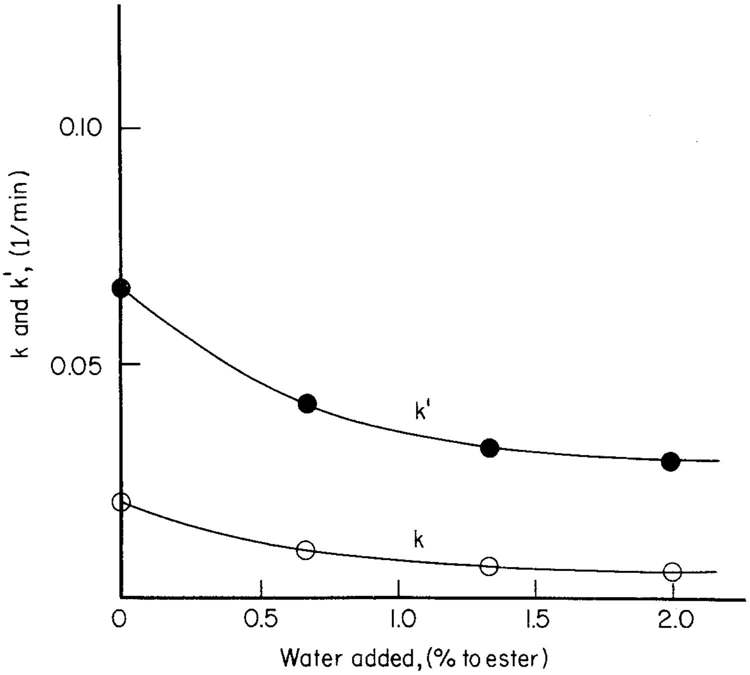

FIG. 4. Poisoning action of water.

Reaction of Water and Carbon Monoxide on the Copper Chromite Catalyst

Lawson *et al.* (*11*) have stated that there is a possibility that the water-gas reaction may take place on the copper catalyst. Of the experiments shown in Fig. 3 one experiment in which, for instance, 0.60% of water was added, is illustrated in Fig. 5, which shows the course of the decrease of S.V. and I.V. with reaction time. At the reaction time zero, i.e., immediately after the hydrogen pressure is built up to 120 kg/cm^2, I.V. is 68, which is much less than 102, the I.V. of the starting ester. This

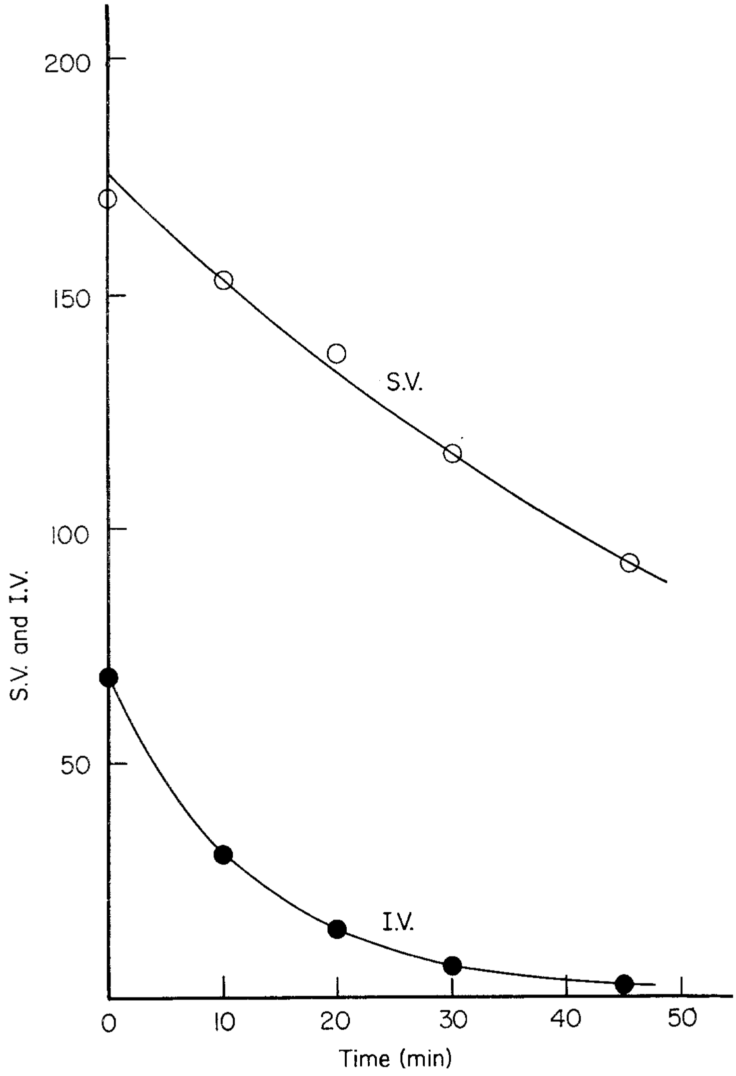

FIG. 5. Decrease of S. V. and I. V. when ester added with 0.6% of water and carbon monoxide was reduced in the presence of Cu/Cr_2O_3. (Refer to Fig. 3.)

suggests that hydrogen is formed from carbon monoxide and water by the water-gas reaction during the heating-up of the reaction system. We have verified further in the following way that this reaction does occur on the copper chromite catalyst. Fundamentally, whether the reaction really takes place or not must be studied under conditions where the catalyst is suspended in ester. But this is not feasible, because in this case the ester would be subjected to hydrolysis to form methanol, which would further be decomposed to carbon monoxide and water, and there is a possibility that the carbon monoxide will form carbon dioxide by the reactions $2CO \rightarrow C + CO$, and $2CO + 2H_2 \rightarrow CH_4 + CO_2$ etc. Thus there exists a possibility of a substantial amount of carbon dioxide being formed when a large amount of water is used. Therefore, Cu/Cr_2O_3 was suspended in higher alcohol, to which water and carbon monoxide were added, and whether the reaction, $CO + H_2O \rightarrow CO_2 + H_2$, takes place or not was examined.

There is, of course, a possibility in this case also that the above side reactions may occur. But in these side reactions only 1 mole of carbon dioxide is formed from 2 moles of carbon monoxide. [The water-gas reaction is an equilibrium reaction. But the equilibrium constant K_p is about 56 (*12*) at 275°C, so that the equilibrium will be far to the right.] Therefore, formation of a nearly equimolar amount of carbon dioxide from original carbon monoxide will undoubtedly indicate the occurrence of the water-gas reaction.

A new catalyst was reduced in ester under severe conditions to yield Cu/Cr_2O_3. This was washed several times with coconut higher alcohol. An aliquot which was equivalent to 4.5 g of $CuO/CuCr_2O_4$ was suspended in 150 g of coconut fatty alcohol. This was further added with 2 g of water and was heated up to 275°C under the initial carbon monoxide pressure of 30 kg/cm^2 and was kept at that temperature for 1 hr. By analysis of the composition of the gas phase, carbon dioxide equivalent to 95% of added water was found. Thus it can be said that the water-gas reaction takes place on Cu/Cr_2O_3.

From the above it is possible to deduce as follows:

When new catalyst is reduced, $CuO/CuCr_2O_4$ changes partly into Cu/Cr_2O_3 and partly into $Cu/Cr_2O_3 \cdot (H_2O)_{ad}$. If water is added to this, $Cu/Cr_2O_3 \cdot (H_2O)_{ad}$ increases. By the action of carbon monoxide, $Cu/Cr_2O_3 \cdot (CO_2)_{ad}$ is formed, which turns into Cu/Cr_2O_3 by the evacuation. Cu/Cr_2O_3 thus formed is more active than the original Cu/Cr_2O_3. This increase in activity is caused by the increase in "activity" itself rather than the increase in the number of so-called "active centers."

The reasons for this deduction are as follows: As described previously, when only water is added, the larger the amount of added water, the larger the amount of adsorbed water, thus making the activity smaller. Therefore, the active part of the catalyst is Cu/Cr_2O_3 and not $Cu/Cr_2O_3 \cdot (H_2O)_{ad}$, or at least, the activity of $Cu/Cr_2O_3 \cdot (H_2O)_{ad}$ is smaller than that of Cu/Cr_2O_3. When the amount of water becomes larger the amount of Cu/Cr_2O_3 becomes less. On the other hand, in the case where water and then carbon monoxide are added, followed by the evacuation, a larger amount of water would never result in a smaller portion of catalyst remaining as $Cu/Cr_2O_3 \cdot (H_2O)_{ad}$ if it might ever result in a larger portion. Therefore, the portion which takes the form of Cu/Cr_2O_3 will be smaller as the amount of water increases. Nevertheless, a larger amount of water results in a larger activity. Therefore, Cu/Cr_2O_3 which has been formed by the treatment of water and carbon monoxide and the evacuation must have a larger activity than that which has not been subjected to this treatment even though the forms are same. But the mechanism is still unknown.

The particle-size distributions of the activated catalyst and the ordinary catalyst were examined by the X-ray small angle scattering method, but no difference was observed between these two.

Reverse Poisoning by Carbon Dioxide.

In the preceding section we described without explanation that the form of the catalyst before evacuation was $Cu/Cr_2O_3 \cdot (CO_2)_{ad}$.

In the experiments of Fig. 1, curve 2, when the initial hydrogen pressure was 50 kg/cm^2, $k = 0.032$ (calibrated for the partial pressure of carbon monoxide) if evacuation was not applied. By evacuation this was raised to 0.072. Therefore, the form before the evacuation may be regarded as $Cu/Cr_2O_3 \cdot (CO_2)_{ad}$. To verify this more closely the following experiments were carried out. To a system containing the above catalyst of the activity of 0.072, 4 kg/cm^2 of carbon dioxide was added and the system was maintained for 10 min at 275°C, then the reaction was carried out; k was lowered to 0.010. On the other hand, if the reaction was carried out after this carbon dioxide was evacuated again, k was restored to 0.047.

It is clear from the above experiments that carbon dioxide is a reverse poison to Cu/Cr_2O_3.

Direct Reduction of the Catalyst by Carbon Monoxide

By evacuation of $Cu/Cr_2O_3 \cdot (CO_2)_{ad}$ the activity of the catalyst was increased. Then it may be expected that the activity will also be increased by evacuating $Cu/Cr_2O_3 \cdot (CO_2)_{ad}$ that is formed by the reduction of $CuO/CuCr_2O_4$ with carbon monoxide. But the results were contrary to the expectation, as described below.

One hundred and fifty grams of ester was added with 4.5 g of $CuO/CuCr_2O_4$ and was heated under the initial carbon monoxide pressure of 30 kg/cm^2. After the temperature reached 275°C, the system was kept at that temperature for 1 hr. A small sample from the gas phase was withdrawn and was analyzed for the amount of carbon dioxide by the usual method. The reduction in percentage was about 90. To match the conditions with the experiments of Fig. 3 as much as possible, the system was once cooled and the gas in the autoclave was discarded, then carbon monoxide was added up to 30 kg/cm^2, and the system was heated to 275°C in 1 hr; after being kept at that temperature for 1 hr, the system was evacuated. Then the reaction was carried out at the hydrogen pressure of 120 kg/cm^2 and at 275°C. The valve $k = 0.0035$ was obtained, i.e., the activity of the catalyst was not increased but on the contrary, decreased.

The ester used here was one containing 0.023% of water. In the case where water was added in varied amounts to this ester, the activity was also scarcely increased. The results are shown in Fig. 6.

On the other hand, k' was also smaller than that of the blank (0.045) when no water was added, but it increased with an increasing amount of water. However, the degree of increase was much smaller than that of Fig. 3.

In the experiments of Fig. 6, water was added at the second step of the carbon monoxide treatment, but the results were almost the same as those of Fig. 6.

Both in the experiments of Fig. 3 and

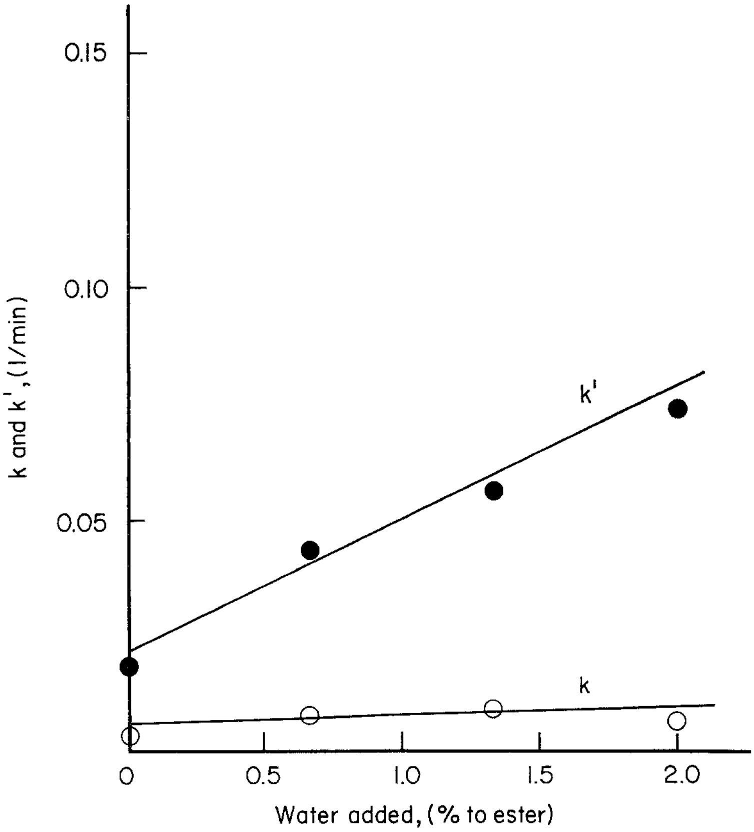

FIG. 6. Activity of the catalyst reduced by carbon monoxide.

Fig. 6, the chemical species existing in the reaction system may be the same. Nevertheless, the results are not the same. But the reasons are still not known.

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