

Selective Hydrogenation of CO into C₁ and C₂ Alcohols by SiO₂-supported RhFe, PtFe, and PdFe Bimetallic Cluster-derived Catalysts

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The cluster-derived bimetallic catalysts prepared from SiO₂-supported Rh₄Fe, Rh₄Fe₂, Pt₃Fe₃, PtFe₄, Pd₆Fe₆, and PdFe₄ carbonyl clusters exhibit high catalytic activities and selectivities for formation of oxygenates, consisting mainly of methanol and ethanol, from CO + H₂.

The chemical modification of solid surfaces, *e.g.*, SiO₂, Al₂O₃, and MgO using molecular metal cluster compounds as precursors has been recently investigated as a means of achieving sophisticated control over metal particle sizes (< 10 Å)¹ and metal compositions.² Such an approach is relevant to the molecular-level design of catalytically active surfaces.³ Additionally, it has been demonstrated that some electropositive ions such as Mn, Ti, Zr, and Fe promote the production of higher oxygenates in the CO + H₂ reaction catalysed on Rh.⁴ In particular, Fe promotion in the conventional Rh-Fe/SiO₂⁵ and Ir-Fe/SiO₂⁶ catalysts is remarkable for enhancing alcohol formation. EXAFS, Mössbauer, and Fourier transform (F.t.) i.r. studies have suggested that this promotion is associated with bimetallic sites consisting of RhFe and IrFe ensembles formed on the Rh and Ir crystallites with Fe.⁷ We report here that as a localized model for the promoted Rh, Pt, and Pd, tailored metal catalysts have been prepared from SiO₂-supported Fe-containing Rh, Pt, and Pd bimetallic carbonyl clusters. They have exhibited strikingly higher activities and higher selectivities for the production of C₁ and C₂ alcohols from CO + H₂, compared to the conventional metal catalysts.

A series of Fe-containing carbonyl clusters, such as [FeRh₄(CO)₁₅][NMe₄], [Fe₂Rh₄(CO)₁₆][TMBA]₂ (TMBA = benzyl trimethylammonium cation), [Fe₃Pt₃(CO)₁₅]-[TMBA]₂, [Fe₄Pt(CO)₁₆][TMBA]₂, [Fe₆Pd₆(CO)₂₄H]-[TMBA]₃, and [Fe₄Pd(CO)₁₆][TMBA]₂, were synthesized and isolated as crystals as reported by Longoni *et al.*^{8,9} The carbonyl clusters were dissolved in tetrahydrofuran (THF), acetone, or acetonitrile and impregnated with SiO₂ gel (Davison no. 57, 10–20 mesh, surface area 280 m²/g) under

an inert atmosphere of nitrogen. After removal of the solvent, the impregnated catalysts were oxidised by O₂ at room temperature overnight, followed by reduction with flowing H₂ under temperature-programmed conditions (293 to 673 K, 0.5–2 wt.% metal loading). Rh₄(CO)₁₂, [Fe₃(CO)₁₁][TMBA]₂, and [Pt₁₂(CO)₂₄][NEt₄]₂ were also used as precursors to prepare the Rh, Fe, and Pt cluster-derived catalysts. The CO + H₂ reaction was conducted at 473–543 K in an open flow mode stainless steel reactor (5–10 kg/cm², CO/H₂ molar ratio 0.5). The products were analysed by thermal conductivity detection (TCD) and flame ionisation detection (FID) gas chromatography (g.c.) using active carbon (1 m) and Al₂O₃-DMF (4 m) for hydrocarbons, CO, and CO₂, and Chromosorb 101 (4 m, 408 K) for oxygenates, respectively. The oxygenate products were collected by bubbling the effluent gas through a water condenser (50 ml of H₂O). The resulting catalysts were characterized by EXAFS,[†] Mössbauer (Austin S-600), and i.r. (Shimadzu FTIR 4100) spectroscopic measurements.

Typical results for a CO hydrogenation at 5 kg/cm² pressure of syngas (CO + H₂) are presented in Table 1, where the specific rates of product formation and selectivities are evaluated on mmol/min/mmol Rh in CO base. It was interesting that the yields of oxygenates, mainly consisting of methanol and ethanol, were substantially enhanced and that selectivities towards alcohols were promoted (15–42% selectivity) on the Rh₄Fe and Rh₄Fe₂ cluster-derived catalysts,

[†] Carried out at the BL 10B SOR Facility, National Laboratory for High Energy Physics (KEK-PF).

Table 1. Catalytic performance of SiO₂-supported RhFe carbonyl cluster-derived catalysts. 250 °C, CO/H₂ 0.5, space velocity 1000 l/h, total pressure 5 kg/cm².

Catalyst precursor/SiO ₂ (2 wt. % metal)	CO conversion (%)	Specific rates of product formation ($\times 10^{-3}$ mmol/min/mmol Rh) [Selectivity in CO base] ^a					Oxygenate selectivity (%)
		CH ₃ OH	CH ₃ CHO	C ₂ H ₅ OH ^b	CH ₄	C ₂₊ ^c	
Rh ₄ (CO) ₁₂	0.5	0.05 [0.4]	0.18 [3]	—	12 [97]	—	3.4
[FeRh ₄ (CO) ₁₅] ²⁻	1.5	3.7 [8]	1.4 [6]	1.7 [7]	39 [79]	—	21
[Fe ₂ Rh ₄ (CO) ₁₆] ²⁻	2.4	7.0 [9]	1.3 [3]	13 [33]	45 [56]	—	45
RhCl ₃ + FeCl ₃ (Fe/Rh 0.2—4 wt. % metal)	3.6	1.3 [3]	0.5 [2]	4.7 [20]	36 [75]	—	25

^a %CE = $(iC_j/\sum iC_j) \times 100$, where i = number of carbon atoms in a product molecule and C_j = concentration of the j molecule. ^b Including ethyl group in the form of acetate. ^c C₂₊ = hydrocarbon >C₂.

Table 2. Catalytic performance of SiO₂-supported PtFe and PdFe carbonyl cluster-derived catalysts. 250 °C, CO/H₂ 0.5, space velocity 1000 l/h, total pressure 5 kg/cm².

Catalyst precursor/SiO ₂ (2 wt. % metal)	CO conversion (%)	Specific rates of product formation ($\times 10^{-3}$ mmol/min/mmol Pt, Pd) [Selectivity in CO base] ^a				Oxygenate selectivity (%)
		CH ₃ OH	CH ₄	C ₂₊ ^c	CO ₂	
[Pt ₁₂ (CO) ₂₄] ²⁻	0.1	4.2 [100]	—	—	—	100
[Fe ₃ Pt ₃ (CO) ₁₅] ²⁻	0.2	13 [100]	—	—	—	100
[Fe ₄ Pt(CO) ₁₆] ²⁻	1.7	12 [7]	31 [18]	23 [26]	88 [50]	7
H ₂ PtCl ₆	0.03	1.5 [100]	tr ^b	tr	—	~100
Fe ₆ Pd ₆ (CO) ₂₄ H] ³⁻	0.5	20 [79]	5.4 [21]	—	—	79
[Fe ₄ Pd(CO) ₁₆] ²⁻	1.1	12 [12]	36 [35]	16 [32]	21 [21]	12
PdCl ₂	0.03	1.5 [100]	tr	tr	—	~100

^a %CE = $(iC_j/\sum iC_j) \times 100$, where i = number of carbon atoms in a product molecule and C_j = concentration of the j molecule. ^b tr = Trace amount. ^c C₂₊ = hydrocarbons >C₂.

compared with those on non-promoted Rh/SiO₂ from Rh₄(CO)₁₂. Fe promotion for alcohol production was found to be greater on the RhFe cluster-derived catalysts than on the conventional H₂-reduced RhFe/SiO₂ prepared by co-impregnation of Rh and Fe chlorides. Additionally, the hydrocarbon selectivities were considerably suppressed on the RhFe cluster-derived catalysts, possibly owing to the site-blocking of Rh ensembles with Fe.¹⁰ Along with the CO + H₂ reaction, we have carried out the atmospheric pressure hydroformylation of ethylene and propene to evaluate the catalytic CO insertion activity on the RhFe cluster-derived catalysts. The hydroformylation rates to produce alcohol-rich oxygenates were dramatically enhanced by a factor of 100–300 times on Fe-containing Rh cluster-derived catalysts, rather than on the Rh₄-derived one.

As shown in Table 2, the Fe promotion was also substantiated on the Pt₃Fe₃ and Pd₆Fe₆ cluster-derived catalysts, which gave methanol in higher yields and selectivities (79–100% selectivity) in the CO + H₂ reaction, compared to the conventional Pt and Pd catalysts and even more remarkable

than the Pt₁₂ carbonyl cluster-derived catalyst. While methane and higher hydrocarbons were obtained in appreciable amounts on the catalysts derived from PtFe₄ and PdFe₄ carbonyl clusters, this might be due to the segregation of both binary clusters to make isolated Fe ensembles active for a typical Fischer–Tropsch synthesis of hydrocarbons.

The Fourier transform *K*-edge EXAFS of Rh and Fe on the H₂-reduced sample (4 wt. % total metal) prepared from SiO₂-supported [Fe₂Rh₄(CO)₁₆][TMBA]₂ suggest that the RhFe bimetallic particles are highly dispersed in the size range ca. 10 Å, having direct Rh–Fe–O bonding [Rh–Rh: coordination no. (C.N.) 7.2, *R* 2.65 Å; Fe–Rh: C.N. 1.8, *R* 2.54 Å; and Fe–O: C.N. 3.0, *R* 1.99 Å]. On the other hand, Mössbauer studies on the Fe₂Rh₄ and Pt₃Fe₃ cluster-derived catalyst showed absorption bands which could be resolved into a singlet and a pair of quadrupole doublets and which are reasonably assigned to Fe⁰ and Fe³⁺, respectively. No band for Fe²⁺ was observed. The results indicate that Fe atoms mostly exist (above 65% abundance) in the Fe³⁺ state even after H₂ reduction at 673 K on the Rh₄Fe₂ and Pt₃Fe₃

cluster-derived catalysts. The EXAFS and Mössbauer studies imply that Fe³⁺ in the highly dispersed RhFe and PtFe bimetallic catalysts are located in the metal-support (silica) interface in forming Rh- (or Pt-)Fe³⁺ ensembles. This also seems to serve as an anchor for Rh (or Pt and Pd) clusters, reducing sintering. In fact, the catalytic performance of the Fe-containing Rh, Pt, and Pd derived catalysts was found to be good, maintaining their activities and selectivities for alcohol formation in a long time-on-stream reaction of CO + H₂.

In conclusion, we have evidence for the potential benefits of molecular clusters as precursors for the preparation of tailored bimetallic catalysts which provided higher activities and selectivities for alcohol formation in the CO + H₂ reaction, compared with the conventional metal catalysts. Fe promotion for oxygenate formation could be explained in terms of C- and O-bonded CO chemisorption with the adjacent RhFe, PtFe, and PdFe bimetallic sites to enhance the migratory insertion of CO with M-H and M-alkyl, as previously proposed in the alkene hydroformylation catalysed on Ru-Co¹¹ and Rh-Zn¹² bimetallic catalysts.

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