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Catalytic Properties of Potassium- or Lanthanum-Promoted Co/γ-Al_2O_3 Catalysts in Carbon Monoxide Hydrogenation

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Abstract−The effects of potassium or lanthanum additives on the catalytic properties of alumina-supported cobalt catalysts were examined through carbon monoxide hydrogenation reaction. The catalysts were characterized by hydrogen or carbon monoxide chemisorption, oxygen titration, and temperature-programmed desorption. The reactions were carried out at 270 °C and atmospheric pressure. When a small amount of potassium was added to alumina-supported cobalt catalysts, the amount of hydrogen adsorption decreased more significantly than that of carbon monoxide adsorption, and the extent of reduction also decreased. With the addition of potassium, the overall carbon monoxide conversion decreased, while the selectivity to higher hydrocarbon and olefin increased. The effect of lanthanum on activity and selectivity in carbon monoxide hydrogenation was less significant than the effect of potassium. Temperature-programmed desorption showed that the presence of additives changed the adsorbed state of CO on cobalt.

Key words: Cobalt, Alumina, Potassium, Lanthanum, Carbon Monoxide Hydrogenation

INTRODUCTION

Cobalt-based catalysts are widely used in CO hydrogenation, especially when high molecular weight paraffins are desired. Cobalt catalysts are preferred for Fisher-Tropsch synthesis due to their activity, high selectivity to long chain hydrocarbons, and low activity for the competitive water-gas shift reaction. To increase their activity, cobalt is usually supported on a high surface area support to obtain high metal dispersion. The commonly used supports include silica, alumina, titania, zirconia and zeolites [Lee et al., 1988; Shin et al., 1996; Choi et al., 1997; Riedel et al., 1999; Zhao et al., 2003].

The widely studied effect of potassium promotion on various catalysts in the Fisher-Tropsch synthesis is generally reported as the surface basicity effect. The addition of potassium is known to result in an increase in the selectivity of Fisher-Tropsch products, while the activity decreases because of the electronic effect caused by the basicity of potassium [Gonzalez and Miura, 1982; Lee and Ahn, 1990; Xu et al., 1995; Yoon and Kim, 1995; Wang et al., 2003]. Designing a catalyst that mitigates the decrease of activity and improves selectivity is therefore necessary. In some studies, an element with redox centers can reportedly mitigate the decrease of activity and rare-earth metal oxide has a similar basicity to the element with redox centers [Goldwasser and Hall, 1981; Barrault and Guilleminot, 1986].

In this paper, the characteristics of cobalt containing γ-Al_2O_3 in CO hydrogenation were discussed. The effect of potassium or lanthanum oxide on the catalytic activity and selectivity of CO hydrogenation was investigated. The catalyst samples were characterized with hydrogen or carbon monoxide chemisorption, oxygen titration, and temperature-programmed desorption.

EXPERIMENTAL

1. Catalysts

Powder of γ-Al_2O_3 was provided by Strem Chemicals and had a mean diameter of 74 µm, a pore volume of 0.27 cm^3/g, and a surface area of 227 m^2/g. Hydrogen and helium (Matheson, 99.999%) were further purified by using a Deoxo catalyst followed by a molecular sieve trap. Carbon monoxide (Takachiho, 99.95%) was passed through the molecular sieve trap to remove the water and metal carbonyl.

Alumina-supported cobalt catalysts were prepared by the incipient wetness method. After the pores of the alumina were filled with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (Aldrich, 99.9%) and KNO_3 (Aldrich, 99.9%) or $La(NO_3)_3 \cdot 6H_2O$ (Aldrich, 99.9%) to an appropriate metal loading, the catalysts were dried overnight in air at 100 °C. Following calcination with oxygen at 500 °C for 24 h, the catalysts were reduced with hydrogen by being heated to 500 °C at 2 °C/min and the temperature was maintained for 10 h.

2. Characterization

The extent of reduction was measured by oxygen titration at 400 °C according to the method of Batholomew and Farrauto [1976], where the reduced cobalt metal was assumed to react with oxygen to Co_3O_4 [Chin and Hercules, 1982]. To calculate the extent of reduction of 10 wt% Co/γ-Al_2O_3 catalyst, oxygen titration was conducted by varying the concentration of K or La. When only La was loaded, consumption by oxygen was confirmed. This confirmation was used to correct the value of the extent of reduction.

The adsorption isotherms were measured at 25 °C in a conven-

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[‡] This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

Table 1. Chemisorption data of 10 wt% Co/γ-Al_2O_3 catalysts

Promoter/Co (wt%)	Extent of reduction (%)[a]	irr.H×10^3 (H/Co)	irr.CO×10^3 (CO/Co)	$[CO/H]_{irr}$[b]	Dispersion (%)[c]	d (nm)[d]
-	83	6.1	11.8	1.9	5.3	18.0
K(1)	82	5.6	11.6	2.1	4.9	19.6
K(5)	80	2.7	8.6	3.2	3.1	35.6
K(10)	59	0.9	8.7	9.7	3.2	30.1
La(1)	81	4.6	3.5	0.8	6.7	14.5
La(5)	76	4.6	3.5	0.8	7.1	13.6
La(10)	68	5.9	6.0	1.0	5.0	19.3

[a] Calculated from O_2 titration at 400 °C, assuming the formation of Co_3O_4 [Chin and Hercules, 1982].

[b] Ratio of irreversible uptakes at room temperature.

[c] Dispersion determined from H_2 uptake at room temperature multiplied with adsorption activation factor [Reuel and Bartholomew, 1984].

[d] Cobalt particle size obtained from the relation (d=6.59×s/%D, s=14.6 atoms/nm^2) [Reuel and Bartholomew, 1984].

tional Pyrex glass volumetric adsorption apparatus. The gas uptakes were obtained by extrapolating the straight portion of the isotherms to zero pressure, and the irreversible uptakes were determined by the difference between the total uptakes and the reversible uptakes. The amount of adsorbed hydrogen and CO showed a straight line over 150 torr. The line was back extrapolated to zero pressure. The adsorption amount over the support or K or La was too small to consider.

Reuel and Bartholomew [1984] reported that hydrogen adsorption is part of the activation process over the supported Co catalysts and that the dispersion, which is determined by using the maximum amount of adsorbed hydrogen, agrees well with the dispersion measured by TEM. In addition, the ratio of the maximum amount of adsorbed to the amount of adsorption at normal temperature has been defined as an adsorption activation factor, and the adsorption activation factor of 10 wt% Co/γ-Al_2O_3 was calculated as 1.2. This factor was consequently used in this experiment. The following equation suggested by Reuel and Bartholomew [1984] was used to calculate the dispersion of Co particles:

$$D\ (\%)= 1.2\times X/(Wf),$$

where X is the total amount of adsorbed hydrogen at 398 K under the assumption that hydrogen adsorption is part of activation process and that adsorption amount increases with temperature; W is the weight percentage of cobalt; and f is the fraction of the reduced cobalt metal determined through the oxygen titration experiment. The particle size (d) was calculated by subsequent formula [Reuel and Bartholomew, 1984]:

$$d=6.59\times s/\%D,$$

where s is the surface site density calculated by the weight average of the face (100), (110), and (111) of the fcc cobalt with respect to the supported cobalt crystal. Its value was 14.6 atomic number/nm^2.

For the temperature-programmed desorption (TPD) of carbon monoxide, 0.5 g catalyst was reduced with hydrogen at 500 °C for 30 min under a helium stream. After cobalt metal was saturated with CO, TPD curves were obtained by flowing helium at 60 cc/min as the temperature was linearly increased at 5 °C/min. The stream containing CO was analyzed by a TCD (Hewlett-Packard 5710A) located immediately downstream from the catalyst.

3. Reaction

CO hydrogenation reaction was performed in a differential reactor operating at atmospheric pressure, 250 °C, and a H_2/CO ratio of 3. Products were passed through a heated transfer line to a gas chromatograph (Hewlett-Packard 5890 II) with a TCD and an FID connected in series. Products were separated in a 6 ft×1/8 in. column packed with a Porapak Q (TCD) and in a 50 m×0.2 mm cross-linked methylsilicone-fused silica capillary column (FID). The column temperature was held for 2 min at 50 °C and then heated to 150 °C at 16 °C/min. The rate of CO hydrogenation reached a steady state 1 h after the introduction of the reactant gases into the reactor, and the reaction rates of all catalysts were measured after 2 h.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

Table 1 shows the extent of reduction, the dispersion, the particle size and the adsorption amount with additives. As the concentration of potassium increases, the dispersion decreases and the particle size increases. This sequence coincides with several reports in the literature that potassium promotes sintering. The extent of reduction decreases with the addition of potassium. This result is inferred from the decrease of dispersion. It has been suggested that potassium might decrease the amount of surface cobalt. Furthermore, the amount of adsorbed hydrogen and carbon monoxide decreases with the addition of potassium. This phenomenon occurs because the addition of potassium might decrease the number of active sites on the surface cobalt. In addition, this trend is similar to the decrease of dispersion.

As the concentration of lanthanum increases, the amount of hydrogen chemisorption remains almost constant (Table 1). The amount of carbon monoxide chemisorption over lanthanum-added catalysts is smaller than that over the catalyst without lanthanum. Consequently, the CO/H ratio over lanthanum-added catalysts is smaller than that over the catalyst without lanthanum. Underwood and Bell [1988] reported that lanthanum exists in La_2O_3 and in its partially reduced state LaOx over the Rh/SiO_2 catalyst. They suggested that LaOx controlled the adsorption of carbon monoxide and hardly affected the adsorption of hydrogen. This phenomenon occurs because the chemisorbed hydrogen over the active site of rhodium spills over LaOx's surface. Because the amount of adsorbed carbon monoxide decreases with the addition of lanthanum in the Rh/SiO_2 cata-

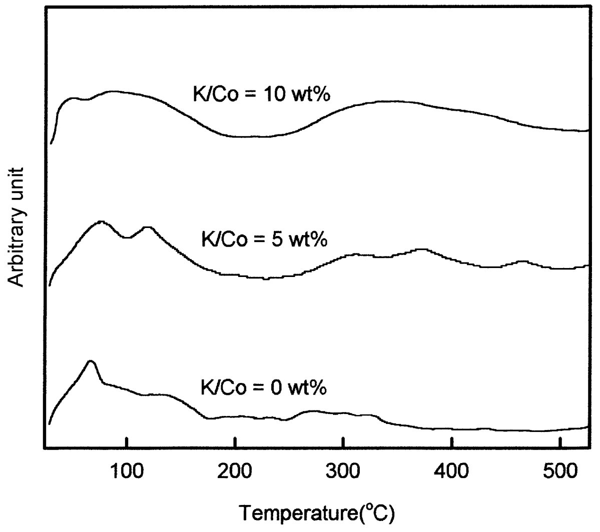

Fig. 1. TPD of CO over K-added 10 wt% Co/γ-Al_2O_3 catalysts.

lyst, Underwood and Bell [1988] also suggested that part of the additive exists on the surface of the rhodium particle. In this study, the extent of reduction decreases with the addition of lanthanum because part of the lanthanum that exists in the oxide state covers the cobalt metal. This phenomenon disturbs the reduction of cobalt and the chemisorption of carbon monoxide.

Fig. 1 shows TPD curves of Co/γ-Al_2O_3 catalysts with the added potassium. The desorption peaks of the carbon monoxide were observed in two temperature ranges: from 50 °C to 200 °C and from 300 °C to 400 °C. Lee et al. [1985] suggested that the peak in the low-temperature range of about 200 °C is caused by desorption of CO molecules adsorbed on a nickel surface over a supported nickel catalyst, and that the high-temperature peak of about 400 °C is produced from the recombination of oxygen from the support and the carbon.

In the results of this experiment, high-temperature peaks seem to be due to the carbon monoxide produced by the recombination of oxygen and the carbon offered in support. Of the two peaks in the low-temperature range, one can be considered as weakly chemisorbed CO and the other as strongly chemisorbed CO. The amount of weakly chemisorbed carbon monoxide decreases with the addition of potassium, while the amount of strongly chemisorbed carbon monoxide increases. The desorption peak also seems to have moved to a high temperature with the addition of potassium. Consequently, the adsorption strength of carbon monoxide increases with the addition of potassium.

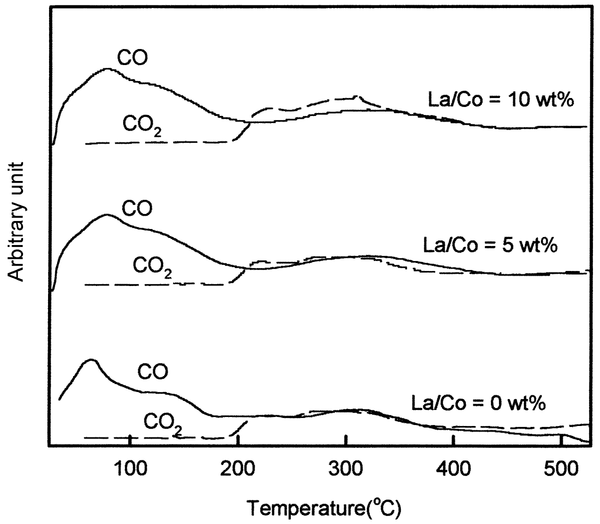

Fig. 2. TPD of CO over La-added 10 wt% Co/γ-Al_2O_3 catalysts.

Fig. 2 shows TPD curves over lanthanum-added Co/γ-Al_2O_3 catalysts. While the amount of desorption for weakly chemisorbed carbon monoxide decreases with the addition of lanthanum, the maximum desorption peak of chemisorbed carbon monoxide moves to a high temperature. The adsorption strength of carbon monoxide increases with the addition of lanthanum. Furthermore, the amount of carbon dioxide produced during carbon monoxide TPD increases with the addition of lanthanum. As carbon dioxide can be produced by the dissociation of carbon monoxide, lanthanum reportedly promotes the dissociation of carbon monoxide. This phenomenon coincides with the tendency of the lanthanum-added Pd/SiO_2 catalyst reported by Rieck et al. [1986].

2. Activity and Selectivity

To elucidate the effect of diffusion on catalytic performance, the conversions were obtained by changing the space velocity (Fig. 3). Because the relationship of the conversion versus W/F (W: catalyst mass; F: reactant velocity of flow) clearly displays a linearity to W/F of 0.3, the hydrogenation reactions of carbon monoxide were carried out within this range to exclude the effect of diffusion in the catalyst bed.

As shown in Table 2, the activity in carbon monoxide hydrogenation over Co/γ-Al_2O_3 decreases with the addition of potassium. The decrease in activity seems to be attributed to covering of the active site of cobalt by potassium. This result is confirmed by a decrease in the extent of reduction and a decrease of dispersion caused by the addition of potassium.

Table 3 shows the effects of potassium addition on product distri-

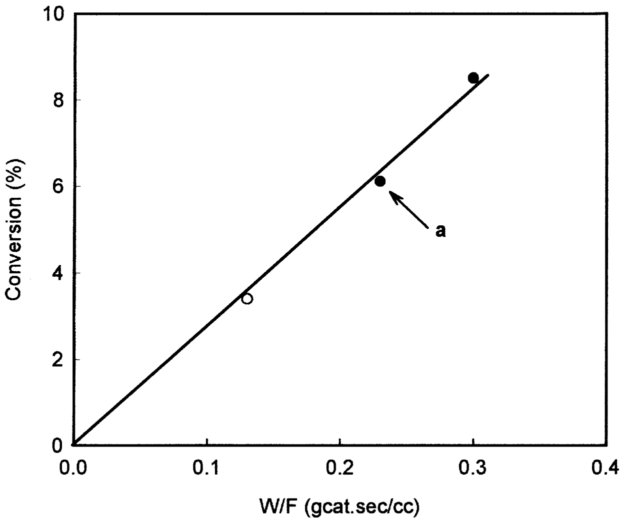

Fig. 3. Absence of external mass transfer resistance for 10 wt% Co/γ-Al_2O_3 (W: catalyst weight, F: reactant flow rate, A: experimental region).

Table 2. Turnover frequency for CO disappearance over 10 wt% Co/γ-Al_2O_3 catalysts

Promoter/ Co (wt%)	Conversion (%)	$R_{CO}\times10^6$ at 270 °C (mol/gcat.sec)	$N_{CO}\times10^3$ at 270 °C (sec^{-1})
-	6.1	4.2	46.1
K(1)	5.0	3.4	34.1
K(5)	4.0	2.8	52.4
K(10)	2.0	1.4	20.9
La(1)	6.2	4.2	37.4
La(5)	6.0	4.1	34.0
La(10)	1.6	1.4	12.9

Reaction conditions: 270 °C, 1 atm, $H_2/CO=2$, W/F=0.23 gcat.sec/cc.

Table 3. Effects of promoters on product distribution over 10 wt% Co/γ-Al_2O_3 catalysts

Promoter/ Co (wt%)	Conv. (%)	Product distribution (wt%)				Olefin selectivity (wt%)	
		C_1	C_2-C_4	C_5-C_{10}	C_{11+}	$\frac{C_2^=}{C_2^=+C_2}$	$\frac{C_3^=}{C_3^=+C_3}$
-	6.1	61.0	29.6	9.4	0.0	18.2	75.8
K(1)	5.0	60.5	29.9	9.6	0.0	26.4	81.2
K(5)	4.0	44.5	34.5	20.1	0.8	54.8	96.3
K(10)	2.0	32.6	30.5	32.2	4.7	96.5	95.0
La(1)	6.2	58.9	32.0	9.3	0.0	23.9	72.8
La(5)	6.0	57.8	30.9	11.4	0.0	22.9	81.2
La(10)	1.6	39.9	37.8	21.7	0.5	83.5	94.0

Reaction conditions: 270 °C, 1 atm, $H_2/CO=2$, W/F=0.23 gcat.sec/cc.

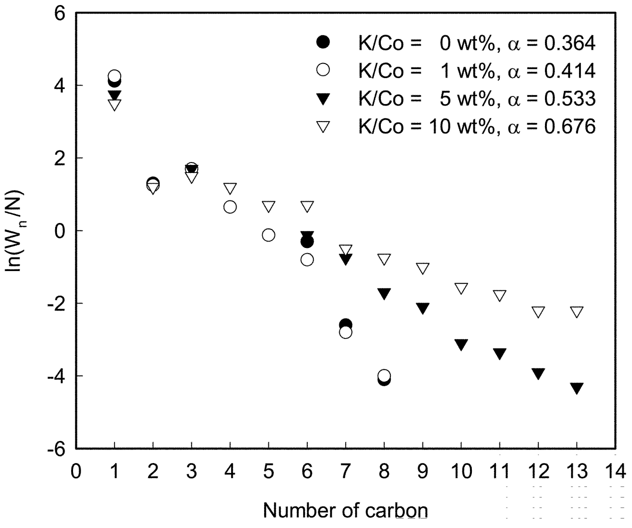

Fig. 4. Anderson-Schulz-Flory plots for the products over K-added 10 wt% Co/γ-Al_2O_3 (270 °C, 1 atm, $H_2/CO=2$, W/F=0.23 gcat.sec/cc).

bution. The addition of potassium causes an increase in the olefin yield of a C_2-C_3 product and in the higher hydrocarbon yield; however it causes methane production to decrease. Fig. 4 shows Schulz-Flory plots for the molecular weight distribution of the produced hydrocarbon. The chain propagation probability (α) calculated from the plots increased from 0.364 for the Co/γ-Al_2O_3 catalyst without potassium to 0.676 for the catalyst with potassium at a K/Co's ratio of 10 wt%. This result seems to be due to the increase of residence time for the carbonaceous species on the catalyst surface.

The electron density over cobalt surface increases with the addition of potassium. This increase possibly occurs because potassium donates some electrons to the cobalt surface. Accordingly, the bond between cobalt and carbon monoxide is reinforced. This result is attributed to the backdonation of cobalt's d electron orbitals to π^* antibonding orbital of CO. Consequently, carbon monoxide is chemisorbed more strongly on a cobalt surface. This explanation is confirmed by the chemisorption results in which the ratio of chemisorbed CO/H increases with the addition of potassium. It is also confirmed by the TPD results in which the bond strength of the CO on the catalyst increases with the addition of potassium. Strengthening the bond between the metal and the adsorbed molecular CO by adding potassium coincides with the results on a Ni/SiO_2 catalyst reported by Praliaud et al. [1986].

The addition of lanthanum has a similar effect to the addition of potassium on catalytic performance, though its effect is less noticeable than that of potassium. As shown in Table 2, the conversion of carbon monoxide and turn-over-frequency (TOF) remain almost constant with the addition of lanthanum to 5 wt% La/Co, whereas they decrease significantly with the addition of 10 wt% La/Co. As shown in Table 3, the product distribution does not change significantly with the addition of lanthanum to 5 wt% La/Co, though the selectivity toward higher hydrocarbons and the selectivity towards olefins in C_2-C_3 products increase significantly with the addition of 10 wt% La/Co. Fig. 5 shows Schulz-Flory plots for the molecular weight distribution of the produced hydrocarbon. The chain propagation probability (α) calculated from the plots increases from 0.364 for the Co/γ-Al_2O_3 catalyst without lanthanum to 0.558 for the catalyst with lanthanum at the La/Co ratio of 10 wt%, though the increase of α is less pronounced than that of potassium.

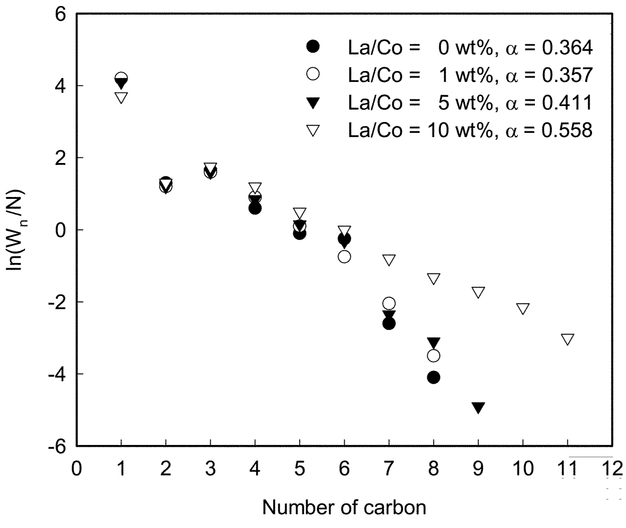

Fig. 5. Anderson-Schulz-Flory plots for the products over La-added 10 wt% Co/γ-Al_2O_3 (270 °C, 1 atm, $H_2/CO=2$, W/F=0.23 gcat.sec/cc).

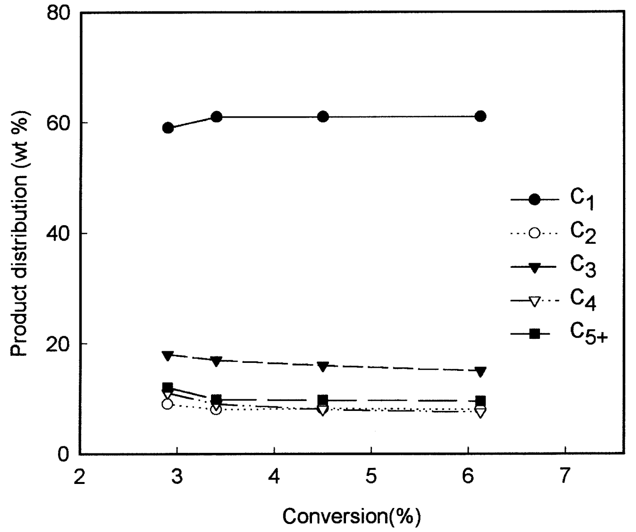

Fig. 6. Dependence of product distribution on conversion in CO hydrogenation over 10 wt% Co/γ-Al_2O_3 (270 °C, 1 atm, H_2/CO=2).

On the other hand, the effect of varying the carbon monoxide conversion on product selectivity has been tested. Fig. 6 shows the product distribution in carbon monoxide hydrogenation with a changing space velocity over a 10 wt% Co/γ-Al_2O_3 catalyst. The product distribution remains almost constant with the decrease of the conversion from 6.2% to 2.8%. The effect of conversion on selectivity is therefore excluded. Consequently, the addition of potassium or lanthanum modifies the surface of catalysts, and increases the production of higher hydrocarbons and olefins.

CONCLUSION

By adding a small amount of potassium to an alumina-supported cobalt catalyst, H_2 adsorption decreases more significantly than carbon monoxide adsorption. The extent of reduction also decreases. With the addition of potassium, the overall carbon monoxide conversion decreases, while the selectivity to higher hydrocarbon and olefin increases. The effect of lanthanum on activity and selectivity in carbon monoxide hydrogenation is less significant than the effect of potassium. The TPD shows that the presence of additives changes the adsorbed state of carbon monoxide on cobalt.

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