



# Silica-supported rhodium-cobalt catalysts for Fischer–Tropsch synthesis

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## ABSTRACT

The effects of the addition of Ag, Au, or Rh to a 15 wt% Co/SiO<sub>2</sub> catalyst on the Fischer–Tropsch (FT) synthesis were studied. Both Au and Rh showed a promoting effect on the FT activity, whereas the addition of Ag decreased the activity. The addition of a small amount of Rh (0.1–0.5 wt%) increased the CO conversion by 50% without affecting the selectivity. It was found that Rh catalyzed the reduction of cobalt oxides, but it did not change the number of surface cobalt atoms. It is proposed that the higher activity of Rh-promoted catalysts is due to the hydrogen spillover from Rh to Co during FT synthesis.

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## 1. Introduction

Supported cobalt catalysts have been extensively studied for Fischer–Tropsch synthesis (FTS) because of their high activity and selectivity for linear hydrocarbons [1–6]. The promoting effects of the addition of a second metal to supported cobalt catalysts, including increased FT activity, higher reducibility of cobalt oxides, and improved catalyst stability [7], have been reported in numerous studies. Ru [7,8], Re [9], Pt [10], and Pd [11] are among the most studied promoters. For example, Vada et al. [10] reported that the addition of Pt or Re to Co/Al<sub>2</sub>O<sub>3</sub> significantly increased the FT activity, whereas the selectivity remained unchanged. They suggested that the higher activity was due to increased reducibility and increased number of surface cobalt atoms. Similarly, Kogelbauer et al. [8] reported that the addition of Ru to Co/Al<sub>2</sub>O<sub>3</sub> catalysts facilitated the reduction of cobalt oxides, resulting in a higher FT activity. The addition of Ru also significantly increased the turnover rates on Co/SiO<sub>2</sub> and Co/TiO<sub>2</sub> catalysts, and it was proposed that Ru inhibited the deactivation of cobalt catalysts by catalyzing the hydrogenolysis of carbonaceous deposits [7]. Recently, Jacobs et al. [12] reported that the addition of small amounts of Group 11 metals (Cu, Ag, Au) to Co/Al<sub>2</sub>O<sub>3</sub> improved the reducibility of cobalt oxides, and in the cases of Ag and Au, increased the density of surface cobalt sites.

The proposed mechanisms for these promoting effects include hydrogen spillover and formation of bimetallic particles. Hilmen et al. [9] studied the effect of Re on the reduction of Co/Al<sub>2</sub>O<sub>3</sub> catalysts and found that the promoting effect of Re for an intimate mixture of Re/Al<sub>2</sub>O<sub>3</sub> and Co/Al<sub>2</sub>O<sub>3</sub> was similar to that for a co-impregnated Re–Co/Al<sub>2</sub>O<sub>3</sub> catalyst. They proposed that hydrogen spillover from Re promoted the reduction of cobalt oxides.

The formation of bimetallic particles can modify the electronic properties of cobalt catalysts, and thus change their catalytic performance for FT synthesis. Using energy dispersive spectroscopy (EDS), Tsubaki et al. [11] showed the formation of Ru–Co, Pt–Co, and Pd–Co bimetallic particles in the noble metal-promoted Co/SiO<sub>2</sub> catalysts prepared by co-impregnation. It was found that Ru was enriched at the surface of cobalt particles, while Pt or Pd formed a uniform alloy with cobalt. Carlsson et al. [13] showed that, for alumina-supported bimetallic Pd–Co particles, the binding energy of carbon monoxide to both Pd and Co sites was lowered.

Compared to those noble metals (Ru, Pd, and Pt) that have been discussed, there have been very limited studies of FTS on Rh-promoted cobalt catalysts [14–16]. A Rh–Co/SiO<sub>2</sub> catalyst was studied using temperature-programmed reduction, oxidation, and extended X-ray absorption fine structure (TPR, TPO, and EXAFS), and it was found that Rh catalyzed the reduction of cobalt oxides and Rh–Co bimetallic particles formed after reduction [14]. Noronha et al. [16] reported that the addition of Rh to niobia-supported cobalt catalysts increased both the FT activity and the selectivities to C<sub>5+</sub> hydrocarbons and oxygenates. In this work, we report

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the promoting effect of Rh on Co/SiO<sub>2</sub> FTS catalysts, as well as the results on silica-supported Ag-Co and Au-Co catalysts.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

Cobalt-based bimetallic catalysts were prepared by incipient wetness co-impregnation of silica with aqueous solutions containing cobalt and a second metal. The silica support (Davison, Grade 952) was calcined at 773 K before impregnation. The metal salts used in this study were cobalt(II) nitrate hexahydrate, silver nitrate, hydrogen tetrachloroaurate(III) hydrate, and rhodium(III) chloride hydrate. After impregnation, the samples were dried at 353 K overnight and calcined in air at 673 K for 3 h. Five silica-supported catalysts were prepared, including Co, 1.0 wt% Ag-Co, 1.0 wt% Au-Co, 0.1 wt% Rh-Co, and 0.5 wt% Rh-Co. The nominal loading of cobalt in these samples was 15 wt%. The actual concentrations of metals and chlorine were determined by neutron activation analysis.

Hydrogen chemisorption and temperature-programmed experiments were carried out using a Micromeritics AutoChem II 2920 system, which employs a thermal conductivity detector (TCD) to monitor the changes in gas composition. After reduction at 673 K for 12 h, the sample (~0.2 g) was cooled to room temperature slowly in flowing hydrogen, and then further cooled to about 200 K using an isopropyl alcohol/liquid nitrogen slurry before purging with argon carrier gas. The temperature was then increased to 673 K at 10 K/min and the hydrogen desorption spectrum was recorded. The reducibility of cobalt catalysts was measured by injecting oxygen pulses at 573 K after H<sub>2</sub> TPD. The volume of the sample loop was calibrated by injections of a known volume of gas using a syringe. TPR experiments were carried out from room temperature to 1073 K at 10 K/min using 10% H<sub>2</sub>/Ar after the calcined catalyst was heated to 473 K in flowing helium to remove adsorbed water.

Transmission electron microscopy (TEM) images were recorded by a FEI Tecnai G2 F20 TEM using passivated samples prepared by oxidizing the reduced catalysts at room temperature in 1% O<sub>2</sub>/He flow. X-ray diffraction (XRD) patterns were collected on both calcined and passivated samples with a Bruker D8 Advance diffractometer using Cu K $\alpha$  radiation. Cobalt particle sizes were calculated from XRD line broadening and from the amount of chemisorbed hydrogen according to the methods in the literature [17,18].

### 2.2. Fischer–Tropsch synthesis

FTS was carried out at 493 K and 5 bar in a stainless steel plug flow reactor (8 mm i.d.) after the catalyst (40–60 mesh, 0.5 g) was reduced in flowing hydrogen at 673 K for 12 h. A N<sub>2</sub>/CO (1:3) mixture (99.99%) was passed through a hot trap kept at 513 K to remove metal carbonyls, and hydrogen (99.995%) was used without further purification. A gas composition of 1:3:6 N<sub>2</sub>/CO/H<sub>2</sub> and a total flow rate of 40 mL/min were used for all the experiments. The reactants and gaseous products (C<sub>1</sub>–C<sub>8</sub>) were analyzed with an online HP 5890 GC equipped with TCD and FID, and products with higher molecular weight were collected in a hot trap (393 K) and a cold trap (273 K). The CO conversion was calculated using nitrogen as an internal standard.

## 3. Results and discussion

### 3.1. Characterization of catalysts

The catalysts were investigated by elemental analysis, XRD, TEM, and H<sub>2</sub> chemisorption. In the calcined samples, Co<sub>3</sub>O<sub>4</sub> was

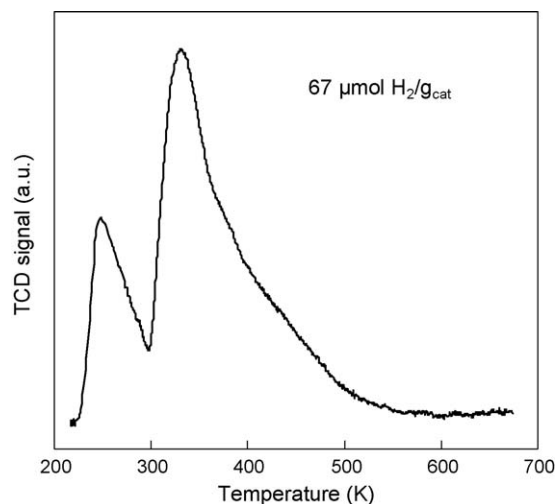


Fig. 1. H<sub>2</sub> TPD profile from 15 wt% Co/SiO<sub>2</sub>.

the only cobalt phase detected by XRD, and metallic cobalt was the only cobalt phase detected in the passivated samples. The diffraction patterns of gold particles (> 30 nm) were observed in the Au-Co catalyst. The results of elemental analysis showed that the concentration of cobalt in the calcined 15 wt% Co/SiO<sub>2</sub> sample was 13.7 wt%, corresponding to 14.4 wt% in the reduced sample, or a 96% efficiency of impregnation. The efficiencies of impregnation for cobalt and other metals in all the samples were greater than 92%. For the Rh-Co samples, it was found that 40–50% of the chloride from rhodium chloride precursors remained in the catalysts after calcination.

The dispersion of cobalt in the Co/SiO<sub>2</sub> catalyst was 5.8%, as determined from the amount of hydrogen desorbed, and the corresponding H<sub>2</sub> TPD profile is shown in Fig. 1. The average cobalt particle size calculated from TEM and H<sub>2</sub> TPD was 17 ± 2 nm for the Co/SiO<sub>2</sub> catalyst. No notable difference in hydrogen chemisorption or cobalt particle size was observed for the Rh-Co samples compared to those of the unpromoted Co/SiO<sub>2</sub>. The results of pulse oxidation experiments after H<sub>2</sub> TPD showed that the Co<sub>3</sub>O<sub>4</sub> in both Co/SiO<sub>2</sub> and Rh-Co/SiO<sub>2</sub> catalysts was completely reduced to metallic cobalt after the reduction step at 673 K.

Fig. 2 shows the TPR profiles of Co/SiO<sub>2</sub> and two Rh-Co/SiO<sub>2</sub> samples. It is generally believed that the two peaks in TPR are due to a two-step reduction of Co<sub>3</sub>O<sub>4</sub> to CoO and then to metallic cobalt [19,20]. Apparently the addition of Rh to Co/SiO<sub>2</sub> lowered the reduction temperatures of cobalt oxides. For the 0.5 wt% Rh-promoted sample, the two TPR peaks of Co/SiO<sub>2</sub> shifted by 120 K and 60 K to lower temperatures, respectively. The same promoting effect of noble metals on the reduction of cobalt oxides has been widely reported in the literature [4]. It is noteworthy from the TPR profiles that the reduction of cobalt oxides was completed at temperatures below 673 K for both Co and Rh-Co samples. The amount of H<sub>2</sub> consumed during TPR was also consistent with the complete reduction of Co<sub>3</sub>O<sub>4</sub> to metallic cobalt below 673 K. This is different from alumina-supported cobalt catalysts (see Ref. [21] for an example), which often show TPR features at temperatures much higher than 673 K. The reduction temperature of silica-supported cobalt catalysts, particularly the CoO to Co step, is dependent on cobalt particle size and the properties of silica support [20]. Some TPR profiles of Co/SiO<sub>2</sub> catalysts in the literature [22,23] also showed the complete reduction of cobalt oxides below 673 K.

The characterization results discussed above showed that the addition of Rh to Co/SiO<sub>2</sub> did not change the cobalt particle size, and cobalt oxides in both Co and Rh-Co catalysts were completely

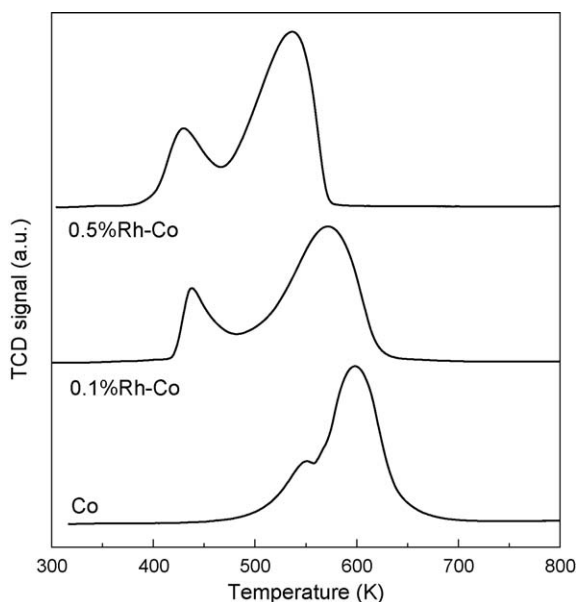


Fig. 2. TPR profiles of Co/SiO<sub>2</sub>, 0.1 wt% Rh-Co/SiO<sub>2</sub>, and 0.5 wt% Rh-Co/SiO<sub>2</sub>.

reduced following reduction in H<sub>2</sub> at 673 K for 12 h. Therefore, the number of surface cobalt atoms was the same for Co and Rh-Co catalysts, and this is also consistent with hydrogen chemisorption results.

### 3.2. FTS activity and selectivity

The CO conversions as a function of time on Co and bimetallic Co catalysts are shown in Figs. 3 and 4. Both Au-Co and Rh-Co catalysts showed an induction period of about 40 h, during which the CO conversion increased significantly. It is believed that the initial low activities were caused by the residual chloride from the precursors, which poisons the active metal sites. It has been reported that chloride can be removed by the water vapor produced under CO hydrogenation conditions [24]. This is consistent with the gradually increased activity on the fresh catalyst and the disappearance of the induction period on the regenerated catalyst, as shown in Fig. 4 for

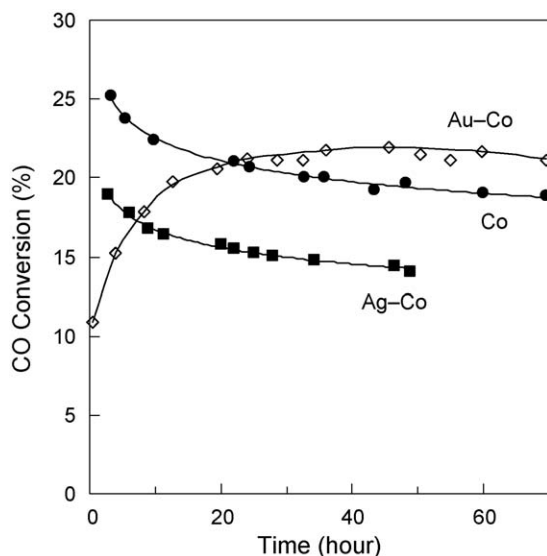


Fig. 3. CO conversion as a function of time on Co/SiO<sub>2</sub>, 1.0 wt% Ag-Co/SiO<sub>2</sub>, and 1.0 wt% Au-Co/SiO<sub>2</sub>.

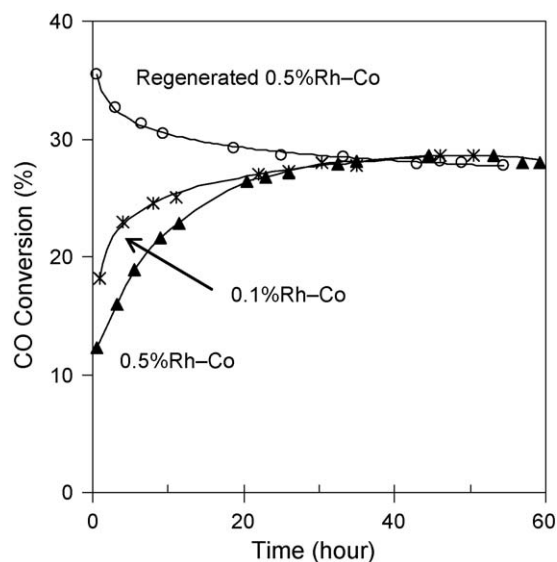


Fig. 4. CO conversion as a function of time on Rh-promoted 15 wt% Co/SiO<sub>2</sub> (Regeneration conditions for 0.5%Rh-Co: H<sub>2</sub>, 673 K, 12 h).

the 0.5% Rh-promoted catalyst. Elemental analysis showed that the concentration of chlorine in the 0.5% Rh-Co catalyst decreased from 0.2 wt% to below the detection limit ( $\sim 0.02$  wt%) after the reaction.

The steady-state activity of the Au-Co catalyst was slightly higher than that of Co/SiO<sub>2</sub>, while the Ag-Co catalyst was less active than unpromoted Co/SiO<sub>2</sub>. The higher activity of Au-promoted cobalt catalysts has also been reported for Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> supported catalysts [12,25]. Recently Jacobs et al. [12] reported that, due to the higher extent of cobalt reduction and therefore higher number of active cobalt sites, Ag-promoted Co/Al<sub>2</sub>O<sub>3</sub> catalysts were more active than unpromoted Co/Al<sub>2</sub>O<sub>3</sub>. However, in our study, unpromoted Co/SiO<sub>2</sub> catalyst was completely reduced after the reduction at 673 K. The observed decrease in activity of the Ag-promoted catalyst may be attributed to blocking of surface cobalt sites by Ag.

The addition of a small amount of Rh (0.1–0.5 wt%) to Co/SiO<sub>2</sub> increased the FT activity by  $\sim 50\%$ . The steady-state activities on the 0.1 and 0.5% Rh-promoted catalysts were almost the same, although the initial activity of the 0.1%Rh-Co sample was higher due to a lower concentration of residual chloride. As a control experiment, FTS was also carried out on a 0.1 wt% Rh/SiO<sub>2</sub> catalyst under the same conditions. Only trace amounts of CH<sub>4</sub> and C<sub>2</sub> products were detected, and the CO conversion was less than 0.01%. The results confirmed that the higher activity of Rh-Co catalysts was due to the promoting effect of Rh, instead of the additional FT activity from Rh particles. Noronha et al. reported that the addition of Rh to Co/Nb<sub>2</sub>O<sub>5</sub> increased the FT activity at 533 K and 1 bar [16]. A Rh/Co atomic ratio of 0.09 or higher was used for these niobia-supported catalysts, compared to a Rh/Co ratio of 0.004 for our 0.1 wt% Rh-promoted catalyst.

The deactivated Rh-Co catalysts can be completely regenerated by reduction at 673 K, as shown in Fig. 4. No sintering of cobalt particles was observed after repeated FT reaction and regeneration cycles. The deactivation behavior of the regenerated Rh-Co catalysts was similar to that of the unpromoted Co/SiO<sub>2</sub>, and no induction period was observed due to the removal of chloride by H<sub>2</sub>O vapor during FTS.

The reaction rates and the selectivities to C<sub>5+</sub> products at the steady state (after 48 h of reaction) on the cobalt-based catalysts are summarized in Table 1. Both the addition of Ag and Au resulted in a slightly lower selectivity to C<sub>5+</sub> products. The selectivity to C<sub>5+</sub> products on the Rh-Co catalysts increased with time during the

**Table 1**

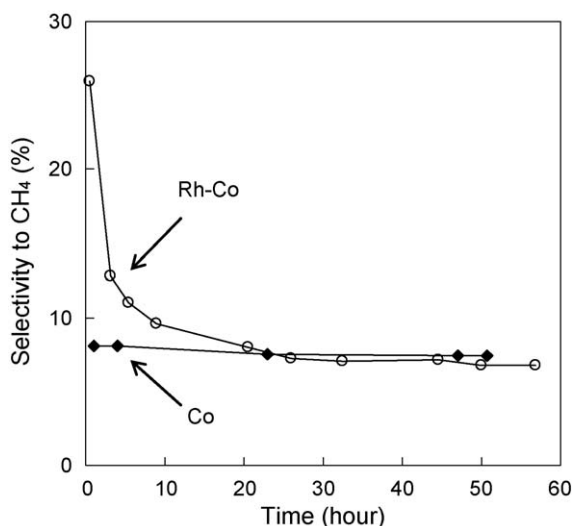
Activity and selectivity after 48 h of reaction ( $T = 493$  K,  $P_{\text{CO}} = 1.5$  bar,  $P_{\text{H}_2} = 3.0$  bar,  $\text{GHSV} = 4.8 \text{ L(STP)}/\text{g}_{\text{cat}}/\text{h}$ ).

Catalyst	CO conversion (%)	TOF <sup>a</sup> ( $\text{s}^{-1}$ )	Selectivity (%)	
			CH <sub>4</sub>	C <sub>5+</sub>
15% Co	19.4	0.026	7.5	85.1
1% Ag–15% Co	14.2	0.019	10.4	77.9
1% Au–15% Co	21.8	0.029	8.1	82.8
0.1% Rh–15% Co	28.6	0.038	7.2	85.0
0.5% Rh–15% Co	28.5	0.038	7.1	84.9

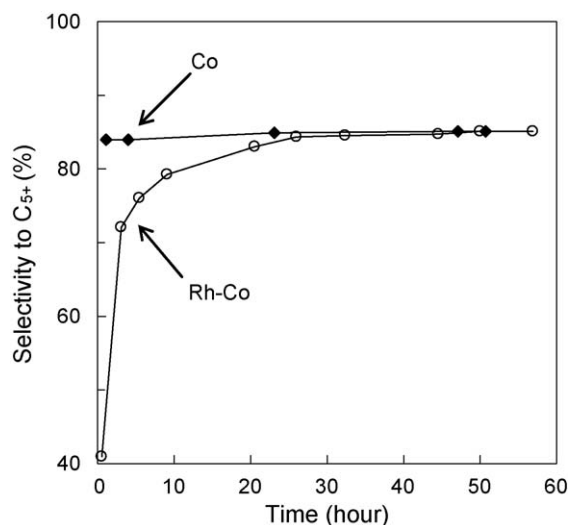
<sup>a</sup> TOF (turnover frequency) was calculated using the number of surface cobalt atoms based on H<sub>2</sub> chemisorption.

induction period, and the selectivity to CH<sub>4</sub> decreased, as shown in Figs. 5–7. The chain growth probability obtained from C<sub>3</sub>–C<sub>8</sub> hydrocarbons on the 0.5% Rh–Co catalyst was 0.77 after 3 h of reaction, and increased to 0.88 after 24 h. At the steady-state conditions, the selectivities and product distributions on the Rh–Co catalysts were almost the same as on the unpromoted Co/SiO<sub>2</sub>.

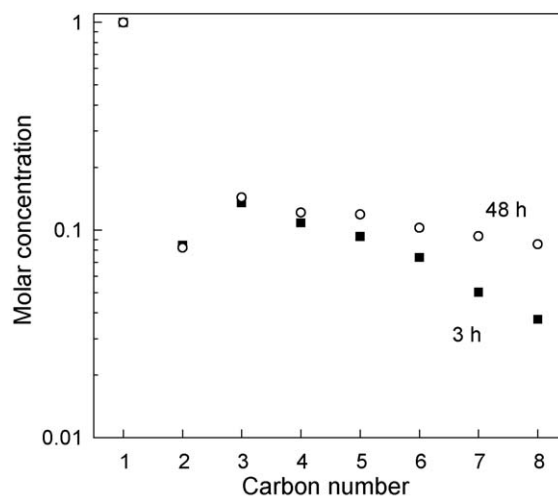
The results in this study show that, although the addition of Rh catalyzes the reduction of cobalt oxides, this does not account for the higher activity of Rh-promoted cobalt catalysts. Given that



**Fig. 5.** Selectivity to CH<sub>4</sub> as a function of time on Co/SiO<sub>2</sub> and 0.5% Rh–Co/SiO<sub>2</sub>.



**Fig. 6.** Selectivity to C<sub>5+</sub> products as a function of time on Co/SiO<sub>2</sub> and 0.5% Rh–Co/SiO<sub>2</sub>.



**Fig. 7.** Anderson–Schulz–Flory distributions of C<sub>1</sub>–C<sub>8</sub> products after 3 h and 48 h of reaction on 0.5% Rh–15% Co/SiO<sub>2</sub>.

cobalt oxides in both Co and Rh–Co catalysts were completely reduced after reduction at 673 K, the number density of surface cobalt atoms was the same for Co and Rh–Co catalysts. Therefore, the higher activity of Rh–Co catalysts is due to some promoting effect of Rh during FT reaction, most likely the spillover of hydrogen from rhodium to metallic cobalt particles. The phenomenon of hydrogen spillover is very common in heterogeneous catalysis [26,27], and has been observed on various supported rhodium catalysts, including Rh/SiO<sub>2</sub>, Rh/Al<sub>2</sub>O<sub>3</sub>, Rh/TiO<sub>2</sub>, and Rh/CeO<sub>2</sub> [28–31]. For FTS, the spillover of hydrogen would result in a higher surface coverage of hydrogen on cobalt, thus increasing the formation rates of monomers and chain initiators (CH<sub>x</sub> species). Therefore, the overall FT activity will be higher.

The fact that very low concentrations of Rh in the catalysts (Rh/Co atomic ratio = 1:250 for 0.1 wt% Rh–15 wt% Co) showed a significant promoting effect suggests that Rh is enriched at the surface of the cobalt particles. For the 0.1 wt% Rh-promoted sample, if we assume all of the Rh is at the surface, the surface Rh/Co atomic ratio would be 1:15. The surface Rh/Co ratio of the 0.5% Rh-promoted sample should be close to that of the 0.1% Rh–Co, since their catalytic properties were the same. Because the Rh/Co ratio is so low even at the surface, the cobalt surfaces are likely decorated with Rh atoms or small clusters, instead of forming a stable surface alloy with Rh.

#### 4. Conclusions

Cobalt oxides in the silica-supported cobalt catalysts were completely reduced to metallic cobalt after reduction at 673 K, as shown by TPR and pulse oxidation experiments. The addition of Rh lowered the reduction temperatures of cobalt oxides; however, the cobalt particle size and the number of surface cobalt atoms were not changed. The FT activity on the cobalt-based bimetallic catalysts follows an order of Rh–Co > Au–Co > Co > Ag–Co. The addition of a small amount of Rh (0.1–0.5 wt%) to Co/SiO<sub>2</sub> increased the CO conversion by 50%, while the selectivity was not affected. It is proposed that the spillover of hydrogen from rhodium to cobalt during FTS reaction is responsible for the higher activity of Rh-promoted Co/SiO<sub>2</sub> catalysts.

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