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HOMOLOGATION OF METHANOL CATALYZED BY MIXED TRANSITION METAL CLUSTERS CONTAINING COBALT

Masanobu HIDAI,* Masami ORISAKU, Makoto UE, and Yasuzo UCHIDA
Department of Industrial Chemistry, Faculty of Engineering,
University of Tokyo, Hongo, Tokyo 113

Katsutoshi YASUFUKU and Hiroshi YAMAZAKI
The Institute of Physical & Chemical Research, Wako-shi, Saitama 351

Syntheses of mixed transition metal clusters containing cobalt and their catalytic activities for homologation of methanol were investigated. The reaction of $RuCl_3$ with $Na[Co(CO)_4]$ gave a reddish brown complex $Na[RuCo_3(CO)_{12}]$. The cluster easily underwent a cation exchange to give the Cs^+ and $[Et_4N]^+$ salts. These clusters showed a remarkable catalytic activity for homologation of methanol. The selectivity of ethanol was increased up to 51% in ca. 40% conversion in case of $[Et_4N]^+$ salt. Catalytic activities of some other mixed metal clusters were also examined.

Current energy and resources crises emphasize the potential increased availability of synthesis gas from gasification of coal and other carbon resources.[1)] This has spurred a number of researches of the catalytic formation of useful chemicals from synthesis gas by using heterogeneous[2)] and homogeneous[3)] catalysts. We have now started our studies on the reaction of methanol with synthesis gas, i.e., homologation of methanol to ethanol (equation 1), n-butanol, or higher alcohols because methanol is easily derived from synthesis gas.

$$CH_3OH + CO + 2H_2 \longrightarrow CH_3CH_2OH + H_2O \qquad (1)$$

Since the first report on homologation of methanol by Wender et al.,[4)] many studies have been done by using cobalt or cobalt-iodide systems as catalysts.[5)] However, the yield and the selectivity of ethanol were relatively low. Recently it was claimed that employing CoI_2-PR_3 system as catalyst and octane as solvent was achieved the selectivity for ethanol up to 89.4% at low conversion(13.2%).[6)] There are also reports and patents dealing with the direct syntheses of ethanol by using rhodium carbonyl clusters supported on SiO_2, TiO_2, or ZrO_2.[2)] Our studies are now focused on finding mixed transition metal catalysts which are effective for homologation of methanol, since a combination of the different metals in mixed metal clusters may show reactivity pattern significantly different from homo-clusters. Although many transition metal clusters including mixed metal clusters have been prepared and their structures have been determined by X-ray analyses,[7)] only a few clusters were found to be effective for catalytic reactions.[7)8)] Rhodium carbonyl clusters, for example, showed significant catalytic activities for addition of arenes to ketene or isocyanates,[9)] synthesis of ethylene glycol,[3a)] and oxidation of alcohols and ketones.[10)]

We have now prepared mixed transition metal clusters of cobalt and other transition metals since cobalt is known to be effective for homologation of methanol and the combination with appropriate metals is expected to give a more effective catalyst. The following mixed clusters were first prepared accoding to equation 2.

$$[(\mathrm{dpe})\mathrm{MCl_2}] \;+\; 2\mathrm{Na[Co(CO)_4]} \longrightarrow [(\mathrm{dpe})\mathrm{MCo_2(CO)_7}] \qquad (2)$$

$$\underline{1} : \mathrm{M = Pd}\ , \quad \underline{2} : \mathrm{M = Pt}$$

$$\mathrm{dpe = Ph_2PCH_2CH_2PPh_2}$$

When a THF solution of $\mathrm{Na[Co(CO)_4]}$ was added to the suspension of $[(\mathrm{dpe})\mathrm{MCl_2}]$ (M = Pd, Pt) in THF, the color of the solution immediately turned dark red, and the mixture was allowed to stand at 50°C for 2 hr. After filtration, the solution was evaporated to dryness and the residue was recrystallyzed from $\mathrm{CH_2Cl_2}$/hexane to give $[(\mathrm{dpe})\mathrm{PdCo_2(CO)_7}]$ 1 or $[(\mathrm{dpe})\mathrm{PtCo_2(CO)_7}]$ 2 in good yields(1 ; 89%, 2 ; 78%).[11)] The cluster 2 has previously been prepared by the same method.[12)] The compound 2 was also prepared by the reaction of $[(\mathrm{dpe})\mathrm{Pt(\text{-}C{\equiv}CPh)_2}]$ with $[\mathrm{Co_2(CO)_8}]$. The infrared spectra of these clusters 1 and 2 showed three terminal ν(CO) at 2040, 2000, and 1979 $\mathrm{cm^{-1}}$ and one band at 1720 $\mathrm{cm^{-1}}$ which is ascribed to a bridging carbonyl group.[13)] The results of homologation of methanol by using these mixed clusters are shown in Table 1. In the case of the cluster 1, the rate of methanol carbonylation to acetaldehyde increased compared with $[\mathrm{Co_2(CO)_8}]$ or $[\mathrm{Co_4(CO)_{12}}]$, but the reduction to ethanol was not enhanced. On the other hand, use of the cluster 2 slightly increased the yield of ethanol. When the cluster $[\mathrm{RhCo_3(CO)_{12}}]$[14)] was used as catalyst, the yield of methyl acetate slightly increased.

Preparation of a mixed cluster containing cobalt and ruthenium has also been attempted since there are some claims that the yield of ethanol is improved by the addition of a small amount of ruthenium chloride[15)] or $[\mathrm{Ru_3(CO)_{12}}]$[5b)] (Ru/Co ratio = ca. 1/10). When a red solution of ruthenium chloride in methanol was treated with an excess of a THF solution of $\mathrm{Na[Co(CO)_4]}$, the color of the mixture immediately changed dark blue. The mixture was allowed to stand at room temperature for 10 hr. After the color of the mixture turned dark red, the solution was evaporated to dryness and the residue was extracted with THF. After evaporating the solvent, a reddish brown compound was obtained. The solid was recrystallyzed from THF/hexane to give $\mathrm{Na[RuCo_3(CO)_{12}]}$ 3 in 68% yield.

$$\mathrm{RuCl_3{\cdot}3H_2O} \;+\; \text{excess } \mathrm{Na[Co(CO)_4]} \longrightarrow \mathrm{Na[RuCo_3(CO)_{12}]} \qquad (3)$$

The addition of CsCl or $[\mathrm{Et_4N}]\mathrm{Cl}$ to a water solution of the cluster 3 precipitated a brown solid which contains $\mathrm{Cs^+}$(4) or $[\mathrm{Et_4N}]^+$(5) as a cation.[16)] A similar mixed cluster $[\mathrm{HRuCo_3(CO)_{12}}]$ was previously prepared by the reaction of $[\mathrm{Ru_3(CO)_{12}}]$ with $[\mathrm{Co_2(CO)_8}]$ in acetone followed by acidification with hydrochloric acid, but the yield was only 7%.[17)] The infrared spectra of these clusters 3, 4, and 5 exhibit absorptions at 1990, 1960, and 1800 $\mathrm{cm^{-1}}$ characteristic of carbonyl ligands, which are very similar to those of an iron-cobalt cluster $[\mathrm{Et_4N}][\mathrm{FeCo_3(CO)_{12}}]$.[18)] The cluster $[\mathrm{HFeCo_3(CO)_9\{P(OCH_3)_3\}_3}]$ has a closed metal tetrahedron with three bridging carbonyl

Table 1. Homologation of Methanol Catalyzed by Mixed transition Metal Clusters a)

Catalyst		Conver-sion(%)	Yield (%) b)					Selectivity(%) c)	
			AcH	DMA d)	EtOH	AcOMe	Me_2O	Total C_2	EtOH
$[Co_2(CO)_8]$ e)		46	3.9	25	0.7	2.5	22	31	1.4
$[Co_4(CO)_{12}]$ f)		48	4.0	29	0.6	2.8	23	32	1.2
$[(dpe)PdCo_2(CO)_7]$ e)	1	61	10	30	0.8	5.9	18	39	1.3
$[(dpe)PtCo_2(CO)_7]$ e)	2	49	6.0	24	1.6	3.7	19	36	3.3
$[RhCo_3(CO)_{12}]$		52	6.0	27	0.8	8.4	16	39	1.6
$Na[RuCo_3(CO)_{12}]$	3	46	1.3	5.6	16	4.4	20	41	30
$Cs[RuCo_3(CO)_{12}]$	4	43	0.7	2.6	18	5.6	16	51	41
$[Et_4N][RuCo_3(CO)_{12}]$	5	41	0.5	1.7	21	0.4	15	54	51
$[Et_4N][Ru_3Co(CO)_{13}]$ f)	6	40	0	0.4	9.1	2.6	27	26	23
$[Ru_3(CO)_{12}]$		18	0	0	2.8	0.7	31	11	10

a)Unless otherwise noted, the catalyst(0.13 mmol), methanol(500 mmol), CH_3I(5 mmol), and benzene(10 mmol) as internal standard were charged in a 200 ml stainless-steel autoclave lined with titanium. Carbon monoxide(40 kg/cm^2) and hydrogen(80 kg/cm^2) were then introduced and the mixture was stirred for 3 hours at 180°C. b)The yield was calculated by (CH_3OH consumed for product)/(CH_3OH charged) x 100. c)The selectivity was obtained by [product(mmol)/CH_3OH reacted(mmol)] x 100. d)DMA means acetaldehyde dimethylacetal. e)The amount of the catalyst used was 0.2 mmol. f)The amount of the catalyst employed was 0.1 mmol.

ligands between the each two cobalt atoms.19) Based on the similarity of the infrared spectra(vide supra), it may be reasonable to postulate the structure of $[RuCo_3(CO)_{12}]^-$ to be similar to that of the above iron-cobalt mixed cluster.

Compared with $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$, the mixed cluster 3, 4, and 5 showed remarkable catalytic activities for homologation of methanol as shown in Table 1. It is to be noted that the yield and the selectivity of ethanol depend upon the counter cation. The cluster 5 gave a liquid product mainly composed of ethanol and the selectivity of ethanol was 51% at ca. 40% conversion. The other cobalt-ruthenium mixed cluster $[(Ph_3P)_2N][Ru_3Co(CO)_{13}]$ recently prepared by Geoffroy et al.,20) gave ethanol in over 9.1% yield, but the selectivity was rather low. Work is now in progress to elucidate the reaction mechanism.

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