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CATALYTIC REDUCTION OF CO_2 TO CO USING SULFUR VAPOR AS A REDUCING REAGENT

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The catalytic reduction of CO_2 to CO by sulfur vapor was studied at the temperatures higher than 650°C over various metal oxides and sulfides, and on the basis of the results from the kinetic studies and the X-ray diffraction measurements, the reaction scheme was tentatively proposed as follows:

$$\text{metal oxides} + S_2(g) \longrightarrow \text{metal sulfides} + SO_2$$
$$\text{metal sulfides} + CO_2 \longrightarrow \text{metal oxides} + CO + SO_2.$$

From the view point of energy resources, hydrogen formation from water has been of current interest and has been investigated at temperatures as high as 800°C[1]. The reduction of CO_2 to CO is also attractive for energy problems because CO can be easily converted to hydrogen by the well-established Shift Water-Gas Reaction.

The purpose of the present work is to obtain fundamental data on the reaction of CO_2 with sulfur vapor by the catalysis of various metal oxides and sulfides. The experiments were performed with a conventional flow reactor (made of quartz tube with 10 mm in diameter), in which 7 ml of catalysts crushed to 1mm in diameter were packed. The specific surface areas and the weights of catalysts used were summarized in Table 1. The reaction was carried out at the temperatures of 650 to 800°C under the space velocity of $1{,}000h^{-1}$. The sulfur vapor was supplied by the flow of carbon dioxide which passed through a sulfur reservoir heated at 250°C. The sulfur vapor at 250°C was 14.5 mmHg under an atmosphere so as the ratio of $S_2(g)$ to CO_2 was around 0.02. Whole apparatus shown in Fig.1 were made of glass tube with 10 mm in diameter and were heated at 280°C by tape heaters so that no solid sulfur deposited on the surface of glass tube of the apparatus. The reactor was placed in a heater of an infrared radiation type, which can heat the reactor promptly to the reaction temperatures.

The products of the reaction were merely CO and SO_2 at 650 to 750°C under the space velocity of $1{,}000h^{-1}$. No COS was observed by means of both infrared and mass spectroscopic measurements, under the reaction conditions[2]. The amount of CO produced was measured by means of gas chromatography using a column packed with molecular sieves 13X, and that of SO_2 was measured by an SO_2 analyser of NDIR type or by permeation tubes for SO_2 (obtained from Komyo Rikagaku Co.). The formation of CO by the metal oxides and by the metalsulfides were shown in Figs. 2 and 3, respectively. Of all the substances employed, MnO, MnS, Cr_2O_3 and MoS_2 were active for the present reaction, and CuO and CuS were fairly active.

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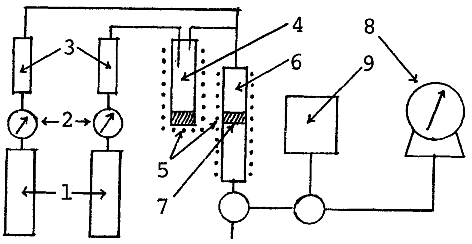
While the others were not so active even at the temperatures so high as 800°C. To clarify the differences in their activities, the study was made using MnO and MnS as the active substances and using Fe_2O_3 as the inactive one. Also the study was done using FeS which was active only at the first stage of the reaction.

In the case of the catalysis by MnO, the X-ray diffraction analysis revealed that the composition of the catalyst changed with the reaction time. It is shown that MnO reacts with sulfur vapor to form SO_2 during the reaction. At the steady state of the reaction, the catalyst became the mixture of MnO and MnS. The things were similar when MnS was employed as a starting material. MnS reacts with CO_2 to form MnO as well as CO and SO_2, and at the steady state the mixture of MnS and MnO was observed. In the case of Fe_2O_3, however, it did not change to FeS by the reaction even at 800°C, and remained in the form of Fe_2O_3 during the reaction. FeS reacted with CO_2 to produce CO and SO_2 with changing to Fe_3O_4. Its activity was decreased, however, with the reaction time and became zero after 20hs of the reaction. The X-ray diffraction spectrum of the sample used for 20h showed Fe_3O_4 and not FeS.

The kinetic studies were done on MnO and MnS by changing the temperature and the space velocity, from 650 to 800°C and from 1,000 to 20,000h^{-1}, respectively. From the results shown in Fig.4, values of the activation energy for the present reaction on MnO and on MnS were calculated. As can be seen in Fig.5, these values were just the same and were 22.0 kcal/mole. (CO_2 conversion in Fig.4 were measured at the steady state of the reaction. The steady states of the reaction on MnO and on MnS can be reached in 5h and in 12h, respectively.) This seems to mean that the reaction schemes on MnO and on MnS are the same at the steady state of the reaction, hence the composition of the catalysts are the similar, ascertained by the X-ray diffraction analysis, at the steady state.

Catalysts	Surface Area (m^2/g)	Weights (g/7ml)
MnO	5.5	8.1
Cr_2O_3	6.0	7.0
Fe_2O_3	4.0	7.1
Co_3O_4	4.5	13.0
NiO	6.0	14.3
CuO	4.0	11.5
MnS	-	8.5
FeS	-	18.3
CoS	-	6.8
NiS	-	6.9
CuS	-	6.1
MoS_2	-	13.5

Table 1; surface area and weights of the catalysts used



1; CO_2 cylinder 2; pressure reducer
3; rotor meter 4; sulfur reservior
5; heater 6; reactor
7; catalyst bed 8; gas flow meter
9; gas chromatography or NDIR analyser

Fig. 1; Apparatus for the experiments

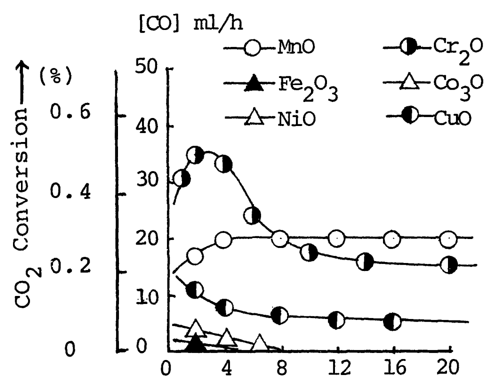


Fig.2; CO formation on metal oxides at 700°C under the space velocity of 1,000 h^{-1}

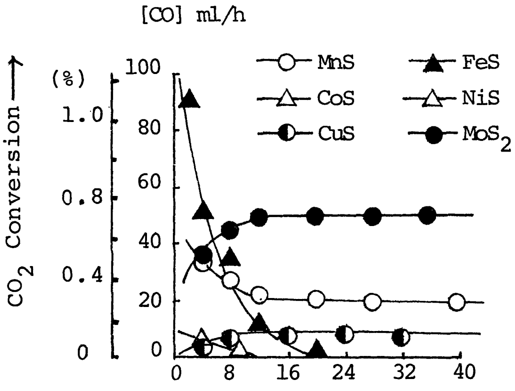
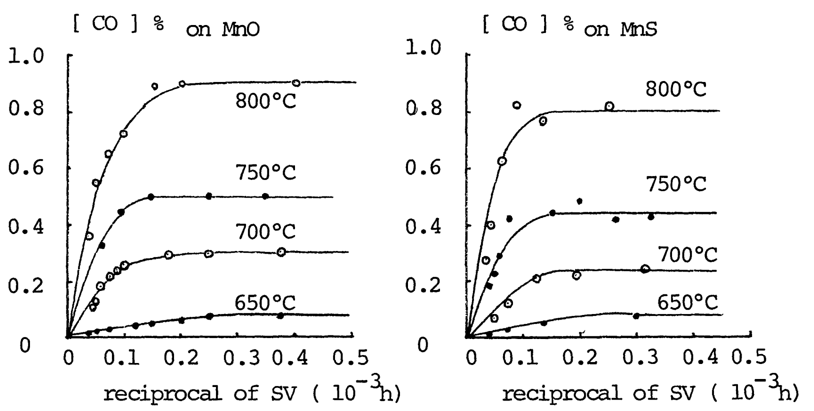


Fig.3; CO formation on metal sulfides at 700°C under the space velocity of 1,000 h^{-1}

Fig.4; CO$_2$ conversion on MnO and MnS catalysts



On the basis of the results obtained, the reaction scheme on MnO or MnS was tentatively proposed as follows:

$$MnO + 3/2\ S_2(g) \longrightarrow MnS + 1/2\ SO_2 + \Delta H_1 \qquad (1)$$

$$MnS + 3\ CO_2 \longrightarrow MnO + SO_2 + 3\ CO + \Delta H_2 \qquad (2),$$

where ΔH represents the enthalpy change of the reaction. Accordingly, at the steady state of the reaction, the reaction might proceed through the sulfurization of MnO (1) and the oxidation of MnS (2), repeatedly. Assuming the change in the entropies in the reactions (1) and (2) could be ignored because of no change in the phase of the reactants, the equilibrium constant K would be expressed as follows:

$K_1 = \exp(-\Delta H_1/RT)$ (3) and $K_2 = \exp(-\Delta H_2/RT)$ (4), and from these equations,

$$-\Delta H_1 + \Delta H_2 = (RT)(\ln(K_1/K_2)) \qquad (5).$$

The equation (5) means that the difference between $(-\Delta H_1)$ and $(-\Delta H_2)$ comes from the ratio of K_1 to K_2, and the extremely large difference between them will result in too much existence of either the metal oxides or the sulfides at the steady state of the reaction. For example, the difference in the enthalpies of FeS-Fe$_2$O$_3$ system is as large as 114.8kcal/mole as can be seen in Table 2, so FeS can be oxidised by

CO_2 forming Fe_2O_3 (or Fe_3O_4 experimentally), but Fe_2O_3 is hard to be sulfurised to FeS. Therefore, the repeating of the oxidation of FeS and the sulfurization of Fe_2O_3 can not be expected. While in the case of MnS-MnO system, the difference in the enthalpies is around 24kcal/mole so that the repeating of the oxidation and sulfurization of MnS and MnO, respectively, can proceed. In the Table 2, the enthalpies of the oxidation of sulfides and the sulfurization of oxides at 1,000°K were given[3]. The differences in the enthalpies between them were less than 25kcal/mole for Mn, Mo and Cu, which are active or fairly active for the present reaction. On the contrary, the differences were as large as ~100kcal/mole for Ni and Fe, which are not so active for the reaction. The overall reaction can be described in the following equation:

$$2\ CO_2 + 1/2\ S_2 \longrightarrow 2\ CO + SO_2.$$

This equation represents that the ratio of [CO produced]/[SO_2 produced] should be 2, and the results obtained from the present experiments were 2.38 on MnO and 2.44 on MnS, respectively, as is shown in Fig.6.

(The enthalpies in Table 2 were calculated by the equation of $\Delta H_{1,000} = \Delta H_{298} + \int_{298}^{1,000} C_p dT$.)

Table 2; Themodynamical values at 1,000°K

a) -ΔH for the sulfurization of oxides

oxides + S_2 → sulfides + SO_2	-ΔH kcal/mole
$MnO + 3/2\ S_2 \rightarrow MnS + 1/2\ SO_2$	17.9
$MoO_3 + 7/4\ S_2 \rightarrow MoS_2 + 3/2\ SO_2$	80.4
$2\ CuO + S_2 \rightarrow Cu_2S + SO_2$	39.1
$Fe_2O_3 + 7/4\ S_2 \rightarrow 2\ FeS + 3/2\ SO_2$	11.1
$NiO + 3/2\ S_2 \rightarrow NiS + 1/2\ SO_2$	95.1

b) -ΔH for the oxidation of sulfides

sufides + CO_2 → oxides + CO	-ΔH kcal/mole
$MnS + 3\ CO_2 \rightarrow MnO + 3\ CO + SO_2$	41.8
$MoS_2 + 7CO_2 \rightarrow MoO_3 + 7\ CO + 2\ SO_2$	98.7
$Cu_2S + 4CO_2 \rightarrow 2\,CuO + 4\ CO + SO_2$	15.0
$2\ FeS + 7\ CO_2 \rightarrow Fe_2O_3 + 7\ CO + 2SO_2$	125.9
$NiS + 3\ CO_3 \rightarrow NiO + 3\ CO + 2\ SO_2$	13.1

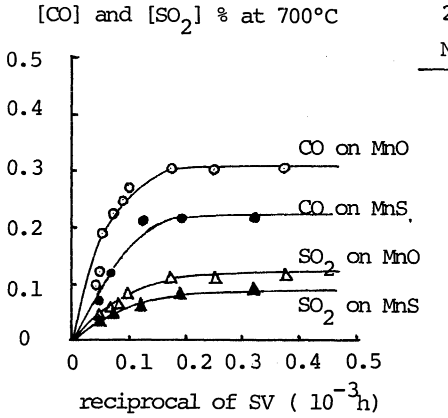


Fig.6; The ratio of CO to SO_2 formed on MnO and MnS at 700°C

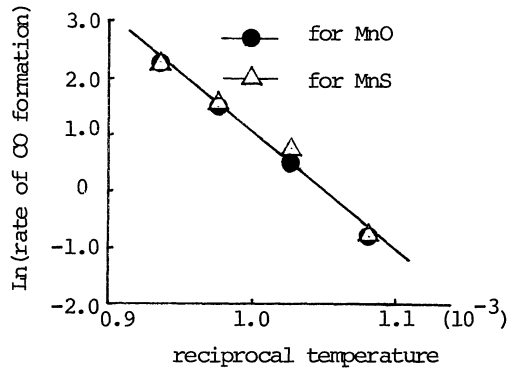


Fig.5; Activation energies on MnO and MnS

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(In the private communication from Dr. M.Dokiya, the small amounts of COS were observed at 800°C under the space velocity of ~$100h^{-1}$.)

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