

Combined homogeneous and heterogeneous catalysts. Rhodium carbonyl thiolate complexes tethered on silica-supported metal heterogeneous catalysts: olefin hydroformylation and arene hydrogenation

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Abstract

The rhodium carbonyl thiolate complex, $\text{Rh}_2[\mu\text{-S}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2(\text{CO})_4$ (Rh–S) was tethered to phosphine-modified Pd–SiO₂ (P–(Pd–SiO₂)), which was prepared by tethering the phosphine ligand $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$ to Pd–SiO₂, to give the tethered complex catalyst Rh–S/P–(Pd–SiO₂). Also, the phosphine-substituted $\text{Rh}_2[\mu\text{-S}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2(\text{CO})_2$ (Rh–S–P) was tethered to several silica-supported metal heterogeneous catalysts M–SiO₂ (M = Pd, Pt, Ru, Ir) to give Rh–S–P/M–SiO₂. These complex catalysts, consisting of a tethered complex on a supported-metal (TCSM), were used to catalyze the hydroformylation of olefins and the hydrogenation of toluene under atmospheric pressure. In the presence of phosphorus donor-ligands, all the TCSM catalysts are active for the hydroformylation of olefins under the mild conditions of 60°C and 1 atm of H₂ and CO (1:1). The most active catalysts, Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂, give maximum TOF values of 1.04 and 0.88 (mol aldehyde/mol Rh min), respectively, and TO values of 905 and 703 (mol aldehyde/mol Rh) during 22.5 h and 23.5 h in the hydroformylation of 1-octene. The Rh–S–P/Pd–SiO₂ ~ PPh₃ catalyst system maintains its activity through three cycles and 68 h to give a total turnover of 2118 mol aldehyde/mol Rh. These activities are higher than those of the homogeneous rhodium thiolate complex catalyst (Rh–S–P) and the rhodium thiolate complex catalysts tethered on just SiO₂ (Rh–S/P–SiO₂ and Rh–S–P/SiO₂). The effects of the phosphorus ligand and PR₃/Rh mole ratio on the hydroformylation rates, conversions, and chemo- and regioselectivities for aldehyde were also investigated. The Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂ catalysts are also active for the hydrogenation of toluene under the mild conditions of 40°C and 1 atm of H₂; they are much more active than the homogeneous rhodium thiolate complex catalyst Rh–S–P, the simple silica-supported heterogeneous palladium catalyst (Pd–SiO₂) and the rhodium thiolate complex catalysts tethered on just SiO₂ (Rh–S/P–SiO₂ and Rh–S–P/SiO₂). The synergistic advantages of the two components (tethered complex and supported metal) of the TCSM catalysts are greater for the hydrogenation of toluene than for the hydroformylation of 1-octene. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium carbonyl thiolate complexes; Supported metal catalysts; TCSM; Tethered complex catalysts; Silica; Palladium; Nickel; Gold; Hydroformylation; Toluene hydrogenation

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1. Introduction

Homogeneous metal complex catalysts are generally more active and selective than heterogeneous metal catalysts, but an important technical problem is the separation and recovery of homogeneous catalysts from reaction solutions. In order to overcome this problem, much work has focused on tethering homogeneous complex catalysts to insoluble supports to combine the advantage of easy catalyst recovery with the high activity and selectivity of soluble complexes [1–18]. Both organic polymers and inorganic oxides have been used as supports to tether metal complex catalysts, but for industrial use, inorganic oxides are often preferred because of their rigid structure and tolerance to various conditions of temperature and reaction medium. Silica is widely used as a support since transition metal complexes can be easily tethered to its surface through a ligand in the complex which has alkoxy- or chlorosilane functional groups that react with surface hydroxyl groups on SiO_2 . Similarly, we have tethered transition metal complexes to silica-supported metal heterogeneous catalysts such as Pd-SiO_2 [19]. The resulting combined homogeneous-heterogeneous catalyst, consisting of a tethered complex on a supported metal (TCSM), not only has the advantages of conventional silica-tethered complex catalysts but also the synergistic action of the two catalyst components. The rhodium complex catalysts, $\text{RhCl}(\text{CO})[\text{CN}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2$ and $\text{RhCl}[\text{CN}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_3$, tethered on the silica-supported metal heterogeneous catalyst Pd-SiO_2 exhibit catalytic activities for the hydrogenation of arenes that are much higher than those of the separate homogeneous rhodium complex catalysts, the separate silica-supported metal heterogeneous catalyst (Pd-SiO_2), or the rhodium complex catalysts tethered on only SiO_2 [19].

In the present study, the rhodium carbonyl thiolate complexes, $\text{Rh}_2[\mu\text{-S}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2(\text{CO})_4$ (Rh-S) and $\text{Rh}_2[\mu\text{-S}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]_2[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3]_2(\text{CO})_2$

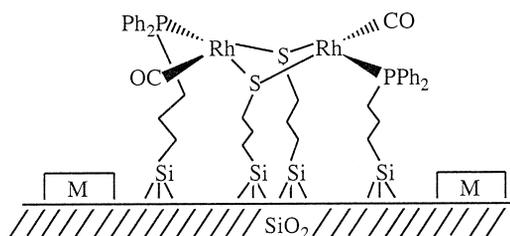


Fig. 1. Representation of the TCSM catalysts Rh-S-P/M-SiO_2 ($\text{M} = \text{Pd, Pt, Ru, Ir}$).

(Rh-S-P), were tethered on silica-supported metal heterogeneous catalysts M-SiO_2 ($\text{M} = \text{Pd, Ru, Pt, Ir}$) and on phosphine-modified Pd-SiO_2 ($\text{P-(Pd-SiO}_2)$) to give the TCSM catalysts, Rh-S-P/M-SiO_2 and $\text{Rh-S/P-(Pd-SiO}_2)$ (Fig. 1). The activities of these TCSM catalysts in the hydroformylation of olefins and the hydrogenation of toluene under atmospheric pressure are reported. Previously, we described [20] the hydroformylation activities of catalysts resulting from the immobilization of Rh-S and Rh-S-P on SiO_2 . The current investigation examines the effects of adding a supported metal to those catalysts.

2. Experimental

2.1. Materials and analysis

$\text{Rh}_2\text{Cl}_2(\text{CO})_4$ was purchased from Strem. Silica gel 100 (B.E.T. surface area, $400 \text{ m}^2/\text{g}$) and 3-mercaptopropyltrimethoxysilane were obtained from Fluka. $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$ was prepared according to the literature method [21]. Solvents were dried by refluxing over CaH_2 under nitrogen prior to use. All other reagents were commercial samples and were used as purchased.

FTIR and DRIFT spectra were recorded on a Nicolet 560 spectrophotometer equipped with a TGS detector in the main compartment and a MCT detector in the auxiliary experiment module (AEM). The AEM housed a Harrick diffuse reflectance accessory. The solution IR spectra were measured in the main compartment using a solution cell with NaCl salt plates. The DRIFT spectra were recorded on samples in the Harrick

microsampling cup. A Varian 3400 GC interfaced to a Finnigan TSG 700 high-resolution magnetic sector mass spectrometer with electron ionization (70 eV) was used for all GC-MS measurements. Gas chromatographic analyses were performed with a HP-6890 GC using a 32 m HP-1 capillary column with a FID detector.

The rhodium analyses of the silica-tethered catalysts were determined by atomic emission spectroscopy. Each sample was prepared for analysis by first treating the catalyst (50 mg) with 5 ml of aqua regia at 90°C for 5–10 min; then 5 ml of aqueous HF (5%) was added to the mixture, which was heated at 90°C for 5–10 min. The resulting solution was diluted with water to 25 ml.

2.2. Preparation of the catalysts

2.2.1. Preparation of silica-supported metal heterogeneous catalysts $M\text{-SiO}_2$ ($M = \text{Pd}, \text{Ru}, \text{Pt}, \text{Ru}$)

2.2.1.1. Pd-SiO₂. This SiO₂-supported palladium was prepared by a procedure similar to that described in the literature [22]. An aqueous solution of H₂PdCl₄, prepared by dissolving 1.2 g of PdCl₂ in 80 ml of aqueous HCl (0.2 M), was added to a flask containing 7.0 g of SiO₂. After the mixture was stirred at room temperature overnight, the water was removed by slow evaporation in a rotary evaporator at 80°C. The resulting solid was dried in an oven at 110°C for 5 h and then calcined at 500°C in an air flow for 4 h in a tube furnace. The calcined sample was subsequently reduced in a H₂ flow for 4 h at 380°C and then passivated under a flow of air at room temperature for 1 h to give the black Pd-SiO₂ (Pd, 10 wt.%) powder.

2.2.1.2. Ir-SiO₂. This SiO₂-supported iridium was prepared by a procedure similar to that used for the preparation of a SiO₂-supported rhodium heterogeneous catalyst [23]. An aqueous solution of H₂IrCl₆ · 6H₂O, prepared by dissolving

2.38 g of H₂IrCl₆ · 6H₂O in 24 ml of H₂O, was added to a beaker containing 8.0 g of SiO₂. After the mixture was stirred at room temperature for 1 h, the water solvent was evaporated by stirring the mixture on a hot plate. The resulting solid material was dried in an oven at 110°C overnight and then transferred to a glass tube and heated in a furnace at 200°C with a flow of N₂ for 2 h to remove most of the water. The sample was first reduced under a H₂ flow at 200°C for 3 h and then at 250°C for 5 h to give the black Ir-SiO₂ (Ir, 10 wt.%) powder.

2.2.1.3. Ru-SiO₂ [24]. An aqueous solution of RuCl₃, prepared by dissolving 1.9 g of RuCl₃ · xH₂O (Ru, 42%) in 30 ml of water, was added to a flask containing 8.0 g of SiO₂. After the mixture was stirred at room temperature overnight, the water was removed by continuously stirring the mixture at 120°C for 3 h. The resulting solid was calcined under a flow of air at 500°C for 6 h and then a flow of oxygen for 1 h at 400°C. The sample was finally reduced with a flow of H₂ at 500°C for 5 h to give the black Ru-SiO₂ (Ru, 10 wt.%) powder.

2.2.1.4. Pt-SiO₂. Pt-SiO₂ (Pt, 10 wt.%) was prepared following the same procedure as that used for the preparation of Ru-SiO₂, except using H₂PtCl₆ instead of RuCl₃ · xH₂O.

2.2.2. Preparation of rhodium carbonyl thiolate complexes

2.2.2.1. Rh₂[(μ-S(CH₂)₃Si(OCH₃)₃)₂(CO)₄ (Rh-S). Rh-S was prepared as described previously [20] and identified by its spectra. IR, ν(CO) (toluene): 2074 (m), 2056 (s), 2004 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 3.57 (s, 18H, OCH₃), 3.11 (t, 4H, SCH₂), 1.91 (m, 4H, CH₂CH₂CH₂), 0.82 (m, 4H, CH₂Si).

2.2.2.2. cis-Rh₂[(μ-S(CH₂)₃Si(OCH₃)₃)₂-[Ph₂P(CH₂)₃Si(OC₂H₅)₃]₂(CO)₂ (Rh-S-P). Rh-S-P was synthesized according to the previously reported procedure [20] and identified

by its spectra. IR $\nu(\text{CO})$ (toluene): 1970 (s), 1956 (s) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 200 MHz): δ 21.92 (d, $J_{\text{Rh-P}} = 122$ Hz).

2.2.3. Preparation of the tethered rhodium complex catalysts

2.2.3.1. Rh-S-P/M-SiO₂ (M = Pd, Ru, Pt, Ir) and Rh-S-P/SiO₂. The rhodium thiolate complex Rh-S-P (0.18 g, 0.12 mmol) was refluxed in 15 ml of toluene for 4 h with M-SiO₂ (0.80 g) that had been dried in vacuum at 100°C for 2 h. After filtration of the mixture, the separated solid was washed with toluene (4 × 10 ml) and then dried in vacuum at room temperature. The rhodium analyses of the catalysts were as follows: 1.70 wt.% for Rh-S-P/Pd-SiO₂, 1.95 wt.% for Rh-S-P/Pt-SiO₂, 2.15 wt.% for Rh-S-P/Ru-SiO₂ and 1.60 wt.% for Rh-S-P/Ir-SiO₂. The rhodium thiolate complex catalyst Rh-S-P/SiO₂, with a rhodium content of 2.45 wt.%, was prepared by the same procedure as that used for the preparation of Rh-S-P/M-SiO₂ except SiO₂ was used instead of M-SiO₂. The IR (DRIFT) spectrum of each catalyst exhibits one $\nu(\text{CO})$ band: 1979 cm^{-1} for Rh-S-P/Pd-SiO₂, 1972 cm^{-1} for Rh-S-P/Pt-SiO₂, 1974 cm^{-1} for Rh-S-P/Ru-SiO₂, Rh-S-P/Ir-SiO₂, and 1978 cm^{-1} for Rh-S-P/SiO₂. These spectra, containing only one band, are quite different than that (1970 (s), 1956 (s) cm^{-1} in toluene) of the precursor *cis*-Rh₂[μ -S(CH₂)₃Si(OCH₃)₃]₂[Ph₂P(CH₂)₃Si(OC₂H₅)₃]₂(CO)₂ complex. However, the 1972–1979 cm^{-1} bands are very similar to that (1975 cm^{-1}) of the *trans* isomer of the dirhodium complex [Rh(μ -SC₆H₅)(PPh₃)(CO)]₂ [25]. According to the literature [26], the product of the reaction between Rh₂(μ -SC₆F₅)₂(CO)₄ and 2 equiv of PPh₃ at low temperature (–5°C) is *cis*-[Rh(μ -SC₆F₅)(PPh₃)(CO)]₂ ($\nu(\text{CO})$: 1994 (s), 1977 (s) cm^{-1}), but the product is *trans*-[Rh(μ -SC₆F₅)(PPh₃)(CO)]₂ ($\nu(\text{CO})$: 1984 cm^{-1}) when the reaction is run at room temperature. Our IR experiments show that *cis*-Rh-S-P also isomerizes to *trans*-Rh-S-P ($\nu(\text{CO})$: 1978 cm^{-1}) upon

heating in toluene at 80°C for 40 min. Thus, it appears that the tethering reaction in refluxing toluene causes the *cis*-Rh-S-P complex to isomerize to *trans*-Rh-S-P.

2.2.3.2. Rh-S/P-(Pd-SiO₂) and Rh-S/P-SiO₂. A mixture of 0.80 g of Pd-SiO₂ (or SiO₂) and Ph₂P(CH₂)₃Si(OC₂H₅)₃ (2.4 g, 0.64 mmol) in 10 ml of toluene was refluxed for 4 h. After the mixture was filtered, the solid was washed with toluene (3 × 10 ml) and dried in vacuum at room temperature to give the phosphine-modified P-(Pd-SiO₂) or P-SiO₂. The P-(Pd-SiO₂) (or P-SiO₂) was stirred with Rh-S (84 mg, 0.13 mmol) in 10 ml of toluene at room temperature for 2 h. After the solid was separated by filtration, it was washed with toluene (4 × 10 ml) and then dried in vacuum at room temperature to give the tethered rhodium thiolate complex catalysts Rh-S/P-(Pd-SiO₂) and Rh-S/P-SiO₂. The rhodium content was 1.2 wt.% for Rh-S/P-(Pd-SiO₂) and 1.7 wt.% for Rh-S/P-SiO₂. The two catalysts had the same DRIFT spectrum which showed three $\nu(\text{CO})$ bands at 2056 (s), 1995 (s) and 1975 (s) cm^{-1} , which are very similar to those (2050 (s), 1990 (s) and 1972 (s) cm^{-1} in hexadecane) of [Rh(μ -S-t-C₄H₉)(CO)₂(PMe₂Ph)]₂, in which the Rh centers are 5-coordinate [27]. This suggests that the major species on the Rh-S/P-(Pd-SiO₂) and Rh-S/P-SiO₂ catalysts is the tethered five-coordinate rhodium thiolate complex Rh₂[μ -(CH₂)₃Si(OCH₃)₃]₂[Ph₂P(CH₂)₃Si(OC₂H₅)₃]₂(CO)₄.

2.3. Catalytic reactions

2.3.1. Hydroformylation of olefins

The hydroformylation reactions were carried out in a three-necked, jacketed glass vessel containing a stirring bar and closed with a self-sealing silicon rubber cap; the vessel was connected to a vacuum/CO-H₂ line and a constant-pressure gas buret. The temperature of the ethylene glycol that circulated through the vessel jacket was maintained with a constant temperature

bath. The reaction temperature and CO–H₂ (1:1) pressure were 60°C and 1 atm, respectively. After the catalyst and phosphorus ligand were added and the atmosphere in the vessel was replaced with CO–H₂, toluene and olefin were added by syringe with vigorously stirring, and the uptake of CO–H₂ was followed with the constant-pressure gas buret. After the reaction was stopped, the reaction mixture was analyzed by GC.

In all experiments, the hydroformylation products were 1-nonanal and 2-methyloctanal. In most cases, the only isomerization products were *trans*-2-octene and *cis*-2-octene. But when P(OPh)₃ co-catalyst was used, *cis*- and *trans*-3-octene and *cis*- and *trans*-4-octene were also formed. No hydrogenation products of the aldehydes, 1-octene or the toluene solvent were detected. There was no evidence for products resulting from the hydroformylation of the internal olefins 2-, 3-, or 4-octene.

2.3.2. Hydrogenation of toluene

The hydrogenation reactions were performed with the same apparatus as that used for the hydroformylations. The reaction temperature and H₂ pressure were 40°C and 1 atm, respectively. After the catalyst was added and the atmosphere in the vessel was replaced with hydrogen, toluene was added, and the uptake of hydrogen was followed with the constant-pressure gas buret.

3. Results and discussion

3.1. Hydroformylation of olefins over the TCSM catalysts

Hydroformylation of olefins to produce aldehydes and/or alcohols is one of the most important industrial methods for the functionalization of C=C bonds [28–31]. In a previous paper [20], we showed that the rhodium carbonyl thiolate complexes, Rh₂[μ-S(CH₂)₃Si(OCH₃)₃]₂-(CO)₄ (Rh–S) and Rh₂[μ-S(CH₂)₃Si(OCH₃)₃]₂-

[Ph₂P(CH₂)₃Si(OC₂H₅)₃]₂(CO)₂ (Rh–S–P), tethered on SiO₂ are highly active catalysts for the hydroformylation of 1-octene under the mild conditions of 60°C and 1 atm. Because we demonstrated previously [19] that catalysts consisting of both tethered complexes and supported metals (TCSM) were much more active than catalysts with only tethered complexes for the hydrogenation of arenes, we sought to determine whether such TCSM catalysts were also more active for hydroformylations. Thus, we prepared the TCSM catalysts Rh–S–P/M–SiO₂ (M = Pd, Pt, Ru, Ir) and Rh–S/P–(Pd–SiO₂) for study of their catalytic activities in the presence of a phosphorus-donor co-catalyst in the hydroformylation of 1-octene under the mild conditions of 60°C and 1 atm. All the silica-supported metal heterogeneous catalysts M–SiO₂ (M = Pd, Ru, Pt, Ir) were found to be inactive for the hydroformylation of 1-octene under the same conditions. The results (Table 1) show that all of the tethered rhodium thiolate complex catalysts are more active (TOF and TO) than the homogeneous Rh–S–P complex catalyst. As the most active catalyst, Rh–S/P–(Pd–SiO₂) has a maximum TOF of 1.04 mol aldehyde/mol Rh min and a TO of 905 mol aldehyde/mol Rh during a 22.5 h time period; these TOF and TO values are about 10 and 4.5 times greater than those of the homogeneous Rh–S–P catalyst and the rhodium complex Rh–S tethered on phosphine-modified SiO₂ (Rh–S/P–SiO₂), respectively. To our knowledge, this TCSM catalyst is the most active immobilized rhodium complex catalyst system for the hydroformylation of olefins under such mild conditions. Hydroformylations of olefins over tethered rhodium complex catalysts reported previously [32–38] are generally performed under a high pressure (normally ≥ 40 atm) of H₂ and CO.

The activities of the TCSM catalysts (Table 1) are strongly affected by the metal on the SiO₂ support. With the same tethered Rh–S–P complex, the activities of Rh–S–P/M–SiO₂ (M = Pd, Ru, Pt, Ir) decrease in the order: Pd–SiO₂ > Ru–SiO₂ > Pt–SiO₂ > Ir–SiO₂.

Table 1

Hydroformylation of 1-octene over tethered rhodium catalysts with PPh_3 co-catalyst^a

Catalyst	P/Rh ^b	Reaction time (h)	Maximum TOF ^c	TO ^d	Conversion ^e (%)	Aldehyde ^f selectivity (%)	n/i ^g	Isomerization ^h products (%)
Rh-S-P ⁱ	6.0	28	0.11	129	44.1	91.4	5.3	3.8
Rh-S-P/SiO ₂	7.4	21	0.49	499	98.2	95.2	4.2	4.7
Rh-S-P/Pd-SiO ₂	6.9	23.5	0.88	703	98.6	92.2	3.8	7.7
Rh-S-P/Pt-SiO ₂	6.5	22.5	0.36	432	69.8	92.0	3.9	5.6
Rh-S-P/Ru-SiO ₂	6.0	26.5	0.41	544	95.5	92.9	4.1	6.8
Rh-S-P/Ir-SiO ₂	6.0	25.5	0.20	213	27.3	95.3	4.5	1.3
Rh-S/P-SiO ₂	6.0	23	0.24	218	30.8	91.2	4.2	2.7
Rh-S/P-(Pd-SiO ₂)	6.5	22.5	1.04	905	95.0	87.1	3.8	12.3

^aReaction conditions: 50 mg of solid catalyst; 5 ml of toluene solvent; PPh_3 as the phosphorus-donor co-catalyst; 1 ml of 1-octene; 60°C, 1 atm.

^bMole ratio of PPh_3 co-catalyst/Rh complex.

^cMaximum TOF is defined as moles of aldehyde formed per mole rhodium per min.

^dMoles of aldehyde formed per mole rhodium during the given reaction time.

^eConversion of 1-octene determined by GC.

^fAldehyde selectivity (total yield of moles of both aldehydes per mole of 1-octene converted) determined by GC.

^gMole ratio of normal aldehyde to branched aldehyde determined by GC.

^hYield of isomerization products (total yield of moles of 2-, 3-, and 4-octenes per mole of 1-octene used initially) determined by GC.

ⁱA total of 10 μmol of Rh-S-P complex.

While the TCSM catalyst Rh-S-P/Pd-SiO₂ is almost two times more active than Rh-S-P/SiO₂, the activities of the Rh-S-P/Ru-SiO₂, Rh-S-P/Pt-SiO₂ and Rh-S-P/Ir-SiO₂ catalysts are lower than that of Rh-S-P/SiO₂. These results demonstrate that only the two catalysts with rhodium thiolate complex tethered on Pd-SiO₂, Rh-S-P/Pd-SiO₂ and Rh-S-P-(Pd-SiO₂), are more active than either the homogeneous rhodium complex Rh-S-P or the rhodium thiolate complexes tethered on just SiO₂ (Rh-S-P/SiO₂ and Rh-S/P-SiO₂). It is clear that the supported-palladium metal does promote the hydroformylation activity of the rhodium thiolate complexes tethered on Pd-SiO₂.

Fig. 2 shows kinetic curves for the hydroformylation of 1-octene over the tethered rhodium thiolate complex catalysts, Rh-S-P/M-SiO₂ (M = Pd, Pt, Ru, Ir), Rh-S-P/SiO₂, Rh-S/P-(Pd-SiO₂) and Rh-S/P-SiO₂, with PPh_3 co-catalyst. Except Rh-S-P/Pd-SiO₂, which is active from the outset (Fig. 2b), the other catalysts exhibit an induction period. The Rh-S-P/Ir-SiO₂ and Rh-

S/P-SiO₂ catalysts give the longest induction period (Fig. 2f and g), while the induction periods with the Rh-S-P/Pt-SiO₂ (50 min), Rh-S-P/Ru-SiO₂ (50 min), Rh-S-P/SiO₂ (45 min) and Rh-S/P-(Pd-SiO₂) (45 min)

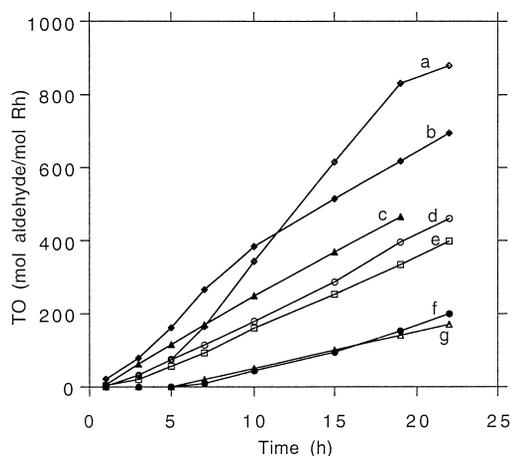


Fig. 2. Kinetic curves for the hydroformylation of 1-octene over the tethered rhodium thiolate complex catalysts: (a) Rh-S-P-(Pd-SiO₂), (b) Rh-S-P/Pd-SiO₂, (c) Rh-S-P/SiO₂, (d) Rh-S-P/Ru-SiO₂, (e) Rh-S-P/Pt-SiO₂, (f) Rh-S-P/Ir-SiO₂, (g) Rh-S/P-SiO₂. Reaction conditions are the same as those in Table 1.

catalysts are about the same (Fig. 2a, c, d and e).

With regard to the chemoselectivity for aldehyde and regioselectivity (n/i , mole ratio of 1-nonanal/2-methyloctanal), the homogeneous catalyst Rh–S–P gives a regioselectivity of 5.3, which is greater than that of the tethered complex catalysts (Table 1). The supported metal (M) in the TCSM catalysts has a small effect on both the chemo- and regioselectivity, although the chemo- and regioselectivities of the Rh–S–P/Ir–SiO₂ catalyst are slightly higher than those of the other tethered complex catalysts.

IR (DRIFT) spectra were recorded on the used catalysts, which were isolated at the end of the reaction time (Table 1) by filtering the catalysts from the reaction mixtures, washing them with toluene and drying under vacuum. The IR spectra of all the used TCSM catalysts isolated from the Rh–S–P/M–SiO₂ ~ PPh₃ catalyst systems (M = Pd, Pt, Ru, Ir) are about the same and show two $\nu(\text{CO})$ bands at 2050–2060 (w) and 1965–1975 (s) cm⁻¹, which are very similar to those (2065 (w) and 1975 (s) cm⁻¹) of the used catalyst isolated from the Rh–S–P/SiO₂ ~ PPh₃ catalyst system discussed previously [20]. This result suggests that the supported-metal on SiO₂ does not affect the structures of the tethered rhodium carbonyl thiolate complexes; that is, there is no strong interaction between the supported metal and the tethered complex. Although the IR spectra of the unreacted catalysts Rh–S/P–(Pd–SiO₂) and Rh–S/P–SiO₂ are different from those of the Rh–S–P/M–SiO₂ and Rh–S–P/SiO₂ catalysts, the used catalysts isolated from these two Rh–S catalyst systems both give two $\nu(\text{CO})$ absorptions at 2060 (w) and 1968 (s) cm⁻¹. Thus, the DRIFT spectra of the used Rh–S–P/Pd–SiO₂ and Rh–S/P–(Pd–SiO₂) catalysts are the same, yet Rh–S/P–(Pd–SiO₂) is slightly more active and gives a somewhat different distribution of products than Rh–S–P/Pd–SiO₂. On the basis of detailed IR spectral studies of Rh–S/SiO₂ and Rh–S–P/SiO₂ in our previous paper [20], we proposed that the pre-

dominant species present on the used catalysts was Rh(SR)(CO)(PR'₃)₂, in addition to a smaller amount of a species of the type Rh(SR)(CO)₂(PR'₃) which was more abundant on the most active catalyst systems.

The effect of different phosphorus ligand co-catalysts on the rate, conversion, and selectivity of 1-octene hydroformylation with the TCSM catalysts Rh–S–P/Pd–SiO₂ and Rh–S/P–(Pd–SiO₂) was investigated (Table 2) under the same conditions as those in Table 1. If no phosphorus ligand is added, the catalysts are inactive which indicates that the tethered phosphine in both of these catalysts is unable to substitute for the added co-catalysts used in these hydroformylation reactions. For both catalysts, the highest hydroformylation rates (TOF = 1.32 min⁻¹ for Rh–S/P–(Pd–SiO₂) and 1.87 min⁻¹ for Rh–S–P/Pd–SiO₂) were achieved when P(OPh)₃ was used as the co-catalyst. The catalyst systems with P(OPh)₃ co-catalyst also give the highest regioselectivity (n/i = 8.0) for the normal aldehyde, which is about two times greater than those observed with the phosphine co-catalysts. However, the chemoselectivity for aldehyde in the P(OPh)₃ system is much worse than that observed in the phosphine systems. While the Rh–S/P–(Pd–SiO₂) ~ P(OPh)₃ and Rh–S–P/Pd–SiO₂ ~ P(OPh)₃ catalyst systems give a 1-octene conversion of 98.1%, their selectivities for aldehyde are only 63.7% and 63.1%, respectively, and the yields of isomerization products are over 35.5%. For the three phosphine ligands, both the hydroformylation rates and the selectivities for aldehyde with the Rh–S/P–(Pd–SiO₂) catalyst decrease in the order: PPh₃ > P(C₆H₄OMe-*p*)₃ > P(C₆H₄F-*p*)₃. With the Rh–S–P/Pd–SiO₂ ~ PR₃ catalyst system, the hydroformylation rates decrease in the order: PPh₃ > P(C₆H₄F-*p*)₃ > P(C₆H₄OMe-*p*)₃; but the selectivities for aldehyde decrease in the order: PPh₃ > P(C₆H₄OMe-*p*)₃ > P(C₆H₄F-*p*)₃. Of all the phosphine-donor co-catalysts, P(C₆H₄F-*p*)₃ gives the highest n/i ratio with both Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂. These re-

Table 2

Hydroformylation of 1-octene over Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂ with different phosphorus ligands^a

Phosphorus	Reaction time (h)	Maximum TOF ^c	TO ^d	Conversion ^e (%)	Aldehyde ^f selectivity (%)	<i>n/i</i> ^g	Isomerization products (%) ^h
<i>Rh–S/P–(Pd–SiO₂) catalyst</i>							
P(OPh) ₃	23.5	1.32	685	98.1	63.7	8.0	35.5
PPh ₃	22.5	1.04	905	95.0	87.1	3.8	12.3
P(<i>p</i> -C ₆ H ₄ OMe) ₃	22.0	0.59	591	62.4	86.3	3.4	8.5
P(<i>p</i> -C ₆ H ₄ F) ₃	23.0	0.23	262	32.1	74.4	4.0	8.2
<i>Rh–S–P/Pd–SiO₂ catalyst</i>							
P(OPh) ₃	18.5	1.87	479	98.1	63.1	8.0	36.2
PPh ₃	23.5	0.88	703	98.6	92.2	3.8	7.7
P(<i>p</i> -C ₆ H ₄ OMe) ₃	25.0	0.39	479	68.6	90.2	3.5	6.7
P(<i>p</i> -C ₆ H ₄ F) ₃	25.0	0.72	646	97.9	85.3	4.0	14.2

Reaction conditions and footnotes are the same as those in Table 1.

sults indicate that both electron withdrawing and donating substituents on the phenyl rings are unfavorable for the hydroformylation. This trend is different than that observed for the hydroformylation of 1-octene with the Rh–S/SiO₂ ~ PR₃ catalyst system [20], in which electron withdrawing substituents on the phenyl rings increase the hydroformylation rates.

The P/Rh mole ratio also strongly affects the rate, conversion, and selectivity of 1-octene hydroformylation with the TCSM catalysts, Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂ catalysts. As the data illustrate in Table 3, without

added phosphine ligand, both catalysts are inactive for the hydroformylation of 1-octene under these mild conditions, despite the presence of the tethered phosphine on the catalyst surface. An increase in the PPh₃/Rh mole ratio increases the hydroformylation rate, aldehyde selectivity, and 1-nonanal/2-methyloctanal (*n/i*) mole ratio for both catalysts. For the Rh–S/P–(Pd–SiO₂) catalyst, the hydroformylation rate (TOF) reaches a maximum value of 1.04 mol aldehyde/mol Rh min when the PPh₃/Rh mole ratio is 6.5. Although the TOF declines slightly with further increases of the PPh₃/Rh mole

Table 3

Effect of PPh₃/Rh mole ratio on the hydroformylation of 1-octene over Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂^a

PPh ₃ /Rh	Reaction time (h)	Maximum TOF ^c	TO ^d	Conversion ^e (%)	Aldehyde ^f selectivity (%)	<i>n/i</i> ^g	Isomerization products (%) ^h
<i>Rh–S/P–(Pd–SiO₂) catalyst</i>							
0.0	23.0	0	0	23.7	0	–	23.7
3.3	23.5	0.39	421	54.1	71.0	3.7	15.7
6.5	22.5	1.04	905	95.0	87.1	3.8	12.3
9.7	21.5	0.93	944	96.3	89.4	3.9	10.2
13.0	22.0	0.84	943	97.0	90.0	3.8	9.7
<i>Rh–S–P/Pd–SiO₂ catalyst</i>							
0.0	8.0	0	0	11.6	0	–	11.6
2.3	23.5	0.28	240	47.3	65.5	3.6	9.4
4.6	24.0	0.80	676	98.5	88.7	3.6	11.1
6.9	23.5	0.88	703	98.6	92.2	3.8	7.7
9.3	24.0	1.19	680	98.0	89.8	4.0	10.0

Reaction conditions and footnotes are the same as those in Table 1.

ratio, the TO increases from 905 to 943 mol aldehyde/mol Rh during a period of about 22 h. For the Rh–S–P/Pd–SiO₂ catalyst, the highest TO and selectivity for aldehydes are reached when the PPh₃/Rh mole ratio is 6.9, but the maximum TOF increases slightly when the PPh₃/Rh mole ratio is increased to 9.3.

Table 4 shows data for the hydroformylation reactions of different olefins over the TCSM catalysts, Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂. For both catalysts, as the olefin hydrocarbon chain increases, the hydroformylation rate, chemoselectivity for aldehyde, and regioselectivity for linear aldehyde decrease. The hydroformylation rate for styrene is lower than those of the three terminal olefins.

The durability of the Rh–S–P/Pd–SiO₂ ~ PPh₃ catalyst with a PPh₃/Rh mole ratio of 4.6 was evaluated in three successive hydroformylations of 1-octene under the conditions in Table 1. In the first cycle, the maximum TOF was 0.80 and TO was 676 after 24 h. Then, the catalyst was filtered from the mixture, washed with toluene and dried under vacuum at room temperature. It was observed that in the second hydroformylation cycle, the addition of PPh₃ is still essential for the reaction. Using the same PPh₃/Rh mole ratio as in the first cycle, this catalyst system gave a maximum TOF of 0.88 and TO value of 750 after 24 h. After treating

the catalyst as described after the first cycle including the addition of PPh₃, it was used in a third cycle for which the maximum TOF was 0.72 and TO was 692 after 21.5 h. Thus, during the third cycle, the catalyst had essentially the same TO activity as in the first cycle. For the three cycles over 68 h, the total turnover number was 2118 mol aldehyde/mol Rh. In the DRIFT spectrum of the used catalyst after the third cycle, the positions and relative intensities of the $\nu(\text{CO})$ bands are the same as those of the used catalyst in the first cycle ($\nu(\text{CO})$ at 2060 (w) and 1970 (s) cm⁻¹) even though excess PPh₃ (PPh₃/Rh = 4.6) was added to the reaction solution for each cycle. In order to determine if any of the rhodium leached from the solid Rh–S–P/Pd–SiO₂ catalyst during the hydroformylation, the liquid phases from the first, second and third cycles were analyzed for Rh by atomic emission spectroscopy. It was found that 5.3% of the total rhodium on the catalyst leached into the liquid phase in the first cycle. In the second and third cycles, 2.7% and 1.0%, respectively, of the rhodium complex leached into the liquid phases. The liquid phases separated from the three cycles were also used for the hydroformylation of 1-octene under the same conditions as those used with the solid catalyst. After the first cycle (24 h), 1.0 ml of 1-octene was added to the solution phase. The hydro-

Table 4
Hydroformylation of different olefins over Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂^a

Substrate	Reaction time (h)	Maximum TOF ^c	TO ^d	Conversion ^e (%)	Aldehyde ^f selectivity (%)	<i>n</i> / <i>i</i> ^g	Isomerization products (%) ^h
<i>Rh–S/P–(Pd–SiO₂) catalyst</i>							
1-Octene	22.5	1.04	905	95.0	87.1	3.8	12.3
1-Decene	23.5	0.58	699	99.2	77.6	3.8	22.2
1-Dodecene	23.0	0.47	509	98.2	67.0	3.7	32.4
Styrene	23.5	0.29	371	30.0	82.5	0.5	5.3 ⁱ
<i>Rh–S–P/Pd–SiO₂ catalyst</i>							
1-Octene	23.5	0.88	703	98.6	92.2	3.8	7.7
1-Decene	20.5	0.46	428	99.0	83.4	3.8	16.4
1-Dodecene	24.0	0.45	402	98.4	71.6	3.9	17.9
Styrene	23.5	0.23	248	31.8	90.9	0.44	2.9 ⁱ

Reaction conditions and footnotes are the same as those in Table 1.

ⁱYield of ethylbenzene determined by GC.

formylation rate (milliliters of CO and H₂ uptake per minute) of the solution phase was about one-fifth of that of the first cycle with the solid catalyst (Rh–S–P/Pd–SiO₂). However, the solution phases from the second and third cycles were inactive for the hydroformylation of 1-octene under the reaction conditions. Thus, in the first cycle, about 20% of the hydroformylation could have been catalyzed by Rh that leaches into the solution, but in the second and third cycles, the hydroformylation is catalyzed only by the Rh that is tethered on the Pd–SiO₂ surface even though a small amount of Rh leached into the solution during the second and third hydroformylation cycles. Also, the activity of the catalyst in the third cycle appears not to be diminished by the loss of Rh in the first and second cycles. No $\nu(\text{CO})$ absorptions were detected in the IR spectrum of the solution after the first cycle, despite the observation that the solution showed catalytic activity.

3.2. Hydrogenation of toluene to methylcyclohexane

Although immense success has been achieved in the field of homogeneous transition metal complex-catalyzed hydrogenations of olefins, the related field of arene hydrogenation has been underdeveloped. We previously reported [19] that TCSM catalysts (Rh–CNR₃/Pd–SiO₂ and Rh–CNR₂/Pd–SiO₂) containing the rhodium isocyanide complexes, RhCl[CN(CH₂)₃Si(OC₂H₅)₃]₃ and RhCl(CO)[CN(CH₂)₃Si(OC₂H₅)₃]₂ tethered on Pd–SiO₂ are very active for the hydrogenation of arenes under the mild conditions of 40°C and 1 atm. The TCSM catalysts, Rh–S–P/Pd–SiO₂ and Rh–S/P–(Pd–SiO₂), were also used to catalyze the hydrogenation of toluene to methylcyclohexane under the mild conditions of 40°C and 1 atm of H₂. Table 5 shows the rates (TOF and TO) of hydrogenation of toluene in the presence of the two TCSM catalysts, the homogeneous rhodium thiolate complex catalyst, and the heterogeneous Pd–SiO₂ catalyst. It can be

Table 5
Hydrogenation of toluene to methylcyclohexane over tethered rhodium thiolate complex catalysts^a

Catalyst	Reaction time (h)	Maximum TOF ^b	TO ^c	H ₂ uptake ^c (mmol)
Pd–SiO ₂	21.5	–	–	1.52
Rh–S–P ^d	8.0	0	0	0
Rh–S–P/ SiO ₂	23.0	0.09	77	0.92
Rh–S–P/ Pd–SiO ₂	21.0	0.95	630	6.43
Rh–S/ P–SiO ₂	25.0	0.08	104	0.86
Rh–S/ P–(Pd–SiO ₂)	23.5	0.91	896	5.21

^aReaction conditions: 50 mg of solid catalyst; 5 ml of toluene; 40°C, 1 atm.

^bMaximum TOF defined as moles of H₂ uptake per mole Rh per min.

^cTurnover (moles of H₂ per mole Rh) and H₂ uptake correspond to the reaction time.

^dA total of 10 μmol of Rh–S–P complex.

seen that under the reaction conditions in Table 5, the homogeneous catalyst Rh–S–P is inactive for the hydrogenation of toluene, even though the amount (10 μmol) of Rh–S–P in solution is greater than that (8.25 μmol) in the TCSM catalysts. However, the TCSM catalysts Rh–S–P/Pd–SiO₂ and Rh–S/P–(Pd–SiO₂) are active for the reaction. The activity (TOF = 0.95, TO = 630 in a 21 h time period) of the Rh–S–P/Pd–SiO₂ catalyst is at least four times greater than that of the simple heterogeneous SiO₂-supported palladium (Pd–SiO₂) and eight times that of the catalyst consisting of Rh–S–P tethered to just SiO₂ (Rh–S–P/SiO₂). Similarly, Rh–S/P–(Pd–SiO₂) is about three and nine times more active than Pd–SiO₂ and the SiO₂-tethered catalyst Rh–S/P–SiO₂, respectively.

The IR (DRIFT) spectrum of the used Rh–S–P/Pd–SiO₂ catalyst, which was isolated at the end of the hydrogenation (Table 5) by filtering the catalyst from the reaction mixture, washing with toluene and drying under vacuum, shows one $\nu(\text{CO})$ band at 1982 cm^{-1} , which is the same as that of the unreacted Rh–S–P/Pd–SiO₂ catalyst. Moreover, like the unreacted Rh–S–P/Pd–SiO₂ catalyst, when the used Rh–S–P/Pd–SiO₂ catalyst was stirred in toluene

under a CO atmosphere at room temperature overnight, the IR (DRIFT) spectrum of the resulting sample gave three $\nu(\text{CO})$ adsorptions at 2077 (m), 2064 (s) and 2010 (s) cm^{-1} , which indicates that the tethered rhodium complex Rh–S–P is converted to the tethered Rh–S complex (Rh–S/Pd–SiO₂) [20]. All these results suggest that during the hydrogenation reaction the rhodium in the TCSM catalyst Rh–S–P/Pd–SiO₂ remains tethered as the original Rh–S–P complex.

By comparing the data in Tables 1 and 5, it can be seen that the difference between the activities of the TCSM catalysts (Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂) and the conventional SiO₂-tethered complex catalysts (Rh–S/P–SiO₂ and Rh–S–P/SiO₂) is much greater for the hydrogenation of toluene than for the hydroformylation of 1-octene. Thus, it is clear that the synergistic function of the two catalyst components of the TCSM catalysts is more favorable for hydrogenation than for hydroformylation. The greater toluene hydrogenation rate enhancement caused by the Pd in the TCSM catalysts may be explained by the hydrogen spillover mechanism that we proposed previously [19] for the hydrogenation of arenes over the Rh–CNR₂/Pd–SiO₂ and Rh–CNR₃/Pd–SiO₂ TCSM catalysts. This mechanism involves dissociative adsorption of H₂ on Pd, followed by spillover of hydrogen onto the SiO₂ surface [39–42] where it is transferred to an arene substrate that is coordinated to the Rh in a tethered complex. Thus, both the Pd metal and the tethered Rh complex play roles in promoting the hydrogenation of arenes. On the other hand, in hydroformylation, adsorption of H₂ is disfavored because CO adsorbs more strongly than H₂ to Pd [43]. This CO adsorption interferes with the generation of spillover hydrogen on Pd; therefore, the effect of Pd on the activity of the tethered Rh–S–P catalyst is relatively small. Thus, the TOF and TO values for Rh–S–P/Pd–SiO₂ are less than twice as large as those for Rh–S–P/SiO₂ in 1-octene hydroformylation. But the TOF and TO values for Rh–S–

P/Pd–SiO₂ are more than eight times as large as those for Rh–S–P/SiO₂ in toluene hydrogenation. These TOF and TO values for the hydrogenation of toluene with Rh–S–P/Pd–SiO₂ (0.95, 630 for 21.0 h) and Rh–S–P–(Pd–SiO₂) (0.91, 896 for 23.5 h) are, however, substantially lower than those of the isocyanide rhodium TCSM catalysts, Rh–CNR₂/Pd–SiO₂ (4.8, 1750 for 8.5 h) and Rh–CNR₃/Pd–SiO₂ (5.5, 2420 for 8.5 h).

4. Summary

The TCSM catalysts, Rh–S–P/M–SiO₂ (M = Pd, Pt, Ru, Ir) and Rh–S–P–(Pd–SiO₂), are active for the hydroformylation of olefins in the presence of phosphorus donor ligands under the mild conditions of 60°C and 1 atm of H₂ and CO (1:1). While catalysts that contain the rhodium thiolate complexes tethered on Pd–SiO₂ (Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂) exhibit activities for the hydroformylation of 1-octene that are higher than that of the simple tethered complex catalyst Rh–S–P/SiO₂, the Rh–S–P/M–SiO₂ (M = Pt, Ru, Ir) catalysts are somewhat less active than Rh–S–P/SiO₂. Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂ are also active for the hydrogenation of toluene at 40°C and under 1 atm of H₂. The activities of Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂ for both hydroformylation and hydrogenation are higher than those of the homogeneous rhodium thiolate complex catalyst Rh–S–P, the simple silica-supported heterogeneous palladium catalyst (Pd–SiO₂) and the rhodium thiolate complex catalysts tethered on just SiO₂ (Rh–S/P–SiO₂ and Rh–S–P/SiO₂). The effect of the supported palladium metal on the activities of Rh–S/P–(Pd–SiO₂) and Rh–S–P/Pd–SiO₂ is larger for the hydrogenation of toluene than for the hydroformylation of 1-octene. The results suggest that the design of a TCSM catalyst with high activity depends on the proper choice of the two catalyst components (tethered complex and supported metal).

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References

- [1] F.T. Hartley, *Supported Metal Complexes*, Reidel, Dordrecht, 1985.
- [2] T. Iwasawa, *Tailored Metal Catalysts*, Reidel, Tokyo, 1986.
- [3] P. Panster, S. Wieland, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1996, p. 605.
- [4] W.T. Ford, *Polymeric Reagents and Catalysts*, ACS, Washington, DC, 1986.
- [5] P.C. L'Argentière, D. Liprandi, D.V. Marconetti, N.S. Fígoli, *J. Mol. Catal. A: Chem.* 118 (1997) 341.
- [6] F. Verpoort, A.R. Bossuyt, L. Verdonck, B. Coussens, *J. Mol. Catal. A: Chem.* 115 (1997) 207.
- [7] R. Giannandrea, P. Mastroianni, G. Zaccaria, C.F. Nobile, *J. Mol. Catal. A: Chem.* 109 (1996) 113.
- [8] W. Keim, P. Mastroianni, C.F. Nobile, N. Ravasio, B. Corain, M. Zecca, *J. Mol. Catal.* 81 (1993) 167.
- [9] S. Shimazu, K. Ro, T. Sento, N. Ichikuni, T. Uematsu, *J. Mol. Catal. A: Chem.* 107 (1996) 297.
- [10] P.M. Lausarot, G.A. Vaglio, M. Valle, *J. Organomet. Chem.* 204 (1981) 249.
- [11] K.G. Allum, R.D. Hancock, I.V. Howell, T.E. Lester, S. McKenzie, R.C. Pitkethly, P.J. Robinson, *J. Catal.* 43 (1976) 331.
- [12] B.J. Pugin, *J. Mol. Catal. A: Chem.* 107 (1996) 273.
- [13] A. Kinting, H. Krause, M. Capka, *J. Mol. Catal.* 33 (1985) 215.
- [14] A. Carmona, A. Corma, M. Iglesias, A. San José, F. Sánchez, *J. Organomet. Chem.* 492 (1995) 11.
- [15] M.G.L. Petrucci, A.K. Kakkar, *J. Chem. Soc., Chem. Commun.* (1995) p. 1577.
- [16] J. Cermák, M. Kvícalová, V. Blechta, M. Capka, Z. Bastl, *J. Organomet. Chem.* 509 (1996) 77.
- [17] A. Corma, M. Iglesias, C. Del Pino, F. Sánchez, *J. Organomet. Chem.* 431 (1992) 233.
- [18] A. Carmona, A. Corma, M. Iglesias, F. Sánchez, *Inorg. Chim. Acta* 244 (1996) 79.
- [19] H. Gao, R.J. Angelici, *J. Am. Chem. Soc.* 119 (1997) 6937.
- [20] H. Gao, R.J. Angelici, *Organometallics* 17 (1998) 3063.
- [21] M. Capka, *Synth. React. Inorg. Met.-Org. Chem.* 7 (1977) 347.
- [22] A.M. Kazi, B. Chen, J.G. Goodwin Jr., G. Marcelin, N. Rodriguez, R.T.K. Baker, *J. Catal.* 157 (1995) 1.
- [23] T. Ioannides, X.E. Verykios, *J. Catal.* 140 (1993) 353.
- [24] J. Inukai, K. Asakura, Y. Iwasawa, *J. Catal.* 143 (1993) 22.
- [25] E.S. Bolton, R. Havlin, G.R. Knox, *J. Organomet. Chem.* 18 (1969) 153.
- [26] J.J.G. Fierro, M. Martínez-Ripoll, M.D. Merchán, A. Rodríguez, P. Terreros, H. Torrens, M.A. Vivar-Cerrato, *J. Organomet. Chem.* 544 (1997) 243.
- [27] Ph. Kalck, R. Poilblanc, *Inorg. Chem.* 14 (1975) 2779.
- [28] H.M. Colquhoun, D.J. Thompson, M.V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*, Plenum, New York, 1991.
- [29] B. Cornils, in: J. Falbe (Ed.), *Hydroformylation in New Syntheses with Carbon Monoxide*, Springer, Berlin, 1980, p. 1.
- [30] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, *J. Mol. Catal. A: Chem.* 104 (1995) 17.
- [31] C.D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, 1996, p. 29.
- [32] J. Blum, A. Rosenfeld, N. Polak, O. Israelson, H. Schumann, D. Avnir, *J. Mol. Catal. A: Chem.* 107 (1996) 217.
- [33] C.U. Pittman Jr., A. Hirao, *J. Org. Chem.* 43 (1978) 640.
- [34] L. Hong, E. Ruckenstein, *J. Mol. Catal.* 90 (1994) 303.
- [35] B. Lee, H. Alper, *J. Mol. Catal. A: Chem.* 111 (1996) 17.
- [36] D. Cauzzi, M. Lanfranchi, G. Marzolini, G. Predieri, A. Tiripicchio, M. Costa, R. Zanon, *J. Organomet. Chem.* 488 (1995) 115.
- [37] F.R. Hartley, S.G. Murray, P.N. Nicholson, *J. Mol. Catal.* 16 (1982) 363.
- [38] H. Arai, *J. Catal.* 57 (1978) 135.
- [39] W.C. Conner Jr., J.L. Falconer, *Chem. Rev.* 95 (1995) 759.
- [40] F. Roessner, U. Roland, *J. Mol. Catal. A: Chem.* 112 (1996) 401.
- [41] W.C. Conner Jr., G.M. Pajonk, S.J. Teichner, *Adv. Catal.* 34 (1986) 1.
- [42] V.V. Rozanov, O.V. Krylov, *Russ. Chem. Rev.* 66 (1997) 107.
- [43] G.C. Bond, *Heterogeneous Catalysis*, 2nd edn., Oxford Science Publication, 1987.