

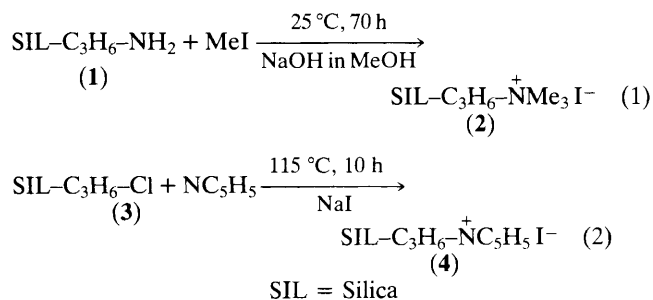
Anchoring of an Anionic Triruthenium Cluster to Functionalized Silica and Its Catalytic Properties for the Water-gas Shift Reaction

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 $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$, 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 $[\text{Ru}_3\text{H}(\text{CO})_{11}]^-$ 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



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 $(\text{EtO})_3\text{Si}[\text{CH}_2]_3\text{NH}_2$ 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 $(\text{MeO})_3\text{Si}[\text{CH}_2]_3\text{Cl}$ 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, $[\text{Ru}_3\text{H}(\text{CO})_{11}][\text{NMe}_3\text{-C}_3\text{H}_6\text{-SIL}]$ (5) and $[\text{Ru}_3\text{H}(\text{CO})_{11}][\text{NC}_5\text{H}_5\text{-C}_3\text{H}_6\text{-SIL}]$ (6), were prepared in methanol at 25 °C by an anionic-exchange reaction of the functionalized silicas (2) and (4) respectively with $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$. 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 $\text{Ru}_3 : \text{N}$ molar ratios of

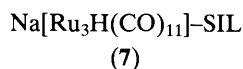
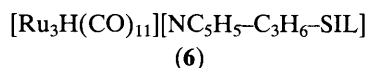
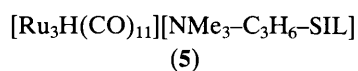


Table 1. Activities of the various catalysts in the water-gas shift reaction.^a

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, $P(\text{CO})$ 200 Torr, $P(\text{H}_2\text{O})$ 15 Torr, reaction time 6 h. ^b mol- H_2 per mol- Ru_3 after 6 h.

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 $[\text{Ru}_3\text{H}(\text{CO})_{11}][\text{NEt}_4]$ (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.

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 $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$ 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 $\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$ 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).

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