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NOTES

Catalysis by Supported Metal Crystallites Prepared from Metal Carbonyl Clusters

III. Catalytic Vapor-Phase Hydroformylation of Olefins over Rh, Bimetallic Rh–Co, and Co Crystallites Prepared from the Carbonyl Cluster Compounds Dispersed on Zinc Oxide

The dispersion of a metal plays, in many cases, an important role in providing high activity and selectivity with supported catalysts. In particular, if the metal is bimetallic, its electronic properties may be associated with its composition and dispersion at the surface. Various devices thus have been proposed for highly dispersed metal and bimetallic alloy, for instance, conventional impregnation methods or ion-exchange methods (*1*). In some cases, molecular metallic cluster compounds have been also used as precursors to produce highly dispersed metallic crystallites including bimetallic systems (*2*). It was previously reported by this author (*3*) that highly dispersed Pt crystallites could be prepared by pyrolysis of $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n 2NEt_4$ (n = 2–5) on γ-Al_2O_3 and silica gel. These materials specifically catalyzed dehydrocyclization of *n*-hexane. In this paper, our work was extended to Rh, bimetallic Rh–Co, and Co catalysts similarly prepared on ZnO from carbonyl clusters. These materials demonstrated catalytic vapor-phase hydroformylation of olefins under mild reaction conditions.

Various metal carbonyl clusters such as $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh_2Co_2(CO)_{12}$ $RhCo_3(CO)_{12}$, and $Co_4(CO)_{12}$ were synthesized and isolated by Chini's methods (*4*). Each cluster was deposited (0.1–0.5 wt% Rh loading) on ZnO (Kadox 25, New Jersey Zinc Co.) from hexane or tetrahydrofuran solutions. At temperatures below 90°C, $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ on ZnO were catalytically inactive for the hydroformylation reaction with C_2H_4 (or C_3H_6), CO, and H_2 (65 cm Hg). At temperatures above 90°C they became active aldehyde formation catalysts after some induction period, when the carbonyl clusters partially decomposed evolving CO.

Cluster decomposition has been observed at 130 and 145°C for $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ on ZnO by temperature-programmed desorption under hydrogen flow. Even with complete removal of CO by evacuation (10^{-4} Torr) at 120 to 150°C, Rh on ZnO catalyzed hydroformylation reactions.[1] No significant difference in the specific rates and linear isomer selectivities was observed in the dispersed $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ catalysts after pyrolysis *in vacuo* or activation under oxo synthesis gas, as shown in Table 1. Infrared spectral results suggested that terminal (2020 and 2070 cm^{-1}) and bridging (1795 cm^{-1})

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[1] It should be noted here that the conventional supported Rh catalysts (0.5–2.0 wt% Rh loading) on ZnO, γ-Al_2O_3, and silica gel, prepared from $RhCl_3$ impregnation followed by hydrogen reduction, produce negligible aldehyde under hydroformylation reaction conditions.

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TABLE 1

Rates and Isomer Distributions from Ethylene and Propene Hydroformylation over $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ on ZnO

	Pretreatment	$C_2H_4 + CO + H_2 = C_2H_5CHO$[a]			$C_3H_6 + CO + H_2 = C_3H_7CHO$[b]		
		Rate (mmol g_{Rh}^{-1} h^{-1})	Aldehyde selectivity[c] (%)	A.E. (kcal mol^{-1})	Rate (mmol g_{Rh}^{-1} h^{-1})	Normal isomer (%)	A.E. (kcal mol^{-1})
$Rh_4(CO)_{12}$–ZnO (0.15 mmol, 20 g)	Pyrolysis *in vacuo*[d]	96	99	11	20	58	13.5
	Activation under oxo atmosphere[e]	86	99	12	16	60	14
$Rh_6(CO)_{16}$–ZnO (0.11 mmol, 20 g)	Pyrolysis *in vacuo*	35	98	13	11.5	70	15.6
	Activation under oxo atmosphere	30	99	13.5	9.8	72	16

[a] $C_2H_4:CO:H_2 = 20:20:20$ cm Hg.

[b] $C_3H_6:CO:H_2 = 18:18:20$ cm Hg.

[c] Aldehyde selectivity = (aldehyde)/(aldehyde) + (alcohol) × 100 expressed in mol.

[d] After evacuating (10^{-4} Torr) at 160°C for 1 h.

[e] After heating at 110–130°C under olefin (18–20 cm Hg), CO (20 cm Hg), and H_2 (20 cm Hg).

carbonyl absorption bands of dispersed $Rh_6(CO)_{16}$ on ZnO diminished in parallel and completely disappeared when the catalyst was evacuated at 150°C. By exposing the pyrolyzed catalyst to 10 cm Hg of CO at 25°C relatively broad bands, with about half the intensity of those observed with the starting sample, reappeared in the 1985 and 1780 cm^{-1} regions. Under a mixture of C_2H_4, CO, and H_2 (molar ratio 1:1:1, 45 cm Hg) the characteristic carbonyl bands of ZnO-supported $Rh_6(CO)_{16}$ shifted to 1985 and 1785 cm^{-1} and a weak new band appeared at 1650 cm^{-1}. The intensities of these bands decreased to half their initial value upon raising the temperature above 110°C. When propionaldehyde was catalytically produced in the ir cell, the carbonyl absorption spectra resembled those of $Rh_6(CO)_{15}^{2-}$ and $Rh_6(CO)_{14}^{4-}$ in solution (*5*). These results suggest that the dispersed Rh crystallites on ZnO prepared by pyrolysis *in vacuo* may reconstruct to form carbonyl species similar to partially decarbonylated Rh clusters, which are catalytically active for olefin hydroformylation under mild conditions.

The results presented in Table 1 show that hydroformylation rates and linear isomer proportions obtained with pyrolyzed cluster catalysts are relatively structure sensitive to the precursor carbonyl clusters. The catalyst prepared by pyrolysis of $Rh_4(CO)_{12}$ exhibited specific rates of aldehyde formation 1.5 to 2.8 times larger than that from $Rh_6(CO)_{16}$; however, the former showed a lower proportion of linear isomer. The linear isomer selectivity in propene hydroformylation with each of these catalysts was nearly independent of temperature (90–160°C), CO partial pressure (5–45 cm Hg), and conversion.

The hydroformylation reaction also pro-

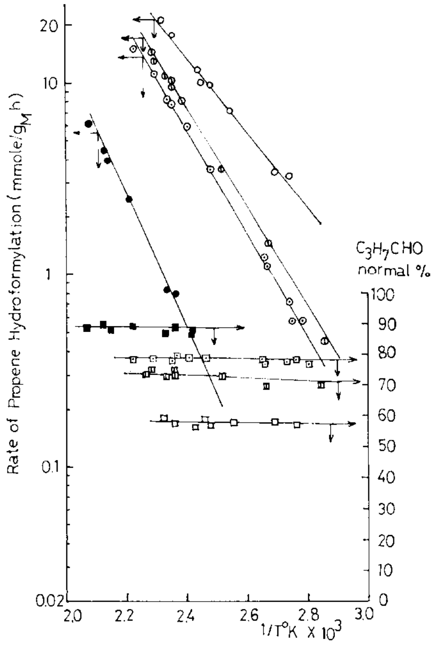

Fig. 1. Temperature dependence of rates (mmol g_M^{-1} h^{-1}, where g_M = weight of dispersed metal) and proportions of linear isomer in propene hydroformylation over ZnO-supported $Rh_4(CO)_{12}$(○, □), $Rh_2Co_2(CO)_{12}$(◐, ◫), $RhCo_3(CO)_{12}$(⊙, ⊡), and $Co_4(CO)_{12}$(●, ■). Catalyst preparation: carbonyl clusters (0.15 mmol) deposited on ZnO (20 g) from hexane solutions. Pyrolysis at 160°C under evacuation. Reaction condition: C_3H_6:CO:H_2 = 18:18:20 cm Hg. The total volume of the closed circulating Pyrexreactor was ca. 420 ml.

ceeded over bimetallic Rh–Co and Co crystallites prepared on ZnO by pyrolysis of $Rh_2Co_2(CO)_{12}$, $RhCo_3(CO)_{12}$, and $Co_4(CO)_{12}$. The temperature dependence on specific rates and linear isomer selectivity in propene hydroformylation is shown for each catalyst in Fig. 1. A decreasing order of hydroformylation rates was obtained over catalysts prepared from the following carbonyl clusters: $Rh_4(CO)_{12}$ (100), Rh_2Co_2 $(CO)_{12}$ (60), $RhCo_3(CO)_{12}$ (42), and Co_4 $(CO)_{12}$ (5.2). The figures in parentheses are relative rates of aldehyde formation at 160°C. Catalysts from clusters having larger cobalt contents produced higher proportions of linear aldehyde.

It is interesting to note that pyrolyzed $Co_4(CO)_{12}$ on ZnO exhibited the highest selectivity to linear aldehyde (above 90%), but had the lowest specific activity.[2] For bimetallic Rh–Co catalysts, the yield of aldehyde per Rh is comparable to that observed with the pyrolyzed $Rh_4(CO)_{12}$ catalyst under similar reaction conditions; however the normal isomer selectivity is markedly higher with catalysts prepared from larger cobalt clusters. This suggests that cobalt atoms in dispersed bimetallic Rh–Co crystallites behave as an "electronic donor-ligand," possibly due to their lower ionization potential, to stabilize a normal intermediate on top of rhodium sites in olefin hydroformylation reactions.

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[2] The supported cobalt catalysts prepared from Co-acetate or nitrate impregnated on ZnO and reduced by hydrogen were catalytically inactive for ethylene and propene hydroformylation under our reaction conditions.