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Selective Olefin Hydroformylation on Carbon-supported Ru and Ru-Co Carbonyl Cluster-derived Catalysts

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High activities and selectivities toward normal-alcohols were achieved in the vapor-phase hydroformylation of ethylene and propylene on the carbon-supported Ru-Co bimetallic carbonyl cluster-derived catalysts under an atmospheric pressure.

One promising method of obtaining well-defined metal catalysts is employing organometallic compounds as the precursors. Such an approach may provide a molecular-level elucidation of the elementary steps of heterogeneous catalysis in terms of organometallic chemistry.$^{1)}$ Metal clusters have been paid much attention as the starting organometallic compounds because they can give highly-dispersed metal ensembles with uniform composition, and supported cluster-derived catalysts provide differences and/or advantages over the conventional metal catalysts prepared by coimpregnation or ion-exchange techniques.$^{2)}$ In fact, recent works$^{3-4)}$ supported that bimetallic cluster-derived catalysts exhibited a promotion of the catalytic activity and selectivity in some catalytic reactions, e.g., $CO + H_2$ conversion to oxygenates and hydrocarbons, which are markedly different from those of the catalysts of constituent metals. Generally, the catalytic, electronic, and structural properties are associated with the metal compositions of surface bimetallic species and geometric situation of metal ensembles. In homogeneous olefin hydroformylation reaction, ruthenium carbonyls exhibit a poor activity even under high pressure conditions compared with cobalt or rhodium carbonyls, but the competitive hydrogenation of olefin to paraffin preferentially occurs.$^{5)}$ It was previously reported$^{6)}$ that $Co_2(CO)_8$+$Ru_3(CO)_{12}$ mixture showed the synergistic rate enhancement in homogeneous hydroformylation. We report here that carbon-supported Ru and Ru-Co bimetallic catalysts derived from the carbonyl clusters gave higher catalytic activity to selectively produce normal alcohols in the vapor-phase hydroformylation of ethylene and propylene under an atomospheric pressure.

The precursor complexes such as $[NEt_4][HRu_3(CO)_{11}]$,$^{7)}$ $[NEt_4][Ru_3Co(CO)_{13}]$,$^{8)}$ $H_3Ru_3Co(CO)_{12}$,$^{8)}$ and $HRuCo_3(CO)_{12}$$^{9)}$ were synthesized according to published procedures. $Co_4(CO)_{12}$ was purchased from Strem Chem. Inc. and purified by recrystallization from pentane. An amorphous carbon (Wako Pure Chem. Ind. Ltd., surface area 800 m^2 g^{-1}, 12-20 mesh) was treated at 300 °C under vacuum for 2 h. Each carbonyl cluster was impregnated from the organic solutions under N_2 onto the amorphous carbon (1 wt.% total metal loading). The organic solvent was carefully

Table 1. Hydroformylation of ethylene on carbon-supported Ru, Ru-Co, Co carbonyl cluster-derived catalysts[a)]

Precursor/Carbon	Atomic ratio Co/Ru	Rate of formation:T.O.F.[b)] C_2H_6 min^{-1}	$C_2H_5CHO+C_3H_7OH$ min^{-1}	Sel. for oxygenates[c)] mol %	Sel. for alcohol[d)] mol %
$[NEt_4][HRu_3(CO)_{11}]$	0	0.06(1)[e)]	0.007(1)[e)]	11	1
$[NEt_4][Ru_3Co(CO)_{13}]$	0.33	0.24(3.9)[e)]	0.033(4.5)[e)]	12	19
$H_3Ru_3Co(CO)_{12}$	0.33	0.27(4.4)[e)]	0.037(5.0)[e)]	12	10
$HRuCo_3(CO)_{12}$	3.0	1.1(18)[e)]	0.13(17)[e)]	10	47
$Co_4(CO)_{12}$	-	0.009[f)]	0.0008[f)]	8	0

a) Temperature 172 ± 1 °C; $C_2H_4:CO:H_2 = 20:20:20$ ml min^{-1}, 1 atm.

b) mmol Ru-mmol^{-1} min^{-1}. c) $(C_2H_5CHO+C_3H_7OH)/(C_2H_6+C_2H_5CHO+C_3H_7OH)\times100$.

d) $C_3H_7OH/(C_2H_5CHO+C_3H_7OH)\times100$. e) Relative activity. f) mmol Co-mmol^{-1} min^{-1}.

removed by a vacuum distillation, follwed with H_2-reduction at 200 °C. The hydroformylation reactions were carried out using an open flow-mode reactor. A mixture gas of C_2H_4 (or C_3H_6), CO and H_2 (1:1:1 molar ratio under total pressure of 1 atm) was passed through the catalyst bed (3-4 g of catalyst) at the total flow rate of 60 ml min^{-1}. The oxygenated products such as aldehydes and alcohols were collected in a water condensor (50 ml of H_2O) by bubbling the effluent gas. The analysis of the products were conducted by TCD and FID gas chromatography having Al_2O_3/DMF and Porapak Q columns.

The results of the atmospheric pressure hydroformylation of ethylene and propylene in vapor-phase were presented in Table 1 and Table 2. It is of great interest to find that carbon-supported $[NEt_4][HRu_3(CO)_{11}]$-derived catalyst gave higher activities rather than $Co_4(CO)_{12}$-derived one. Further hydrogenation of the aldehyde to the alcohol did not occurred on the Ru cluster-derived one. Total selectivities for hydroformylation by Ru or Ru-Co carbonyl cluster-derived catalysts were ca. 10% for ethylene and ca. 5% for propylene. On the catalyst derived from $Co_4(CO)_{12}$, the rate of a simple hydrogenation as well as a hydroformylation reaction comparatively much low rather than Ru carbonyl cluster-derived catalyst. These results suggest that ruthenium carbonyl hydrides as active species for a olefin hydroformylation may be formed on the carbon support under the mild conditions.

The activities for hydroformylation (aldehyde + alcohol) per Ru atom are markedly enhanced with increasing the Co contents in the Ru-Co bimetallic cluster-derived catalysts, compared with that by the catalyst prepared from $[NEt_4][HRu_3(CO)_{11}]$ or $Co_4(CO)_{12}$ alone. The catalyst derived from $HRuCo_3(CO)_{12}$

Table 2. Hydroformylation of propylene on carbon-supported Ru, Ru-Co, Co carbonyl cluster-derived catalysts[a]

Precursor/Carbon	Rate of formation:T.O.F.[b]		Sel. for oxygenates[c]	Sel. for alcohols[d]	Sel. for n-isomers[e]
	C_3H_8	$C_3H_7CHO+C_4H_9OH$			
	min^{-1}	min^{-1}	mol %	mol %	mol %
$[NEt_4][HRu_3(CO)_{11}]$	0.040(1)[f]	0.0017(1)[f]	4	1	80
$[NEt_4][Ru_3Co(CO)_{13}]$	0.15 (3.8)[f]	0.0029(1.7)[f]	2	0	74
$H_3Ru_3Co(CO)_{12}$	0.17 (4.3)[f]	0.0029(1.7)[f]	6	1	81
$HRuCo_3(CO)_{12}$	0.55(14)[f]	0.027(16)[f]	5	76	96
$Co_4(CO)_{12}$[g]	0.006[h]	0.0004[h]	1	2	81

a) Temperature 194 ± 1 °C; $C_3H_6:CO:H_2$ = 20:20:20 ml min^{-1}, 1 atm.

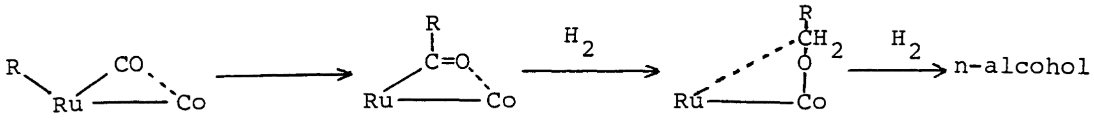
b) mmol Ru-mmol^{-1} min^{-1}. c) $(C_3H_7CHO+C_4H_9OH)/(C_3H_8+C_3H_7CHO+C_4H_9OH)$x100.

d) $C_4H_9OH/(C_3H_7CHO+C_4H_9OH)$x100. e) (butanal+butanol)/$(C_3H_7CHO+C_4H_9OH)$x100.

f) Relative activity. g) Temperature 203 ± 1 °C. h) mmol Co-mmol^{-1} min^{-1}.

provided sixteen times higher rate for propylene hydroformylation than $[NEt_4][HRu_3(CO)_{11}]$-derived one. The selectivities for alcohols on the Ru-Co carbonyl cluster-derived catalysts were much higher than that on $[NEt_4][HRu_3(CO)_{11}]$or $Co_4(CO)_{12}$-derived catalyst. Additionally, the selectivities toward normal alcohol formation were substantially improved by increasing Co contents in the catalysts derived from Ru-Co bimetallic carbonyl clusters. For a propylene hydroformylation, it was found that highest selectivity toward normal alcohol were achieved by $HRuCo_3(CO)_{12}$-derived catalyst, i.e., the selectivity for alcohol formation was 76% and the selectivity for normal-isomers was 96%, although the $[NEt_4][HRu_3(CO)_{11}]$-derived catalyst gave 80% of normal-isomers selectivity. The results suggest that Co atoms are associated with the promotion for normal alcohol formation in a hydroformylation reaction catalyzed by Ru carbonyls.

Such higher rates and higher selectivities to normal alcohol production on the Co-rich Ru-Co bimetallic carbonyl cluster-derived catalysts cannot be explained simply by the additional formation of aldehyde and alcohol from the individual Ru and Co carbonyl clusters, i.e., a physical mixture of $[NEt_4][HRu_3(CO)_{11}]$ and $Co_4(CO)_{12}$, on carbon. It was previously reported that the Co atoms in Rh-Co carbonyl cluster-derived catalysts markedly enhanced normal-isomer selectivities for propylene hydroformylation.[3] The Co atoms in the Rh-Co carbonyl clusters may play a role as a ligand to stabilize n-alkyl intermediates and to accelerate a migratory CO insertion into the alkyl-metal bond. Furthermore, they act effectively as a inert braker to devide the Ru ensemble into an isolated Ru atom. The CO insertion is accelerated by the Ru-Co bi-site interaction, i.e., an oxygen atom of coordinated CO on Ru bound with the positively charged Co atom which has lower ionization potential than Ru, as shown in the following proposed model of an active site(Scheme 1). In fact, Shriver et al. reported that Lewis acids such as $AlBr_3$ and BF_3 could greatly enhance the rate of the migratory CO insertion reaction due to the adduct formation between organometallic carbonyls and the Lewis acid reagents.$^{10)}$



R = C_2H_5, C_3H_7

Scheme 1.

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