A Study of Catalysis by Uranium Oxide and Its Mixed Catalysts. IX.[1]
A Catalytic Reduction of Nitric Oxide with Carbon Monoxide

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The reduction of NO with CO over the uranium oxide catalyst and its mixed catalysts with alkali metal oxide or alkaline earth metal oxide has been investigated using conventional flow and pulse reactors at temperatures of 250 to 450 °C under atmospheric pressure. The activity of the uranium oxide catalyst without any additive was higher than that of the Fe_2O_3 catalyst, although it was inferior to that of the CuO-Cr_2O_3 catalyst. The addition of alkali metal oxide or alkaline earth metal oxide to uranium oxide, particularly in the case of Cs_2O or K_2O, was effective in enhancing the catalyst activity. The W/F-conversion curves revealed that the reduction of NO to N_2 proceeds consecutively, passing through N_2O as a gas-phase intermediate. The reaction rates were formulated as $r=kP_{\mathrm{CO}}^{1.0}P_{\mathrm{NO}}^{0.4}$. The kinetic study suggested a redox reaction sequence. The oxidation states of the catalysts were discussed on the basis of X-ray diffractograms.

The catalytic reduction of NO with CO, H_2 or NH_3 has recently been investigated very actively as part of a comprehensive study of air pollution control, and much useful information has been presented in both fundamental study and development research.[2] In spite of the considerable number of publications on the catalysts, however, few reports have been published about the uranium oxide catalyst. Our preliminary study has revealed that uranium oxide has a high activity for NO–CO reaction.

In this paper, we will describe the behavior of uranium oxide as a catalyst and the influence of the addition of alkali metal oxide or alkaline earth metal oxide upon the catalytic activity. In addition, the results of a kinetic study and details of the catalyst structure will be given.

Experimental

Catalyst Preparation. The uranium oxide catalyst without additive (to be subsequently referred to as the U catalyst) was prepared by the method described in a previous paper.[3] The mixed catalysts with alkali metal oxide or alkaline earth metal oxide were prepared by the wet mixing method: the prescribed amount of an aqueous solution of Cs_2CO_3, KOH, NaOH, $Ca(OH)_2$, or $Mg(OH)_2$ was added to the yellow precipitate $(NH_4)_2U_2O_7$, obtained from $UO_2(NO_3)_2$ by precipitation with NH_4OH. The respective slurries were followed by drying in an air oven at the temperature of 110 °C. The resulting paste-like solid masses were well-mixed by a knead-machine for 3 hr, and were then extruded to obtain the desired pellet size. (These mixed catalysts will subsequently be referred to as the U–Cs catalyst, the U–K catalyst, *etc.*) A series of catalysts containing a certain kind of metal oxide in different proportions was prepared by the same method. The compositions of the mixed catalysts were expressed by the atomic M/(U+M) ratio, where M represents the species of the metals added to the catalyst as an oxide. All the catalysts were calcined at 500 °C for 2 hr in a stream of air before use in the catalytic tests. After calcination, the U catalyst was green-black in color; all of the mixed catalysts with alkali metal oxide or alkaline earth metal oxide were tan-orange, although their chroma was somewhat different from one another, depending upon the catalyst composition. The specific surface areas of the catalysts were determined according to the BET method, using nitrogen as the adsorbate.

In order to characterize the U catalyst, three kinds of commercial catalysts were used; the CuO–Cr_2O_3 catalyst (Nissan-Kemetron, Inc., type G-22; CuO 42%, Cr_2O_3 40%, BaO 12%), the Pt–Al_2O_3 catalyst (Nippon-Engelhard, Inc., Pt 0.5%), and the Fe_2O_3 catalyst (Shell, Inc., type 105; Fe_2O_3 93%, Cr_2O_3 5%, K_2CO_3 2%). These catalysts were also calcined at 500 °C for 2 hr in a stream of air before use.

Apparatus and Analysis. Most of the catalytic-activity measurements were carried out on a conventional flow apparatus consisting of a 18 mmϕ glass reactor. The reactor contained a packed bed consisting of 1.0 g of the catalyst and small glass-beads in the ratio of 1 : 10 by volume, thereby improving the isothermal conditions during the course of reaction. Before the start of the experiments, the catalyst was heated in a stream of helium to 500 °C for 1 hr, and then cooled to the reaction temperature. A mixture of NO and CO was admitted into the reactor at a constant rate of flow. After we had ascertained that the flow system had attained a stationary state, we began to analyze the product stream. The reaction products and the reactor feed were introduced at regular time intervals into a gas-chromatographic unit consisting of a 0.5-m column of Porapak Q and a 1-m column of Molecular Sieve 13X. The columns were operated at room temperature, with helium as the carrier gas; a detector of a thermal-conductivity type was placed between the Porapak and Molecular Sieve columns. Such a procedure permitted a satisfactory analysis of the mixture consisting of N_2, N_2O, NO, CO, and CO_2, even with the injection of only one sampling.

Considering the stoichiometry of the reaction, the conversion of NO, x_{NO}, and the selectivity, $S_{\mathrm{N_2}}$, for nitrogen formation were given by:

$$x_{\mathrm{NO}} = \frac{\mathrm{N_2+N_2O}}{\mathrm{N_2+N_2O+1/2\,NO}} \tag{1}$$

$$S_{\mathrm{N_2}} = \frac{\mathrm{N_2}}{\mathrm{N_2+N_2O}} \tag{2}$$

In order to elucidate the reaction mechanism, some of the experiments were carried out on a conventional pulse-reaction method, using helium as the carrier gas. The gas-chromatographic unit described above served as an analytical tool.

X-Ray Diffractograms of the Catalysts. X-Ray diffraction measurements were made for the purpose of qualitatively identifying the catalysts. The X-ray diffractograms of the powdered samples were obtained at room temperature by using Ni-filtered copper radiation (Rigaku Denki Co., Geigerflex D-3F spectrometer).

Results and Discussion

Activity of the U Catalyst and the Pressure-dependency of Reaction Rates. The change in the catalyst activity during the course of the reaction was practically negligible throughout the catalytic tests.

In Fig. 1, the activity and the selectivity of the U catalyst are compared with those of commercial catalysts. Figure 1 indicates that the catalytic activity decreases in this order: $CuO-Cr_2O_3 > U > Fe_2O_3 > Pt-Al_2O_3$; the $Pt-Al_2O_3$ catalyst does not begin to be active until much higher temperatures than the other catalysts, but, in such a case, the degree of reaction approches the level of 90%, the relative activity of the Pt catalyst is rather higher than those of the U and Fe_2O_3 catalysts. The selectivity, S_{N_2}, for nitrogen formation was inclined to increase with an increase in the reaction temperature in every catalyst. In the case of the U catalyst, the selectivity curve appears to have its minimum at temperatures near 300 °C. However, a steep dip as described in the literature[4,5)] was not observed under the reaction conditions of this work.

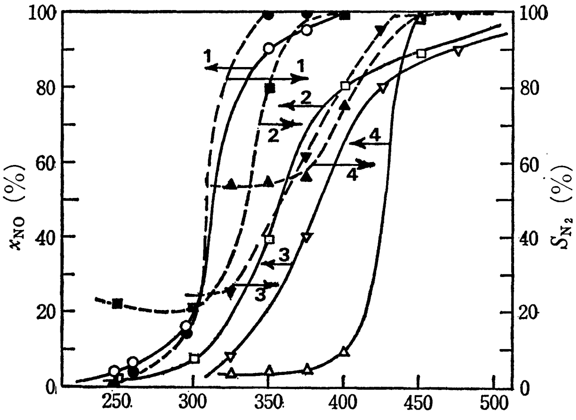

Fig. 1. Activities and selectivities of various catalysts. 1: $CuO-Cr_2O_3$, 2: U, 3: Fe_2O_3, 4: $Pt-Al_2O_3$. Catalyst weight (W): 1.0 g, NO/CO feed ratio (m): 1.0, Flow rate of feed gas (F): 50 ml/min.

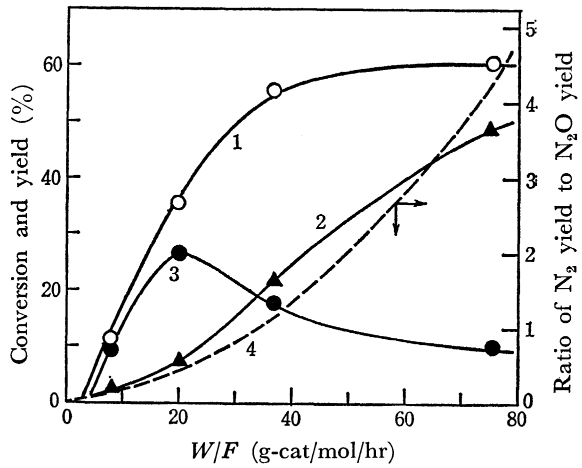

Fig. 2. Effects of W/F on the catalytic reaction. 1: x_{NO}, 2: N_2 yield ($=x_{NO}\times S_{N_2}$), 3: N_2O yield ($=x_{NO}-x_{NO}\cdot S_{N_2}$), 4: Ratio of N_2 yield to N_2O yield. Reaction temperature (t): 310 °C, m: 1.0.

It must be noted that the U catalyst has a high activity for the NO–CO reaction; nevertheless, uranium oxide belongs to the class of heavy metal oxides which also includes MoO_3, V_2O_5, and WO_3. The MoO_3, V_2O_5, and WO_3 catalysts exhibited very little activity; the x_{NO} values were only a few %, even when the reaction temperature was raised to 500 °C. The fact that the activity of the U catalyst for the NO–CO reaction was exceptionally high for a heavy metal oxide catalyst was quite similar to the finding previously reported in the study of $CO-O_2$ reaction.[3)]

Figure 2 shows the influence of W/F on the results of the reaction. The N_2O yield–W/F curve reaches a maximum. In addition, the curve of the ratio of the N_2 yield to the N_2O yield passes through the point of origin, as it increases with an increase in W/F. These facts suggest that the reduction of NO to N_2 proceeds consecutively, passing through N_2O as a gas-phase intermediate.

The rate measurements were conducted in a low range of W/F, in which one may assume the differential reactor. The reaction rate, r, can be obtained from the slopes of the linear relationship between $y_0 \cdot x_{NO}$ (y_0: mol-fraction of NO at the inlet of the reactor) and W/F. The dependence of the reaction rates on the partial pressure of NO or CO is illustrated in Fig. 3. It can be seen from Fig. 3 that the reaction rates are expressed by this equation:

$$r = kP_{CO}^{0.1}P_{NO}^{0.4} \tag{3}$$

where k is the reaction rate constant in mol/g-cat hr atm$^{1.4}$.

Influences of the Addition of Alkali Metal Oxide or Alkaline Earth Metal Oxide upon the Activity of the Uranium Oxide Catalyst. Temperature-conversion curves over the U–Cs catalysts containing cesium oxide in different proportions are shown in Fig. 4. Since the selectivity, S_{N_2}, for nitrogen formation showed a behavior similar to that in Fig. 1, the conversion datum alone is plotted in Fig. 4 as a function of the reaction temperature.

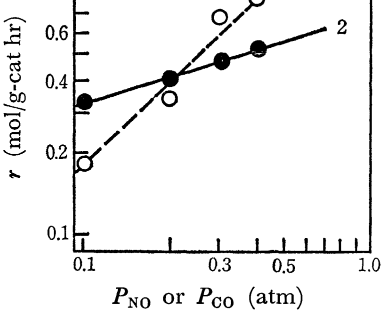

Fig. 3. Reaction rates as a function of NO or CO partial pressure.
1: Effect of CO partial pressure (P_{NO} was kept at constant pressure of 0.1 atm).
2: Effect of NO partial pressure (P_{CO} was kept at constant pressure of 0.1 atm).
Total pressure ($\pi = P_{CO}+P_{NO}+P_{He}$): 1 atm, t: 310 °C.

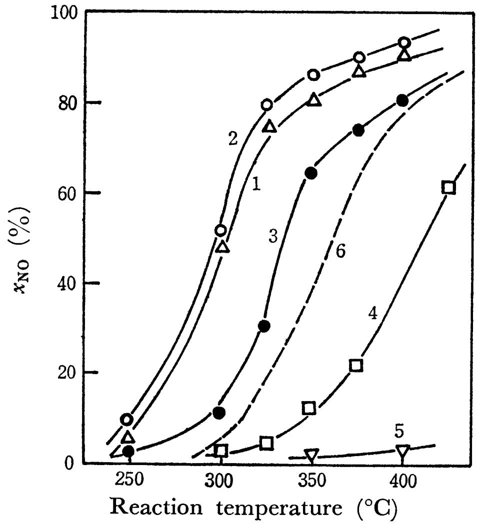

Fig. 4. Temperature-conversion curves over the catalysts containing Cs_2O in a different proportion.
Catalyst composition in atomic Cs/(U+Cs) ratio—1: 0.1, 2: 0.2, 3: 0.3, 4: 0.4, 5: 0.5, 6: 0.0 (U catalyst without Cs_2O).
Reaction conditions are the same as for Fig. 1.

Figure 4 indicates that the U–Cs catalysts with an adequate composition are much more active than the U catalyst without Cs_2O. In order to make a quantitative expression of the results, the rate constants, k_{flow}, were calculated according to a conventional manner for the ideal tubular flow reactor: at the point in the reactor where the conversion is x_{NO}, P_{NO} and P_{CO} may be written as $P_{NO}=P_{CO}=(1-x_{NO})/(2-0.5x_{NO})$ by taking into account the stoichiometry of the reaction and the feed NO/CO ratio of 1.0. Thus,

$$k_{flow}=\frac{y_0}{W/F}\int_0^x\frac{dx}{r}=\frac{0.5}{W/F}\int_0^{x_{NO}}\left(\frac{2-0.5x_{NO}}{1-x_{NO}}\right)^{1.4}dx_{NO} \quad (4)$$

From the series of conversion data shown in Fig. 4, the values of k_{flow} at 350 °C were evaluated by means of a graphical integral in Eq. (4) for each experimental point. The values are plotted in Fig. 5 as a function of the catalyst composition, together with the data relating to the BET surface area of the catalysts. Figure 5 shows that the catalyst activity increases with an increase in the atomic (Cs/U+Cs) ratio, passes through a maximum at about 0.2, and then almost disappears above 0.5. The k_{flow} value of the U–Cs catalyst with an atomic ratio of 0.2 was about five times that of the U catalyst without any additive. An increase in the activity upon the addition of Cs_2O was achieved in the range with a lower atomic Cs/U+Cs ratio than 0.3, and the further addition of (Cs_2O) resulted in a decrease in the activity. The correlation between the surface area of the catalysts and the composition of the catalysts leads us to the conclusion that the enhancing of activity attributable to Cs_2O addition is independent of the change in the surface area of the catalysts.

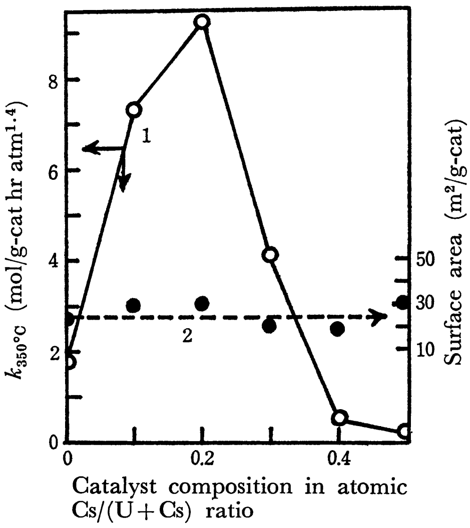

Fig. 5. Rate constant and surface area of U–Cs catalyst as a function of catalyst composition.
1: Rate constant *vs.* catalyst composition.
2: Surface area *vs.* catalyst composition.

The temperature-conversion curves over the other mixed catalysts are shown in Fig. 6. Figure 6 depicts that the addition of K_2O, Na_2O, CaO or MgO is in every cases effective in the modification of catalyst activity, although the influence of CaO and MgO upon the enhancing of activity is very slight. The effect of K_2O on activity was particularly noteworthy, by analogy with the Cs_2O addition. The modified catalysts with Cs_2O or K_2O added were superior in activity to the $CuO-Cr_2O_3$ catalyst, or at least to a catalyst of comparable magnitude. Thus, it appears established that the enhancing of the activity of the uranium oxide catalyst can be realized by the addition of small amounts of Cs_2O or K_2O, which are alkali metal oxides with lower electronegative properties.

A Plausible Reaction Mechanism. The results of an experiment in which the pulse-reaction method was employed to characterize the reduction and re-oxidation processes of the catalyst are shown in Figs. 7 and 8. Figure 7 suggests that the re-oxidation of

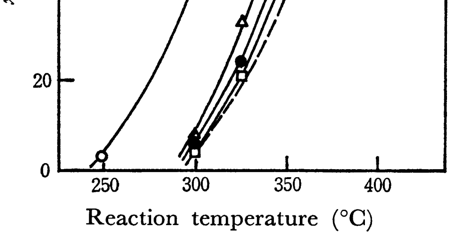

Fig. 6. Temperature-conversion curves over the catalysts containing various additives.
1: U-K, 2: U-Na, 3: U-Ca, 4: U-Mg, 5: U-without additive
Catalyst composition: M/(U+M)=0.2, Reaction conditions are the same as for Fig. 1.

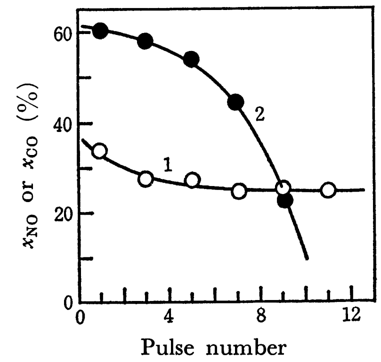

Fig. 7. Changes in conversion with repeated sample injections in pulse-reaction method.
1: Change in CO conversion, when CO pulses were injected to the fresh U catalyst.
2: Change in NO conversion, when NO pulses were injected to the reduced U catalyst.
W: 0.2 g, t: 350 °C, Pulse size: 0.5 ml, Helium flow rate as a carrier gas (F'): 20 ml/min.

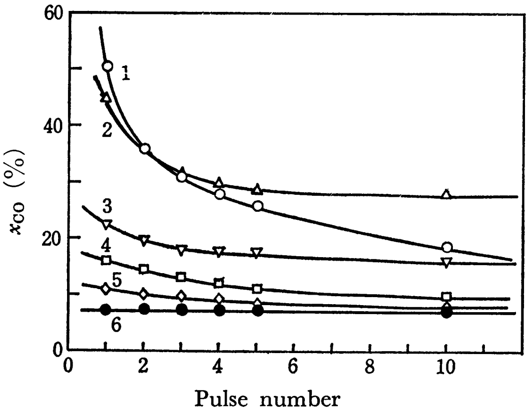

Fig. 8. Comparison of reduction rates in the catalysts with and without additive.
Catalyst—1: U-Cs, 2: U-K, 3: U-Na, 4: U-Ca, 5: U-Mg, 6: U-without additive.
Composition of the catalysts containing additive is 0.2 in atomic M/(U+M) ratio.
W: 0.1 g, t: 350 °C, Pulse size of CO: 0.8 ml, F': 30 ml/min.

the reduced catalyst with NO pulses takes place more rapidly than the reduction of the catalyst with CO pulses. Figure 8, in which the facilities and regularities in the reduction of various catalysts are compared to one another, indicates that the ease of reduction decreases in this order: U-Cs>U-K>U-Na>U-Ca>U-Mg>U; this order is in accord with that of the catalyst activity. On the basis of information obtained in Figs. 7 and 8, we have speculated on a mechanism for the NO–CO reaction featuring the following reduction-reoxidation sequence:

$$\text{CAT-O} + \text{CO} \xrightarrow{A} \text{CAT} + \text{CO}_2 \tag{5}$$

$$\text{CAT} + \text{NO} \longrightarrow \text{CAT-O} + 1/2\text{N}_2 \tag{6}$$

where CAT-O and CAT represent an active site on the catalyst and its site as reduced by CO respectively. Provided that the rate-limiting step in the redox sequence is a reduction process of the catalyst by CO, as is shown by Eq. (5), both the results of Fig. 7 and the kinetic orders of Eq. (3) are readily understandable.

In order to make the successive order of the reduction rates of various catalysts clearer, we have analyzed the conversion data of Fig. 8 by two methods. One of the methods is to calculate the rate constant from the values of x_{CO} at the first pulse, using the rate equation for a pulse-reaction system:[6)]

$$k_{\text{pulse, CAT-O+CO}} = \frac{1}{273R\ W/F} \ln \frac{1}{1-x_{CO}} \tag{7}$$

The other method is to determine the coefficient of the variation in the CO conversion at the initial stage; $(\Delta x_{CO}/\text{pulse number})_0$ was evaluated from the conversion data of the first and second pulses for each catalyst.

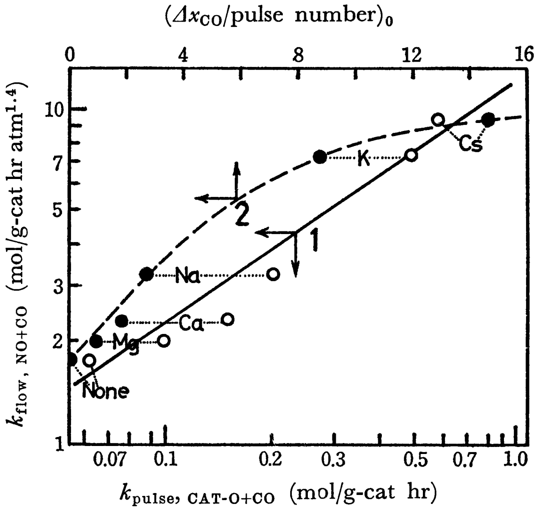

Fig. 9. Correlation between activity of the catalysts and reducibility of the catalysts.
1: $k_{\text{pulse, CAT-O+CO}}$ vs. $k_{\text{flow, NO+CO}}$.
2: $(\Delta x_{CO}/\text{pulse number})_0$ vs. $k_{\text{flow, NO+CO}}$.

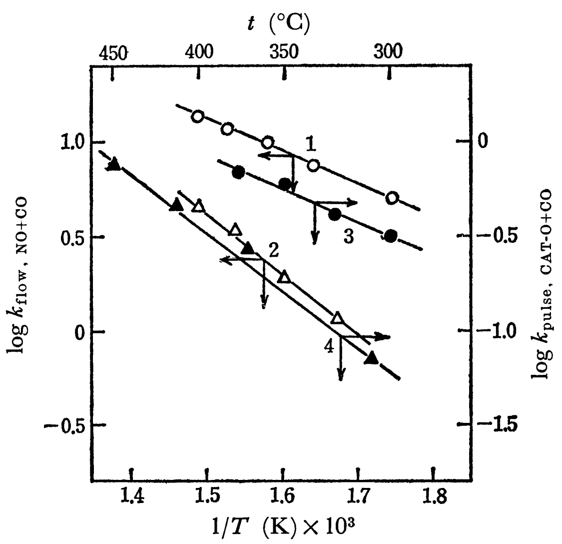

Fig. 10. Arrhenius plots for the rate constants.
1: Rate constants of NO-CO reaction over U-Cs catalyst in flow method, 2: Rate constant of NO-CO reaction over U catalyst in flow method, 3: Reduction rate constant of U-Cs catalyst in pulse method, 4: Reduction rate constant of U catalyst in pulse method.

In Fig. 9, the resulting two parameters by which the ease of reduction by CO is represented are correlated to k_{flow}. Figure 9 shows that there is a direct correlation between k_{flow} and the k_{pulse} parameter or $(\Delta x_{\text{CO}}/\text{pulse number})_0$.

Arrhenius plots of the rate constants for the U and U–Cs catalysts are illustrated in Fig. 10. Both log k_{flow} and log k_{pulse} are correlated to $1/T$ by straight lines. The apparent activation energy was found to be about 8 kcal/mol for the U–Cs catalyst and about 15 kcal/mol for the U catalyst. The finding to be emphasized here is that the activation energy observed in a flow-reaction method is entirely consistent with that of the reduction process of CAT-O by CO in a pulse-reaction method. This is suggestive of the redox mechanism which is expressed in the forms of Eqs. (5) and (6). However, a more detailed experiment, *e.g.*, tracer work labeled with an oxygen-18 isotope, is necessary to confirm the reaction mechanism. In this paper, it can only be said that all the experimental results have been interpreted satisfactorily on the basis of the redox mechanism.

X-Ray Diffractograms of the Catalysts. The X-ray diffractograms of the catalyst samples are shown in Fig. 11. Diagram 4, for the U catalyst, reveals that the sample consists mainly of U_3O_8. In contrast, Diagram 1, 2, and 3 for the catalysts containing Cs_2O, K_2O, and Na_2O respectively, show, without exception, that the definite peaks attributable to $UO_3 \cdot 2H_2O$ are present, together with minor peaks the assignment of which is unknown. The $UO_3 \cdot 2H_2O$ compound results when UO_3 is allowed to stand in contact with air containing moisture; the hydrate is quickly reconverted into UO_3 by heating above 200 °C, as has previously been described.[7] The peaks attributable to $UO_3 \cdot 2H_2O$ were likewise observed in the catalysts containing CaO or MgO; however, in such cases the diffraction lines were weak in intensity.

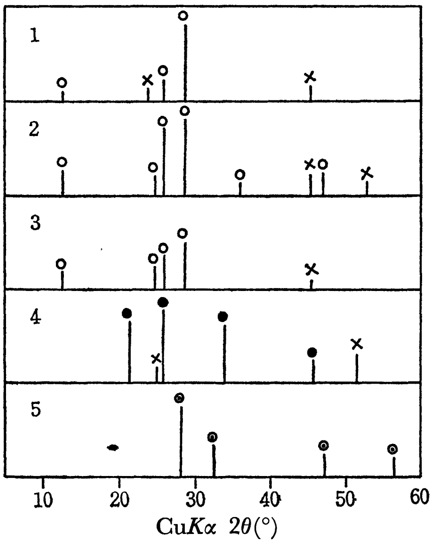

Fig. 11. X-ray diffractograms of the catalysts.
1: U–Cs catalyst (atomic Cs/(U+Cs) ratio: 0.2) before use for reaction, 2: U–K catalyst (atomic K/(U+K) ratio: 0.2) before use for reaction, 3: U–Na catalyst (atomic Na/(U+Na) ratio: 0.2) before use for reaction, 4: U catalyst before and after use for reaction, 5: U–Cs catalyst (atomic Cs/(U+Cs) ratio: 0.2) after use for reaction.
○: Peak attributable to $UO_3 \cdot 2H_2O$ (Ref. ASTM card 13—408), ●: Peak attributable to U_3O_8 (Ref. ASTM card 2-276), ⊙: Peak attributable to U_3O_7 (Ref. ASTM card 15—4), ×: Unknown peak for assignment.

Thus, it may be concluded that the addition of small amounts of alkali metal oxide or alkaline earth metal oxide can be used to elevate the oxidation state of U_3O_8 to UO_3. This can also readily be understood from the great difference in color between the U catalyst without any additive and the mixed catalysts; the former was green-black, characteristic of U_3O_8, whereas the latter was tan-orange, characteristic of UO_3.

The X-ray diffraction pattern of the U catalyst was entirely unchanged even after the catalyst had been used for the catalytic reaction. In contrast, the diffractogram of the U–Cs catalyst after having been used for the reaction (Diagram 5) was greatly different from Diagram 1, and the peaks were identified as belonging to those of U_3O_7. Therefore, one is forced to consider that, during the reaction, the oxidation state of uranium oxide is lower in the U–Cs catalyst than in the U catalyst. This fact is in conflict with the redox mechanism described in the previous section, because the oxidation state of the catalysts is considered to remain unaltered through the NO–CO reaction provided it proceeds *via* the sequence of Eqs. (5) and (6). This problem has not yet been completely elucidated, but it has been speculated that the U–Cs catalyst is more liable than the U catalyst to lead the formation of N_2O and that its use results in an excess of CO by unbalancing the redox reaction sequence of Eqs. (5) and (6), whereupon the reduction to the lower oxidation state takes place in the case of the U–Cs catalyst. However, a further investigation of the surface structure directly responsible for the catalytic reaction is required for a comprehensive understanding of the uranium oxide as a catalyst.

In the X-ray diffractograms of the catalysts containing alkali metal oxide or alkaline earth metal oxide, the peaks corresponding to the normal uranate and/or polyuranate structures were completely missing. The uranate K_2UO_4, which was prepared by a soaking method in a separate batch, showed only a very low activity in the NO–CO reaction.

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