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NOTE

Evidence for Site Isolation in Rh–Mo Bimetallic Catalysts Derived from $CpRhMo(CO)_3(PPh_3)_2$

Recently, several investigations have focused on promoted rhodium catalysts with particular emphasis on the effects of molybdenum and the utilization of organometallic precursors (1–7). Miessner and co-workers (1, 2) have published investigations of bimetallic cluster-derived Rh–Mo catalysts. These cluster-derived catalysts have shown significant oxygenate selectivity in CO hydrogenation when compared with bimetallic catalysts made from metal salts (1, 3, 4). In their recent paper (6), Miessner and co-workers excluded molybdenum suboxide migration; instead, they explained that the Mo promotion results in oxidative disruption of Rh_x particles and prevents the sintering of Rh. Similar structural arguments were put forth by us in earlier work on Rh–Mo catalysts derived from separate rhodium and molybdenum carbonyl precursors (8). We concluded that the role of molybdenum on alumina was to site-isolate rhodium in a highly dispersed form with a higher propensity for oxygenate production than larger rhodium particles. The site-isolated form of rhodium approaches the limit of ultrahigh atomic dispersion through textural promotion. In this investigation of Rh–Mo bimetallic catalysts, we provide reactivity and infrared spectral results that indicate the promotion of rhodium by molybdenum leads to a site-isolation effect which is enhanced by synthesis of the catalyst with a bimetallic complex precursor.

The bimetallic complex, $(PPh_3)_2RhMo(CO)(\mu\text{-}CO)_2Cp$, was synthesized following the method reported by Preston and co-workers (7). Initial complexes $RhCl(PPh_3)_3$, $Mo(CO)_6$, NaCp/THF, $RhH(CO)(PPh_3)_3$, and $[Mo(CO)_3Cp]_2$ were purchased (Strem and Aldrich) and were used without further purification. Silica (BET surface area = 320 m^2/g) and γ-alumina (American Cyanamid, BET surface area = 250 m^2/g) were heated at 200°C in air for 24 hr before catalyst preparation. Appropriate amounts of the bimetallic complex, $(PPh_3)_2RhMo(CO)(\mu\text{-}CO)_2Cp$, or separate complexes, $RhH(CO)(PPh_3)_3$ and $[Mo(CO)_3Cp]_2$, were dissolved in dichloromethane and the solution was added to corresponding amounts of support under a nitrogen atmosphere. The mixture was stirred for 2 hr and the solvent was removed by vacuum evaporation. Elemental analysis results and chemisorption data of the samples are shown in Table 1. Hydrogen and carbon monoxide chemisorptions were measured after the samples were reduced at 350°C with flowing H_2 for 4 hr and evacuated at the same temperature to 10^{-5} Torr (1 Torr = 133.3 N m^{-2}) for 16 hr. Carbon monoxide or dioxide hydrogenation reactions were carried out over the catalysts in a fixed-bed high-pressure reactor. Detailed descriptions of the reactor system, product analysis, and pretreatment of gases have been reported elsewhere (8). The reactor was charged with 1.0 g of catalyst (60 × 100 mesh), which was oxidized at 200°C in flowing air (30 ml/min) for 4 hr and then reduced at 350°C for 6 hr in flowing H_2 (40 ml/min). After the catalyst activity reached a steady state, reaction data were collected at different reaction conditions: 200–350°C; 1.0–3.0 MPa; CO/H_2 or CO_2/H_2 = 2–0.33; GHSV = 1200–2400 hr^{-1}. Fourier transform infrared (FTIR) spectra were recorded *in situ* for all catalysts after reduction at 350°C, CO absorption at 50°C, and evacuation at room temperature.

The CO hydrogenation reaction conditions and results are summarized in Table 2. The results indicate that compared with the nonbimetallic-complex-derived catalysts, designated as $Rh,Mo/SiO_2$ and $Rh,Mo/Al_2O_3$, the bimetallic-complex-derived catalysts show higher selectivities for oxygenate formation. In addition, the alumina-supported bimetallic-complex-derived catalyst showed particularly higher activity. Beyond these differences, the different supports also alter the oxygenate distribution: methanol is

TABLE 1

Elemental Analysis and Chemisorption Data of the Rh–Mo Bimetallic Catalysts

Catalysts	% Rh	% Mo	% P	CO/Rh	H/Rh
$RhMo/SiO_2$	0.51	0.47	0.28	1.06	0.16
$Rh,Mo/SiO_2$	0.36	0.38	0.25	1.00	0.00
$RhMo/Al_2O_3$	0.58	0.66	0.39	1.19	0.04
$Rh,Mo/Al_2O_3$	0.31	0.39	0.33	1.28	0.56

Note. RhMo and Rh,Mo represent catalyst derived from $RnMo(CO)_3Cp(PPh_3)_2$ and the mixture of $RhH(CO)(PPh_3)_3$ and $[Mo(CO)_3Cp]_2$, respectively.

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TABLE 2

CO_2-Free Selectivity of Rh–Mo Bimetallic Catalysts for CO Hydrogenation

Catalysts	H_2/CO	T (°C)	P (MPa)	C_xH_y	MeOH	Me_2O	EtOH	ΣOxy.	r^a	TON^b
$RhMo/SiO_2$	2	300	2.0	21.6	73.5	0.3	4.4	78.2	9.80	9.52
$Rh,Mo/SiO_2$	2	300	2.0	48.0	41.5	—	10.5	52.0	12.5	12.9
$RhMo/Al_2O_3$	2	250	1.87	24.8	17.8	44.9	12.4	75.1	55.2	47.8
$Rh,Mo/Al_2O_3$	2	300	2.0	37.4	19.9	42.7	—	62.5	3.87	3.11

[a] Reaction rate expressed as 10^{-6} × Mol CO/g Rh/sec.

[b] Turnover number expressed as 10^{-4}/sec.

the main oxygenate on silica-supported catalysts, while a much higher percentage of dimethyl ether is formed on the alumina-supported catalysts compared to other oxygenates. Methanol is dehydrated readily to dimethyl ether (i.e., dimethyl ether is a secondary product) on alumina-supported catalysts because of its significant Lewis acidity.

Table 3 summarizes the reaction conditions and results for CO_2 hydrogenation over these catalysts. It can be seen that the overall rates for CO_2 hydrogenation are lower than those for CO hydrogenation, but again, the bimetallic-complex-derived catalysts show distinctly higher selectivities toward oxygenates compared with catalysts derived from separate complexes. The differences in the product distributions from those of CO hydrogenation are that methanol is the main oxygenated component for both kinds of oxide-supported catalysts. Nevertheless, dimethyl ether was also formed on the alumina-supported catalysts.

Temperature dramatically changed the selectivity of CO and CO_2 hydrogenation on both the bimetallic-complex-derived and mononuclear-complex-derived catalysts. The bimetallic-complex-derived catalysts show higher selectivity to oxygenates at lower temperatures compared with the corresponding mononuclear-complex-derived catalysts. Methanol selectivity, for example, is approximately twice as high (80% compared to 45%) at 250°C over the $RhMo/SiO_2$ than over the $Rh,Mo/SiO_2$. The bimetallic-complex-derived catalysts are stable after break-in of approximately 4 hr, the CO hydrogenation rate and methanol selectivity over $RhMo/SiO_2$ remain unchanged for nearly 100 hr on stream.

An FTIR spectroscopy study on the used, re-reduced catalysts indicates that CO chemisorption on the bimetallic-complex-derived catalysts leads mainly to gem-dicarbonyl CO-coordination, while in contrast it leads principally to linear-CO coordination on the mononuclear-complex-derived catalysts (Fig. 1). The carbonyl absorption characteristics of the IR spectra on the catalysts also show some variation with the oxide support used. For $RhMo/SiO_2$, the strong gem-dicarbonyl absorption appeared at 2103 and 2033 cm^{-1}, a broad, weak-bridging absorption appeared at 1900 cm^{-1}, and almost no linear-CO absorption was observed. In contrast, for $RhMo/Al_2O_3$, there was a distinct linear-CO absorption (2065 cm^{-1}) besides the similar gem-dicarbonyl (2096, 2026 cm^{-1}) and broad weak-bridging (1863 cm^{-1}) CO absorption. The differences in CO absorption between the mononuclear complex-derived catalysts and the bimetallic-complex-derived catalysts are evident in both the silica- and alumina-supported cases. Not only were there no gem-dicarbonyl bands on the mononuclear-complex-derived catalysts, but also the linear-CO peak positions are shifted from 2075 cm^{-1} to 2055 and 2033 cm^{-1} for Rh, Mo/SiO_2, and from 2065 to 2076 cm^{-1} for $Rh,Mo/Al_2O_3$ (see Fig. 2).

It has been reported (3–5) that the doublet of the gem-dicarbonyl becomes the main feature of the infrared spectrum of CO chemisorbed on supported rhodium–molybdenum catalysts only when the Mo/Rh ratio is high (>4). The gem-dicarbonyl feature also was shown to be correlated with high dispersions of rhodium (5). However, in this study, the strong gem-dicarbonyl absorptions were ob-

TABLE 3

CO-Free Selectivity of Rh–Mo Bimetallic Catalysts for CO_2 Hydrogenation

Catalysts	H_2/CO_2	T (°C)	P (MPa)	C_xH_y	MeOH	Me_2O	EtOH	ΣOxy.	r	TON
$RhMo/SiO_2$	1	300	2.0	36.3	61.9	—	1.9	63.8	1.75	1.70
$Rh,Mo/SiO_2$	1	350	2.0	59.5	39.5	—	1.0	40.5	3.47	3.57
$RhMo/Al_2O_3$	1	300	2.0	43.4	44.1	8.7	3.9	56.6	1.72	1.49
$Rh,Mo/Al_2O_3$	1	350	2.0	55.8	43.0	1.2	—	44.2	3.10	2.50

Note. The rate and turnover number are calculated as in Table 2.

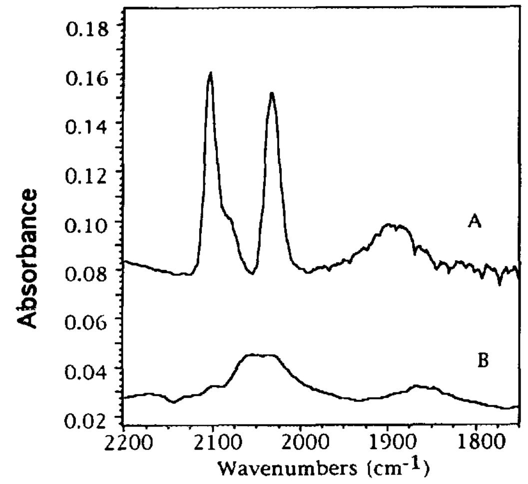

FIG. 1. (A) CO-absorbed RhMo/SiO_2 evacuated at RT. (B) CO-absorbed Rh,Mo/SiO_2 evacuated at RT.

served on the bimetallic-complex-derived catalysts even when the Mo/Rh ratio was only 1. After comparison with the IR spectra of CO on the reduced mononuclear-complex-derived catalysts at nearly the same metal loading, it is evident that the gem-dicarbonyl feature of the bimetallic-complex-derived catalysts is not a result simply of low metal loadings, an issue of concern, since low Rh loading was found to give rise to a gem-dicarbonyl on other supported Rh catalysts (9). Therefore, the prominence of the gem-dicarbonyl feature in the CO absorption spectra on the bimetallic-complex-derived catalysts points to more effective dispersion and hence site isolation of rhodium by molybdenum on both the alumina and silica surfaces.

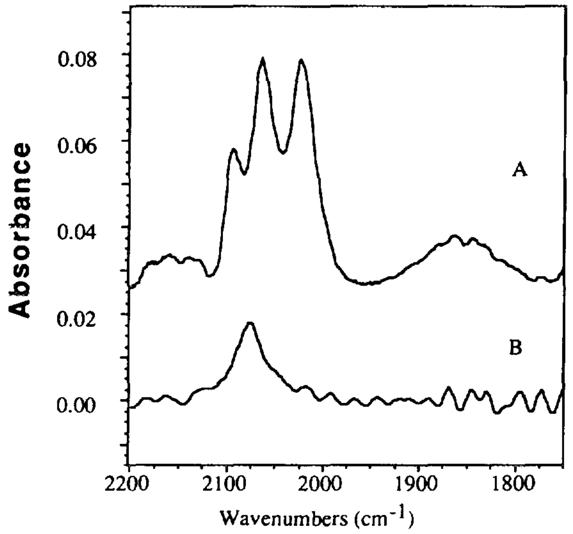

FIG. 2. (A) CO-absorbed RhMo/Al_2O_3 evacuated at RT. (B) CO-absorbed Rh,Mo/Al_2O_3 evacuated at RT.

Rh–Mo catalysts derived from the bimetallic complex, $(PPh_3)_2RhMo(CO)(\mu\text{-}CO)_2Cp$, show enhanced oxygenate-selectivities in the CO and CO_2 hydrogenation reactions compared with catalysts derived from the mononuclear complexes, $RhH(CO)(PPh_3)_3$ and $[Mo(CO)_3(C_5H_5)]_2$. The alumina-supported catalyst derived from the bimetallic complex precursor also displays unusually high activity for CO hydrogenation. The propensity for oxygenate formation on the bimetallic-complex-derived catalysts was confirmed by data derived from apparent activation energies and reaction orders which will be discussed in full detail elsewhere. The gem dicarbonyl was the main feature of the IR spectra of CO-absorbed on the bimetallic-complex-derived catalysts. These results suggest that promotion of Rh by Mo is enhanced in the bimetallic-complex-derived catalysts and the enhancement may arise through more effective site isolation.

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