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Fixation of Carbon Dioxide to Carbon by Catalytic Reduction over Metal Oxides

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The catalytic reduction of CO_2 to carbon with hydrogen was studied on the oxide catalysts for the fixation of carbon dioxide. Carbon dioxide was reduced to carbon and carbon monoxide selectively on the oxide catalysts. The catalyst, WO_3, is highly active for reducing carbon dioxide to carbon.

On a global scale, carbon dioxide concentration in atmosphere have increased by nearly 25% since the industrial revolution.[1,2] Carbon dioxide is one of the so-called "greenhouse gases" and makes a significant contribution to the global warming.[3] Therefore, a CO_2 fixation should be demanded urgently for preventing the greenhouse effect. Several methods have been proposed for the CO_2 fixation.[4-6] Catalytic fixation of carbon dioxide has an advantage in a fast rate for CO_2 fixation, and so this method can treat a large quantity of CO_2 at a time.[7] In this study, the catalytic reduction of carbon dioxide to carbon over the metal oxides was investigated for the CO_2 fixation from the large CO_2 emission sources such as electric power plants. This is because that the amount of CO_2 evolution is extremely large and a high reaction temperature could be obtained easily in these large CO_2 emission sources.

Commercial metal oxides with an extra pure grade were used without further purification. Catalysts were reduced in a hydrogen stream at 773 K for 5 h prior to the CO_2 reduction. Catalytic reduction of carbon dioxide with hydrogen was performed in a conventional flow system at an atmospheric pressure from 573 K to 973 K. A gaseous mixture of H_2 (25 mol%), CO_2 (12.5 mol%), and an internal standard, N_2 (62.5 mol%), was fed to the catalyst bed at W/F=10 g-cat. h/mol (where W stands for the catalysts weight, and F the total flow rate of reactants). The reaction products were analyzed by the gas chromatographs using a molecular sieve column for CO and N_2, silica gel column for CO_2 and N_2, and an active aluminum column for hydrocarbons.

The amounts of CO_2 and CO were corrected by the amount of the internal standard, N_2, and so the errors in the carbon balance were within plus or minus 1 percent or so. Therefore, the amount of formed carbon during the CO_2 reduction can be estimated based on the material balance.

Table 1 shows the activities in the reduction of CO_2 with hydrogen over the metal oxides. The conversions at the optimum temperature for the reduction of carbon dioxide to carbon were listed in Table 1. Catalytic reduction of CO_2 proceeded on the oxides of the alkaline earth elements and the transition elements, but did not on the oxides of the typical elements and without catalyst. Metal catalysts have been generally applied to the catalytic reduction with hydrogen, and alkanes or alcohols were formed in the CO_2 hydrogenation over the metal catalyst.[8-10] However, carbon monoxide and carbon were produced but no hydrocarbons on the oxide catalysts. Since the hydrogenation activity is generally far lower on the oxide catalysts than the metal catalysts, carbon dioxide may be converted into carbon and carbon monoxide selectively. These product distributions on the oxide catalysts are desirable for the purpose of the fixation of CO_2 because of no by-products. Conversion into carbon increased with the

Table 1. Reduction of CO_2 with H_2 over the oxide catalysts

Metal[a] oxide	Temp[b] / K	Conversion[c] /% of CO_2	into C	into CO	into Hydrocarbon
WO_3	973	69.9	27.6	42.3	0.0
Y_2O_3	973	55.9	21.3	34.6	0.0
ZnO	973	68.2	17.5	50.7	0.0
Cr_2O_3	973	65.3	14.5	50.8	0.0
CeO_2	973	64.3	13.2	51.1	0.0
Mn_2O_3	973	61.2	11.7	49.5	0.0
MgO	973	46.2	11.1	35.1	0.0
V_2O_5	673	14.9	10.9	4.0	0.0
ZrO_2	973	62.1	10.5	51.6	0.0
MoO_3	873	51.0	10.4	40.6	0.0
TiO_2	573	6.6	6.6	0.0	0.0
Sb_2O_3	---	0.0	0.0	0.0	0.0
PbO	---	0.0	0.0	0.0	0.0
SnO_2	---	0.0	0.0	0.0	0.0
Al_2O_3	---	0.0	0.0	0.0	0.0
SiO_2	---	0.0	0.0	0.0	0.0

a) Oxide phases before reaction. b) Optimum temperature for CO_2 reduction to carbon. c) Calculation based on carbon dioxide elevating temperature, and thus it attained the maximum at 973 K on the most catalysts. While the CO_2 conversion goes up to over 50% on the most oxide catalysts at 973 K, CO_2 reduction with hydrogen terminated in the step of carbon monoxide, so that the conversion into carbon became low. The metal oxide of W, Y, and Zn, however, exhibited a rather high activity for the reduction of CO_2 to carbon. In particular, WO_3 catalyst is highly active for the reduction of CO_2 into C.

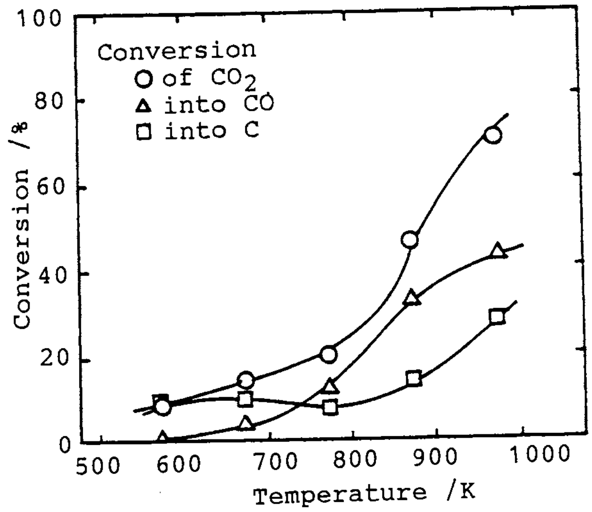

Fig. 1. Temperature dependence of the activity of WO_3 catalyst.

Temperature dependences of activity in CO_2 reduction on the WO_3 catalyst were shown in Fig. 1. Carbon dioxide can be reduced on WO_3 catalyst even at 573 K, but a low conversion. Conversion of CO_2 increased linearly with an increase in temperature. The formation of carbon was dominant below 773 K, whereas carbon monoxide formation became dominant above 873 K. The following two reaction paths are considered for the carbon formation in the reduction of CO_2 with H_2; (1) Carbon formation by the direct CO_2 reduction with H_2, (2) Carbon formation by the consecutive reduction or disproportionation of carbon monoxide, which is a primary product in CO_2 reduction. It is expected from the thermodynamic calculations that carbon formation by the direct CO_2 reduction is favorable in a low temperature, but CO formation comes to be favorable above 873 K. Since the amount of CO formation remarkably increased above 773 K, most of the carbon may be formed via CO at the elevated temperature.

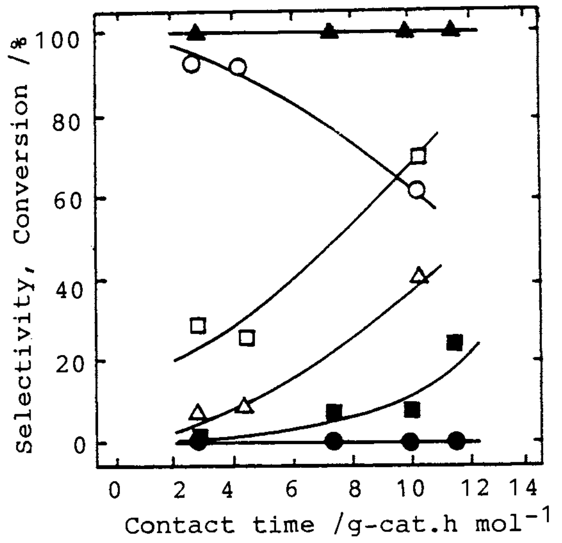

Fig. 2. Effects of contanct time on CO_2 reduction.

CO_2 Conv. ■ at 573 □ at 973 K

Selectivity

● of CO ▲ of C at 573 K

○ of CO △ of C at 973 K

Effects of contact time on the product distribution were further studied on the WO_3 catalyst at 573 K and 973 K. Conversion of CO_2 increased linearly with the increase in the contact time. Selectivities to

C decreased with increasing the contact time at 973 K. This is in a manner contrary with the selectivities to CO. However, both of the selectivities to C and CO were independent of the contact time at 573 K. These results confirmed the predictions that carbon formed directly from carbon dioxide at a low temperature but formed consecutively via CO in a high temperature.

The activity of WO_3 catalyst for the CO_2 reduction at 973 K were plotted as a function of the reaction time in Fig. 3. Although the CO_2 conversion and the conversion into C slightly decreased within 15 min after the initiation of reaction, the CO_2 conversion as well as the product distributions were almost independent of the reaction time within 45 min. This suggests that the reduction of carbon dioxide with hydrogen proceeds catalytically on WO_3. Since the color of catalyst bed changed to black and a black powder, which seems to be carbon, was remained when the used WO_3 catalysts were dissolved into the concentrated nitric acid, it is undoubted that free carbon was formed on the surface of WO_3 catalysts during CO_2 reduction. Since the deposited carbon may be easily removed from the catalysts by a mechanical exfoliation process, catalytic reduction of CO_2 is one of the promising methods for the chemical fixation of CO_2.

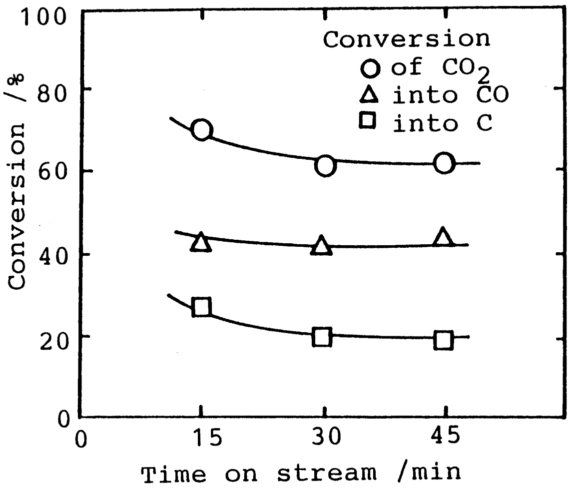

Fig. 3. Activity of WO_3 catalyst for CO_2 reduction as a function of reaction time.

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