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THE ENHANCED FORMATION OF C_2-OXYGENATES IN THE HYDROGENATION OF CARBON MONOXIDE OVER THE MODIFIED COBALT CATALYSTS

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The formation of C_2-oxygenates was enhanced by the modification of Co/SiO_2 catalyst, prepared from cobalt(II) acetate, with transition metal (Ru or Re) and alkaline earth in the hydrogenation of carbon monoxide. The X-ray photoelectron spectra suggest that the cobalt is kept in the moderate oxidation state by synergetic effects of transition metal and alkaline earth. The formation of C_2-O occurrs on the partly reduced cobalt site.

In recent years, rhodium catalysts have extensively been developed for the syngas-based synthesis of C_2-oxygenates (C_2-O), i.e., acetaldehyde, ethanol, and acetic acid.1-3) However, transition metals other than rhodium have low activities for the synthesis of C_2-O.4-9) The hydrogenation of carbon monoxide over cobalt4) and ruthenium5) catalysts has usually yielded a wide range of hydrocarbons, and the formation of C_2-O was negligibly small. On the other hand, methanol was obtained seletively over rhenium,6) iridium,7) platinum,7,8) and palladium7-9) catalysts. The investigations of multimetallic catalysts have been required for the selective synthesis of C_2-O. The modifications of cobalt catalysts with copper10) and molybdenum11) have been studied for the synthesis of ethanol and other alcohols. We have previously found that the cobalt of Co/SiO_2 prepared from cobalt(II) acetate was kept in the divalent state during the treatment in a hydrogen stream up to 600 °C, and was inactive for the formation of C_2-O.12) In this letter, we wish to describe the enhanced formation of C_2-O by the modification of the Co/SiO_2 catalyst with transition metal (Ru or Re) and alkaline earth (Sr, Ba, Ca, or Mg).

$Co(A)/SiO_2$ and $Co(N)/SiO_2$ catalysts were prepared by impregnation of silica gel (Davison Grade 57, specific surface area: 330 m^2/g, dried in vacuo at 200 °C for 2 h) with aqueous solutions of cobalt(II) acetate and nitrate, respectively. $Co(A)-M/SiO_2$ catalysts (M=Sr, Ba, Ca, or Mg) were prepared from cobalt(II) and alkaline earth acetates in a similar manner. These catalysts were treated in a hydrogen stream at 300 °C for 3 h. The modifications of $Co(A)/SiO_2$ and $Co(A)-M/SiO_2$ catalysts with rhenium were carried out by impregnating them with aqueous solutions of ammonium perrhenate. The modifications with ruthenium were done by impregnation with a hexane solution of triruthenium dodecacarbonyl. Before use, all catalysts were activated in a hydrogen stream at 450 °C for 3 h. The hydrogenation of carbon monoxide was carried out at 21 kg/cm^2 of syngas of molar ratio: $CO:H_2:Ar=30:60:10$ by the use of a fixed bed-type reactor made of stainless steel, argon being used as an internal standard. The effluent gas was analyzed by gas chromatography after the reaction reached a stationary state. Product selectivities were determined as

Table 1. The hydrogenation of carbon monoxide over the modified cobalt catalysts a)

Catalyst b)	Temp °C	Conv CO %	Product selectivity/% EtOH c)	AcH	C_2-O d)	MeOH e)	CH_4	C_{2-8} f)
Co(N) (5)	250	23.0	0.7	0.6	1.2	0.4	9.5	36.5
Co(A) (5)	250	1.7	0.8	0.1	0.9	1.8	32.1	46.3
Re (5)	250	0.30	0	0	0	0	37.0	28.0
Ru (2.71)	250	23.8	0.1	0.5	0.8	0	6.7	13.7
Co(A)-Re (5:5)	220	7.7	10.8	0.9	11.8	3.4	30.8	41.0
Co(A)-Ru (5:2.71)	220	17.4	5.7	1.5	7.9	1.0	21.5	49.8
Co(A)-Re-Sr (5:5:5)	250	5.0	20.2	3.2	25.0	2.8	18.2	39.3
Co(A)-Ru-Sr (5:2.71:5)	250	4.5	22.5	5.5	30.4	4.4	17.5	32.2
Co(A)-Ru-Ba (5:2.71:7.84)	250	2.8	16.1	5.0	22.1	3.8	19.9	36.8
Co(A)-Ru-Ca (5:2.71:2.29)	250	11.8	17.8	3.1	22.8	2.6	19.8	42.4
Co(A)-Ru-Mg (5:2.71:1.39)	220	10.5	13.5	2.6	16.4	2.4	30.2	37.4

a) Reaction conditions: CO:H_2:Ar=30:60:10; Pressure: 21 kg/cm^2; GHSV=2000/h. b) Supported on SiO_2. Numbers in parentheses express grams of each component on 100 g of SiO_2. The gram-atomic amounts of Ru and alkaline earths were the same as those of Re and Sr, respectively. c) Including ethyl moiety of ethyl acetate. d) Sum of ethanol, acetaldehyde, and acetic acid. e) Including methyl moiety of methyl acetate. f) Sum of C_2-C_8 hydrocarbons.

carbon efficiency on the basis of reacted carbon monoxide. The major products were alcohols and hydrocarbons. Hydrocarbons higher than C_9 were produced especially in the cases of Co(N)/SiO_2, Ru/SiO_2, and Co(A)-Ru/SiO_2 catalysts. Propanol, butanol, methyl and ethyl acetates, and carbon dioxide were also obtained in small amounts. The acetates were considered to be formed from alcohols and acetic acid. The X-ray photoelectron spectroscopic measurements were carried out after an in situ activation in a hydrogen stream at 300 °C. The compensations for the effects of charge-up were made using Si(1s) line with the binding energy of 103.4 eV.

Table 1 summarizes the hydrogenation of carbon monoxide over the modified Co/SiO_2 catalysts. Co(N)/SiO_2 catalyst had a high activity for Fischer-Tropsch reaction to yield a wide range of hydrocarbons. However, Co(A)/SiO_2 catalyst had a very low activity, and no formation of oxygenates was observed. Ru/SiO_2 and Re/SiO_2 catalysts had quite different activities: the former had a very high activity for the formation of hydrocarbons, whereas the rate of the hydrogenation were very slow over the latter catalyst. The modification of Co(A)/SiO_2 catalyst with ruthenium or rhenium enhanced markedly the hydrogenation of carbon monoxide, and acetaldehyde and ethanol were produced in addition to a mixture of hydrocarbons. A significant improvement of the selectivity of C_2-O was observed by the double modification with transition metal (Ru or Re) and strontium, although the activity was decreased. A large part of the decrease of the activity was ascribed to the decrease of the hydrocarbon formation. The selectivity of C_2-O was in the order: Co(A)-Ru-Sr/SiO_2 > Co(A)-Re-Sr/SiO_2 >> Co(A)/SiO_2. Figure 1 shows the effects of

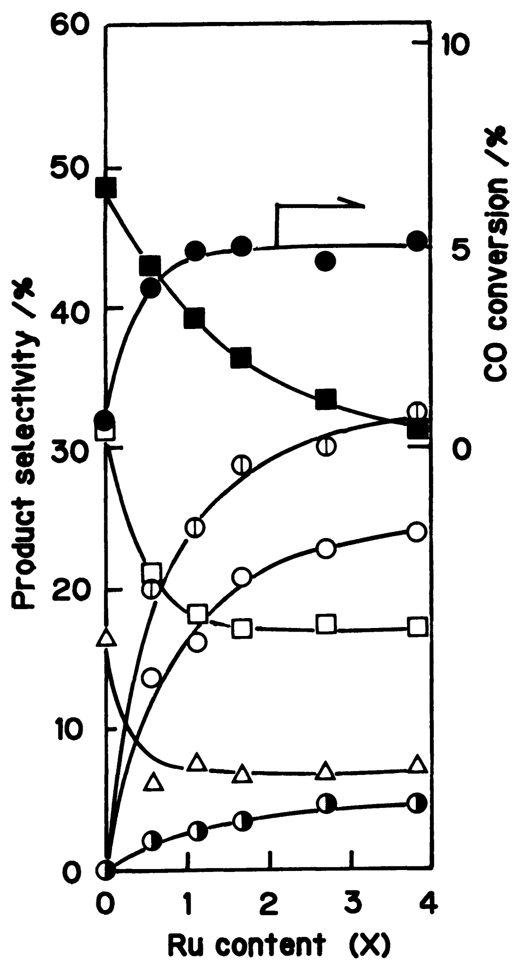

Fig. 1. The effects of Ru on the hydrogenation of carbon monoxide over Co(A)-Ru-Sr/SiO_2 catalysts. Co:Ru:Sr=5:X:5 (weight ratio); 250 °C; 21 kg/cm^2; GHSV=2000/h.
○: EtOH; ⦶: C_2-O; ◑: MeOH;
□: CH_4; ■: C_{2-8}; △: CO_2.

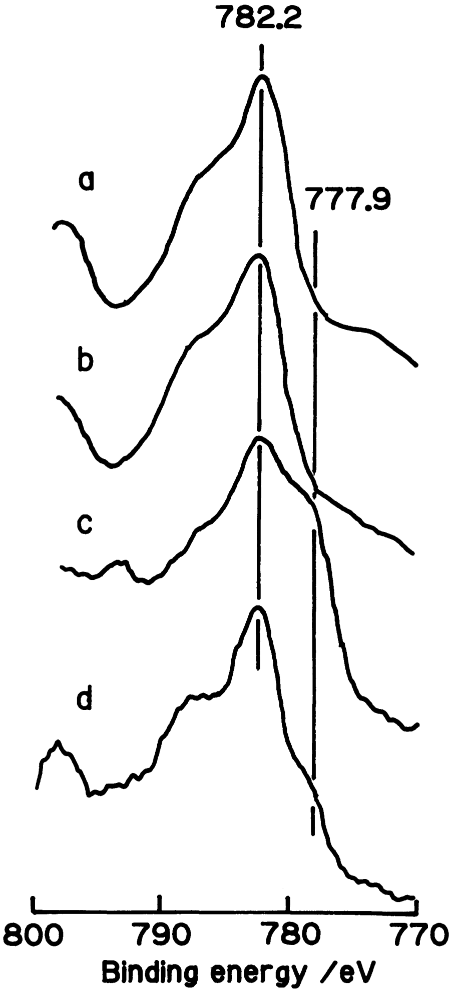

Fig. 2. The X-ray photoelectron spectra of Co-Ru-Sr catalyst system.

a: Cobalt(II) acetate;
b: Co(A)/SiO_2 (5:100);
c: Co(A)-Ru/SiO_2 (5:2.71:100);
d: Co(A)-Ru-Sr/SiO_2 (5:2.71:5:100).

the amount of ruthenium on the hydrogenation of carbon monoxide over Co(A)-Ru-Sr/SiO_2 catalyst. The catalytic activity was increased by the addition of ruthenium, but reached constant at ca. 1 wt% of ruthenium. The formation of C_2-O was increased monotonously with the marked decrease of the hydrocarbon formation: the best selectivity of C_2-O was 32%. The alkaline earths other than strontium have also improved the selectivity of C_2-O in the order: none $<<$ Mg $<$ Ca $\leq$ Ba $<$ Sr, as shown in Table 1. However, the catalytic activity was decreased in the order: none $>$ Mg $>>$ Ca $>$ Sr $>$ Ba. The effects of rhenium and alkaline earths on Co(A)-Re/SiO_2 catalyst were similar to those of ruthenium and alkaline earths on Co(A)-Ru/SiO_2 catalyst.

These observations over the modified cobalt catalysts suggest that the roles of ruthenium and rhenium in the formation of C_2-O resemble to each other, although ruthenium and rhenium originally have quite different activities, and that the formation of C_2-O occurrs on a cobalt site, but not on a ruthenium or rhenium site.

The X-ray photoelctron spectroscopic studies of the Co-Ru-Sr catalyst system were undertaken in order to know the change of the state of the cobalt by the modification. The spectra are shown in Fig 2. The cobalt on the Co(A)/SiO_2 surface was found to be present in the divalent state with the binding energy of 782.2 eV, which was the same as that of cobalt(II) acetate. A discernible shoulder at 777.9 eV appeared by the modification with ruthenium. Although the peak is small and vague, we can assign it to Co^0(2p3/2). However, the height of shoulder was decreased by the modification of Co(A)-Ru/SiO_2 catalyst with strontium. On the other hands, Ruthenium was found to be present in the metallic state on these catalysts. These results indicate that some parts of the divalent cobalt are reduced to the metallic state in the presence of ruthenium, and that strontium suppresses the reduction of the divalent cobalt. The spectra of the Co-Re-Sr system are similar to those of the Co-Ru-Sr system.

A possible mechanism of the modification of Co(A)/SiO_2 catalyst with transition metal (Ru or Re) and alkaline earth (Sr, Ba, Ca, or Mg) is as follows. Ruthenium or rhenium promotes to reduce some parts of the divalent cobalt during the activation in a hydrogen stream. Alkaline earth keeps the cobalt in the moderate oxidation state, preventing the cobalt from an excessive reduction. The formation of C_2-O occurrs on the partly reduced cobalt site, and the hydrogen to hydrogenate carbon monoxide is activated on ruthenium or rhenium site. These synergetic effects of cobalt, transition metal and alkaline earth enhance the formation of C_2-O in the hydrogenation of carbon monoxide.

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