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EXAFS characterization and selective olefin hydroformylation on Rh_4, Rh_2Co_2 and $RhCo_3$ carbonyl clusters attached to tris-hydroxymethylphosphine-grafted silica

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$Rh_{4-x}Co_x(CO)_{12}$ ($x = 0, 2, 3$) are attached by carbonyl substitution to THP (tris-hydroxymethylphospine)-grafted silica keeping their cluster frameworks. They have been characterized by Rh K-edge EXAFS (extended X-ray absorption fine structure) and Fourier transform IR spectroscopy. They exhibited high catalytic activity with $> 98\%$ selectivity in gas phase hydroformylation of ethene and propene to give aldehydes under mild conditions (40 kPa and 300–373 K).

Keywords: Surface-bound $Rh_{4-x}Co_x(CO)_{12}$; THP-grafted silica; olefin hydroformylation

1. Introduction

Bimetallic carbonyl cluster compounds such as $Rh_2Co_2(CO)_{12}$ and $Rh_4Fe_2(CO)_{15}^{2-}$ grafted on SiO_2 and ZrO_2 and $Rh_{6-x}Ir_x(CO)_{16}$ ($x = 1, 2, 4$) occluded in zeolite pores have been used as molecular precursors for rational preparation of tailor-made catalysts [1,2] having well-defined metal ensembles and metal compositions, and applied to some probing catalytic reactions, e.g., olefin hydroformylation [3,4], $CO + H_2$ reaction [5] and alkane hydrogenolysis [6]. Nevertheless, so far it is difficult for SiO_2- and Al_2O_3-bound metal carbonyl clusters such as $Rh_4(CO)_{12}$ and $Os_3(CO)_{12}$ to keep their original cluster frameworks without

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further degradation and aggregation under the impregnation and prevailing reaction conditions [7,8]. Here we use THP (tris-hydroxymethylphosphine) grafted on silica surface to uniformly immobilize Rh and RhCo bimetallic carbonyl clusters, e.g., $Rh_{4-x}Co_x(CO)_{12}$ ($x = 0, 2, 3$), which have been characterized by EXAFS and FTIR spectroscopy. They exhibited high activity and selectivity in the vapor-phase hydroformylation of ethene and propene at less than 1 atm and 300–373 K.

2. Result and discussion

THP is obtained by the reaction of terakis-hydroxymethyl phosphonium chloride (Albright Wilson Co. LTD, 99%) with NEt_4Cl and purified by distillation in colorless syrup [9]. THP is impregnated (≈ 13 wt% loading) from ethanol solution with silica gel (Aerosil-200, surface area 250 m^2 g^{-1}; 1.25×10^{23} OH/g SiO_2 dehydrated by evacuation at 473 K). IR spectra of attached THP are shown in figs. 1a–1d. After the impregnation of THP on SiO_2 at 300 K, ν(CH) and δ(CH) of the methylene groups of THP appeared at 2990, 2910 cm^{-1} and 1440 cm^{-1}, respectively, and ν(OH) of hydrogen bonded OH at 3350 cm^{-1} accompanied with a sharp decrease of the isolated terminal OH groups on the silica surface ($\nu(OH) = 3700$ cm^{-1} in fig. 1a). The intensity of ν(OH) at 3350 cm^{-1} decreased by evacuation with increasing temperature (303–403 K), whereas that of ν(CH) remained unchanged. This suggests that THP successively grafted with silica surface by a dehydration reaction between THP and surface OH on silica, eventually forming $P(CH_2OSi{\equiv})_3/SiO_2$ (I) (figs. 1b–1e). $Rh_4(CO)_{12}$ ($\nu_{CO} = 2076$(s), 2043(w) and 1878(m) cm^{-1}) is instantaneously and completely immobilized (2–4 wt% Rh loading) from hexane solution with (I) under formation of CO at 300 K. No Rh carbonyl complex was detected in the filtered solution by atomic absorption analysis and IR observation, indicative of no leaching. It was found that 2.7 mol of CO per 1 mol of Rh_4 cluster were evolved at 300 K during the impregnation with THP/SiO_2. After removal of the hexane solvent at 300 K by evacuation, the resulting orange-colored sample (II) showed the lower-frequency shifted IR bands (fig. 1g) at 2044(s) and 1840(m) cm^{-1} probably due to the carbonyl substitution of $Rh_4(CO)_{12}$ with two or three phosphine ligands of (I). The IR spectra resemble those of $Rh_4(CO)_{10}(PPh_3)_2$ ($\nu_{CO} = 2085$(w), 2060(s), 2040(m), 2024(w), 1840(m), 1818(w) cm^{-1} [10]) and $Rh_4(CO)_9\{P(OCH_2)_3CEt\}_3$ ($\nu_{CO} = 2085$(w), 2060(s), 2040(s), 2024(w), 1848(m) cm^{-1} [11]). There are no other CO IR bands assignable to subcarbonyls such as $Rh(CO)_2$ and $Rh_6(CO)_{16}$ upon impregnation and by thermal treatments upto 353 K, as shown in figs. 1h–1j. The results suggested that Rh_4 carbonyl cluster is substantially stabilized with the THP-grafted silica surface. By contrast, we found that $Rh_4(CO)_{12}$ is unstable on SiO_2 and Al_2O_3, and readily converted into $Rh_6(CO)_{16}$ ($\nu_{CO} = 2086$(s), 2045(s) and 1805(m) cm^{-1}), being accompanied

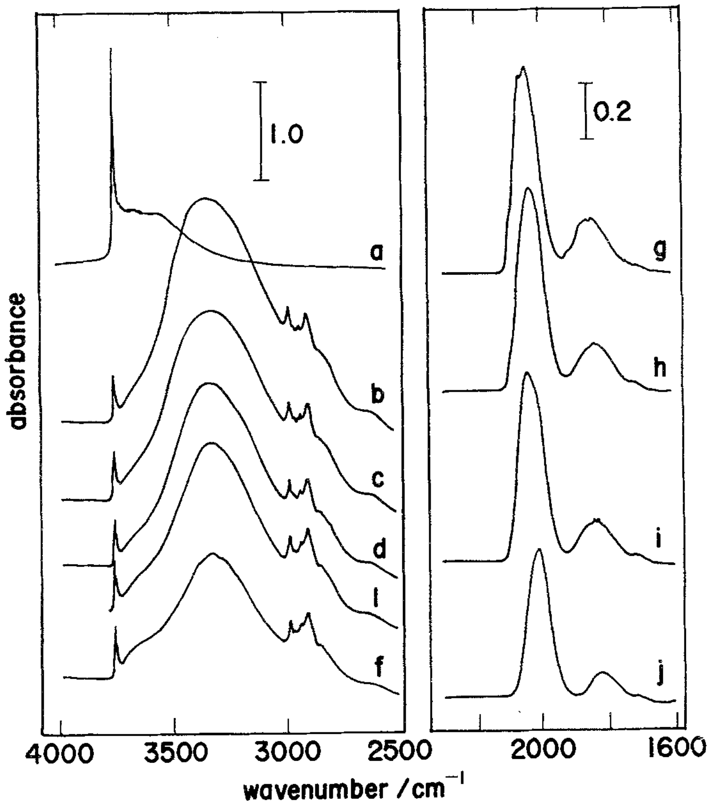


Fig. 1. Fourier transform IR spectra of tris-hydroxylmethylphosphine(THP)-grafted SiO_2 (I), (a)–(f), and $Rh_4(CO)_{12}$ attached to THP/SiO_2 (II), (g)–(j). (a) SiO_2 partially dehydrated at 473 K, (b) after impregnation of THP from ethanol solution, followed by evacuation at 303 K to remove the solvent, (c) after evacuation at 323 K, (d) at 363 K, (e) at 383 K, and (f) at 403 K; (g) upon impregnation of $Rh_4(CO)_{12}$ from hexane solution with (I) after evacuation at 403 K, (f) followed by the successive evacuation at 303 K, (h) at 323 K, (i) at 343 K, and (j) at 353 K. The spectrum of THP/SiO_2 (I) (f) is subtracted from each of (g)–(j).

with gem-$Rh(CO)_2$ ($\nu_{CO} = 2109$, 2097(sym) and 2022, 2001(asym) cm^{-1}), as previously reported [7]. In situ EXAFS data were conducted for sample (II) on the SOR beam line 10B of the National Laboratory for High Energy Physics (KEK-PF). The EXAFS was recorded with transmittance mode at room temperature. The Fourier transform of the EXAFS oscillation $k^3X(k)$ on sample (II) is shown in fig. 2, and the results of the curve-fitting analyses are summarised in table 1. The spectra were analyzed with program EXAFS2 and theoretical parameters [12]. Rh K-edge EXAFS analysis of the Rh–Rh frameworks and Rh–P coordination in terms of coordination number (Nc) and atomic distances (R) for sample (II) provided direct evidence for retention of the tetrahedral Rh cluster moiety attached to THP grafted silica (I). For Rh–Rh bond, $R = 0.276$ nm with $Nc = 2.4$ and for Rh–P bond, $R' = 0.234$ nm with $Nc' = 0.5$ were

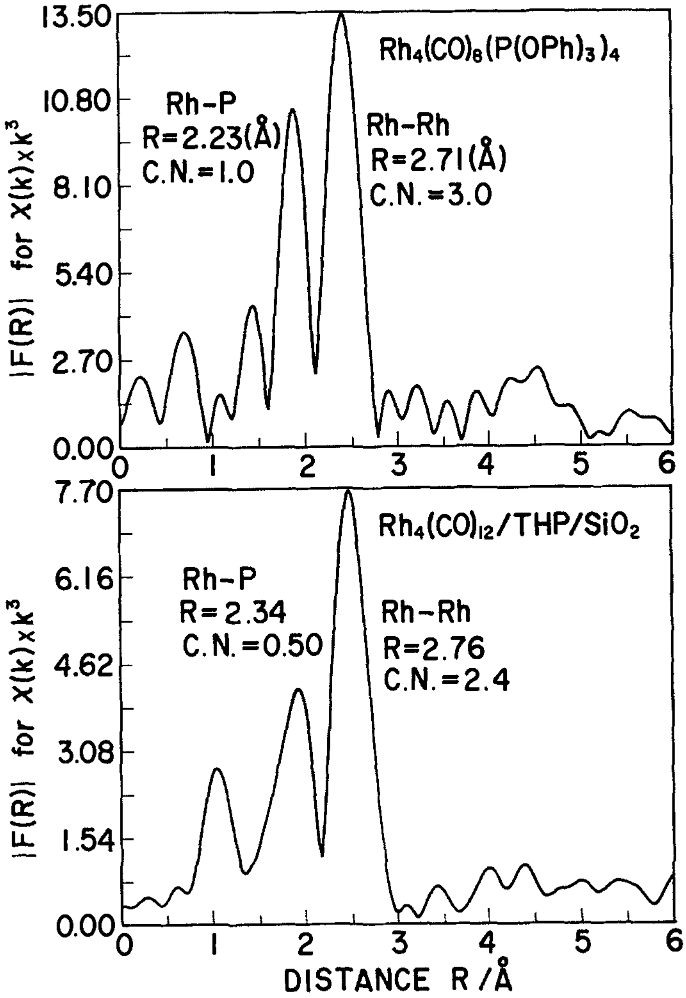
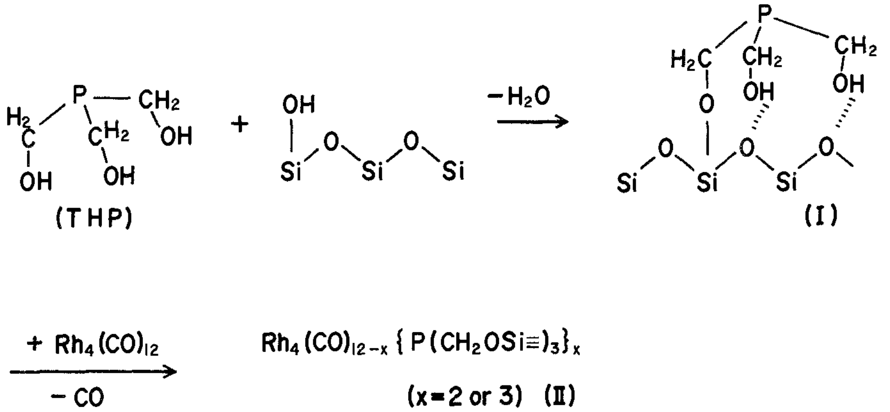


Fig. 2. Fourier transform of EXAFS oscillation $k^3X(k)$ of $Rh_4(CO)_{12}$ attached on THP/SiO_2 (II) (a), and $Rh_4(CO)_8\{P(OPh)_3\}_4$ as the reference (b).

Table 1
EXAFS parameters of Rh clusters

Compound	Bond	R (Å)	Nc	ΔE_0	σ	Error	R (Å) (XRD)
$Rh_4(CO)_8(P(OPh)_3)_4$	Rh–Rh	2.71	3.0	−8.35	0.060	0.039	2.72 (ave)
	Rh–P	2.23	1.0	−3.26	0.049	0.074	2.20–2.25
$Rh_4(CO)_{12}$/THP/SiO_2	Rh–Rh	2.76	2.4	4.79	0.069	0.041	
(fresh)	Rh–P	2.34	0.50	7.30	0.060	0.063	
$Rh_4(CO)_{12}$/THP/SiO_2	Rh–Rh	2.77	2.4	6.46	0.069	0.041	
(after reaction)	Rh–P	2.32	0.43	6.18	0.067	0.072	



obtained by curve-fitting of the EXAFS oscillation data. These structural values are in good agreement with those observed by EXAFS for crystalline reference of $Rh_4(CO)_{12}$ (for Rh–Rh, $R = 0.269$ nm with $Nc = 3.0$) and $Rh_4(CO)_8(PPh_3)_4$ (III) (for Rh–Rh, $R = 0.271$ nm with $Nc = 3.0$, and for Rh–P, $R' = 0.223$ nm with $Nc' = 1.0$). The EXAFS results also suggest that Rh_4 carbonyl clusters retain their frameworks coordinated at average with two phosphines grafted on silica. Furthermore, considering the van der Waals distance (≈ 0.70 nm) of two adjacent phosphine ligands on (I), it is of interest to find that the Rh–Rh and Rh–P distances in (II) are relatively lengthened and Rh_4 is slightly distorted, compared with those of $Rh_4(CO)_{12}$ and reference (III).

The hydroformylation reaction was performed at 323–363 K and reduced pressure of ethene + CO + H_2 ($p(C_2H_4) = p(CO) = p(H_2) = 13.3$ kPa) using a closed circulating pyrex glass reactor charged with each sample of $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh_2Co_2(CO)_{12}$, $RhCo_3(CO)_{12}$ and $Rh_2(CO)_4Cl_2$, which were similarly attached on THP-grafted silica (I). As shown in table 1, $Rh_4(CO)_{12}$ attached to THP-grafted silica (II) exhibited remarkably high activities in ethene hydroformylation giving C_2H_5CHO with more than 98% selectivity. A trace of ethane was formed as by-product in a simple hydrogenation of ethene. No propanol was detected. The catalytic performances reached in a few minutes and kept stationary conversions and selectivities on (II) at 368 K. The samples of $Rh_6(CO)_{16}$ and $[Rh(CO)_2Cl]_2$ as precursors attached to (I) offered considerably smaller TOF (turn of frequency) of propanol formation at 368 K, 1/1000 and 1/10 of those for $Rh_4(CO)_{12}$ as a precursor. The EXAFS analysis of (II) indicated that the Rh–Rh and Rh–P bondings are basically not changed in terms of atomic distances and coordination numbers before and after the ethene hydroformylation at 368 K, as shown in fig. 2 and table 2. The in situ IR studies suggested that there was no appreciable change in their carbonyl bands associated with linear and edge-bridging CO of the sample (II) without any appearance of gem-$Rh(CO)_2$ as the degradation species during the ethene hydroformy-

Table 2
Catalytic performance of Rh and Rh–Co bimetal clusters attached on THP/SiO_2 in the hydroformylation of ethene and propene

Catalyst [a]	TOF [b,c] (s^{-1})	Selectivity [b]	E_a [a] (kJ mol^{-1})	n/i [e]
ethene hydroformylation				
$Rh_4(CO)_{12}/THP/SiO_2$	3.1×10^{-3}	98%	26.5	
$Rh_2Co_2(CO)_{12}/THP/SiO_2$	1.7×10^{-3}	98%	52.0	
$RhCo_3(CO)_{12}/THP/SiO_2$	1.2×10^{-3}	98%	56.8	
$Rh_6(CO)_{16}/THP/SiO_2$	5.9×10^{-6}	> 98%	27.8	
$[Rh(CO)_2Cl]_2/THP/SiO_2$	3.6×10^{-4}	> 98%	39.5	
propene hydroformylation				
$Rh_4(CO)_{12}/THP/SiO_2$	5.6×10^{-4}	> 98%	19.0	0.91
$Rh_2Co_2(CO)_{12}/THP/SiO_2$	3.6×10^{-4}	> 98%	35.0	1.51
$RhCo_3(CO)_{12}/THP/SiO_2$	1.7×10^{-4}	> 98%	50.8	3.14

[a] THP/SiO_2 denote THP grafted SiO_2, 2 wt% of metals were loaded on THP/SiO_2 on each catalyst.

[b] Reaction condition; $T = 338$ K, $p(H_2) = p(CO) = p(C_2H_4)$ (or $p(C_3H_6)) = 13.3$ kPa, volume of reactor = 260 cm^3.

[c] TOF = mol/metal atom/s.

[d] Activation energy (E_a) was measured at 323–373 K.

[e] n/i = normal/iso molar ratio of butanal.

lation to give propanal. Accordingly, it is reasonably proposed that the Rh_4 carbonyl cluster attached to (I) is much more catalytically active and selective for the gas phase hydroformylation reaction towards aldehydes than $Rh_6(CO)_{16}$ and $Rh(CO)_2$ species similarly attached to THP/SiO_2 (I), which have been characterized by IR and EXAFS spectroscopy.

For propene hydroformylation, table 1 shows TOF and selectivities for butanal and normal/iso isomer ratios of butanal observed on $Rh_2Co_2(CO)_{12}$ and $RhCo_3(CO)_{12}$ attached to THP grafted on silica (I). Butanal was catalytically produced in more than 99% selectivity with a trace of propane by-product at 338–373 K. It is of interest to find that the TOF of butanal formation decreased systematically on the catalysts prepared from RhCo bimetallic clusters having larger Co contents, whereas the normal/iso selectivity of butanal substantially pronounced for $Rh_2Co_2(CO)_{12}$ and $RhCo_3(CO)_{12}$ as precursors. The trends for activity and normal/iso selectivity are consistent with those previously reported in propene hydroformylation on $Rh_{4-x}Co_x(CO)_{12}$ ($x = 0, 2, 3, 4$) impregnated on ZnO [3], where it is suggested that Co atoms in RhCo bimetallic clusters may play the role of electron-donor to stabilize normal-acyl intermediates favorable for linear-chained aldehyde formation.

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