Hydroformylation of Cyclohexene Catalysed by Homogeneous Bimetallic Systems[1]

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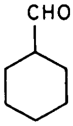
Homogeneous bimetallic systems such as $Co_2(CO)_8$–$Ru_3(CO)_{12}$ and $[Et_4N][FeCo_3(CO)_{12}]$ show high catalytic activity for the hydroformylation of cyclohexene compared with $Co_2(CO)_8$ alone.

Our previous results[1] indicated that in the homologation of methanol by cobalt–ruthenium mixed metal catalysts, ruthenium was not only involved in the hydrogenation of acetaldehyde to ethanol,[2] but also slightly but notably enhanced acetaldehyde formation.[3] These observations led us to expect that bimetallic systems might also show high catalytic activity for hydroformylation of olefins since both processes involve alkyl and acyl complexes as common intermediates. We describe here the preliminary results of cyclohexene hydroformylation catalysed by cobalt–ruthenium and cobalt–iron bimetallic systems, which both show synergism for the two metals. Recently, Laine[4] reported that ruthenium–iron mixed metal catalysts were very effective for the hydroformylation and aminomethylation reactions of pent-1-ene using the water gas shift reaction.



(1)

As summarized in Table 1, the yield of cyclohexanecarbaldehyde (**1**) was greatly increased on using $Co_2(CO)_8$–$Ru_3(CO)_{12}$ mixed catalysts compared with $Co_2(CO)_8$ or $Ru_3(CO)_{12}$ alone. The yield of (**1**) in Run 4 was much higher than the sum of the yields of (**1**) from Run 1 and Run 6, indicating a synergistic effect for cobalt and ruthenium. At Ru : Co 9.9 : 1, the conversion of cyclohexene into (**1**) approached 100% and the initial rate was *twenty seven times*

Table 1. Hydroformylation of cyclohexene with Co–Ru and Co–Fe mixed metal catalysts.[a]

Run	Catalyst	Ru:Co or Fe:Co	Yield of (**1**),%[b]	Initial rate (V_o)[c]
1	$Co_2(CO)_8$	—	14	1.0
2	$Co_2(CO)_8 + Ru_3(CO)_{12}$	0.34	32	3.6
3	$Co_2(CO)_8 + Ru_3(CO)_{12}$	0.95	52	5.9
4	$Co_2(CO)_8 + Ru_3(CO)_{12}$	3.2	62	8.4
5	$Co_2(CO)_8 + Ru_3(CO)_{12}$	9.9	100[d]	27
6[e]	$Ru_3(CO)_{12}$	—	2.7	0.29
7	$[Et_4N][FeCo_3(CO)_{12}]$	0.33	27	2.3
8[f]	$Co_2(CO)_8 + Fe_3(CO)_{12}$ $+ [Bu_4N]Cl$	0.35	10	1.1
9	$Co_2(CO)_8 + Fe_3(CO)_{12}$	0.91	9.2	1.0
10	$[Et_4N][Fe_3Co(CO)_{13}]$	3.0	0.2	0.0

[a] Cyclohexene, 80 mmol; tetrahydrofuran as solvent, 10 ml; toluene as internal standard, 5 mmol; reaction temp., 110 °C; reaction time, 4 h; $CO:H_2$ 40:40 kg/cm^2, initial pressure at room temp. The amount of Co was kept at 0.2 mg atom throughout. [b] The yield of (**1**) included the 2,4,6-tricyclohexyl-1,3,5-trioxane formed, because the latter quantitatively decomposed to (**1**) under the conditions of our direct g.l.c. analysis. [c] Relative to $Co_2(CO)_8$ alone (Run 1). [d] Small amount of cyclohexanemethanol formed. [e] Ru 0.6 mg atom. [f] Co : Fe : [Bu_4N] 3.0 : 1.0 : 1.0.

faster than that with $Co_2(CO)_8$. It is noteworthy that as more $Ru_3(CO)_{12}$ was added to $Co_2(CO)_8$, the initial rate increased. This result is in sharp contrast with that of methanol homologation by the $Co_2(CO)_8$–$RuCl_3 \cdot 3H_2O$ mixed catalyst which showed maximum activity at Ru : Co 1 : 3.[1] When the conversion of cyclohexene increased above *ca.* 50%, 2,4,6-tricyclohexyl-1,3,5-trioxane was formed together with (**1**). The trioxane may be formed *via* trimerization of (**1**) by hydridocarbonyl compounds such as $HCo(CO)_4$. In the reaction with bimetallic catalysts, neither cyclohexanemethanol nor cyclohexane were formed under the reaction conditions described in footnote a, Table 1, although a small amount of cyclohexanemethanol was formed at very high conversion of cyclohexene. Kinetic studies show that the rate of the aldehyde formation is given by equation 1. Recent

$$V_o = k_{obs}\,[Co]^{1.0}[Ru]^{0.6}[cyclohexene]^{0.5}P(H_2)^{0.9}P(CO)^{-1.0} \quad (1)$$

evidence shows that in the hydroformylation of olefins by $Co_2(CO)_8$, the final C–H bond forming step is a dinuclear process, involving a reaction between $HCo(CO)_4$ and an acyl complex.[5] We tentatively propose that in the cobalt–ruthenium mixed metal systems, this step may be accelerated by the attack of ruthenium hydrides such as $[HRu_3(CO)_{11}]^-$ on the acylcobalt complex. Interestingly, the rate is dependent on the half-order of the concentration of cyclohexene in the bimetallic systems, but on the first-order for $Co_2(CO)_8$ alone.[6]

A similar synergistic effect was also observed if the mixed metal cluster $[Et_4N][FeCo_3(CO)_{12}]$ was used as the catalyst. However, $[Et_4N][Fe_3Co(CO)_{13}]$ exhibited little activity. Although it was claimed by Doyle[7] that a mixture of $Co_2(CO)_8$, $Fe(CO)_5$, and $[Bu_4N]I$ as well as $[Et_4N][FeCo_3(CO)_{12}]$ showed a high catalytic activity for methanol homologation, addition of $Fe_3(CO)_{12}$ with or without $[Bu_4N]Cl$ to $Co_2(CO)_8$ did not improve the yield of (**1**) in the hydroformylation of cyclohexene.

The bimetallic catalysts discussed herein were also effective for the hydroformylation of other olefins such as hex-1-ene.

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References

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