Catalysis Letters 2 (1989) 227–234

Fe-PROMOTED SELECTIVE METHANOL SYNTHESIS IN CO HYDROGENATION CATALYZED ON SiO_2-SUPPORTED Ir_4Fe AND Pd_6Fe_6 BIMETALLIC CARBONYL CLUSTER-DERIVED CATALYSTS

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Received 14 December 1988; accepted 6 March 1989

The bimetallic catalysts prepared from Ir_4Fe and Pd_6Fe_6 carbonyl clusters exhibited high activities and selectivities towards methanol from $CO+H_2$. In contrast, hydrocarbons and CO_2 were preferentially obtained on the catalyst prepared from Fe-rich $PdFe_4$ cluster. The promotion towards methanol synthesis on the SiO_2-supported Ir_4Fe and Pd_6Fe_6 cluster catalysts was proposed to be associated with Pd-Fe^{3+} and Ir-Fe^{3+} sites located at the metal-support interface.

1. Introduction

Some bimetallic carbonyl cluster compounds have been used as the precursor to offer the tailored metal catalyst having a higher metal dispersion in less than 10 Å of the metal particle size with well-defined metal composition, compared with the conventional catalysts prepared by coimpregnation and ion-exchange of the metal salts [1–3].

It has been previously reported that in the catalytic CO hydrogenation on promoted Rh, Pt, Pd, and Ir catalysts [4], electropositive ions such as Mn, Ti, and Zr increase CO conversion due to the enhancement of CO dissociation. In contrast, Fe, Mo, and Zn substantially improve the selectivities towards oxygenates such as alcohols. The recent EXAFS and Mössbauer studies on conventional Rh-Fe/SiO_2 catalysts have demonstrated that a promoter Fe is enriched in the surface layer of Rh particles in forming the Rh-Fe ensembles at the metal support (SiO_2) interfaces [5]. Accordingly, as precursor compounds for the located model of Fe-promoted Rh/SiO_2 catalysts, RhFe bimetallic carbonyl clusters, e.g., $[FeRh_5(CO)_{16}]^{2-}$, $[Fe_2Rh_4(CO)_{16}]^{2-}$, and $[FeRh_4(CO)_{15}]^{2-}$ having the different

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Fe/Rh atomic ratios were employed to impregnate the RhFe bimetallic ensembles highly dispersed on SiO_2. The marked promotion of direct alcohol production in a $CO + H_2$ reaction and olefin hydroformylations was observed on the RhFe bimetallic cluster-derived catalysts [6].

We report here catalytic performances of SiO_2-supported $[FeIr_4(CO)_{15}]^{2-}$, $[Fe_6Pd_6(CO)_{24}H]^{3-}$ and $[Fe_4Pd(CO)_{16}]^{2-}$ bimetallic carbonyl clusters. They gave a marked promotion towards methanol synthesis in a $CO + H_2$ reaction, and towards 1-propanol in a hydroformylation of ethene. The electronic and structural characterization of the Pd_6Fe_6, $PdFe_4$, and Ir_4Fe bimetallic cluster-derived catalysts was conducted by means of Mössbauer, EXAFS, and FTIR spectroscopies. The origin of Fe promotion on the SiO_2-supported Ir_4Fe and Pd_6Fe_6 bimetallic clusters are discussed.

2. Experimental

$[TMBA]_2[FeIr_4(CO)_{15}]$ was originally synthesized and other clusters such as $[TMBA][HIr_4(CO)_{11}]$, $[TMBA]_3[Fe_6Pd_6(CO)_{24}H]$, $[TMBA]_2[Fe_4Pd(CO)_{16}]$, and $[TMBA]_2[Fe_3(CO)_{11}]$ (TMBA = NMe_3 (CH_2Ph)) were prepared by literature methods [7]. Each carbonyl cluster was impregnated onto SiO_2 (Davison GR-10303, 10–20 mesh, surface area = 330 m^2/g) from the THF solution under N_2. After removal of the solvent, the SiO_2-impregnated catalyst was gently oxidized at 423 K for 2 h in an O_2 flow (1 atm). The oxidized sample was reduced with flowing H_2 (1 atm) by programmed heating at 673 K for 2 h. Salt-derived Ir-Fe/SiO_2 and Pd-Fe/SiO_2 catalysts were prepared by coimpregnation of SiO_2 with the EtOH solution of $IrCl_4 \cdot H_2O$, $PdCl_2$, and $FeCl_3$.

A pressurized $CO + H_2$ reaction and an atmospheric pressure hydroformylation of ethene were performed with a flow-mode stainless-steel reactor (i.d. = 14 mm; 240 mm long tubing). Oxygenate products were collected in a water-condenser (50 ml H_2O) by bubbling the effluent gas. Products were analyzed by TCD and FID g.c using different columns, e.g., active carbon (1 m, 293 K), DMF/Al_2O_3 (4 m, 293 K), and Porapak Q (4 m, 343 K) for hydrocarbons, CO, and CO_2; Chlomosorb 101 (4 m, 408 K) for oxygenates.

For spectroscopic studies the catalysts were pressed into wafers (30 mg, 20 mm diameter), and reduced by H_2 at 673 K for 2 h. ^{57}Fe Mössbauer spectra were obtained at 298 K with a Shimadzu MEG-3 spectrometer. Isomer shifts were given relative to α-Fe. EXAFS measurements were conducted at 293 K with the SOR beam line (BL-10B) in the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF). IR spectra were recorded at 298 K with an FTIR spectrometer (Shimadzu FTIR-4100). CO (150 torr) was absorbed on the freshly reduced catalyst at 298 K for 10 min in an in situ IR cell, and the IR cell was evacuated at 10^{-4} torr.

3. Results and discussion

The results of 5 kg/cm^2 pressure CO hydrogenation are presented in table 1, where the specific rates of product formation and the selectivities are evaluated on mmol/min/(Ir or Pd mmol) in CO base. Interestingly, the rate of methanol production on the $[FeIr_4(CO)_{15}]^{2-}$ cluster-derived catalyst was dramatically enhanced by a factor of over 200 times magnification compared with the Fe-free $[HIr_4(CO)_{11}]^-$-driven catalyst. Thus the selectivity towards methanol was effectively improved up to 90% and the selectivity towards methane was suppressed to 9% on the Ir_4Fe/SiO_2 catalyst. $[Fe_3(CO)_{11}]^{2-}$-derived catalyst had no catalytic activity under the reaction conditions of 5 kg/cm^2 and 523 K. To compare the Fe promotion for methanol production, two Ir-Fe/SiO$_2$ catalysts were prepared from $IrCl_4 \cdot H_2O + FeCl_3$ and from a physical mixture of homometallic clusters $[TMBA]_2$-$[HIr_4(CO)_{11}]$ and $[TMBA]_2[Fe_3(CO)_{11}]$ at the same Fe/Ir atomic ratio of 0.25 as the bimetallic cluster $[FeIr_4(CO)_{15}]^{2-}$. Both catalysts gave higher rates for methanol production than did the Ir_4 cluster-derived catalyst, but the rate enhancement was much lower than that with the $[FeIr_4(CO)_{15}]^{2-}$-derived catalyst. On the catalysts prepared from salts and homometallic clusters, methanol selectivities were 60–80% and methane was substantially produced (above 20%

Table 1
CO hydrogenation on IrFe and PdFe cluster-derived catalysts [a]

Precursor/SiO$_2$ (2 wt% metal)	Fe/Ir or Fe/Pd	Specific rates of formation ($\times 10^{-3}$ min^{-1}) [b]				
		CH_3OH	C_2H_5OH	CH_4	H.C.(C_2^+)	CO_2
$[HIr_4(CO)_{11}]^-$	0	0.2	–	0.3	< 0.1	–
		(40)		(48)	(12)	
$[FeIr_4(CO)_{15}]^{2-}$	0.25	45	–	4.3	0.4	–
		(90)		(9)	(1)	
$IrCl_4.H_2O+FeCl_3$	0.25	7.8	0.4	3.4	0.6	–
		(61)	(6)	(27)	(6)	
$[HIr_4(CO)_{11}]^-$	0.25	3.0	tr	0.8	0.1	–
$+[Fe_3(CO)_{11}]^{2-}$		(79)		(20)	(2)	–
$PdCl_2$	0	1.5	–	tr	tr	–
		(100)				
$[Fe_6Pd_6(CO)_{24}H]^{3-}$	1.0	20	–	5.4	–	–
		(79)		(21)		
$PdCl_2+FeCl_3$	1.0	5.4	0.2	11	4.8	9.2
		(17)	(1)	(34)	(20)	(28)
$[Fe_4Pd(CO)_{16}]^{2-}$	4.0	12	–	36	16	21
		(12)		(35)	(32)	(21)

[a] Reaction conditions: total metal loading 2 wt%, $CO/H_2 = 0.5$ molar ratio, SV = 1000 h^{-1}, total pressure 5 kg/cm^2, 523 K.

[b] mmol/min/(Ir or Pd mmol), values in parentheses are selectivities calculated from carbon efficiencies: $iCi/\Sigma iCi \times 100$ (%).

Table 2
Hydroformylation of ethene on SiO_2-supported Ir_4, Ir_4Fe, and Pd_6Fe_6 carbonyl cluster-derived catalysts [a]

Precursor/SiO_2	Reaction temp. (K)	Specific rates of formation ($\times 10^{-3}$ min^{-1}) [b]		Sel. for [c] alcohol (mol%)
		C_2H_6	$C_2H_5CHO + 1\text{-}C_3H_7OH$	
$[HIr_4(CO)_{11}]^-$	443	9.4	0.3	70
		(97)	(3)	
$[FeIr_4(CO)_{15}]^{2-}$	443	12	3.9	94
		(97)	(3)	
$PdCl_2$	408	200	0.9	~ 0
		(~ 100)	(< 1)	
$[Fe_6Pd_6(CO)_{24}H]^{3-}$	408	1800	35	79
		(98)	(2)	

[a] Reaction conditions: total metal loading 2 wt%; flow rate $C_2H_4 + CO + H_2 = 20 + 20$ ml/min, total pressure, 1 atm.

[b] mmol/min(Ir or Pd mmol), values in parentheses are selectivities (mol%).

[c] $1\text{-}C_3H_7OH/(C_2H_5CHO + 1\text{-}C_3H_7OH) \times 100$.

sel.). Consequently, the $[FeIr_4(CO)_{15}]^{2-}$-derived catalyst showed most effective Fe promotion for methanol synthesis in the Fe promoted Ir/SiO_2 catalysts.

Similar Fe promotion for methanol production was observed on the $[Fe_6Pd_6(CO)_{24}H]^{3-}$ cluster-derived catalyst; the rate for methanol production was highly increased and the selectivity towards methanol reached to 79%. The Pd-Fe/SiO_2 catalyst prepared from $PdCl_2 + FeCl_3$ (atomic ratio Fe/Pd = 1) gave lower methanol selectivity. Notably, a poor methanol selectivity was obtained with the appreciable formation of CO_2 and hydrocarbons such as CH_4, C_2H_4, and C_3H_6 on the Fe-rich $[Fe_4Pd(CO)_{16}]^{2-}$/SiO_2 catalyst. Probably, the isolated Fe particles which might be produced by the segregation of the impregnated $PdFe_4$ clusters catalyzed a typical Fischer-Tropsch synthesis, resulting in the preferential production of CO_2 and hydrocarbons.

The results of hydroformylation of ethene over IrFe and PdFe cluster-derived catalysts are presented in table 2. It is of interest to find that both the hydroformylation to give propionaldehyde + 1-propanol and the simple hydrogenation to ethane were markedly enhanced on the catalysts derived from Ir_4Fe and Pd_6Fe_6 carbonyls compared with Ir_4/SiO_2 and Pd/SiO_2, respectively. Moreover, the selectivities towards 1-propanol were comparatively increased on the Ir_4Fe and the Pd_6Fe_6 cluster-derived catalysts.

As shown in fig. 1, the Mössbauer spectrum of Pd_6Fe_6 cluster-derived catalyst indicates that Fe atoms are mostly in the state of Fe^{3+} (Fe^{3+}: isomer shift (I.S.) = 0.36 mm/s, quadrupole splitting (Q.S.) = 0.42 mm/s, relative peak area = 64%; Fe^{2+}: I.S. = 1.24 mm/s, Q.S. = 2.5 mm/s, relative peak area = 36%) even after H_2 reduction at 673 K for 2 h. This is consistent with the preferential

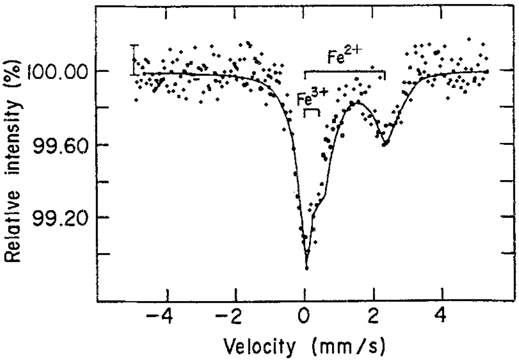


Fig. 1. ^{57}Fe Mössbauer spectrum of SiO_2-supported $[TMBA]_3[Fe_6Pd_6(CO)_{24}H]$ cluster-derived catalyst; 4 wt% metal loading, H_2 reduction at 673 K for 2 h.

existence of Fe^{3+} species in the SiO_2-supported Rh_4Fe_2 catalyst [6]. EXAFS studies were preliminarily performed on the Pd_6Fe_6 and the $PdFe_4$ cluster-derived catalysts after H_2 reduction at 673 K for 2 h. The Fourier transform of Fe K-edge EXAFS $k^3\chi(k)$ of the Pd_6Fe_6/SiO_2 catalyst is shown in fig. 2. The EXAFS results for the Pd_6Fe_6/SiO_2 catalyst showed the preferential contribution of Fe-Pd (2.5 Å) and Fe-O (2.0 Å). Pd K-edge EXAFS study on the Pd_6Fe_6/SiO_2 indicated the presence of Pd-Fe and Pd-Pd bondings without the contribution of Pd-O(support). By contrast, a negligible contribution of Fe-Pd bonding was observed on the $PdFe_4/SiO_2$ catalyst. This is reasonably reflected in the catalytic performance of the $PdFe_4$ catalyst with a poor selectivity in the $CO + H_2$ reaction. Fe-O bonding was not found in the H_2-reduced Pd-Fe/SiO_2 catalyst prepared from $PdCl_2 + FeCl_3$, where Fe atoms are uniformly distributed in the metal particles forming a Pd-Fe^0 alloy [8]. In contrast to the salt-derived Pd-Fe/SiO_2 catalysts, the results of Mössbauer and EXAFS studies on the Pd_6Fe_6 cluster catalyst imply that Fe^{3+} ions are located at the metal-support interface to anchor Pd atoms in forming the Pd-Fe^{3+} sites bound with SiO_2. Thus

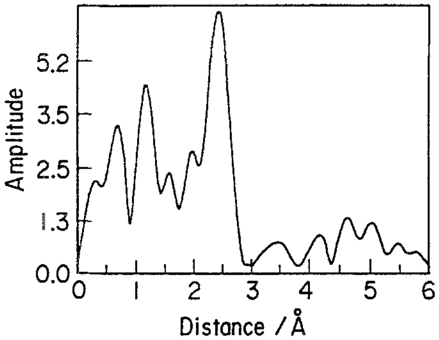
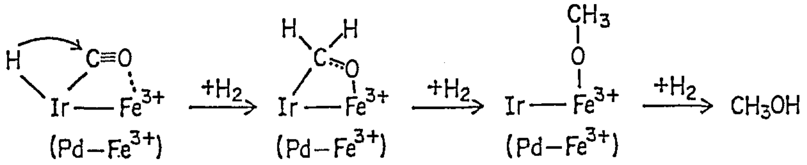


Fig. 2. Fourier transform of Fe K-edge EXAFS $k^3\chi(k)$ for SiO_2-supported $[TMBA]_3[Fe_6Pd_6(CO)_{24}H]$ cluster-derived catalyst; 4 wt% metal loading, H_2 reduction at 673 K for 2 h.

it is likely to predict that Pd-Fe^{3+} sites are essentially active for methanol production on the Pd_6Fe_6 catalyst in the $CO + H_2$ reaction. Similarly, Ir-Fe^{3+} sites are suggested to be formed and to catalyze the methanol synthesis on the $[FeIr_4(CO)_{15}]^{2-}$ cluster-derived catalyst. In the FTIR spectrum of adsorbed CO on the Ir_4Fe/SiO_2 catalyst, a band at 2044 cm^{-1} for the terminal CO shifted to higher wavenumber by 10 cm^{-1} than that on Ir_4 cluster-derived catalyst. Thus the electronical states of Ir in the Ir_4Fe catalyst were influenced by the presence of adjacent Fe ions. From above spectroscopic studies, it is suggested that Fe breaks IR and Pd ensembles in forming Ir-Fe^{3+} and Pd-Fe^{3+} sites in the Ir_4Fe and Pd_6Fe_6 bimetallic cluster-derived catalysts. The bimetallic sites lead to the marked suppression of CO dissociation to methane formation in the $CO + H_2$ reaction, eventually resulting in the marked improvement of methanol selectivity.

4. Conclusion

We have evidence for the benefits of molecular clusters as precursors to prepare $IrFe/SiO_2$ and $PdFe/SiO_2$ catalysts. On Pd_6Fe_6 and Ir_4Fe carbonyl cluster-derived catalysts, higher activities and selectivities for methanol synthesis was achieved in a $CO + H_2$ reaction. CO dissociation was effectively suppressed and the activities for CO insertion and hydrogenation were greatly enhanced, possibly due to Ir-Fe^{3+} and Pd-Fe^{3+} sites located at the metal-support interfaces in Ir_4Fe/SiO_2 and Pd_6Fe_6/SiO_2 catalysts as a following proposed mechanism:



Acknowledgments

We thank Dr. N. Kosugi and Prof. H. Kuroda for discussion on EXAFS evaluation, and we are also grateful to Dr. Y. Sakai and Prof. T. Tominaga for Mössbauer study.

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