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Metal Cluster Catalysis: Preparation and Catalytic Properties of Anionic Triruthenium Clusters Anchored to Functionalized Silica

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Abstract

The anionic triruthenium cluster $[Ru_3H(CO)_{11}]^-$ was anchored on a silica surface, modified with ammonium and pyridinium functions, and used as a catalyst for the water-gas shift reaction and for hydrogenation of ethylene and carbon monoxide. The silica-anchored clusters were stable up to 150 °C and exhibited higher catalytic activities for the hydrogenation of ethylene (70 °C) and the water-gas shift reaction (150 °C) than those of a silica-adsorbed $Na[Ru_3H(CO)_{11}]$. No catalytic activity for the hydrogenation of carbon monoxide was detected at 270 °C over the silica-anchored clusters.

Introduction

The anionic triruthenium hydridocarbonyl cluster $[Ru_3H(CO)_{11}]^-$ has been reported as a homogeneous catalyst for several important reactions, particularly in C_1 chemistry such as the water-gas shift reaction [1, 2], ethylene glycol synthesis from CO and H_2 [3–5], homologation of methanol to ethanol [6], methyl formate synthesis from CO_2, H_2 and CH_3OH [7], and hydroformylation of olefins [8]. In solution, active clusters may react with each other to form various products, causing difficulty in the identification of the catalytic species and a decrease in catalytic activity [9]. Immobilization of metal cluster complexes on a solid surface may prevent the unfavourable intermolecular reactions and offer the practical advantages of heterogeneous catalysts, such as easy separation from reaction products and catalyst re-use.

In a preliminary communication the anionic triruthenium cluster $[Ru_3H(CO)_{11}]^-$ anchored to silica via ammonium or pyridinium functional groups proved to be a highly active catalyst for the water-gas shift reaction [10]. Herein we report a systematic study on the preparation and thermal stability of the silica-anchored clusters and their catalytic properties for the water-gas shift reaction and the hydrogenations of ethylene and carbon monoxide. A silica-adsorbed $Na[Ru_3H(CO)_{11}]$ catalyst was also prepared and its catalytic properties examined.

Experimental

Preparation of Catalyst

The parent cluster $Na[Ru_3H(CO)_{11}]$ was synthesized by a reported method [11]. Porous silica (Davison 952, 350 m^2/g) was used after treatment under vacuum (10^{-3} Torr) at 300 °C for 6 h.

$SIL-(CH_2)_3N^+R_3I^-$ (2)

Ammonium ($-N^+Me_3$ and $-N^+Et_3$)-functionalized silicas (2) were prepared as follows. A toluene solution (50 cm^3) of $(EtO)_3Si(CH_2)_3NH_2$ was added to 5 g of SiO_2 in a glass reactor and the mixture was stirred at boiling temperature (*ca.* 110 °C) of toluene for 6 h, giving rise to an aminated silica, $SIL-(CH_3)_3$-NH_2 (1). The aminated silica (1) was added (2g) in the methanol solution (50 cm^3) of RI (32 mmol, R = Me or Et) and NaOH (10 mmol) and the mixture was stirred for 70 h at 25 °C, giving ammonium-functionalized silica (2). The silica (2) was washed with methanol and dried under vacuum at room temperature. The elementary analysis data for $SIL-(CH_2)_3N^+Me_3I^-$ and $SIL-(CH_2)_3N^+Et_3I^-$ are given in Table I.

TABLE I. Analytical Data of Functionalized Silicas.

Compound	Elements in mmol/g-Silica		
	C	N	I
$SIL-(CH_2)_3N^+Me_3I^-$	3.72	0.64	0.87
$SIL-(CH_2)_3N^+Et_3I^-$	4.83	0.48	0.30
$SIL-(CH_2)_3N^+C_5H_5I^-$	5.07	0.53	0.44

$SIL-(CH_2)_3N^+C_5H_5I^-$ (4)

Pyridinium ($-N^+C_5H_5$)-functionalized silica (4) was prepared as follows. A toluene solution (50 cm^3) of $(MeO)_3Si(CH_2)_3Cl$ was added to 5 g of SiO_2 in

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a glass reactor and the mixture was stirred at the boiling temperature of toluene for 6 h, resulting in the formation of a chlorinated silica, SIL–$(CH_2)_3Cl$ (**3**). The chlorinated silica (**3**) was added (2g) to the pyridine solution (70 cm^3) of NaI (1.2 mmol) and the mixture was stirred at 115 ℃ for 10 h, giving a pyridinium-functionalized silica (**4**) with the content of N, C and I as listed in Table I.

$[Ru_3H(CO)_{11}][NMe_3(CH_2)_3$–SIL] (5)

The anchored cluster (**5**) was prepared as follows. A methanol solution (10 cm^3) of $Na[Ru_3H(CO)_{11}]$ (0.06 mmol) was added to SIL–$(CH_2)_3N^+Me_3I^-$ (**2**) and the mixture was stirred at 25 ℃ for 24 h. The precipitate was washed with methanol and dried under vacuum at 60 ℃. The content of Ru in the anchored catalyst (**5**) was 3.3 mg per g of catalyst.

$[Ru_3H(CO)_{11}][NEt_3(CH_2)_3$–SIL] (6)

A methanol solution (10 cm^3) of $Na[Ru_3H(CO)_{11}]$ (0.06 mmol) was added to SIL–$(CH_2)_3$-$N^+Et_3I^-$ (**2**) and the mixture was stirred at 25 ℃ for 24 h. The precipitate was washed with methanol and dried under vacuum at 60 ℃. The content of Ru in the anchored catalyst (**6**) was 5.5 mg per g of catalyst.

$[Rn_3H(CO)_{11}][NC_5H_5(CH_2)_3$–SIL] (7)

A methanol solution (10 cm^3) of $Na[Ru_3H(CO)_{11}]$ (0.06 mmol) was added to SIL–$(CH_2)_3$-$N^+C_5H_5I^-$ (**4**) and the mixture was stirred at 25 ℃ for 24 h. The precipitate was washed with methanol and dried under vacuum at 60 ℃. The content of Ru in the anchored catalyst (**7**) was 9.0 mg per g of catalyst.

$Na[Ru_3H(CO)_{11}]/SiO_2$ (8)

Silica-adsorbed $Na[Ru_3H(CO)_{11}]$ (**8**) was prepared by evaporating the methanol solvent at 60 ℃ from a suspension of SiO_2 in methanol solution of $Na[Ru_3H(CO)_{11}]$. The content of Ru in the catalyst (**8**) was 20 mg per g.

Catalytic Activity Measurements

The water-gas shift reaction and hydrogenation of ethylene and of carbon monoxide were carried out over the anchored catalysts in a glass reactor (total volume 260 cm^3) operating in a continuous circulating flow mode. Analyses of the products were based on gas chromatographs using Porapak Q (2 m) and VZ-10 (3 m) for hydrocarbons and active carbon (2 m) for CO, CO_2, and H_2.

Results and Discussion

Preparation and Characterization of Catalysts

Ammonium and pyridinium functions were used as anchoring groups. The procedures to prepare the functionalized silicas are outlined in reactions 1–4.

$$SiO_2 + (EtO)_3Si(CH_2)_3NH_2 \xrightarrow[\text{toluene}]{110\ ^\circ\text{C},\ 70\ \text{h}}$$

$$\underset{(1)}{\text{SIL–}(CH_2)_3NH_2} + 3EtOH \qquad (1)$$

$$(1) + RI \xrightarrow[\text{NaOH, methanol}]{25\ ^\circ\text{C},\ 70\ \text{h}} \underset{(2)}{\text{SIL–}(CH_2)_3N^+R_3I^-} \qquad (2)$$

$$SiO_2 + (MeO)_3Si(CH_2)_3Cl \xrightarrow[\text{toluene}]{110\ ^\circ\text{C},\ 6\ \text{h}}$$

$$\underset{(3)}{\text{SIL–}(CH_2)_3Cl} + 3MeOH \qquad (3)$$

$$(3) + NC_5H_5 \xrightarrow[\text{NaI}]{115\ ^\circ\text{C},\ 10\ \text{h}} \underset{(4)}{\text{SIL–}(CH_2)_3N^+C_5H_5I^-} \qquad (4)$$

where SIL = silica, R = CH_3 or C_2H_5.

The aminated silica (**1**) was prepared by the condensation of $(EtO)_3Si(CH_2)_3NH_2$ with the hydroxyl groups on the silica surface leading to elimination of EtOH [12], and was subsequently treated with RI (R = Me or Et) under alkaline conditions to give the ammonium-functionalized silica (**2**). The chlorinated silica (**3**) was prepared by the reaction of $(MeO)_3$-$Si(CH_2)_3Cl$ with SiO_2, followed by treatment with pyridine in the presence of NaI to afford the pyridinium-functionalized silica (**4**). Analytical data of the functionalized silicas are given in Table I. The N contents of the functionalized silicas correspond to 0.8–1.1 pendant functions per nm^2.

Three types of silica-anchored anionic triruthenium clusters (**5**)–(**7**) were prepared in methanol at 25 ℃ by an anionic-exchange reaction of the surface-functionalized silicas (**2**) and (**4**) respectively with $Na[Ru_3H(CO)_{11}]$. Table II lists the infrared data and Ru contents of anchored clusters (**5**)–(**7**). The infrared spectra of carbonyl in the anchored clusters are almost in agreement with the spectrum of $[Ru_3H(CO)_{11}][NEt_4]$, indicative of the preservation of the framework of the triruthenium cluster. The Ru contents were in the range of 3.3–9.0 mg per g of catalyst, which correspond to Ru_3:N molar ratios of 0.017–0.056. For the sake of comparison, a silica-adsorbed $Na[Ru_3H(CO)_{11}]$ (**8**) was prepared by evaporating the methanol at 60 ℃ from a suspension of SiO_2 in a methanol solution of $Na[Ru_3H(CO)_{11}]$.

The thermal-stabilities of the supported clusters (**5**)–(**8**) were explored by gas evolution during the pyrolysis treatment of the catalysts under He (400

TABLE II. Infrared and Analytical Data of Silica-Supported Anionic Triruthenium Clusters.

Compound	IR[a] ν_{CO} (cm^{-1})	Ru content (mg/g-cat.)
$[Ru_3H(CO)_{11}][NEt_4]$[b]	2075vw, 2018vs, 1985s 1945m, 1702w	
$[Ru_3H(CO)_{11}][NMe_3(CH_2)_3-SIL]$ (5)	2025s, 1970s, 1925sh 1745w	3.3
$[Ru_3H(CO)_{11}][NEt_3(CH_2)_3-SIL]$ (6)	2025s, 1970s, 1925sh 1750w	5.5
$[Ru_3H(CO)_{11}][NC_5H_5(CH_2)_3-SIL]$ (7)	2030s, 1970s, 1935sh 1740w	9.0
$Na[Ru_3H(CO)_{11}]/SiO_2$ (8)	2045s, 1985s, 1760w	20

[a] All measurements were made in wafer forms at 25 °C for SiO_2-supported clusters. [b] From Ref. [11].

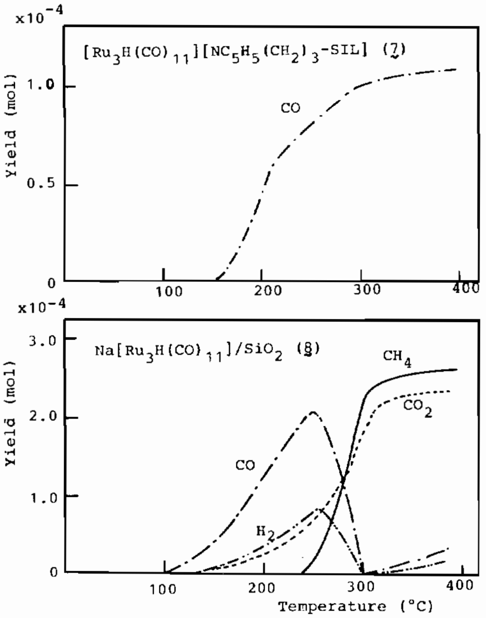

Fig. 1. Amounts of gases evolved during the thermal treatment of silica-supported clusters (7) and (8) under He (400 Torr). (7) = 350 mg and (8) = 500 mg.

Torr) in a closed-circulation glass reactor. Figure 1 shows the total amount of gases evolved during the thermal treatment of $[Ru_3H(CO)_{11}][NC_5H_5(CH_2)_3-SIL]$ (7) and $Na[Ru_3H(CO)_{11}]/SiO_2$ (8). In the case of the anchored cluster (7), no gas evolution was detected up to 140 °C. Evolution of CO was observed above 160 °C, and the evolution increased with temperature until all the CO in the cluster was lost (at 300 °C).

The decomposed complex did not show any carbonyl band in the infrared spectrum in the range 2100–1700 cm^{-1}, indicative of complete decarbonylation. The other anchored clusters $[Ru_3H(CO)_{11}][NMe_3(CH_2)_3-SIL]$ (5) and $[Ru_3H(CO)_{11}][NEt_3(CH_2)_3-SIL]$ (6) exhibited similar thermal-stability to that of (7) and were stable up to 150 °C. On the contrary, the adsorbed cluster (8) showed much lower thermal-stability than those of anchored clusters. The decarbonylation of (8) occurred at temperatures above 100 °C and H_2 was evolved together with CO_2 above 130 °C. The formation of H_2 and CO_2 may arise from the reaction of CO with H_2O adsorbed on the surface of silica. At temperatures above 250 °C, the amounts of CO and H_2 decreased with temperature and CH_4 was formed, indicating that the thermally decarbonylated cluster (8) is active for the hydrogenation of CO.

The supported clusters (5)–(8) were tested as catalysts for the water-gas shift reaction and hydrogenation of ethylene and carbon monoxide.

Water-gas Shift Reaction

The water-gas shift reaction was carried out in the temperature range 100–150 °C under CO (200 Torr) and H_2O (15 Torr) over the catalysts.

Figure 2 shows changes in the rate of H_2 evolution over the anchored catalyst (7) at different reaction temperatures. The reaction was carried out for 36 h by a sequential procedure based on a reversible change in the reaction temperatures of 100–150 °C. At the chosen temperature range H_2 and CO_2 were produced in equimolar quantities, which were proportional to the reaction time. The initial rate of H_2 evolution at 100 °C for 10 h is in agreement with the rate at the later stage (25–36 h, 100 °C), confirming that the anchored catalyst (7) can be re-used without any loss of catalytic activity. The infrared spectrum of the used catalyst was almost identical with that of the original anchored cluster.

Figure 3 shows the yield of H_2 at 150 °C during the course of the water-gas shift reaction over the supported catalysts (5)–(8). In all the anchored catalysts of (5)–(7), the H_2 yield increased in proportion to the reaction time for over 10 h, which

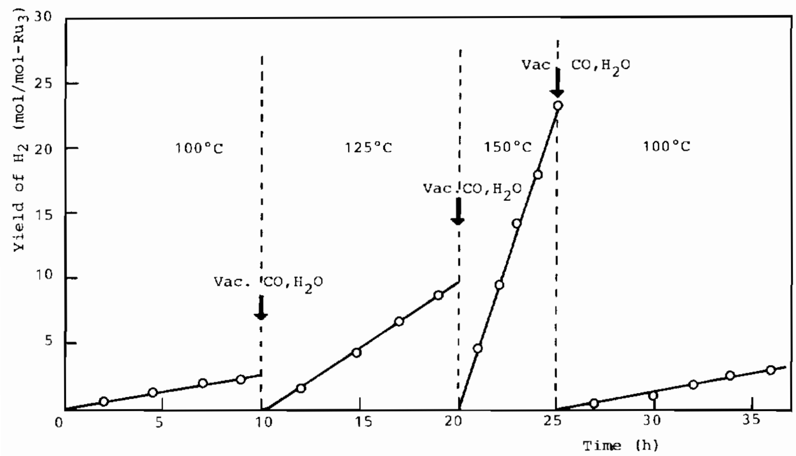

Fig. 2. Changes in the rate of H_2 evolution during the water-gas shift reaction over the silica-anchored cluster (7) at different temperatures of 100–150 °C. Reaction conditions: P_{CO} = 200 Torr, P_{H_2O} = 15 Torr, and catalyst = 100 mg.

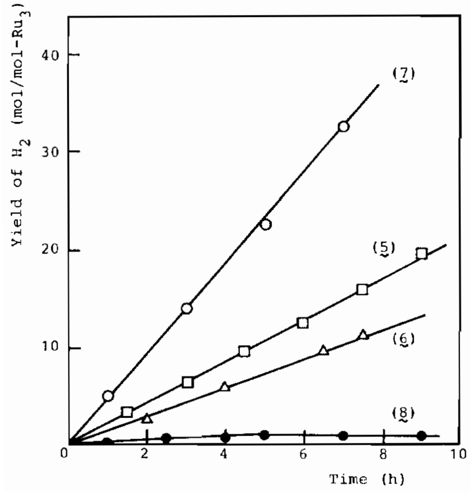

Fig. 3. Yield of H_2 during the course of water-gas shift reaction at 150 °C. (□); $[Ru_3H(CO)_{11}][NMe_3(CH_2)_3\text{-SIL}]$ (5), (△); $[Ru_3H(CO)_{11}][NEt_3(CH_2)_3\text{-SIL}]$ (6), (○); $[Ru_3H(CO)_{11}][NC_5H_5(CH_2)_3\text{-SIL}]$ (7), and (●); $Na[Ru_3H(CO)_{11}]/SiO_2$ (8). Reaction conditions: P_{CO} = 200 Torr, P_{H_2O} = 15 Torr, and catalyst = 100–200 mg.

indicates that the active cluster species are stable during the reaction. On the contrary, the adsorbed cluster (8) was not stable at 150 °C and evolution of H_2 stopped after 5 h. The anchored cluster (7) showed the highest activity, and the activity at 150 °C decreased in the order

$$(7)\ [4.5] > (5)\ [2.2] > (6)\ [1.4] > (8)\ [0.2] \qquad (5)$$

where the values in parentheses are the turnover frequencies represented by mol-H_2 × mol-Ru_3^{-1} × h^{-1}. The catalytic activities of the anchored clusters (5)–(7) are higher by one order of magnitude than the activity of the silica-adsorbed cluster (8).

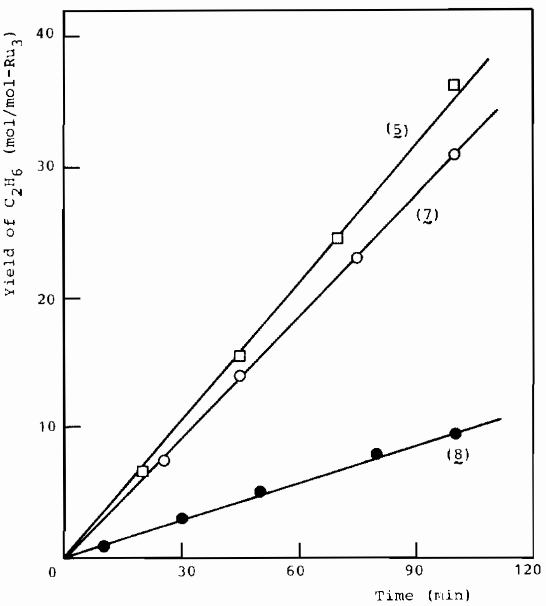

Fig. 4. Yield of C_2H_6 during the course of ethylene hydrogenation at 70 °C. (□); (5), (○); (7) and (●); (8). Reaction conditions: $p_{C_2H_4}$ = 100 Torr, P_{H_2} = 200 Torr, and catalyst = 100 mg.

Hydrogenation of Ethylene

The hydrogenation of ethylene was carried out at 70 °C under C_2H_4 (100 Torr) and H_2 (200 Torr) over the catalysts (5), (7) and (8). The results are shown in Fig. 4. On both anchored and adsorbed clusters the yield of C_2H_6 increased proportionally with reaction time, for 2 h. The rate of C_2H_6 formation was dependent upon the catalyst and decreased in the order:

$$(5)\ [21] \simeq (7)\ [19] > (8)\ [6] \qquad (6)$$

where the values in parentheses are the turnover frequencies represented by mol-C_2H_6 × mol-Ru_3^{-1}

$\times h^{-1}$. The catalytic activities of the anchored clusters (5) and (7) are again higher than the activity of the adsorbed cluster (8) for the hydrogenation of ethylene at 70 ℃.

Hydrogenation of Carbon Monoxide

The hydrogenation of carbon monoxide was carried out at 270 ℃ under CO (100 Torr) and H_2 (200 Torr) over the catalysts (5)–(8). The anchored clusters (5)–(7) did not show any catalytic activity for gas conversion at 270 ℃. On the contrary, the silica-adsorbed cluster (8) showed a high catalytic activity (3.6 mol-CO $\times$ mol-$Ru^{-1} \times h^{-1}$) for hydrogenation of CO, giving a broad spectrum of hydrocarbons ($[CH_4] = 88$, $[C_2H_4 + C_2H_6] = 9$, and $[C_3H_6 + C_3H_8] = 3$ mol %).

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