

EFFECT OF PARTIAL METAL REDUCTION ON THE CATALYTIC PROPERTY OF COBALT

Sang Heup MOON* and Kwang Euy YOON

Department of Chemical Engineering, Korea Advanced Institute of
Science and Technology, Cheongryang P.O. Box 131, Seoul, Korea

(Received 22 April 1987 • accepted 28 July 1987)

Abstract—Effect of partial metal reduction on the catalytic property of cobalt has been studied for Co/Al₂O₃ catalyst reduced to different extents. The sample catalysts have been tested for CO and H₂ adsorption, CO hydrogenation, and Temperature Programmed Surface Reaction (TPSR). Major effect of the incomplete metal reduction on the surface property of cobalt is that hydrogen adsorption is significantly suppressed. This behavior is responsible to enhanced olefin production and retarded CO dissociation as observed for the catalysts of lower metal reduction. Changes in the kinetic parameters of CO hydrogenation on partially reduced cobalt may be explained from its gas adsorption behavior.

INTRODUCTION

Supported cobalt catalysts are used mostly as partially reduced ones because they are reduced slowly in hydrogen[1] and sometimes the oxides react with the support to form stable compounds[2]. We have observed previously[3] that kinetic behavior of cobalt in CO hydrogenation changes when it is reduced incompletely. This behavior has been studied more in this laboratory, and the result will be discussed in this paper.

Although many workers have studied cobalt catalysts previously[4,5,6], only few have reported the percentage reduction of their catalysts, and none has studied the effect of partial metal reduction systematically. Recently, Bartholomew's group[6,7,8] has studied cobalt catalysts reduced to different extents, but their results have to be analyzed with caution because their catalysts have been prepared with different metal loading. Since the amount of metal loading changes not only the extents of metal reduction but also the metal particle size, the two effects have contributed simultaneously to changes in the property of their catalysts.

To avoid complications due to other variables of catalyst preparation, we have prepared the sample catalysts that are different only in their extents of metal reduction. They have been obtained by reducing an identical catalyst at the same temperature but only for

different periods. Using the sample catalysts, we have measured the amounts of H₂ and CO adsorption, the kinetic parameters of CO hydrogenation, and Temperature Programmed Surface Reaction (TPSR) spectra of methane production after the catalysts have been exposed to CO under different conditions. Details of the experiments and the results are described below.

EXPERIMENTAL

As mentioned above, the sample catalysts used in this study are identical except for the extents of metal reduction. The original sample catalyst, 10 wt% Co/Al₂O₃, was prepared from alumina and cobalt nitrate by incipient wetness method[4], dried at 120°C, decomposed of nitrate at 220°C, and finally reduced in H₂ at 375°C for different periods. We varied the reduction period between 15 minutes and 18 hours to obtain sample catalysts of different metal reduction. Materials used in the experiment are described in detail in our previous paper[3].

The percentage reduction of the sample catalysts was measured by oxygen titration which was described by Bartholomew and Farrauto[9]. In this method, cobalt was titrated with oxygen at 400°C assuming that Co₃O₄ formed after titration.

The amount of either hydrogen or CO chemisorption on the catalysts was obtained by extrapolating an isotherm of the irreversible gas uptake to zero pressure as in the work of Reuel and Bartholomew[6]. The irreversible gas uptake is the difference between the total and the reversible gas adsorption. To measure the reversible gas uptake, the catalyst was evacuated for 30

*To whom all correspondence should be addressed. Mailing address: Reaction Engineering Laboratory, Korea Advanced Institute of Science and Technology, Cheongryang P.O. Box 131, Seoul, Korea

minutes after the initial isotherm measurement. Since hydrogen uptake was small in this study, the amount of the total H_2 uptake was also extrapolated to zero pressure and the result is listed in Table 1.

The sample catalysts were tested for CO hydrogenation in a differential fixed-bed glass reactor. The reactant stream with the H_2/CO ratio of 3.0 was flowed through the reactor at the space velocity of 15,000–30,000 hr^{-1} . The reaction temperature, 210–250°C, was lower than the catalyst reduction temperature, 375°C, and so the percentage reduction of the catalysts remained constant during the reaction tests.

TPSR spectra of methane production were observed for two sample catalysts of different metal reduction which were either used for CO hydrogenation at 240°C for 30 min or were preadsorbed with CO at room temperature. Methane production was monitored as hydrogen flowed over the catalyst and as the reactor was heated at the programmed rate of 10°C/min. Details of the experiments are also described elsewhere [10].

RESULTS AND DISCUSSION

1. H_2 and CO adsorption

Table 1 shows the amounts of H_2 and CO adsorption on the catalysts of different metal reduction. Also included are the fractions of reduced metal exposed to the surface that are calculated from the percentage reduction and the gas uptake results. Hydrogen adsorption decreases significantly when the catalysts are reduced incompletely. This result was reported already in our previous paper[3]. In the paper, we excluded sintering of metal particles and metal-support interaction from reasons for the reduced hydrogen uptake. This was because the temperature of catalyst reduction was low enough to prevent sintering and the catalysts were prepared with relatively high metal loading, 10

wt%, on the same alumina support to minimize the metal-support interaction.

This study indicates that the cobalt particles are not contaminated nor encapsulated as a result of poor reduction. If such an effect should occur, it must be accompanied by decrease in the fraction of metal exposure to the surface. But Table 1 shows that the fraction calculated from CO uptake increases slightly when the catalyst is reduced to lower extents.

We therefore conclude that the significant decrease in H_2 uptake is an intrinsic effect of the partial metal reduction. As discussed previously[3], origin of the effect seems to be an electronic interaction between cobalt and the unreduced cobalt oxide. The unreduced cobalt oxide that exists in many different oxidation states and in close contact with the reduced cobalt metal modifies the electronic property of the latter, and this results in suppression of H_2 adsorption on cobalt.

2. Activity in CO Hydrogenation

2-1. Activation Energy

Table 2 shows changes in the kinetic parameters of CO hydrogenation when the catalysts are reduced to different extents. The activation energy for production of different hydrocarbons changes in different manner with the extent of metal reduction. That is, the energy for methanation decreases slightly but that for ethane and ethylene production increases as the catalysts are reduced incompletely. The trends are clear when the results are plotted as in Figure 1.

Decreasing activation energy for methanation was also observed by other worker[11,12] on partially reduced metal foil or on oxygen-contaminated single crystal. Recently, Reuel and Bartholomew[7] have reported a similar trend for their supported cobalt catalysts. But, as mentioned above, their results are complicated due to changes in both the extent of metal reduction and the surface crystal structure.

Table 1. Percentage reduction and gas uptake of 10% Co/ Al_2O_3 catalysts

Catalyst (a) Reduction	Percentage (b) Reduction / %	Gas Uptake at 25°C/ $\mu\text{mol}(\text{gcat})^{-1}$			Surface Exposure of (e) Reduced Metal / %		
		Total H_2 (c)	Irrev. H_2 (c)	Irrev. CO (d)	Total H_2	Irrev. H_2	Irrev. CO
R(375,0.25)	21.3	0.8	0.4	14.0	0.4	0.2	3.9
R(375,1.0)	28.0	4.2	3.4	19.5	1.8	1.4	4.1
R(375,5.0)	45.5	19.5	14.5	23.5	5.1	3.8	3.0
R(375,11.0)	52.8	27.0	19.5	24.0	6.0	4.4	2.7
R(375,18.0)	57.5	34.0	25.0	31.0	7.0	5.1	3.2

(a) R(T,t) designates a catalyst reduced at T°C for t hours.

(b) Estimated by O_2 titration of reduced sample at 400°C assuming formation of Co_3O_4 .

(c) Estimated by zero pressure extrapolation of adsorption isotherm at room temperature.

(d) Amounts of gas uptake after 30-min evacuation.

(e) The dispersion is defined as surface metal/reduced metal instead of surface metal/total metal.

Table 2. Kinetic parameters of partially reduced 10% Co/Al₂O₃ catalysts.

Catalyst ^(a) Reduction	Extent of Reduction/%	Kinetic Parameters								
		CH ₄			C ₂ H ₄			C ₂ H ₆		
		X ^(b)	Y ^(b)	Ea ^(c)	X ^(b)	Y ^(b)	Ea ^(c)	X ^(b)	Y ^(b)	Ea ^(c)
R(375,0.25)	21.3	0.99	-0.58	32.0	0.59	0.41	24.2	1.17	-0.98	45.3
R(375,1.0)	28.0	1.04	-0.55	32.4	0.55	0.43	22.7	1.60	-0.90	45.3
R(375,5.0)	45.5	1.09	-0.58	32.5	0.45	0.75	22.0	1.68	-0.84	44.1
R(375,11.0)	52.8	1.11	-0.60	32.7	0.39	0.76	20.6	1.68	-0.74	42.5
R(375,18.0)	57.5	1.12	-0.57	33.0	0.45	0.78	20.2	1.69	-0.78	42.5

a. R(T,t) designates a catalyst reduced at T°C for t hours.

b. Rate = $K \cdot P_{H_2}^X \cdot P_{CO}^Y$

c. Activation energy of reaction/kcal(gmol)⁻¹

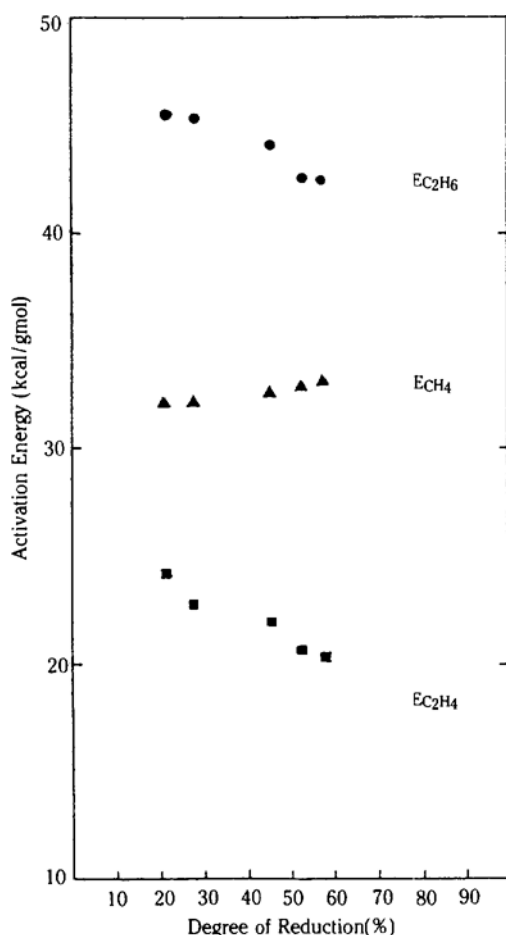
**Fig. 1. Effect of percentage reduction on activation energy of CO hydrogenation.**

Table 2 indicates that the activation energy for hydrogenation of the surface carbon species, which is the rate determining step of methanation[4], is lowered by

decreased cobalt reduction. However, it should be mentioned here that this does not necessarily mean enhancement of the overall methanation rate because a simultaneous decrease in hydrogen adsorption on cobalt reduces the concentration of surface hydrogen necessary for methanation. The overall turnover rate is determined by both the activation energy and their surface hydrogen concentration.

Activation energy increase for ethane and ethylene production on partially reduced catalysts was not reported before. Since the rate determining step of ethylene production is chain propagation of the surface carbon species[5], this result indicates that activation energy of the propagation step is raised by incomplete metal reduction. The activation energy increase is less significant for ethane production than for ethylene. This is because ethane is produced through both steps of propagation and hydrogenation[5] and therefore its activation energy shows an intermediate trend of methanation and ethylene production.

2.2. Dependence on Reactant Pressure

Table 2 and Figure 2 show dependence of the reaction rate on the reactant partial pressure when the rate is expressed by an empirical power law. It has been discussed by Vannice[4] that the order to hydrogen partial pressure represents the number of hydrogen atoms involved in hydrogenation of the surface carbon species. The negative order to CO partial pressure for methane and ethane production arises because CO behaves as an inhibitor to the reaction by covering majority of the catalyst surface. The order is positive, however, for ethylene production because in this case rate determining step is not hydrogenation but propagation of the surface carbon species. In other words, the rate of ethylene production is not inhibited but enhanced by high CO partial pressure.

Figure 2 shows clearly that the pressure dependence changes when the catalysts are reduced to different extents. A trend for methane and ethane production is

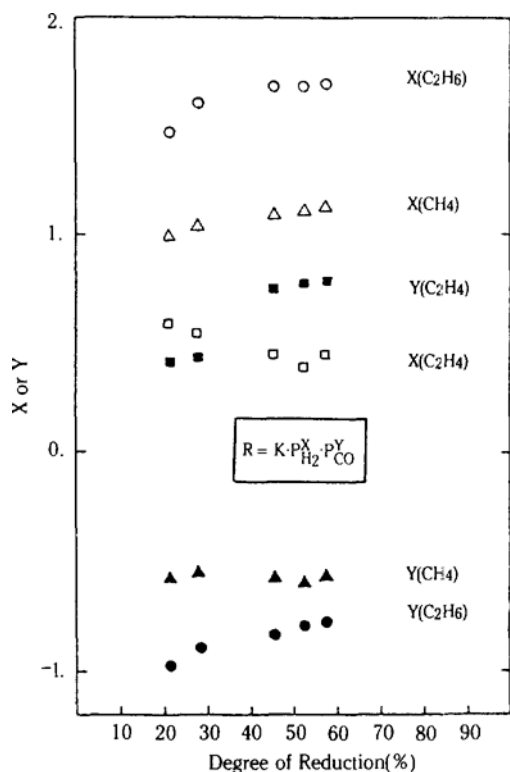


Fig. 2. Rate dependence on reactant partial pressure in CO hydrogenation.

that the positive order to hydrogen pressure decreases and the negative order to CO pressure increases in absolute magnitude with lower metal reduction. This indicates that the number of hydrogen atoms involved in hydrogenation step decreases and the inhibiting effect of CO on the catalyst surface increases. Increased inhibition by CO agrees well with our gas uptake result in Table 1, which shows that CO is adsorbed more and H₂ adsorbed less on cobalt when the catalysts are reduced incompletely.

For ethylene production, the pressure dependence changes in different manner than for methane and ethane production, i.e., the order to hydrogen pressure increases and that to CO pressure decreases with lower metal reduction. Increasing order to hydrogen pressure suggests that more hydrogen atoms are involved in the hydrogenation step. This is an opposite trend to that for paraffin production. Decreasing order to CO pressure is again due to enhanced CO adsorption on the partially reduced catalysts. That is, the overall rate of ethylene production is positively dependent on CO pressure as discussed above, but its dependence becomes smaller for the partially reduced catalysts because their surface adsorbs CO relatively strongly.

3. Olefin/Paraffin Product Ratio

In our previous paper[3], we reported that the olefin/paraffin ratio among the hydrocarbon products of CO hydrogenation increased significantly when the cobalt catalysts were reduced to lower extent. Also observed was that the overall reaction rate per catalyst weight decreased with incomplete catalyst reduction. Accordingly, conversion in the reaction experiment varied with the extent of catalyst reduction, e.g., from 1.8% to 0.2% as the percentage reduction changed from 57.5% to 21.3%.

According to Amelse et al.[13] and Varma et al.[14], the olefin/paraffin product ratio in CO hydrogenation on cobalt is enhanced when the reaction is carried out at low conversion. They have explained that this is because the water-gas shift reaction is retarded at low conversion and therefore hydrogen concentration on the catalyst surface is lower than in the case of high conversion.

To observe the intrinsic effect of incomplete metal reduction on the product selectivity, we have carried out reaction experiments at different conversions for two sample catalysts. Figure 3 shows that the olefin/paraffin ratio is higher at lower conversions, but also clear is that the product ratio increases about twofold when the percentage reduction decreases from 57.5% to 21.3%.

Accordingly, the conclusion made in our previous paper[3] is still valid, i.e., olefin production on cobalt

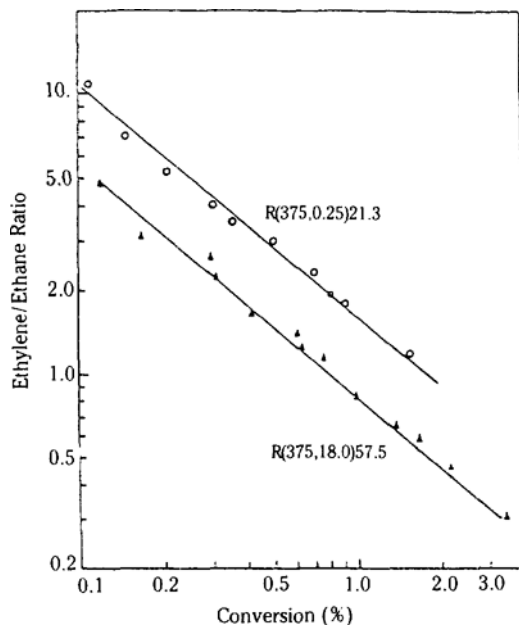


Fig. 3. Effect of conversion and percentage reduction on ethylene/ethane ratio.

catalyst may be enhanced simply by lowering the extent of metal reduction. The primary reason for the enhanced olefin production is suppression of hydrogen adsorption on the partially reduced catalysts.

4. TPSR Results

Figure 4 shows the TPSR spectra of methane production on two sample catalysts of different metal reduction. They are obtained by flowing hydrogen on the catalysts which have been used for CO hydrogenation at 240°C for 30 minutes. Since carbon deposits on the catalyst during CO hydrogenation[5], the methanation rate in Figure 4 represents the hydrogenation rate of the surface carbon species at different temperatures.

The spectra show two major peaks: an intense peak below 300°C and a less intense and broader peak of complex structure above 300°C. We will discuss mostly about the peak below 300°C because temperatures of CO hydrogenation in our kinetic study have been below 300°C. McCarty and Wise[15] have studied hydrogenation of carbon on nickel and suggested that the peak below 300°C is by hydrogenation of the alpha-carbon species which is relatively active and is therefore mostly responsible to methanation.

In Figure 4, two spectra show the peak below 300°C almost at the same position, i.e., near 200°C. This suggests that the activation energy for hydrogenation of the alpha-carbon is almost same for the two catalysts. It agrees with the result of our kinetic measurements

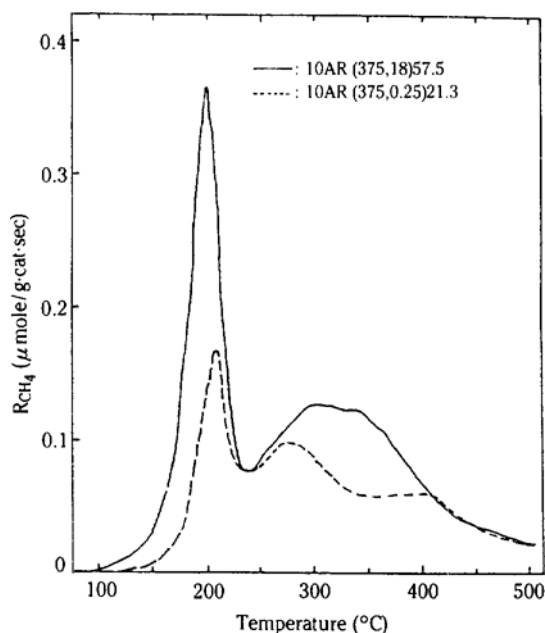


Fig. 4. TPSR spectra after CO hydrogenation at 240°C for 30 min.

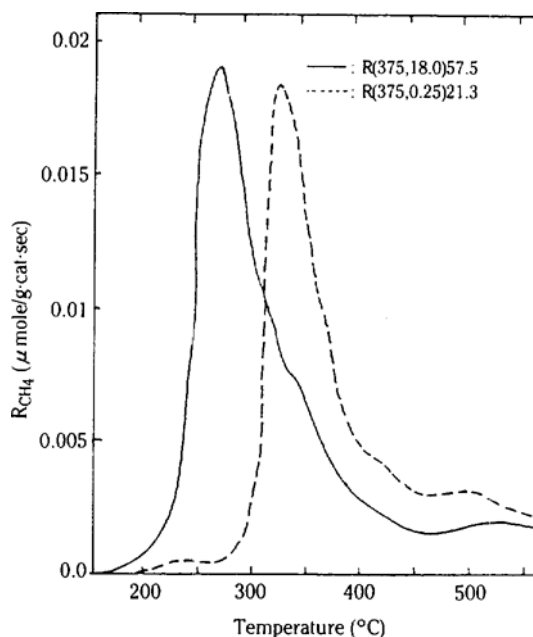


Fig. 5. TPSR spectra after CO adsorption at room temperature.

in Table 2, which also shows that the activation energy of methanation changes only slightly with different metal reduction.

The two spectra are different, however, in the peak intensity showing a smaller peak on the (375, 0.25) catalyst. An obvious reason for this is that the poorly reduced (375, 0.25) catalyst has a smaller cobalt surface area than the other catalyst. But, the result of another TPSR experiment, Figure 5, indicates that this is not the only reason for the intensity difference. Figure 5 indicates that the rate of carbon deposition per reduced cobalt surface also changes with the extent of metal reduction.

The spectra in Figure 5 are obtained by flowing hydrogen on the two sample catalysts after they have been exposed to CO at room temperature. The result is different from that of Figure 4 because in Figure 5 methane is produced through both steps of carbon deposition and its hydrogenation whereas in Figure 4 it is produced only by hydrogenation of the surface carbon species.

Figure 5 shows that the peak near 250°C on the (375, 18) catalyst shifts to higher temperature by more than 50°C as the metal reduction is lowered from 57.5% to 21.3%. Since it has been observed in Figure 4 that the peak position for hydrogenation of the carbon species is almost same for the two catalysts, the large peak shift in Figure 5 is due to difference in the rate of carbon deposition on the two catalysts. The difference occurs

because carbon deposition is a H₂-assisted process as described below.

As studied by Low and Bell[16] for Ru and by Bianchi and Bennett[17] for Fe, CO dissociation on transition metals is enhanced by the presence of hydrogen in the reactant stream. This is because hydrogen reacts readily with oxygen produced by CO dissociation and eventually removes it from the catalyst surface. However, the assistance by hydrogen becomes small on the poorly reduced, (375, 0.25) catalyst because the catalyst adsorbs hydrogen only in small amount as shown in Table 1. In other words, the hydrogen-assisted CO dissociation is retarded by suppression of hydrogen adsorption on the partially reduced catalyst, and this results in the peak shift observed in Figure 5.

CONCLUSION

This work is done as a further study of our previous one[3] to demonstrate that the catalytic property of cobalt changes when cobalt is reduced incompletely. Gas uptake on cobalt changes with partial metal reduction, i.e., H₂ adsorption decreases significantly and CO adsorption increases slightly. Changes in the kinetic parameters of CO hydrogenation observed in this study may be explained from the above gas uptake result. Olefin is produced more on cobalt when the catalyst is reduced to lower extent. This is important industrially because the product selectivity may be modified simply by changing the extent of catalyst reduction. Although this work is limited to CO hydrogenation on Co/Al₂O₃, we have shown enough evidence that the extent of metal reduction is an important variable in preparation of metal catalysts.

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