Promotional Effect of Noble Metal to Co-based Fischer-Tropsch Catalysts Prepared from Mixed Cobalt Salts

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Addition of very small amount of Ru, Pt and Pd exhibited great effect on the Co-based catalysts prepared by mixing impregnation of cobalt (II) nitrate and cobalt (II) acetate. Added small amount of Ru to this kind of catalyst showed extremely high activity, while no apparent CH_4 selectivity change was observed. However, added Pt and Pd hardly exerted effect on the activity of Co-based catalyst, but increased CH_4 selectivity remarkably.

Cobalt-containing catalysts are known to be effective in CO hydrogenation.[1,2] Recent studies indicated that Fischer-Tropsch synthesis (FTS) activity of Co catalysts depended on the active-site number after the reduction. The active-site number should be determined by the Co particle size, loading amount and reduction degree.[3,4] Synthesis of highly dispersed Co catalysts requires the initial formation of fine CoO or Co_3O_4 crystalline. The formation of such small oxide clusters is controlled by strong interactions between the support and Co precursors, but in turn such strong interactions generally make lower the reduction degree of such precursors to Co metal.[5]

The present authors have reported that the catalyst prepared from the mixture of cobalt nitrate and cobalt acetate (condition b) exhibited higher activity than the catalyst prepared from mono-precursor salt (condition a),[6] because the metal reduced from cobalt nitrate promoted the reduction of Co^{2+} to metallic state in cobalt acetate by H_2 spillover mechanism during catalyst reduction process. But its reduction degree was still not enough. Here, it is reported that adding very small amount of noble metal to this kind of catalysts had significant influence on the activity, methane and CO_2 selectivity. Addition of very small amount of Ru exhibited remarkably high activity and low CH_4 selectivity. As shown in Table 1, the activity of RuCo (condition b) was higher than that of RuCo (condition a).

The supported cobalt catalysts were prepared by incipient-wetness coimpregnation of cobalt nitrate, cobalt acetate and noble metal salts on silica gel (ID gel, Fuji Davison, 270 $m^2 g^{-1}$, pore volume 1.22 $cm^3 g^{-1}$), drying in air at 393 K for 12 h, and then calcining at 723 K for 2 h in air. The compositions of the catalysts were listed in Table 1. The weight ratio of noble metal to cobalt was 1/50. After calcination, catalysts were activated in flowing hydrogen at 673 K for 10 h. At last, the catalysts were passivated by 1% O_2 in N_2.

Catalysts were tested in a semi-batch slurry-phase reactor (volume: 80 ml). The amount of catalyst was 1 g. 20 ml of n-$C_{16}H_{34}$ was used as liquid medium.

FT-IR spectra were recorded using a Nicolet Magna 550 spectrophotometer. Each sample of 30 - 40 mg was pressed into a disk. The disk was placed in an infrared cell, equipped with CaF_2 windows. CO was adsorbed on the fresh catalysts at room temperature (P_{co} = 200 Torr) for 10 min. Then, the cell was evacuated for 5 min.

Table 1. Catalytic behaviors of various Co (10 wt%)/SiO_2 FTS catalysts

Catalyst	CO conv. / %	CH_4 sel. / %	CO_2 sel. / %	TOF[c] $*10^2 s^{-1}$
Co[a]	29.8	6.6	1.6	7.2
Co[b]	33.5	8.9	1.3	9.3
RuCo[b]	72.3	8.5	3.3	12.7
PtCo[b]	49.5	13.8	9.5	4.2
PdCo[b]	57.9	17.8	5.0	5.9
Ru	2.5	4.8	0.1	/
RuCo[a]	56.7	6.6	3.3	/

Total cobalt loading amount: 10 wt%. [a]Catalyst precursor was only cobalt nitrate. [b]Catalyst precursor was the mixture of cobalt nitrate and cobalt acetate, molar ratio of nitrate to acetate was 1; noble metal loading amount was 0.2 wt%. Reaction conditions: 1.0 MPa, 513 K, W/F = 5 g-cat.h/mol, CO/ H_2 = 1/2. Noble metal precursors were $Ru(NO_3)_3$, $Pt(NO_2)_2(NH_3)_2$ and $Pd(NO_2)_2(NH_3)_2$ respectively. [c]Calculated by TOF(s^{-1}) = CO_{conv}.s^{-1}/ surface Co. Surface Co atom number was determined by static H_2 adsorption.

Table 2. Structure difference of various catalysts

Catalyst	Reduction degree / %[a]	Dispersion / %[b]	Particle size / nm	
			$H_{2(ad)}$[c]	TEM
Co*	50	8.63	12.02	4.52
RuCo**	100	6.91	13.09	6.45
PtCo**	56	22.67	4.15	2.94
PdCo**	63	16.62	5.63	4.15

*Catalyst precursor was the mixture of cobalt nitrate and cobalt acetate. **Same as the [b] in Table 1. [a]After 673 K reduction, assuming the noble metals are completely reduced and following reactions occur during the oxidation at 673 K: $3Co+2O_2 \blacktriangleright Co_3O_4$, $Pt+1/2O_2 \blacktriangleright PtO$, $Pd+1/2O_2 \blacktriangleright PdO$ and $Ru+3/4O_2 \blacktriangleright 1/2Ru_2O_3$. [b]Assuming the stoichiometry H_{ad}/Co_s or M_s=1 (M=Ru, Pt and Pd). [c]Calculated by d_s(nm) = 96/D(%) according to Ref. 7

The reaction results are compared in Table 1. Although the CO conversion of Co was 33.5%, the RuCo's was as high as 72.3%. However, if the catalyst precursor was only cobalt nitrate and also promoted by 0.2 wt% Ru, the CO conversion was only 56.7%. According to the Table 1, the CO conversion was in the order of RuCo > PdCo > PtCo > Co > 0.2 wt% Ru.

The catalysts promoted by Pd and Pt exhibited higher methane and CO_2 selectivity than the catalyst promoted by Ru or Co only. Table 1 shows that RuCo catalyst exhibited large turnover frequency (TOF) value of CO. But the catalyst promoted by Pt or Pd showed small TOF value and higher methane and CO_2 selectivity. Their TOF values were even lower than those of cobalt catalyst without noble metal addition.

As shown in Table 2, with the addition of small amount of Ru, the reduction degree increased sharply from 50% to 100%, indicating that no cobalt existed in oxide form. At the same time the cobalt particle size increased also. Small amount of the added Pt or Pd had slightly influenced the reduction degree, but the Co particle size decreased obviously.

In Table 2, the particle size determined from H_2 adsorp-

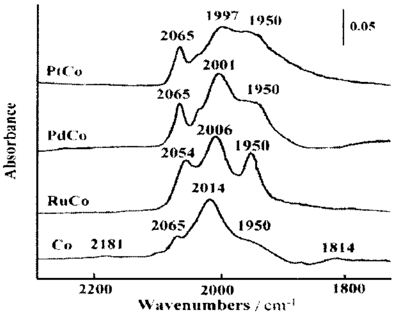

Figure 1. FT-IR spectra of CO adsorbed on various catalysts reduced at 673 K.

tion was different from that from TEM. In TEM experiment, a catalyst pellet was embedded into resin and then cut by microtome method. Due to the limitation of the number of the pellets observed by TEM, it is considered that particle size from H_2 adsorption was more precise. According to the theory of FTS,[8] large supported metallic crystallines showed larger TOF value than smaller ones. From Tables 1 and 2, it seems that this theory is correct here. TOF exhibited the same changing trend to metallic particle size.

Individual metal particles in the bimetallic RuCo, PtCo and PdCo were analyzed by EDS attached to TEM. The results gave clear evidence that the noble metals had intimate interaction with Co, and alloy of RuCo, PtCo and PdCo formed with different composition. It was found that Ru was very rich in alloy RuCo (95.9 wt%), compared to its original composition (2 wt%). Composition of alloy PtCo (5.2 wt%) and PdCo (7.9 wt%) was near to the preparation ratio (2 wt%). The difference of the formed alloy composition seemed to change the reduction degree and the size of metallic crystalline during the catalyst preparation.

The FT-IR spectra of the adsorbed CO for the reduced catalysts are compared in Figure 1. For catalyst Co, an intense peak at 2014 cm^{-1} with two shoulder peaks at 2065, 1950 and weak peaks at 2181, 1814 cm^{-1} were observed. The 2014 cm^{-1} peak was assigned to CO adsorbed on cobalt metal in linear geometry.[9,10] The 2065 cm^{-1} shoulder peak could be assigned to the surface carbonyl species, Co $(CO)_x$ (where X>1), which readily happened to corner sites on the cobalt metal, and the 1950 cm^{-1} shoulder peak was due to the bridged CO on Co sites.[11] The 1814 cm^{-1} weak peak was assigned to an adsorbed CO onto multifold sites.[12] The peak at 2181 cm^{-1} was assigned to the CO adsorbed on Co^{n+} (n = 2,3) species.[12] as surface cobalt oxide species were difficult to be completely reduced on supported cobalt acetate.

For the catalyst PtCo and PdCo, the band of CO adsorbed on cobalt metal in linear-type shifted from 2014 cm^{-1} on catalyst Co to 1997, 2001 cm^{-1} respectively. Similarly, peak 2065 cm^{-1} derived from surface carbonyl species Co $(CO)_x$ and the 1950 cm^{-1} peak was from CO in bridge adsorption state. For the catalyst RuCo, the CO adsorbed as linear-type shifted to 2006cm^{-1}, and 2065 cm^{-1} of Co $(CO)_x$ shifted to 2054 cm^{-1}. Peak 1950 cm^{-1}, the bridge-type adsorbed CO, was very strong on RuCo. It is believed that bridge-type CO was easily formed on large Co particles here. As has been pointed out, the bridge-type CO was much more active than linear-type CO.[13] The high activity of RuCo catalyst can be attributed to the increase in bridge-type adsorbed CO, which was easily dissociated to carbon and oxygen. From EDS, Pt or Pd dispersed very well in cobalt to form alloy of uniform composition. It is considered that electronic effect, legend effect, appeared in PtCo and PdCo catalyst as linear CO peaks of these catalysts shifted remarkably to lower side, even if the Co particle size decreased. Electron transferred from Pt or Pd to anti-bonding orbital of the linearly-adsorbed CO through Co, making CO combination weak. But this electronic transfer did not happen to bridge-adsorbed CO, as no wavenumber shift of bridge-adsorbed CO appeared. From IR spectra of PtCo and PdCo, new peak derived from adsorbed CO with the structure between linear and bridge mode might form, resulting 1950 cm^{-1} peak in shoulder-peak from. It seems that this electronic effect determined the lower TOF and higher methane selectivity.[14] For RuCo, Ru became very rich on cobalt surface from EDS and bulk cobalt contained little Ru. This might lead to large supported cobalt particle and more bridge-type adsorbed CO. Legend effect was not so obvious in RuCo as Ru was enriched at Co particle surface. Shift of linearly-adsorbed CO from 2014 cm^{-1} to 2006 cm^{-1} was mainly due to the Co particle size increase of RuCo catalyst.

From the viewpoint of particle size effect, the wavenumber of linearly-adsorbed CO on PtCo or PdCo should be higher than 2014 cm^{-1}, the analogy on Co catalyst, as the metallic particle size of PtCo and PdCo was smaller than that of Co catalyst. It is estimated that due to the electronic shift from Pt or Pd to CO, the wavenumber of linear CO on PtCo and PdCo was 1997 and 2001 cm^{-1} respectively, lower than that of Co catalyst. This electronic effect might be also the reason why bridge CO on PdCo and PtCo had stronger peak than that of Co catalyst.

From above, it is clear that Ru promoted the Co reduction significantly and supported Co metallic crystalline size was increased. CO adsorbed at bridge state, to form the active CO species, on this RuCo catalyst. As a result, RuCo catalyst exhibited high activity.

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