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Communications

Promoter Effect of Iron on Olefin Hydroformylation Catalyzed by SiO_2-Supported Rhodium–Iron Bimetallic Carbonyl Clusters: Rh–Fe^{3+} Bimetallic Activation of Catalytic CO Insertion

Sir:

Surface organometallic chemistry, particularly involving metal cluster compounds, has been a subject of recent interest,[1] because supported clusters make possible the molecular-level elucidation of heterogeneous catalysis in terms of organometallic chemistry. It has been previously[1,2] reported that metal carbonyl clusters dispersed on SiO_2, Al_2O_3, ZrO_2, or C give discrete ensembles of mono- and bimetal atoms less than 10 Å in size with well-characterized metal composition and are highly dispersed on supports such as SiO_2, Al_2O_3, ZrO_2, or C. They are catalytically active in reactions such as CO + H_2 conversion to oxygenates[3] and lower olefins[4] or hydroformylation of olefins.[5] In the catalytic CO hydrogenation, some electropositive ions such as Mn, Ti, Zr,[6] and Fe[7] promote the production of oxygenates. In fact, the conventional Rh–Fe catalysts prepared from $RhCl_3$ and $FeCl_3$ exhibit a unique activity for producing a mixture of CH_3OH and C_2H_5OH in the CO + H_2 reaction. As judged by TEM, EXAFS,[8] Mössbauer,[9] and IR[10] spectroscopies, conventional SiO_2-supported Rh–Fe catalysts appear to have a Rh surface decorated with Fe^{3+} and Fe^0 that block sites on Rh and reduce multibridged CO chemisorption. This is reflected in suppression of methanation and enhancement of alcohol formation in CO hydrogenation.

In the present study, we have employed Rh–Fe bimetallic carbonyl clusters as molecular precursors for preparation of Rh–Fe bimetallic catalysts. Hydroformylation reactions of ethylene and propylene have been carried out as a diagnostic reaction for migratory CO insertion and a potential model for an elementary step in the formation of oxygenates such as alcohols from CO + H_2.[11] The structural properties of a SiO_2-supported Rh–Fe bimetallic cluster also have been studied by means of Mössbauer and IR spectroscopy of chemisorbed CO. We report here that bimetallic Rh–Fe^{3+} species derived from SiO_2-supported Rh–Fe carbonyl clusters are highly active for migratory CO insertion as judged by the rates of the hydroformylation of ethylene and propylene which are dramatically enhanced.

Carbonyl cluster compounds $Rh_4(CO)_{12}$,[12] $[TMBA]_2[Fe_3(CO)_{11}]$ (TMBA = NMe_3CH_2Ph),[13] $[TMBA][FeRh_5(CO)_{16}]$,[14] $[NMe_4]_2[FeRh_4(CO)_{15}]$,[14] $[TMBA]_2[Fe_2Rh_4(CO)_{16}]$,[14] and $Fe_3Rh_2(CO)_{14}C$[15] were synthesized according to literature methods. SiO_2 gel (Davison no. 57, 10–20 mesh, surface area = 280 $m^2\ g^{-1}$) was impregnated with each carbonyl cluster from a suitable organic solution. After removal of solvent, the impregnated catalysts were oxidized by air at room temperature overnight and reduced by flowing H_2 (1 atm, 60 mL min^{-1}) at a temperature rising from 200 to 400 °C and held at 400 °C for 2 h. Hydroformylation of ethylene and propylene was carried out with a flow-mode Pyrex glass reactor (i.d. = 14 mm; 240 mm long tubing) into which 2.0 g of the catalyst (0.5 wt % total metal loading) was charged. A gas mixture consisting of C_2H_4 (or C_3H_6), CO, and H_2 (1:1:1 volume ratio, total pressure 1 atm) was introduced at 60 mL min^{-1}. The oxygenated products such as aldehydes and alcohols were collected by bubbling the effluent gas through a water trap (50 mL). The analyses of the oxygenated products were conducted by FID gas chromatography with a Chromosorb 101 column (4 m) at 150 °C for ethylene hydroformylation products and 155 °C for propylene products, respectively. The effluent gas was analyzed by TCD gas chromatography with a Porapak Q column (4 m) at 70 °C for C_2H_4/C_2H_6 and a Al_2O_3-DMF column (4 m) at 25 °C for C_3H_6/C_3H_8.

The results for the hydroformylation of propylene are shown in Table I. The catalysts prepared from $Rh_4(CO)_{12}$ gave negligible activity for propylene hydroformylation, but the simple hydrogenation of propylene to propane was observed. On the catalyst derived from $[TMBA]_2[Fe_3(CO)_{11}]$, neither hydroformylation nor simple hydrogenation occurred under similar reaction conditions. The hydroformylation activity was dramatically increased for catalysts derived from $FeRh_5$, $FeRh_4$, Fe_2Rh_4, and Fe_3Rh_2 carbonyl clusters: 130, 260, 300, and 290 times larger, respectively, compared with the Rh_4-derived catalyst. This observation is strikingly similar to that in our earlier work[11a]

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Table I. Hydroformylation of Propylene on SiO_2-Supported Rh, Rh–Fe, and Fe Carbonyl Cluster Derived Catalysts[a]

precursor/SiO_2	at ratio Fe/Rh	specific rates of formation,[b] min^{-1}		selectivity, mol %		
		C_3H_8	PrCHO + BuOH	oxygenates[c]	alcohol[d]	*n*-isomers[e]
$Rh_4(CO)_{12}$	0	~0.001	0.0003 (1)[f]			
$Rh_4(CO)_{12}$[g]	0	0.027	0.0038	13	0	75
$[TMBA][FeRh_5(CO)_{16}]$	0.20	0.078	0.037 (130)	32	46	72
$[NMe_4]_2[FeRh_4(CO)_{15}]$	0.25	0.12	0.075 (260)	38	42	74
$[TMBA]_2[Fe_2Rh_4(CO)_{16}]$	0.50	0.13	0.088 (300)	41	44	73
$Fe_3Rh_2(CO)_{14}C$	1.5	0.10	0.084 (290)	45	63	70
$Rh_4(CO)_{12}$ + $[TMBA]_2[Fe_3(CO)_{11}]$	0.26	0.015	0.010 (34)	41	33	78
$[TMBA]_2[Fe_3(CO)_{11}]$		0	0			

[a] Conditions: total metal loading, 0.5 wt %; reaction temperature, 162 ± 2 °C; flow rate C_3H_6:CO:H_2 = 20:20:20 mL min^{-1}; total pressure, 1 atm. [b] mmol of Rh $mmol^{-1}$ min^{-1}. [c] (PrCHO + BuOH)/(C_3H_8 + PrCHO + BuOH) × 100. [d] BuOH/(PrCHO + BuOH) × 100. [e] (butanal + butanol)/(PrCHO + BuOH) × 100. [f] Values in parentheses are relative activities. [g] Total metal loading, 4 wt %.

of Zn-promoted Rh in enhancing ethylene hydroformylation. Additionally, the Rh–Fe carbonyl cluster derived catalysts improved the activity for the simple hydrogenation, but the relative rate enhancement for the hydrogenation was lower than that for the hydroformylation. Consequently, the selectivity toward hydroformylation was substantially increased on the Fe-containing Rh cluster derived catalysts. Alcohols were also obtained on Fe-containing Rh catalysts, while the $Rh_4(CO)_{12}$-derived catalyst gave only aldehydes as the hydroformylation products. The selectivity for normal isomers of the oxygenates was not affected by the Fe content in the precursor complexes. For example, the selectivity was 75% on the catalyst from $Rh_4(CO)_{12}$, and the Rh–Fe carbonyl cluster derived catalysts gave 70–75% of the normal selectivities. It is interesting to note that although SiO_2-supported $Rh_4(CO)_{12}$-derived catalyst showed much lower catalytic activity, the catalyst gave much more than 70g selectivity toward the normal isomer under the prevailing reaction conditions. In homogeneous catalytic reactions, it is well-known that mono Rh carbonyl species, e.g., $Rh(CO)_4$, exhibit 50–60% selectivity toward normal-isomers in propylene hydroformylation.[16] This analogy suggests that the Rh crystallites derived from $Rh_4(CO)_{12}$ provide higher selectivity than monometallic Rh species for the normal isomer due to steric hindrance around Rh atoms involved in the olefin hydroformylation.

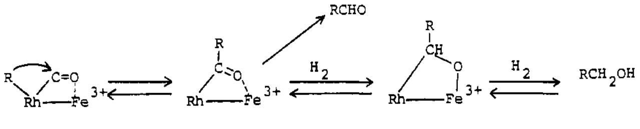
Similarly, Fe promotion was observed in ethylene hydroformylation on Rh–Fe carbonyl cluster derived catalysts.

The hydroformylation activity of the SiO_2-supported Rh–Fe bimetallic clusters was retained for a quite long period (~50 h) after activation.

A physically mixed Rh–Fe catalyst was prepared from a THF solution of $Rh_4(CO)_{12}$ and $[TMBA]_2[Fe_3(CO)_{11}]$ (Fe/Rh atomic ratio = 0.26) impregnated on SiO_2. The resulting H_2-reduced catalyst gave much lower activity for propylene hydroformylation than that from $[NMe_4]_2[FeRh_4(CO)_{15}]$ (Fe/Rh = 0.25). For comparison, a mixture of $Rh_4(CO)_{12}/SiO_2$ with $[TMBA]_2[Fe_3(CO)_{11}]/SiO_2$ (Fe/Rh = 0.24) was prepared and then reduced in hydrogen. This catalyst gave negligible or lower activity for propylene hydroformylation and hydrogenation than that obtained with the catalyst prepared from $Rh_4(CO)_{12}$ alone. These results suggest that Rh–Fe bimetallic carbonyl clusters provide discrete ensembles of Rh–Fe atoms impregnated on SiO_2. The resulting Rh–Fe pairs are highly active for olefin hydroformylation and successive hydrogenation to give higher alcohols.

The valence states of Fe in the bimetallic catalysts prepared from $[TMBA]_2[Fe_2Rh_4(CO)_{16}]$ impregnated on SiO_2 were observed by Mössbauer spectroscopy.[17] It was found that the absorption bands could be resolved into a singlet and a pair of quadrupole doublets and that they were reasonably assigned to Fe^0 and Fe^{3+}, respectively. No band for Fe^{2+} was observed. The isomer shifts relative to α-Fe were found to be 0.17 mm s^{-1} for Fe^0 and 0.46 mm s^{-1} for Fe^{3+},and the quadrupole splitting for Fe^{3+} was 1.00 mm s^{-1}. The Fe^0/Fe^{3+} ratio calculated from the peak areas was 27/73. The Mössbauer data suggest that Fe in the Rh–Fe carbonyl cluster-derived catalysts exists as a mixture of highly dispersed Fe^0 and Fe^{3+} and that Fe atoms are mostly in the state of Fe^{3+} ions even after H_2 reduction at 400 °C. Although there is limited information on the possible location of Fe in the Rh–Fe carbonyl cluster derived catalyst, it is reasonable to postulate that Fe^{3+} ions are bound not only with Rh but also with O atoms of SiO_2 support to form Rh-Fe-O bonding, as was previously suggested from the EXAFS measurements[8] on the conventional Rh–Fe/SiO_2. Fe^{3+} ions derived from Rh–Fe carbonyl cluster seem to play a role in anchoring Rh atoms to prevent a sintering of Rh clusters. They also affect the catalytic performance in promoting the activity for the olefin hydroformylation.

Scheme I



FTIR studies[18] were performed on catalysts derived from Fe_2Rh_4 carbonyl clusters and subsequently exposed to CO. Two absorption bands at 2058 and 1806 cm^{-1} are reasonably assigned to linear carbonyl and bridging carbonyl on Rh atoms, respectively. The bridging CO band was appreciably suppressed in relation to the linear CO band on Fe_2Rh_4/SiO_2, compared with the bridge to linear CO ratio on Rh_4/SiO_2. Moreover, a low-frequency band appeared at 1628 cm^{-1}. This may arise from CO having C-coordinated with Rh and O-coordinated with adjacent electropositive ion Fe^{3+}. It was previously suggested[10] that similar bifunctional activation of CO occurred on conventional SiO_2-supported Rh–Mn, Ti, and Zr catalysts, where a large reduction of the CO stretching frequency was observed. Extensive structural and spectroscopic data demonstrate that stoichiometric adduct formation between organometallic carbonyl complexes and Lewis acids arises from C and O interactions.[19] It is conceivable that Fe atoms act as an inert breaker to divide the Rh ensembles into an isolated Rh atom. On the other hand, electropositive Fe^{3+} contiguous Rh atoms may play a role similar to that found in the Lewis acid promotion of CO insertion seen in organometallic chemistry.[20] The analogous reaction sequence on the bimetallic

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(17) For Mössbauer observation, the sample (total metal loading 4 wt %) was reduced with a H_2 flow at 400 °C for 2 h. Spectra were recorded at 20 °C with a Shimadzu MEG-2 or an Austin Science S-600 spectrometer. In order to determine Mössbauer parameters and relative absorption peak areas, the spectra were fitted as linear combination of Lorentzians with the least-squares method.

(18) For IR observation, the sample (total metal loading 4 wt %) was dried and pressed into a 70-mg wafer (disk diameter = 20 mm), which was reduced in the IR cell containing KBr crystal windows with a H_2 flow at 400 °C for 2 h. The IR spectra were recorded with a double-beam Fourier transform infrared spectrometer (Shimadzu FTIR-4100) at a resolution of 2 cm^{-1}. Generally, 25 interferograms were coadded to improve signal-to-noise ratios. CO was introduced at 25 °C and 22 Torr to the sample disk, and then the cell was evacuated. The background spectra were obtained on the sample wafer, which had been reduced with H_2 but not exposed to CO.

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catalysts might be that shown in Scheme I.

In conclusion, bimetallic Rh-Fe^{3+} ensembles appeared to be generated from Rh-Fe carbonyl clusters supported on SiO_2. They are active for migratory CO insertion as judged by selectivity toward olefin hydroformylation. This activity and selectivity may be due to the bi-site interaction with C- and O-bonded CO. This is reflected in Fe promotion for C_1-C_2 alcohol production from CO + H_2 catalyzed on Rh-Fe catalysts.

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Registry No. $Rh_4(CO)_{12}$, 19584-30-6; $[TMBA][FeRh_5(CO)_{16}]$, 87824-94-0; $[NMe_4]_2[FeRh_4(CO)_{15}]$, 87824-95-1; $[TMBA]_2[Fe_2Rh_4(CO)_{16}]$, 83971-74-8; $Fe_3Rh_2(CO)_{14}C$, 109864-06-4; $[TMBA]_2[Fe_3(CO)_{11}]$, 83971-68-0; ethylene, 74-85-1; propylene, 115-07-1.

Supplementary Material Available: A table listing the results for ethylene hydroformylation and a figure showing the Mössbauer spectrum (2 pages). Ordering information is given on any current masthead page.

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Stabilization of Nickel(III) in a Classical N_2S_2 Coordination Environment Containing Anionic Sulfur

Sir:

Current interest in the factors stabilizing Ni(III)[1] derives in substantial measure from the presence of this oxidation state in many hydrogenases,[2] in which nickel has been suggested to function in catalytic dihydrogen activation.[3] In the enzymes, the Ni(II/III) potential is remarkably negative, falling in the ca. -150 to -400 mV range vs NHE.[3] In synthetic complexes, the higher oxidation states of nickel can often be stabilized by anionic polarizable ligands containing deprotonated amides[4-6] or oximes.[7]

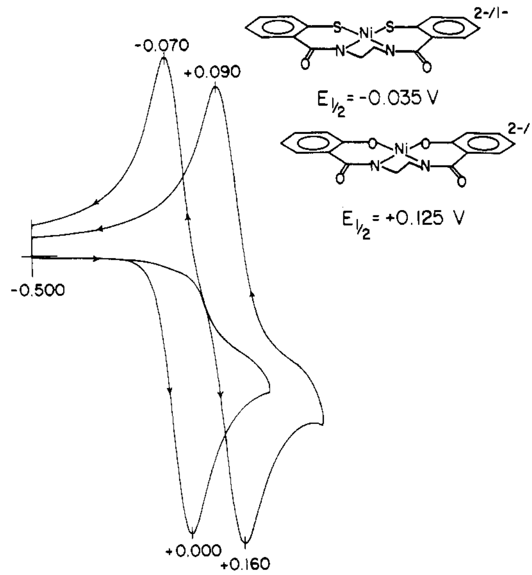

Figure 1. Cyclic voltammograms (100 mV/s) of 1 mM $[1]^{2-}$ and $[2]^{2-}$ in DMF solutions at 25 °C. Peak and half-wave potentials vs SCE are indicated.

Thiolate being a polarizable ligand, it is perhaps not unexpected that the Ni EXAFS of several hydrogenases reveals the presence of (at least three) anionic sulfur ligands.[8,9] Classical nickel(II) thiolate complexes (the non-dithiolene type) can be oxidized,[10] but always irreversibly thus far, and the description of certain products as containing Ni(III) is without substantiation. Our study of this problem has revealed no cases in which the ligand is not irreversibly oxidized to a disulfide,[11] a behavior also demonstrated by others.[10e] We report here one means of effecting *metal*-centered oxidation in a classical (innocent) ligand system containing thiolates and a measure of the relative effect of anionic oxygen and sulfur ligands on nickel redox potentials.

Treatment of *N*,*N'*-ethylenebis(*o*-hydroxybenzamide)[12] (2 equiv of Et_4NOH) and *N*,*N'*-ethylenebis(*o*-mercaptobenzamide)[13] (4 equiv of NaH) in DMF with the indicated bases followed by 1 equiv of $Ni(OAc)_2 \cdot 4H_2O$, and in the latter case also by 2 equiv of Et_4NCl, afforded in good yields red $(Et_4N)_2[1]$ and red-green dichroic $(Et_4N)_2[2]$,[14,15] respectively. ^1H NMR spectra were

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