Anchoring of an Anionic Triruthenium Cluster to Functionalized Silica and Its Catalytic Properties for the Water-gas Shift Reaction

Yoshiharu Doi,* Atsushi Yokota, Hiroto Miyake, and Kazuo Soga

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

The anionic triruthenium cluster $[Ru_3H(CO)_{11}]^-$, anchored to silica *via* ammonium or pyridinium functional groups, exhibits a high catalytic activity for the water-gas shift reaction at low temperatures in the range 100—150 °C.

The anionic triruthenium hydridocarbonyl cluster $[Ru_3H(CO)_{11}]^-$ has been reported to function as a homogeneous catalyst for several important reactions in C_1 chemistry, such as the water-gas shift reaction,[1] ethylene glycol synthesis from CO and H_2,[2,3] and carbonylation of methanol.[4] In solution, the active clusters may react with each other to form various products, which causes difficulty in the identification of the catalytic species and a decrease in catalytic activity.[5] Immobilization of metal cluster complexes on a solid surface may prevent the unfavourable intermolecular reactions. In this communication we report a new method for the

$$\underset{(\mathbf{1})}{\text{SIL–C}_3\text{H}_6\text{–NH}_2} + \text{MeI} \xrightarrow[\text{NaOH in MeOH}]{25\,^\circ\text{C, 70 h}} \underset{(\mathbf{2})}{\text{SIL–C}_3\text{H}_6\text{–}\overset{+}{\text{N}}\text{Me}_3\,\text{I}^-} \qquad (1)$$

$$\underset{(\mathbf{3})}{\text{SIL–C}_3\text{H}_6\text{–Cl}} + \text{NC}_5\text{H}_5 \xrightarrow[\text{NaI}]{115\,^\circ\text{C, 10 h}} \underset{(\mathbf{4})}{\text{SIL–C}_3\text{H}_6\text{–}\overset{+}{\text{N}}\text{C}_5\text{H}_5\,\text{I}^-} \qquad (2)$$

SIL = Silica

preparation of silica-anchored anionic triruthenium clusters and their catalytic properties in the water-gas shift reaction.

Ammonium and pyridinium functions were used as anchoring groups. The procedures to prepare the functionalized silicas are outlined in reactions (1) and (2). The aminated silica (**1**) was prepared by the condensation of $(EtO)_3Si[CH_2]_3NH_2$ with SiO_2 (Davison 952, 350 m^2/g, dried at 300 °C *in vacuo*) with elimination of EtOH,[6] and subsequently treated with MeI under alkaline conditions, giving the ammonium-functionalized silica (**2**) with an N content of 0.64 mmol/g; C, 3.72 mmol/g; and I, 0.87 mmol/g. The N content corresponds to 1.1 pendent ammonium functions per nm^2. The chlorinated silica (**3**) was prepared by the reaction of $(MeO)_3Si[CH_2]_3Cl$ with SiO_2, followed by treatment with pyridine in the presence of NaI to afford the pyridinium-functionalized silica (**4**) with an N content of 0.53 mmol/g; C, 5.07 mmol/g; and I, 0.44 mmol/g. The N content corresponds to 0.9 pendent pyridinium functions per nm^2.

Two types of silica-anchored anionic triruthenium clusters, $[Ru_3H(CO)_{11}][NMe_3–C_3H_6–SIL]$ (**5**) and $[Ru_3H(CO)_{11}]$-$[NC_5H_5–C_3H_6–SIL]$ (**6**), were prepared in methanol at 25 °C by an anionic-exchange reaction of the functionalized silicas (**2**) and (**4**) respectively with $Na[Ru_3H(CO)]_{11}$. The Ru contents were 3.3 mg per g of catalyst for (**5**) and 9.0 mg per g of catalyst for (**6**), which correspond to Ru_3 : N molar ratios of 0.017 and 0.056, respectively. The i.r. spectrum (KBr pellet) of (**5**) showed carbonyl bands at 2025s, 1970s, 1925sh, and 1745w cm^{-1}, in agreement with the i.r. data reported by Johnson *et al.*[7] for $[Ru_3H(CO)_{11}][NEt_4]$ (2075vw, 2018vs, 1985s, 1945m, and 1702w cm^{-1}). The complex (**6**) exhibited i.r. bands at 2030s, 1970s, 1935sh, and 1740w cm^{-1}, indicative of the preservation of the triruthenium cluster framework.

$$[Ru_3H(CO)_{11}][NMe_3–C_3H_6–SIL]$$
(**5**)

$$[Ru_3H(CO)_{11}][NC_5H_5–C_3H_6–SIL]$$
(**6**)

$$Na[Ru_3H(CO)_{11}]–SIL$$
(**7**)

The thermal stabilities of the anchored complexes (**5**) and (**6**) were explored by gas evolution during their pyrolysis under He. No gas evolution was detected up to 140 °C. Evolution of CO and CH_4 was observed from the complex (**5**) above 160 °C, and the evolution increased with temperature, until all the CO in complex (**5**) was lost at 250 °C. The decomposed complex did not show any carbonyl bands in the i.r. spectrum in the range 2100—1700 cm^{-1}, indicative of complete decarbonylation. The other anchored complex (**6**) exhibited similar thermal stability to that of (**5**) and was stable up to 150 °C.

The water-gas shift reaction was carried out for 6 h in the temperature range 100—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 given in Table 1. H_2 and CO_2 were produced in equimolar quantities which were proportional to the reaction time. The anchored complexes (**5**) and (**6**) could be reused without any loss of catalytic activity. For comparison, a silica-adsorbed $Na[Ru_3H(CO)_{11}]$ species (**7**) was prepared in high dispersion (2.0 Ru wt. %) by evaporating the methanol at 25 °C from a suspension of SiO_2 in a methanol solution of $Na[Ru_3H(CO)_{11}]$ and tested as the catalyst; the catalytic activities of the anchored complexes (**5**) and (**6**) are higher by one order of magnitude than the activity of the silica-adsorbed complex (**7**).

Table 1. Activities of the various catalysts in the water-gas shift reaction.[a]

Catalyst	Reaction temperature/°C	Catalytic activity[b]
(**5**)	100	3.0
	125	8.0
	150	20
(**6**)	100	1.8
	125	3.7
	150	27
(**7**)	100	0.3
	150	0.8

[a] 150 mg of catalyst, $P(CO)$ 200 Torr, $P(H_2O)$ 15 Torr, reaction time 6 h. [b] mol-H_2 per mol-Ru_3 after 6 h.

Received, 28th December 1983; Com. 1664

References

1 J. C. Bricker, C. C. Nagel, and S. G. Shore, *J. Am. Chem. Soc.*, 1982, **104**, 1444.

2 B. D. Dombek, *J. Am. Chem. Soc.*, 1981, **103**, 6508.

3 J. F. Knifton, *J. Am. Chem. Soc.*, 1981, **103**, 3959; J. F. Knifton, *J. Chem. Soc., Chem. Commun.*, 1981, 188.

4 D. J. Darensbourg, C. Ovalles, and M. Pala, *J. Am. Chem. Soc.*, 1983, **105**, 5937.

5 R. Ugo and R. Psaro, *J. Mol. Catal.*, 1983, **20**, 53.

6 K. G. Allum, R. D. Hancock, I. V. Howell, S. McKenzie, R. C. Pitkethy, and P. J. Robinson, *J. Organomet. Chem.*, 1975, **87**, 203.

7 B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. Suss, *J. Chem. Soc., Dalton Trans.*, 1979, 1354.