Probing the bimetallic $RhCo_3$ cluster preserved on SiO_2 after thermal treatment under O_2 by hydroformylation

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$RhCo_3(CO)_{12}/SiO_2$, after decarbonylation under atmospheric O_2 at 623 K, exhibits excellent catalytic performances in atmospheric ethylene hydroformylation at 423 K, which is consistent with the corresponding catalysis by the bimetallic cluster catalyst $RhCo_3/SiO_2$.

Keywords: silica-supported $RhCo_3(CO)_{12}$; oxygen treatment; hydroformylation

1. Introduction

In solution and in highly dispersed supported metal catalyst systems, an appropriate catalytic reaction can serve as a probe to obtain evidence of interaction between the atoms of two metallic components [1,2]. Laine has stated the criterion for identifying mixed-metal cluster catalysis: if a specific combination of two and more different transition metals can be used to significantly enhance the catalysis rates or change the product selectivity of a given reaction normally catalyzed by one of the metals, or if the combination allows the catalysis of a reaction not catalyzed independently by one of the metals, then mixed-metal cluster catalysis is suggested [2]. Some heterogeneous bimetallic rhodium catalysts are known to be able to bring about at least 20-fold enhanced rates of formation of oxygenates from syngas compared to monometallic rhodium catalysts [3–8]. Hydroformylation is regarded as an ideal model of the CO insertion reaction resulting in oxygenated products. It can be used as a powerful molecule to distinguish between bimetallic and monometallic rhodium catalysts by comparison of the catalytic behavior of two metallic systems with that of individual metallic systems.

Recently, we have studied the surface chemistry and catalytic behavior of SiO_2-supported $RhCo_3(CO)_{12}$-derived catalysts for ethylene hydroformylation [8–10]. On the basis of our spectroscopic and catalytic results, we found that a considerably high hydroformylation activity can be correlated with the preservation of the $RhCo_3$ cluster on the surface after thermal treatment of $RhCo_3(CO)_{12}/SiO_2$ under H_2. We also further demonstrated that molecular SiO_2-supported $RhCo_3(CO)_{12}$ itself is responsible for the unusual catalysis [10]. In the present communication, we show a strong stability and an even higher catalytic activity of $RhCo_3$ supported on SiO_2 toward ethylene hydroformylation despite that $RhCo_3(CO)_{12}/SiO_2$ undergoes a pretreatment under atmospheric O_2 at 623 K. Its catalytic properties are compared with those of SiO_2-supported catalysts derived from $Rh_4(CO)_{12}$ and $RhCo_3(CO)_{12}$ by H_2 decarbonylation, and from $[Rh_4(CO)_{12} + Co_2(CO)_8]$ (Co : Rh = 3 : 1 atomic ratio) by O_2 decarbonylation, all the rhodium catalysts studied containing 1% Rh.

2. Experimental

$RhCl_3 \cdot nH_2O$ and $Co_2(CO)_8$ were purchased commercially. $NaCo(CO)_4$ was synthesized from $Co_2(CO)_8$ according to ref. [11]. $Rh_4(CO)_{12}$ and $RhCo_3(CO)_{12}$ were synthesized from $RhCl_3 \cdot nH_2O$ and $NaCo(CO)_4$ as described by Martinengo et al. [12,13]. SiO_2 was a silica “Aerosil” supplied by Degussa with a surface area of 380 m^2/g. n-hexane used as the solvent was distilled over P_2O_5 and stored under Ar over activated 5 A molecular sieves. 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 5 A molecular sieves and Mn/MnO.

$Rh_4(CO)_{12}$, $Co_2(CO)_8$ and $RhCo_3(CO)_{12}$ were employed as starting materials to prepare $Rh_6(CO)_{16}/SiO_2$ (1% Rh loading) [14], $Co_4(CO)_{12}/SiO_2$ (1.7% Co loading) [15], $[Rh_6(CO)_{16} + Co_4(CO)_{12}]/SiO_2$ (1% Rh loading, Co : Rh = 3 : 1 atomic ratio) [9] and $RhCo_3(CO)_{12}/SiO_2$ (1% Rh loading) [8,9]. SiO_2 (60–80 mesh granule) was partially dehydroxylated under vacuum at 673 K for 5 h and impregnated with the carbonyl clusters in dry n-hexane under Ar. The impregnated systems were subjected to 2 h of stirring. The solvent was removed by evacuation and the resulting solid samples were dried under vacuum at 1.3×10^{-3} kPa for 1 h. The

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catalyst precursors thus obtained were transferred to the reactor under Ar.

Hydroformylation of ethylene was conducted under atmospheric pressure at 423 K in a glass tubing flow reactor (i.d. = 7 mm) where 0.1 g of catalyst precursor was charged. Prior to admitting a mixture of C_2H_4, CO and H_2 (20 : 20 : 20 ml/min) at 423 K, the supported carbonyl clusters were subjected to the desired decarbonylation procedures in flowing gas at 623 K for 2 h. Data were taken 7 h after the initiation of reaction. Both hydrocarbon and oxygenated products were analyzed on line with gas chromatography, using a 2 m length column of Porapak R and a flame ionisation detector.

The metal contents of the samples studied were determined by X-ray fluorescence spectroscopy.

3. Results and discussion

Table 1 summarized the catalytic results of various supported catalysts derived from those mono- and bimetallic carbonyl clusters in ethylene hydroformylation. $RhCo_3(CO)_{12}/SiO_2$ decarbonylated under H_2 displayed an activity increased by 18 times and a selectivity improved by 17% for the formation of oxygenates at 423 K relative to a $Rh_6(CO)_{16}/SiO_2$-derived monometallic catalyst. This is clearly attributed to the bimetallic effect of supported $RhCo_3$ cluster as we have concluded [10]. Very surprisingly, after $RhCo_3(CO)_{12}/SiO_2$ had been decarbonylated under O_2 and flushed with Ar, the resulting catalyst showed even better catalytic performances to oxygenate formation at 423 K. The activity was 27 times more than that of the $Rh_6(CO)_{16}/SiO_2$-derived monometallic catalyst, the selectivity was much the same as that of the catalyst derived by decarbonylation of $RhCo_3(CO)_{12}/SiO_2$ under H_2. The unusual catalytic results suggest that the $RhCo_3$ cluster was not oxidatively decomposed by O_2 and still preserved intactly on the surface.

In order to ascertain the stablity of SiO_2-supported $RhCo_3$ framework under an O_2 atmosphere at high temperatures, we attempted to determine the catalytic properties of a mixture of rhodium and cobalt oxides supported on SiO_2. $[Rh_6(CO)_{16} + Co_4(CO)_{12}]/SiO_2$ (Co : Rh = 3 : 1 atomic ratio) was obtained via coimpregnation of $Rh_4(CO)_{12}$ and $Co_2(CO)_8$ on SiO_2. The catalyst precursor was treated under the same oxidative conditions before exposure to the reaction gases at 423 K. After 1 h of the reaction, the activity to oxygenates was only 0.24 mol/(Rh mol min) and no propanol was observed. This indicates that a SiO_2-supported mixture of monometallic rhodium and cobalt clusters after oxidation results in a very low catalytic activity under the hydroformylation conditions and that there is no bimetallic active site involved in this system. In this case, it is believed that rhodium and cobalt atoms are fully oxidized to Rh^+, Rh_2O_3 and Co_3O_4 [16–19]. The observed activity for the formation of propanal is lower than that of the monometallic rhodium catalyst. It can be ascribed to the catalysis by part of the rhodium which was reduced to Rh^0 under the H_2-containing reaction gases at 423 K, since the reduction of Rh_2O_3 readily proceeds at temperatures below 423 K [16].

Under the same oxidative conditions, the result with $RhCo_3(CO)_{12}/SiO_2$ is in marked contrast with that with $[Rh_6(CO)_{16} + Co_4(CO)_{12}]/SiO_2$ (Co : Rh = 3 : 1 atomic ratio). We thus consider that the bimetallic $RhCo_3$ cluster is not segregated on SiO_2 following treatment under O_2 at 623 K. Here, it is worth pointing out that thermal treatment of bimetallic particles under O_2 usually leads to bimetallic segregation and concomitant metallic oxidation [16,20,21]. Moreover, it is difficult to reform bimetallic particles by reducing the two monometallic oxides formed after oxidation because of the loss of some specific advantages of alloying [16,22]. In this work, after the supported mixture of monometallic rhodium and cobalt oxides derived from $Rh_4(CO)_{12} + Co_2(CO)_8$ had undergone 2 h of reduction at 623 K, its activity to

Table 1

Catalytic properties of SiO_2-supported mono- and bi-metallic catalysts [a] in atmospheric ethylene hydroformylation (C_2H_4 : CO : H_2 = 20 : 20 : 20 ml/min) at 423 K

Starting material	Co : Rh (atomic ratio)	Activity [b] (mol/(Rh mol min))		Selectivity (mol%)	
		C_2H_6	oxygenates [c]	oxygenates	n-C_3H_7OH
$Co_2(CO)_8$ [d]		0	0	–	–
$Rh_4(CO)_{12}$ [d]		0.42	0.37	47	0
$RhCo_3(CO)_{12}$ [d]		3.63	6.56	64	6
$RhCo_3(CO)_{12}$ [e]		5.32	9.95	65	8
$[Rh_4(CO)_{12} + Co_2(CO)_8]$ [e,f]	3 : 1	0.08	0.24	74	0
$[Rh_4(CO)_{12} + Co_2(CO)_8]$ [g]	3 : 1	1.67	2.82	63	4

[a] With 1% Rh and 1.7% Co loadings.

[b] Data were taken 7 h after the initiation of reaction.

[c] $C_2H_5CHO + n$-C_3H_7OH.

[d] Pretreated under H_2 at 623 K for 2 h.

[e] Pretreated under O_2 at 623 K for 2 h and flushed with Ar at 623 K for 1 h.

[f] Data were taken 1 h after the initiation of reaction.

[g] Pretreated as in e, followed by 2 h of H_2 reduction at 623 K.

oxygenates was only 2.82 mol/(Rh mol min) after 7 h of the reaction and was not comparable to those of the $RhCo_3(CO)_{12}$-derived catalysts as shown in table 1. It follows that the bimetallic Rh–Co particles, if oxidized to monometallic rhodium and cobalt oxides, can be reformed only to a small extent on the surface by H_2 treatment at moderate temperatures (below 623 K). The fact that the $RhCo_3(CO)_{12}$-derived catalyst by O_2 treatment exhibits an activity of approximately 10.0 mol/(Rh mol min) and a selectivity of 65% for the formation of oxygenates is essentially in accordance with the catalytic behavior especially the product selectivity of the known supported $RhCo_3$ cluster which shows the same Rh–Co bimetallic nature or the preservation of $RhCo_3$ cluster in the catalyst. Furthermore, this catalyst displayed a fairly good stability over 115 h of reaction, as shown in fig. 1. With regards to this unexpected stabilization of $RhCo_3$ on the surface of SiO_2, we have recently proposed the existence of a particular cluster–support interaction via a nucleophilic attack of the surface oxygen on the cobalt atoms of $RhCo_3$, with the synergetic enhancement of the Rh–Co bond [8,9]. This kind of interaction may render the $RhCo_3$ framework grafted tightly to the surface and prevent the scission of the Rh–Co bond under drastic conditions, even in the presence of O_2. For $RhCo_3(CO)_{12}/SiO_2$, oxidative treatment gave rise to higher activities in both hydroformylation and hydrogenation than reductive treatment without changing the selectivity. Although this result has not been understood, it is probable that oxidative treatment promotes the interaction between $RhCo_3$ and the surface and thus increases the $RhCo_3$ dispersion. Meanwhile, it is not impossible that increasing the cluster–surface interaction through this approach results in a better stability of $RhCo_3$ cluster on SiO_2. It is generally accepted that oxidative processing of supported metallic carbonyl clusters in the presence of O_2 favors higher metallic dispersions, leading to diminished aggregation of metallic particles [23–27], probably by increasing the interaction between cluster and surface oxygen, thereby reducing cluster mobility on the surface [23]. However, the possibility that thermal treatment under O_2 plays some particular roles in promoting the enhancement of catalytic activity cannot be ruled out.

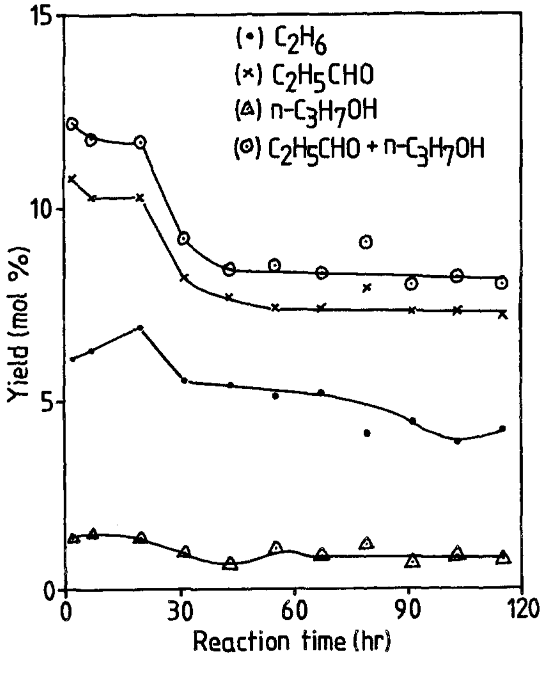

Fig. 1. Dynamic atmospheric ethylene hydroformylation ($C_2H_4 : CO : H_2 = 20 : 20 : 20$ ml/min) at 423 K over a catalyst derived by 2 h of O_2 decarbonylation of $RhCo_3(CO)_{12}/SiO_2$ (1% Rh loading) at 623 K.

In addition, our recent IR study showed that $RhCo_3(CO)_{12}/SiO_2$ can be regenerated under CO after decarbonylation at 623 K under O_2 as well as under H_2 [10].

In summary, the catalytic behavior of $RhCo_3(CO)_{12}/SiO_2$-derived catalyst by decarbonylation under O_2 at 623 K reasonably resembles that under H_2 on which the bimetallic $RhCo_3$ cluster has been spectroscopically characterized. The observed catalysis is therefore ascribed to the preservation of bimetallic $RhCo_3$ framework on SiO_2.

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