Studies on the interaction between ruthenium and cobalt in supported catalysts in favor of hydroformylation

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The interaction between ruthenium and cobalt atoms in SiO_2-supported catalysts prepared from various precursors by H_2 treatment at 350 °C has been studied by ethylene hydroformylation, temperature-programmed reduction (TPR) technique and IR spectroscopy. Incorporation of cobalt with ruthenium gives a catalyst with remarkably enhanced hydroformylation activity with respect to those of monometallic catalysts, irrespective of the ruthenium and cobalt precursors used. The synergistic effect of ruthenium and cobalt on the catalysis is consistent with TPR and IR results. TPR analysis shows regularly a promoted reduction of cobalt due to the "hydrogen spillover" effect, which indicates that ruthenium and cobalt atoms are in intimate contact in the catalysts. CO adsorption IR study demonstrates a strong decrease of CO chemisorption on Ru in the presence of cobalt, proposing that ruthenium and cobalt atoms interact on the SiO_2 surface to form Ru–Co bimetallic particles. The results suggest that the catalysts thus obtained contain Ru–Co bimetallic particles, at least atoms of the two metals in intimate contact. However, *in situ* surface IR spectra of ethylene hydroformylation exhibit little modification by the presence of cobalt on Ru/SiO_2.

Keywords: silica, ruthenium, cobalt, interaction, hydroformylation

1. Introduction

Ruthenium and cobalt are viewed as potential catalytic components to replace rhodium owing primarily to the lower cost. Supported ruthenium and supported cobalt are known to be highly active for Fischer–Tropsch synthesis [1–3]. Nevertheless, they show low catalytic activity and selectivity for olefin hydroformylation because of high catalytic activity for olefin hydrogenation proceeding at the same time [4–9]. It is documented that cobalt is able to enhance greatly the rate of oxygenate formation in olefin hydroformylation, by combination with a variety of noble metals [10–15]. Up to now, little has been devoted to fundamental study concerning ruthenium and cobalt-containing supported hydroformylation catalysts in the literature [10,16,17]. The cause of the high enhancement of oxygenate formation in the copresence of ruthenium and cobalt has not been elucidated. This paper deals with the interaction between ruthenium and cobalt in SiO_2-supported catalysts in association with the rate enhancement of ethylene hydroformylation. Our research is concerned with probing the synergy of ruthenium and cobalt in SiO_2-supported catalysts derived from a variety of precursors by ethylene hydroformylation, characterizing the surfaces of such catalysts by IR spectroscopy and revealing the nature of interaction between supported ruthenium and cobalt atoms by TPR technique.

2. Experimental

$RuCl_3{\cdot}nH_2O$ and $Ru_3(CO)_{12}$ were purchased from Aldrich Chemical Company, Inc. $Co(NO_3)_2{\cdot}6H_2O$ and $CoCl_2{\cdot}6H_2O$ were supplied by Beijing Chemical Reagent Company, Inc. $Co_2(CO)_8$ and $HRuCo_3(CO)_{12}$ were synthesized according to literature procedures [18,19]. SiO_2 was a silica "Aerosil" supplied by Degussa with a surface area of 380 m^2/g. Dichloromethane (CH_2Cl_2) and n-hexane used as solvents were distilled over P_2O_5 under Ar and stored over activated 5A molecular sieves under Ar. The gases H_2, CO, C_2H_4 and Ar had a purity of 99.99%. Before introduction into a sample vessel and a reactor, they were further purified by passage through traps of activated 5A molecular sieves and Mn/MnO.

Metal carbonyl catalyst precursors were prepared by impregnating SiO_2 with solutions of metal carbonyls. SiO_2 (60–80 mesh granule) was predehydroxylated under vacuum at 400 °C for 5 h, and impregnated or coimpregnated with metal carbonyl(s) in dry solvent under Ar in a Schlenk tube. The impregnated systems were stirred for 2 h under Ar. The solvent was removed by evacuation and the resulting solid samples were dried under vacuum (10^{-2} Torr) for 1 h. In this manner, $Co_4(CO)_{12}/SiO_2$, $Ru_3(CO)_{12}/SiO_2$, $(Ru_3(CO)_{12}+Co_4(CO)_{12})/SiO_2$ and $HRuCo_3(CO)_{12}/SiO_2$ were made directly from $Co_2(CO)_8/n$-hexane, $Ru_3(CO)_{12}/CH_2Cl_2$, $(Ru_3(CO)_{12}+Co_2(CO)_8)/CH_2Cl_2$ and $HRuCo_3(CO)_{12}/n$-hexane.

SiO_2-supported metal salts and related catalyst precursors were prepared according to the following procedure.

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First, SiO_2 (60–80 mesh granule) was incipient wetted with an aqueous solution of metal salt(s). Then the resulting slurry after stirring was gently heated under an infrared lamp till it turned into a dry solid sample. The solid sample was subjected to 5 h of calcination in air at 400 °C. Such oxidation calcination is believed to lead to full conversions of $Ru(NO_3)_3$, $RuCl_3$, $Co(NO_3)_2$ and $CoCl_2$ to RuO_2 and Co_3O_4 [20–22]. For making a catalyst precursor from $Ru(NO_3)_3$ or $RuCl_3{\cdot}nH_2O$ and $Co_2(CO)_8$, $Ru(NO_3)_3/SiO_2$ or $RuCl_3/SiO_2$ was impregnated with a n-hexane solution of $Co_2(CO)_8$ under Ar in a Schlenk tube following 5 h of calcination in air at 400 °C. The impregnated system was stirred for 2 h under Ar followed by removal of the solvent under vacuum. The resulting solid sample was dried under vacuum for 1 h.

All ruthenium catalyst precursors prepared contained 1.0% Ru. The atomic ratio of Co : Ru was set to 3 : 1.

Hydroformylation of ethylene was conducted under atmospheric pressure at 150 °C in a glass tubing flow reactor (i.d. = 18 mm) where 0.50 g of catalyst precursor was charged. The detailed experimentation is described elsewhere [23].

For IR and TPR studies, the detailed experimentations are also described elsewhere [23,24].

The metal contents of the samples studied were determined by atomic absorption spectroscopy.

3. Results

3.1. Synergistic effect of ruthenium and cobalt on catalytic ethylene hydroformylation

Table 1 shows comparative catalytic results of atmospheric ethylene hydroformylation at 150 °C over SiO_2-supported monometallic catalysts and ruthenium and cobalt-containing SiO_2-supported catalysts derived from various precursors. Ruthenium and cobalt-containing catalysts derived by combination of any ruthenium and cobalt precursors at an atomic ratio of Co : Ru = 3 : 1 presented to greater extent improved hydroformylation activity as compared to the monometallic catalysts. The great increase in hydroformylation activity accompanied the high activity and selectivity in ethylene hydrogenation and the formation of n-propanol in lesser amounts. For instance, the activity to oxygenates by coimpregnation with $RuCl_3{\cdot}nH_2O$ and $CoCl_2{\cdot}6H_2O$ was 5.7 times greater than that of Ru/SiO_2 made from $RuCl_3{\cdot}nH_2O$; the $HRuCo_3(CO)_{12}$-derived catalyst displayed increased activity to oxygenates by 18.6 times compared to the $Ru_3(CO)_{12}$-derived one; combination of $Ru_3(CO)_{12}$ and $Co_2(CO)_8$ resulted in obviously higher hydroformylation activity than that of the $HRuCo_3(CO)_{12}$-derived catalyst.

The observed tremendous improvement of hydroformylation activity with the $HRuCo_3(CO)_{12}$-derived catalyst is consistent with its catalytic performance for oxygenate formation in previous studies [25–27]. The fact that the ($Ru_3(CO)_{12} + Co_2(CO)_8$) combination is most suitable for the rate enhancement of oxygenate formation is in analogy with previous findings in rhodium and cobalt-containing catalyst systems [13,14]. The above results suggest that there is a synergistic effect between ruthenium and cobalt in supported catalysts on the rate enhancement of ethylene hydroformylation.

3.2. TPR behaviors of catalyst precursors

Figure 1 illustrates TPR profiles of SiO_2-supported $RuCl_3$, $Co(NO_3)_2$ and ($RuCl_3 + Co(NO_3)_2$) following calcination in air at 400 °C. The reduction pattern in figure 1(a)

Table 1
Catalytic properties of SiO_2-supported catalysts[a] in atmospheric ethylene hydroformylation (C_2H_4 : CO : H_2 = 20 : 20 : 20 ml/min) at 150 °C.

Precursor	Co : Rh (atomic ratio)	Activity[b]		Selectivity (mol%)		
		C_2H_6	Oxygenates[c]	C_2H_5CHO	n-C_3H_7O	C_2H_6
$Co(NO_3)_2{\cdot}6H_2O$		0	0	–	–	–
$CoCl_2{\cdot}6H_2O$		0	0	–	–	–
$Co_2(CO)_8$		0	0	–	–	–
$Ru(NO_3)_3$		0	0.14	100	0	0
$RuCl_3{\cdot}nH_2O$		0	0.07	100	0	0
$Ru_3(CO)_{12}$		0	0.07	100	0	0
$HRuCo_3(CO)_{12}$		3.40	1.37	19	10	71
$Ru(NO_3)_3 + Co(NO_3)_2{\cdot}6H_2O$	3 : 1	1.82	1.03	27	9	64
$RuCl_3{\cdot}nH_2O + CoCl_2{\cdot}6H_2O$	3 : 1	0.62	0.47	31	12	57
$Ru(NO_3)_3 + Co_2(CO)_8$	3 : 1	1.47	0.81	29	7	64
$(Ru(NO_3)_3 + Co_2(CO)_8)$[d]	3 : 1	2.96	1.12	19	9	72
$RuCl_3{\cdot}nH_2O + Co_2(CO)_8$	3 : 1	1.66	1.45	32	15	53
$Ru_3(CO)_{12} + Co_2(CO)_8$	3 : 1	5.55	2.46	17	14	69

[a] With 1.0% Ru and 1.7% Co loadings, reduced under H_2 at 350 °C for 2 h.

[b] Expressed by (mol/mol-Co min) for Co/SiO_2 and (mol/mol-Ru min) for Ru-containing catalysts, data were taken 7 h after the initiation of reaction.

[c] $C_2H_5CHO + n$-C_3H_7OH.

[d] $Ru(NO_3)_3/SiO_2$ was precarbonylated under 700 Torr of CO at 100 °C before impregnation with $Co_2(CO)_8/n$-hexane.

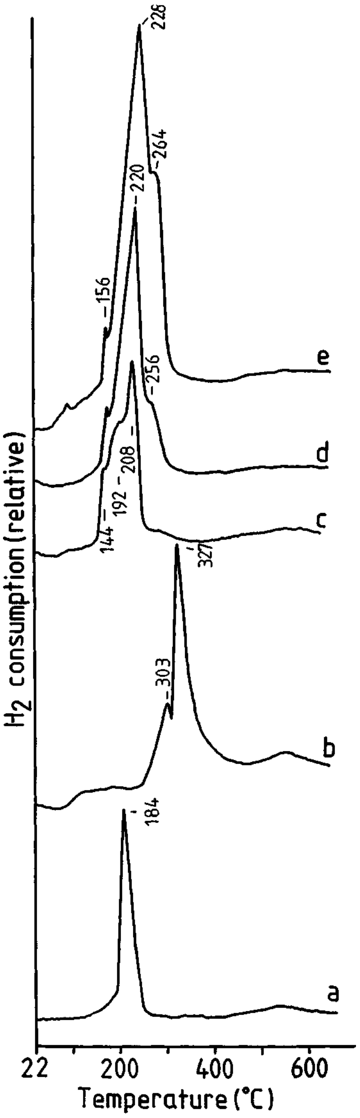

Figure 1. TPR profiles in 5% H_2/N_2 at 8 °C/min of supported precursors following calcination in air at 400 °C. (a) $RuCl_3/SiO_2$ (1.0% Ru loading), (b) $Co(NO_3)_2/SiO_2$ (1.7% Co loading), (c) $(RuCl_3 + Co(NO_3)_2)/SiO_2$ (1.0% Ru loading, Co : Ru = 1 : 3), (d) $(RuCl_3 + Co(NO_3)_2)/SiO_2$ (1.0% Ru loading, Co : Ru = 1 : 1) and (e) $(RuCl_3 + Co(NO_3)_2)/SiO_2$ (1.0% Ru loading, Co : Ru = 3 : 1).

exhibited a single peak at 184 °C, which is assigned to the reduction of RuO_2/SiO_2 in good agreement with a previous result [20]. The reduction pattern in figure 1(b) corresponds to the reduction of Co_3O_4/SiO_2 [21,28]. In the cases of calcined $(RuCl_3 + Co(NO_3)_2)/SiO_2$, the observed reduction patterns deviated from that of either RuO_2/SiO_2 or Co_3O_4/SiO_2, as shown in figure 1 (c)–(e): with Co : Ru = 1 : 3, the TPR curve presented a maximum at 208 °C and two shoulders toward 144 and 192 °C with the absence of reduction peaks for Co_3O_4/SiO_2; with Co : Ru = 1 : 1, the TPR curve showed a dominant peak at 220 °C and two weak shoulders toward 156 and 256 °C; with Co : Ru = 3 : 1, the TPR curve displayed a maximum at 228 and two shoulders toward 156 and 264 °C. Obviously, the reduction maxima of calcined $(RuCl_3 + Co(NO_3)_2)/SiO_2$ were found higher in temperature than the reduction peak of RuO_2/SiO_2. Such a maximum shifted to higher temperatures with increasing Co : Ru atomic ratio. Meanwhile the peak at 264 °C emerged progressively as the cobalt content increased. This peak is assumed to result from the reduction of Co_3O_4 in the presence of ruthenium. The curve in figure 1(e) is actually composed of the reduction peaks for RuO_2/SiO_2 and Co_3O_4/SiO_2. The former shifts to higher temperatures with respect to that of pure RuO_2/SiO_2 and the latter shifts to lower temperatures relative to that of Co_3O_4/SiO_2. The low-temperature shift of Co_3O_4 TPR in the presence of the noble metal ruthenium is explained by the "intraparticle hydrogen spillover" effect [29,30]. The slight high-temperature shift of RuO_2 TPR is due to the superimposition with the peak of Co_3O_4 TPR.

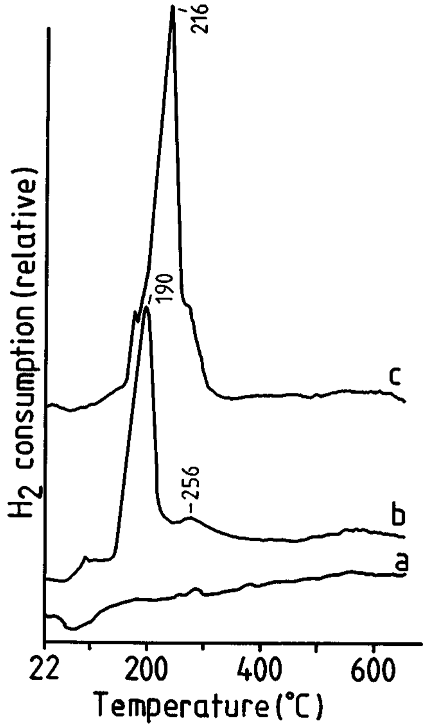

Figure 2. TPR profiles in 5% H_2/N_2 at 8 °C/min of supported precursors following oxidation in air at ambient temperature. (a) $Co_4(CO)_{12}/SiO_2$ (1.7% Co loading), (b) $(RuO_2 + Co_4(CO)_{12})/SiO_2$ (1.0% Ru loading, Co : Ru = 1 : 3) and (c) $(RuO_2 + Co_4(CO)_{12})/SiO_2$ (1.0% Ru loading, Co : Ru = 1 : 1).

Figure 2 illustrates TPR profiles of SiO_2-supported $Co_4(CO)_{12}$ and $(RuO_2 + Co_4(CO)_{12})$ following oxidation in air at ambient temperature. In order to display the TPR signals with cobalt, $Co_4(CO)_{12}/SiO_2$ and $(RuO_2 + Co_4(CO)_{12})/SiO_2$ were converted to Co^{2+}/SiO_2 and $(RuO_2 + Co^{2+})/SiO_2$ by exposure to air at ambient temperature for 24 h [31]. The curve in figure 2(a) presents the TPR result of Co^{2+}/SiO_2 up to 655 °C. No visible reduction peak appeared, indicating that Co^{2+}/SiO_2 derived from $Co_2(CO)_8$ is not easily reduced by H_2. This result has not yet been reported. The possibility of cobalt silicate formation at ambient temperature can be ruled out. Therefore, we suggest that the difficult reduction of Co^{2+} is due to its high dis-

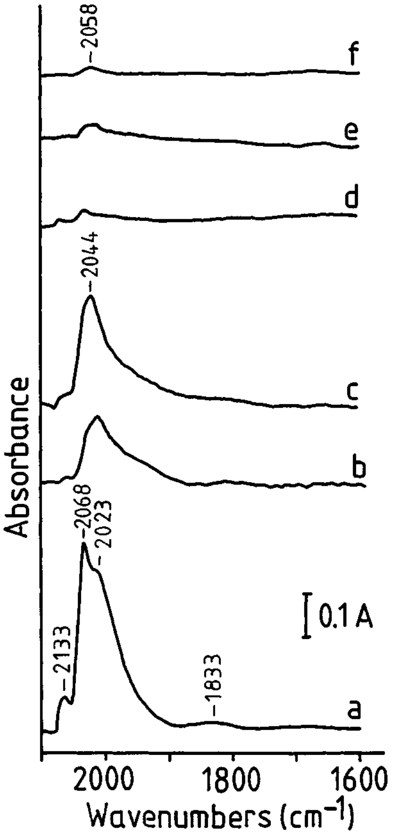

Figure 3. IR spectra of CO adsorbed on catalysts (1.0% Ru loading, adsorption time 24 h) prepared by H_2 treatment at 350 °C of (a) RuO_2/SiO_2, (b) $(RuO_2 + Co_4(CO)_{12})/SiO_2$ (Co : Ru = 3 : 1), (c) $(Ru^{2+}(CO)_3 + Ru_3(CO)_{12} + Co_4(CO)_{12})/SiO_2$, (d) $(RuO_2 + Co_4(CO)_{12})/SiO_2$, (e) $(Ru_3(CO)_{12} + Co_4(CO)_{12})/SiO_2$ and (f) $HRuCo_3(CO)_{12}/SiO_2$.

persion on SiO_2 and strong interaction with surface oxygen [32]. The TPR curve of $(RuO_2 + Co^{2+})/SiO_2$ with Co : Ru = 1 : 3 displayed a sharp peak at 190 °C and a weak broad peak centered at 256 °C. The former is clearly assigned to the reduction of RuO_2/SiO_2 and the latter may be attributed to the reduction of small amounts of Co^{2+}/SiO_2. With Co : Ru = 1 : 1, the TPR curve exhibited mainly an intense peak at 216 °C. The observed reduction maxima shift slightly to lower temperatures compared to that of pure RuO_2/SiO_2. It is thus inferred that the presence of ruthenium makes it possible to reduce partly Co^{2+} to Co^0 at temperature below 300 °C.

3.3. IR characterization of catalysts by adsorption

Figure 3 shows comparative IR spectra of CO adsorbed on catalysts (1.0% Ru loading) prepared by H_2 treatment of a variety of SiO_2-supported precursors at 350 °C. After 24 h of adsorption of CO at 100 Torr and ambient temperature on Ru/SiO_2 derived from $Ru(NO_3)_3$, the surface spectrum presented bands at 2133w, 2068w, 2023s and 1833vw cm^{-1}. The 2023 and 1833 cm^{-1} bands are assigned to the adsorption of CO on Ru^0/SiO_2 [33]. The 2133 and 2068 cm^{-1} bands are attributed to the surface $Ru^{2+}(CO)_3$ species arising from the concerted oxidation of Ru^0 by surface OH^- under CO [33,34]. The easy oxidation of Ru^0 to Ru^{2+} is related to the high dispersion of ruthenium metal particles on SiO_2 (low ruthenium loading). Much the same surface spectra were observed for CO adsorbed on Ru/SiO_2 derived from $RuCl_3{\cdot}nH_2O$ and $Ru_3(CO)_{12}$. There was no band observed for CO adsorbed on Co/SiO_2 (1.7% Co loading) derived from $Co_2(CO)_8$. However, addition of cobalt to Ru/SiO_2 led to reduction in intensity of the linear CO band on Ru^0 and suppression of the carbonyl bands of $Ru^{2+}(CO)_3$. Especially in the cases with $HRuCo_3(CO)_{12}/SiO_2$, $(Ru_3(CO)_{12} + Co_4(CO)_{12})/SiO_2$ and $(RuCl_3 + Co_4(CO)_{12})/SiO_2$, the adsorption of CO was nearly completely inhibited.

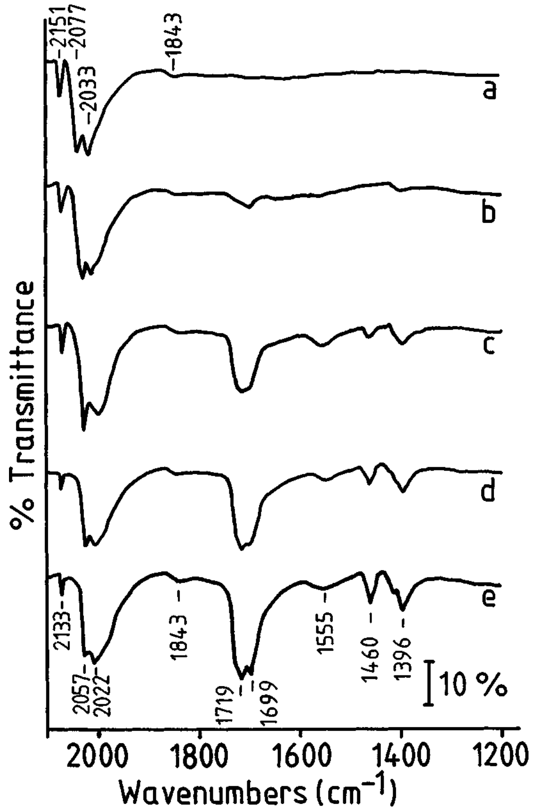

Figure 4. IR spectra on a $Ru(NO_3)_3/SiO_2$-derived catalyst (1.0% Ru loading) under $C_2H_4 + CO + H_2$ (200 : 200 : 200 Torr) at 150 °C in a static IR cell: (a) 3 min, (b) 0.5 h, (c) 13 h, (d) 76 h and (e) 101 h.

In situ ethylene hydroformylation was also studied by IR spectroscopy on typical SiO_2-supported catalysts derived from $Ru(NO_3)_3$, $Co_2(CO)_8$, $(Ru(NO_3)_3 + Co(NO_3)_2{\cdot}6H_2O)$ and $HRuCo_3(CO)_{12}$. Figure 4 gives surface IR spectra taken under steady-state $C_2H_4/CO/H_2$ conditions at 150 °C over Ru/SiO_2 (1.0% Ru loading) prepared from $Ru(NO_3)_3$. At the beginning of reaction, marked bands at 2151 and 2077 cm^{-1} for the surface $Ru^{2+}(CO)_3$ species were observed together with bands at 2033 and 1843 cm^{-1} for CO on Ru^0/SiO_2. As the reaction proceeded, the carbonyl bands for $Ru^{2+}(CO)_3$ decreased somewhat in intensity and still remained in the spectra after 101 h of reaction. In the meantime, bands at 1719 and 1699 cm^{-1} emerged and

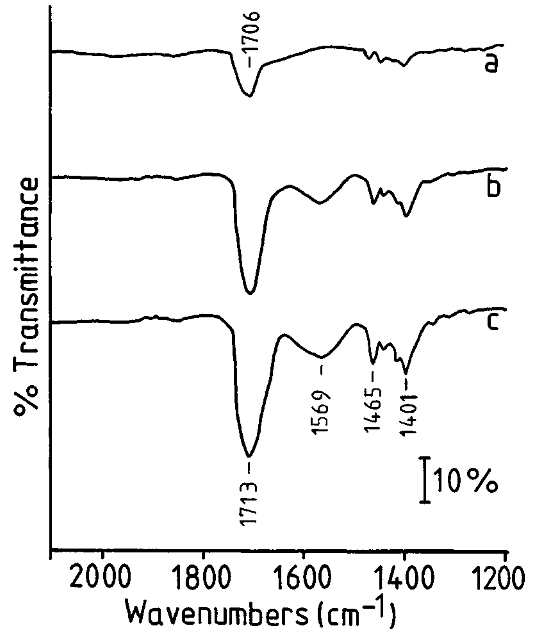

Figure 5. IR spectra on a $Co_4(CO)_{12}/SiO_2$-derived catalyst (1.7% Co loading) under $C_2H_4 + CO + H_2$ (200 : 200 : 200 Torr) at 150 °C in a static IR cell: (a) 12.5, (b) 60 and (c) 106 h.

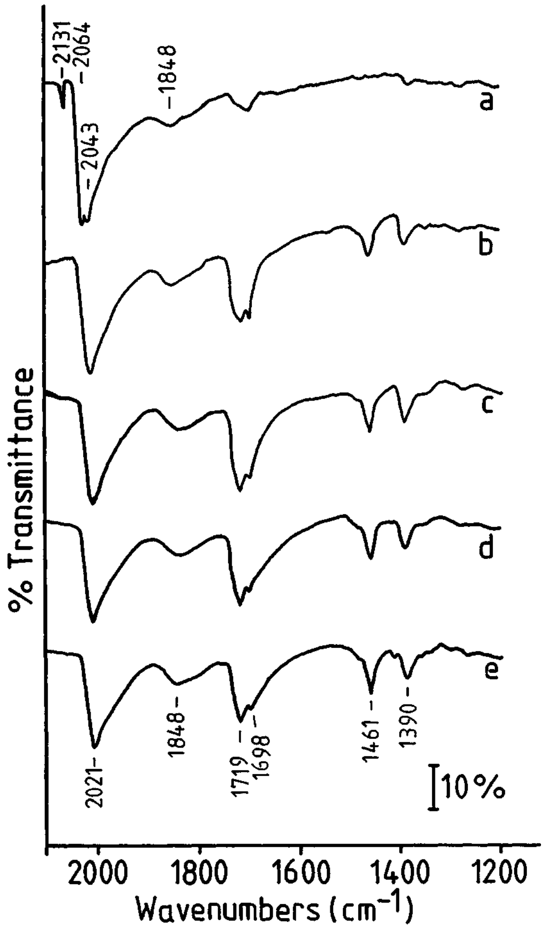

Figure 6. IR spectra on a $(Ru(NO_3)_3 + Co(NO_3)_2)/SiO_2$-derived catalyst (1.0% Ru loading, Co : Ru = 3 : 1) under $C_2H_4 + CO + H_2$ (200 : 200 : 200 Torr) at 150 °C in a static IR cell: (a) 3 min, (b) 5 h, (c) 28 h, (d) 51 h and (e) 100 h.

developed with reaction time. The former corresponds to adsorbed propanal and the latter may be attributed to an acyl species. When the reaction was stopped, the surface spectrum contained the $Ru^{2+}(CO)_3$ bands at 2133 and 2057 cm^{-1}, and the bands at 2022 and 1843 cm^{-1} for CO adsorbed on Ru^0/SiO_2. The linear CO on Rh^0 is recognized to be responsible for CO insertion in hydroformylation [35].

Figure 5 gives surface IR spectra obtained under steady-state $C_2H_4/CO/H_2$ conditions at 150 °C over Co/SiO_2 (1.7% Co loading) derived from $Co_2(CO)_8$. It was noted that no visible band for CO adsorbed on Co/SiO_2 was present except those for adsorbed propanal and an acyl species at 1706–1713 cm^{-1} throughout the reaction.

Figure 6 presents surface IR spectra collected under steady-state $C_2H_4/CO/H_2$ conditions at 150 °C over a SiO_2-supported catalyst (1.0% Ru loading) prepared from $(Ru(NO_3)_3 + Co(NO_3)_2{\cdot}6H_2O)$ (Co : Ru = 3 : 1 atomic ratio). Incorporation of cobalt noticeably attenuated the intensity of the carbonyl bands for $Ru^{2+}(CO)_3$ and thus appeared to promote the reduction of Ru^{2+} to Ru^0. The carbonyl bands of $Ru^{2+}(CO)_3$ at 2131 and 2064 cm^{-1} fully disappeared after 5 h of reaction. The remaining bands at 2021 and 1848 cm^{-1} had little difference from those observed for CO adsorbed on Ru^0/SiO_2. The bands for adsorbed propanal and an acyl species were likewise observed during the reaction.

Figure 7 presents surface IR spectra observed under steady-state $C_2H_4/CO/H_2$ conditions at 150 °C over a SiO_2-supported catalyst (1.0% Ru loading) derived from $HRuCo_3(CO)_{12}$. Cobalt in this catalyst seems to have the same promoting effect on the reduction of Ru^{2+} to Ru^0. The carbonyl bands at 2135 and 2066 cm^{-1} for $Ru^{2+}(CO)_3$ gradually disappeared with reaction time. The remaining bands at 2022 and 1842 cm^{-1} are typical of CO adsorbed on Ru^0/SiO_2. The bands for adsorbed propanal and an acyl species were observed during the reaction, similarly to the above cases.

4. Discussion

Study of cobalt-containing bimetallic catalysts has long been a subject of much interest because of lower cost, good catalytic performances and known oxidation and corrosion resistance [36]. Since cobalt has similarity with many of the noble metals in size, electronic structure and geometric structure, it has been found to form readily alloys with these noble metals [37]. It should be mentioned that ruthenium has a close-packed hexagonal crystal structure [38], and so has cobalt at below 417 °C [36]. Cobalt cannot undergo a transformation to a face-centered cubic form until above 417 °C [36]. Therefore, it is logical to assume that these two metals are totally miscible and can form bimetallic particles by using a temperature of 350 °C at which we

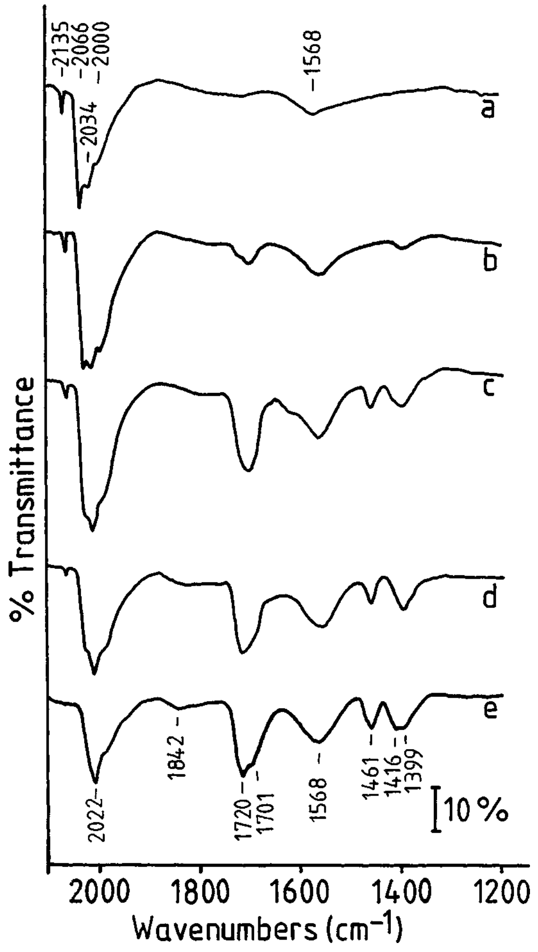

Figure 7. IR spectra on a $HRuCo_3(CO)_{12}/SiO_2$-derived catalyst (1.0% Ru loading) under $C_2H_4 + CO + H_2$ (200 : 200 : 200 Torr) at 150 °C in a static IR cell. (a) 3 min, (b) 0.5 h, (c) 5 h, (d) 27 h and (e) 100 h.

prepared ruthenium and cobalt-containing supported catalysts by H_2 treatment.

An appropriate catalytic reaction can serve as a sensitive probe to study the interaction between the atoms of two metallic components in dilute solutions and in highly dispersed supported metal catalyst systems [39,40]. If two metals do not behave catalytically as separate, independent entities on a carrier, then bimetallic catalysis is suggested [39]. According to the catalytic results in ethylene hydroformylation, the ruthenium and cobalt-containing catalysts studied exhibit increased hydroformylation activity to different extent with respect to either of the ruthenium and cobalt monometallic catalysts. This synergy between ruthenium and cobalt atoms on the catalysis suggests that Ru–Co bimetallic particles or ruthenium and cobalt monometallic particles in intimate contact are formed by H_2 reduction of SiO_2-supported ruthenium and cobalt precursors at 350 °C, by analogy with the viewpoint of Sinfelt [39]. The magnitude of the reaction rate enhancement may be assumed to be dependent on the degree of formation of Ru–Co bimetallic particles. Employ of metal carbonyls as precursors may produce a higher content of Ru–Co bimetallic particles. Similarly, we have recently discovered that considerably increased catalytic activities for ethylene hydroformylation can be achieved over rhodium and cobalt-containing SiO_2-supported catalysts (1.0% Rh and 1.7% Co loadings) derived from various precursors, compared to those of monometallic catalysts [23,41–43]. The synergistic effect is interpreted in terms of the bimetallic catalysis by Rh–Co clusters or particles [23,41–43].

In support of such a synergy via the interaction between ruthenium and cobalt atoms in ethylene hydroformylation, the IR spectroscopic results offer alternative evidence by CO adsorption on the catalyst surfaces. Under identical conditions (1.0% Ru and 1.7% Co loadings, 20.0 mg wafer, 2 h of H_2 treatment at 350 °C and 24 h of CO adsorption at ambient temperature), the incorporation of cobalt with ruthenium on the SiO_2 surface results in the great decrease of CO chemisorption on Ru, assuming that cobalt atoms in the incorporated catalysts do not chemisorb CO. This indicates that the number of ruthenium atoms present on the surface of the particles decreases. The extent of this decrease depends on how much the atoms of two metals interact on the SiO_2 surface to possibly produce bimetallic particles. For example, when ($Ru(NO_3)_3 + Co_2(CO)_8$) is used as a precursor, the resulting catalyst surfaces display a relevant decrease in intensity of the adsorbed CO band relative to Ru/SiO_2, as seen in figure 3 (b) and (c). This is in accordance with an obvious increase of hydroformylation activity over the catalysts compared to that over Ru/SiO_2. In contrast, when $HRuCo_3(CO)_{12}$, ($Ru_3(CO)_{12} + Co_2(CO)_8$) and ($RuCl_3 \cdot nH_2O + Co_2(CO)_8$) are utilized as precursors, the CO adsorption is strongly suppressed on the resulting catalyst surfaces, as shown by the very low band intensities in figure 3 (d)–(f). This is consistent with the appreciably high hydroformylation activity of these three catalysts. In addition to a structural factor, an electronic factor would not be neglected. The presence of cobalt may affect the electronic properties of ruthenium atoms in the particles, so that the strength of bonding of these atoms with reactants and products is modified and the catalytic activity is changed.

Based on the IR observations on both CO adsorption and *in situ* ethylene hydroformylation, the inhibition or weakening of $Ru^{2+}(CO)_3$ formation on SiO_2 in the presence of cobalt may also account for an interaction between ruthenium and cobalt atoms. The possible existence of Ru–Co bimetallic particles on SiO_2 coincides with the known oxidation resistance of cobalt alloys [36]. However, the IR results of *in situ* ethylene hydroformylation on the monometallic ruthenium catalyst and ruthenium and cobalt-containing catalysts show no further significant difference. Under catalytic conditions, only the linear CO on Ru^0 is noticed to be predominantly present as the product of CO adsorption on the surfaces of ruthenium and cobalt-containing catalysts. There are no other adspecies of interest relating to Ru–Co bimetallic particles. Possibly due to the weak adsorption of the hydroformylation reactants and products on Ru–Co bimetallic catalysts, the *in situ* IR study cannot allow us to obtain efficiently specific information on the Ru–Co bimetallic particles and the interaction between ruthenium and cobalt atoms.

It seems intriguing to correlate the TPR results of supported ruthenium and cobalt to the interaction between ruthenium and cobalt atoms in the catalysts studied. The fact that the TPR of RuO_2 is always accompanied by the low-temperature shift of Co_3O_4 or Co^{2+} TPR in any of the $(Ru + Co)/SiO_2$ systems shows a promotion of ruthenium on the reduction of cobalt by the "hydrogen spillover" effect [29,30]. This situation happens certainly with RuO_2 and Co_3O_4 or Co^{2+} in close contact on SiO_2. This implies that the resulting ruthenium and cobalt atoms are not isolated from each other but instead in close contact on SiO_2. From the present TPR results, we cannot determine whether or not the resulting metallic particles are bimetallic. But at least, the formation of ruthenium and cobalt atoms in intimate contact in the catalysts prepared by H_2 treatment of SiO_2-supported ruthenium and cobalt precursors at 350 °C, can be concluded. This can result in a synergy of the two metals on the increase in catalytic activity for ethylene hydroformylation. Despite the fact that sufficiently high temperatures are usually required to form ruthenium alloys and cobalt alloys, the situation of supported bimetallic particles systems may be different and the supports may play an unusual role in the formation of Ru–Co bimetallic particles. In addition, the present TPR analysis is qualitative. It does not enable us to evaluate the percentage of ruthenium and cobalt reduced in the SiO_2-supported catalysts studied. The degree of reduction for oxide-supported metal catalysts depends primarily on the metal dispersion and interaction with the oxide surfaces [32].

5. Conclusions

By combining the results of catalytic study, TPR analysis and adsorption IR characterization, it is thought that the catalysts prepared from SiO_2-supported ruthenium and cobalt precursors by H_2 treatment at 350 °C contain Ru–Co bimetallic particles, at least atoms of the two metals in intimate contact on the SiO_2 surface. Such an interaction between ruthenium and cobalt atoms leads to a synergistic effect on the enhancement in catalytic activity for ethylene hydroformylation to different extent with different precursors. Highly active catalysts may possess higher contents of Ru–Co bimetallic particles on SiO_2 which are found to strongly reduce the adsorption of CO.

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