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Photocatalysis by Metal Cluster: Photoactivation in Catalytic Hydrogenation of Ethylene by the Tetraruthenium Cluster $H_4Ru_4(CO)_{12}$

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Several transition metal cluster complexes have been used as homogeneous catalysts for isomerization and hydrogenation of olefins, and the mechanisms of these thermal catalyses have been studied [1–5]. In contrast, examples of photocatalysis by metal cluster complexes are limited. Recently, Wrighton *et al.* [6, 7] demonstrated that photolysis of iron and ruthenium cluster complexes initiated catalytic olefin isomerization at lower temperatures compared to thermal catalysis. However, the properties of photogenerated catalytic species have not been well understood. In this communication we report our preliminary results concerning the photocatalyzed hydrogenation of ethylene by the tetraruthenium cluster hydride $H_4Ru_4(CO)_{12}$.

The $H_4Ru_4(CO)_{12}$ complex was prepared by a reported method [8]. A heptane solution of $H_4Ru_4(CO)_{12}$ exhibits an intense maximum at 366 nm (ϵ_m 17800) in the near-UV region. The photocatalytic hydrogenations of ethylene with the yellow-orange complex were carried out at temperatures of 2–35 °C in a round-bottomed Pyrex vessel of *ca.* 257 cm^3 with a Teflon-coated stirring bar. After 5 cm^3 of heptane solution of 0.21 m*M* $H_4Ru_4(CO)_{12}$ and the reactants of C_2H_4 (100 Torr) and H_2 (100 Torr) were introduced, the reaction vessel was immersed in a water bath thermostatted at the reaction temperature. Irradiations were conducted using a 450-W medium-pressure Hg lamp equipped with an appropriate Toshiba glass filter ($\lambda \geqslant 310$ nm or $\lambda = 366 \pm 20$ nm). Samples of the gases above the reaction solution were withdrawn at intervals by a syringe through a side arm sealed with silicon rubber, and analyzed quantitatively on a Hitachi 163 FID gas chromatograph using a 2 m column of Porapak Q. When required, carbon monoxide was introduced through the silicon rubber seal by a syringe.

Figures 1(a)–(c) show the changes in the rate of ethane formation during the course of catalytic hydrogenation of ethylene under sequential thermal and photochemical conditions at different temperatures of 2, 26 and 35 °C. Before irradiation the rates of ethane formation are negligible at temperatures below 35 °C. When the light ($\lambda \geqslant 310$ nm) is turned on the rates of ethane formation increase gradually and then attain constant values, depending on the reaction temperature. The existence of induction periods in the ethane formation clearly indicates the photochemical generation of active species from the tetraruthenium cluster precursor $H_4Ru_4(CO)_{12}$. After the light is turned off, the rates of ethane formation decrease gradually toward zero. The time needed to quench catalytic activity increases with a depression in the reaction temperature and is as long as 90 min at 2 °C, indicating a long lifetime of the catalytic active species generated with the help of light. As shown in Fig. 1(b), the ethane formation is again initiated when the light is turned on, and the rate is almost identical to that observed during the first stage of irradiation.

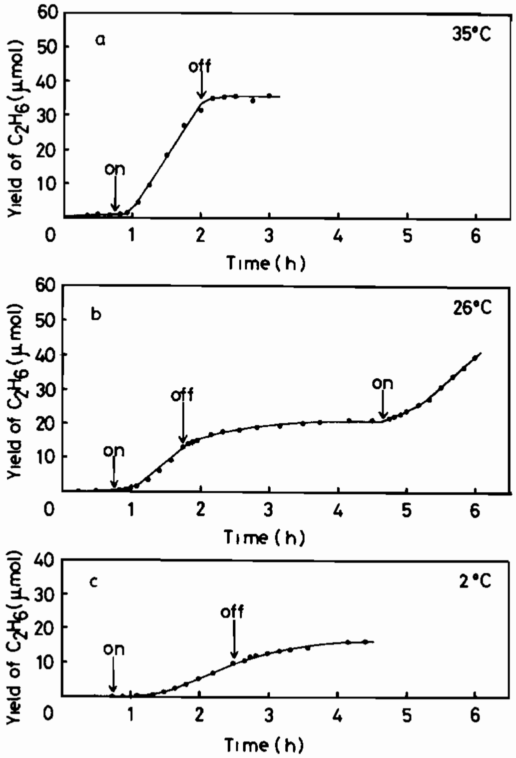

Fig. 1. Changes in the yield of C_2H_6 during the catalytic hydrogenation of ethylene under sequential thermal and photochemical conditions at various temperatures. Reaction conditions: $P_{C_2H_4} = P_{H_2} = 100$ Torr and 0.21 m*M* solution of $H_4Ru_4(CO)_{12}$ = 5 cm^3.

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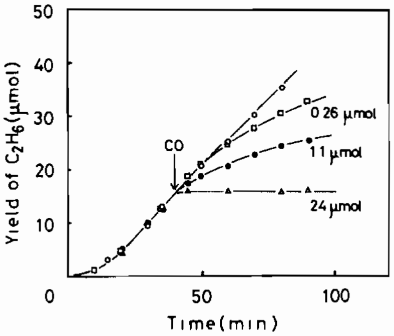
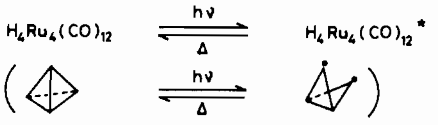


Fig. 2. Changes in the yield of C_2H_6 induced by the addition of CO during the photocatalytic hydrogenation of ethylene. Reaction conditions; 35 ℃, $P_{C_2H_4} = p_{H_2} = 100$ Torr and 0.21 m*M* solution of $H_4Ru_4(CO)_{12} = 5\ cm^3$. The amounts of CO added are shown in the figure.

The quantum yield for ethane formation was measured using 366 nm light (~1 × 10^{-7} einstein/min) at 35 ℃ under 100 Torr of C_2H_4 and 100 Torr of H_2. The quantum yield was found to be 1.8 in excess of unity, which indicates that the ethane formation is catalytic with respect to the number of photons absorbed.

In order to elucidate the properties of active species, the effects of various additives on the hydrogenation rate were examined at 35 ℃. Two types of additives, CCl_4 (5.2 mmol) and O_2 (0.1 mmol), were added into the catalyst solution during irradiation, but neither affected the catalytic activity. In contrast, the addition of carbon monoxide during irradiation caused suppression in the hydrogenation rate, as shown in Fig. 2. The rate decreased with increasing the amount of CO added. At the end of reaction involving 24 μmol of CO in which the catalytic activity almost disappeared, the infrared and electron absorption spectra of catalyst solution were recorded. The detectable Ru compound was $H_4Ru_4(CO)_{12}$, and the recovery of $H_4Ru_4(CO)_{12}$ was found to be almost hundred percent (within experimental error).

The recovery of $H_4Ru_4(CO)_{12}$ under carbon monoxide and the reversible changes in the rate of ethane formation under dark and irradiation (Fig. 1(b)) appear to indicate that the tetraruthenium cluster frameworks themselves provide the catalytic sites without breaking up the cluster into mononuclear fragments. Since the catalyst precursor $H_4Ru_4(CO)_{12}$ is coordinatively saturated, the first steps to initiate the catalytic cycle under photochemical condition must comprise the cleavage of one Ru–Ru bond resulting in an open butterfly structure (eqn. (1)) or the dissociation of a ligand like carbon monoxide (eqn. (2)).



(1)

$$H_4Ru_4(CO)_{12} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} H_4Ru_4(CO)_{11} + CO \qquad (2)$$

A long lifetime of active species and the observed CO inhibition appear to support a first step comprising photoindiced CO dissocation (2). Further work is in progress to explore the mechanism of photocatalyzed hydrogenation of ethylene.

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