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Water-gas Shift Reaction over Ruthenium Carbonyl Complexes Anchored to Silica *via* Phosphine Ligands

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The water-gas shift reaction (WGSR) is of industrial importance, by increasing the hydrogen content in synthetic gas.

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad (1)$$

Commercial operation of the reaction has been carried out at elevated temperatures above 250 ℃ using metal oxide catalysts [1]. Recently homogeneous catalysis of the WGSR has been reconsidered, and several catalyst systems have been found to be active at temperatures of 100–200 ℃ [2, 3]. Examples include carbonyl [4] and phosphine [5] complexes of transition metals. The majority of the homogeneous WGSR have been performed in the presence of organic solvents such as alcohol, acetone and amines, because the metal complexes are insoluble or unstable in water.

Surface-bound transition metal complexes have also been studied as catalysts for the WGSR with vapour-phase reactants. Ruthenium [6], osmium [7], platinum [8] and iridium [9] complexes adsorbed on metal oxides have been shown to be active catalysts.

We have recently found that the anionic triruthenium cluster anchored to silica via ammonium or pyridinium functional groups is one order magnitude more active for the WGSR than the homogeneous catalyst [10]. In this communication we report the syntheses of ruthenium carbonyl complexes anchored to silica via phosphine ligands, $Ru(CO)_4(PPh_2C_2H_4\text{-}SIL)$ (**1**) and $H_4Ru_4(CO)_8(PPh_2C_2H_4\text{-}SIL)_4$ (**2**), and their catalytic properties in the WGSR.

The procedures to prepare the silica-anchored mononuclear complex **1** are outlined by reactions 2–4.

$$Ru_3(CO)_{12} + 3PPh_2C_2H_4Si(OEt)_3 \xrightarrow{60\ ^\circ C,\ 5h} Ru_3(CO)_9[PPh_2C_2H_4Si(OEt)_3]_3 + 3CO \qquad (2)$$

3

$$3 \xrightarrow[CO,\ 50\ bar]{150\ ^\circ C,\ 6h} Ru(CO)_4[PPh_2C_2H_4Si(OEt)_3] \qquad (3)$$

4

$$4 + SiO_2 \xrightarrow{25\ ^\circ C,\ 12h} Ru(CO)_4(PPh_2C_2H_4\text{-}SIL) \qquad (4)$$

5

The reaction of $Ru_3(CO)_{12}$ with $PPh_2C_2H_4Si(OEt)_3$ was carried out in toluene under nitrogen for 5 h at 60 ℃, giving rise to a red trinuclear cluster **3**. A yellowish mononuclear compound **4** was obtained by the treatment of red compound **3** with 50 bar of carbon monoxide in toluene at 150 ℃. The toluene solution of **4** was added to SiO_2 (Davison 952, 350 m^2/g, treated in vacuum for 4 h at 300 ℃), followed by standing at 25 ℃ for 12 h. The precipitate was washed with toluene and dried under vacuum at 100 ℃. The content of Ru in the anchored catalyst **1** was 5 mg per g of catalyst, which corresponds to a coverage of 1.4×10^{-11} mol-Ru/cm^2. The covalent attachment of compound **4** to the silica surface was made *via* the reaction of the $(EtO)_3Si$- functionality in phosphine ligands with the hydroxyl groups on the silica surface [11].

The silica-anchored tetranuclear cluser **2** was prepared by a previously published method [12], as outlined by reactions 5 and 6.

$$H_4Ru_4(CO)_{12} + 4PPh_2C_2H_4Si(OET)_3 \xrightarrow[H_2,\ 60\ bar]{130\ ^\circ C,\ 8h} H_4Ru_4(CO)_8[PPh_2C_2H_4Si(OEt)_3]_4 + 4CO \qquad (5)$$

5

$$5 + SiO_2 \xrightarrow{98\ ^\circ C,\ 6h} H_4Ru_4(CO)_8(PPh_2C_2H_4\text{-}SIL)_4 \qquad (6)$$

2

The content of Ru in the anchored catalyst **2** was 5 mg per g of catalyst.

Table I lists the spectroscopic data for various ruthenium carbonyl complexes **1**–**5**, together with those for related compounds. The infrared and electronic absorption spectra of the complexes **1**–**5** were in agreement with those of related compounds.

The thermal stabilities of the anchored complexes **1** and **2** were explored by gas evolution during the pyrolysis treatment of the complexes under He. No gas evolution was detected up to 140 ℃. Evolution of CO and CH_4 was observed above 150 ℃ from the complex **1**, and the evolution increased

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TABLE I. Spectroscopic Data for Various Ruthenium Compounds.[a]

Compound	IR ν_{CO} (cm^{-1})	UV-vis λ_{max} (nm)	Ref.
$Ru_3(CO)_9[PPh_2C_2H_4Si(OEt)_3]_3$ **3**	2040(vw), 1973(s), 1943(s)	492, 370(sh)	this work
$Ru(CO)_4[PPh_2C_2H_4Si(OEt)_3]$ **4**	2050(s), 1982(m), 1945(vs)	n.d.	this work
$Ru(CO)_4(PPh_2C_2H_4$-SIL) **1**	2045(m), 1990(s), 1940(sh)	n.d.	this work
$H_4Ru_4(CO)_8[PPh_2C_2H_4Si(OEt)_3]_4$ **5**	2008(s), 1981(m), 1948(s) 1920(sh)	407	this work
$H_4Ru_4(CO)_8(PPh_2C_2H_4$-SIL$)_4$ **2**	2008(s), 1978(sh), 1948(s) 1918(sh)	405	this work
$Ru(CO)_4(PPh_2Me)$	2060(s), 1984(m), 1946(vs)	254	[13]
$Ru_3(CO)_9(PPh_2Me)_3$	2042(w), 1970(s), 1943(s)	484, 364(sh)	[13]
$H_4Ru_4(CO)_8(PPh_3)_4$	2015(s), 1984(m), 1952(m) 1930(w)	n.d.	[14]

[a] All measurements were made in toluene solution at 25 °C for soluble complexes and in wafer forms at 25 °C for SiO_2-anchored complexes.

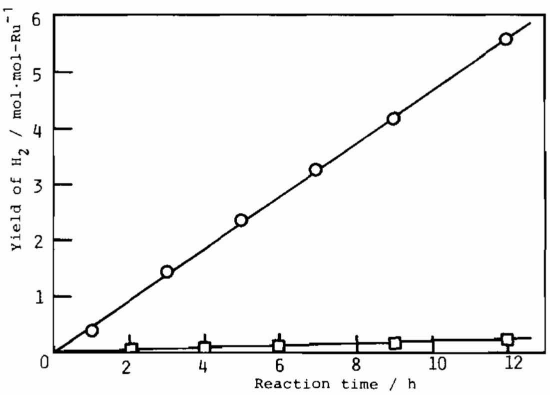

Fig. 1. Yield of H_2 during the course of water-gas shift reaction over the silica-anchored ruthenium complexes (1) and (2) at 150 °C. (○); $Ru(CO)_4(PPh_2C_2H_4$-SIL) (1) and (□); $H_4Ru_4(CO)_8(PPh_2C_2H_4$-SIL$)_4$ (2). Reaction conditions: P_{CO} = 200 torr, P_{H_2O} = 15 torr, and catalyst = 150 mg.

with temperature until all the CO in complex **1** was lost at 350 °C. In the case of complex **2**, evolution of CO, CH_4 and H_2 was observed above 180 °C. Complex **2** showed somewhat high thermal stability relative to that of **1**.

The WGSR was carried out for 12 h at 150 °C under CO (200 torr) and H_2O (15 torr) over the anchored complexes in a closed circulating glass reactor (total volume 260 cm^3). The results are shown in Fig. 1. H_2 and CO_2 were produced at equimolar quantities which were proportional to the reaction time. It is worth noting that the activity (11.2 mol-H_2 × mol-Ru^{-1} × day^{-1}) of mononuclear complex **1** is one order of magnitude higher than that (0.4 mol-H_2 × mol-Ru^{-1} × day^{-1}) of tetranuclear cluster complex **2**.

In both complexes the infrared spectra of the used catalysts were almost identical with those of the original complexes. It was also confirmed that the catalyst **2** could be re-used without any loss of catalytic activity.

In summary, we have demonstrated that the mononuclear ruthenium complex **1** exhibits a high catalytic activity for the WGSR with vapour-phase reactants.

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