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Selective Synthesis of Light Olefins from CO and H_2 with $Na[Ru_3H(CO)_{11}]$ Supported on Metal Oxides

Catalytic synthesis of low-molecular-weight olefins from CO and H_2 is of both commercial and academic interest in C_1 chemistry. The addition of potassium to Fe and Ru catalysts has long been recognized to enhance the selectivity toward olefinic hydrocarbons in the Fischer–Tropsch synthesis (*1, 2*). Potassium, however, facilitates the sintering of metal crystallites, leading to a decrease in the catalytic activity. An approach to this problem seems to be the preparation of a highly dispersed Fe and Ru with potassium on the surface of supports. McVicker and Vannice (*3*) demonstrated that a highly dispersed Fe/K catalyst prepared by thermal decomposition of $K_2Fe(CO)_4$ on Al_2O_3 was active and selective for the formation of C_2–C_4 olefins (50%). Commereuc *et al.* (*4*) found that $HFe_3(CO)_{11}^-$ on Al_2O_3 gave rise to an unusual high selectivity (45%) for propene formation at the initial stage of the hydrogenation of CO. Recently, Hemmerich *et al.* (*5*) showed that $[HFeCo_3(CO)_{12}]^-$ anchored to ammonium-functionalized silica produced selectively olefinic hydrocarbons of C_2–C_{19} with a high activity during the hydrogenation of CO. Okuhara *et al.* (*6*) found that a highly dispersed Ru/K catalyst on Al_2O_3, prepared from $Ru_3(CO)_{12}$ in the presence of K_2CO_3, was much more active and selective for C_2–C_6 olefins (75%). In this note we report that a sodium-anionic triruthenium cluster $Na[Ru_3H(CO)_{11}]$, supported on metal oxides such as TiO_2 and MgO and thermally decomposed under vacuum, selectively yields light C_2–C_5 olefins (69–75%) at 270°C with a high catalytic activity. In addition, a strong support effect on the selectivity in the Fischer–Tropsch synthesis is explored by an X-ray photoelectron spectroscopic (XPS) analysis of the supported $Na[Ru_3H(CO)_{11}]$ catalysts.

$Na[Ru_3H(CO)_{11}]$, which had been prepared according to the method of Johnson *et al.* (*7*), was supported by evaporating the methanol solvent at 30°C from a suspension of metal oxide in the methanol solution of $Na[Ru_3H(CO)_{11}]$. SiO_2 (Davison 952, 350 m^2/g), γ-Al_2O_3 (Nishio, 150 m^2/g), MgO (Wako, 93 m^2/g), and TiO_2 (Koso, 40 m^2/g) were dried under vacuum (10^{-4} Torr) at 300–350°C for 20 h and used as supports. The supported catalysts were activated by heating to 400°C under vacuum. The content of Ru in the catalysts was 20 mg per g of catalyst. The hydrogenation of CO was carried out in a closed circulating glass reactor (total volume 240 cm^3) operating in a continuous circulating flow mode. The products other than methane were collected in a trap kept at liquid-nitrogen temperature to suppress secondary reactions. 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 CH_4, CO, CO_2, and H_2. The catalytic activity and selectivity were determined after attainment of a stationary rate.

The XPS spectra of supported catalysts were recorded on a Shimadzu electron spectrometer ESCA 750 with Mg$K\alpha$ excitation radiation. Sample preparation for XPS measurements was performed in a glove box filled with nitrogen. The C (1*s*) line (E_b = 284.5 eV) of the adsorbed diffusion pump oil was used as standard peak.

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TABLE 1

Activities and Selectivities in Hydrogenation of CO over $Na[Ru_3H(CO)_{11}]$ Supported on Various Metal Oxides[a]

Support	Temp. (°C)	Rate[b]	$S(CO_2)$[c]	Product distribution in hydrocarbons[d]									Fraction of olefins (wt%)
				C_1^-	C_2^-	C_2^{2-}	C_3^-	C_3^{2-}	C_4^-	C_4^{2-}	C_5^-	C_5^{2-}	
SiO_2	270	3.6	3	72	14	1	7	3	2	1	0	0	5
Al_2O_3	270	5.6	2	31	12	8	4	24	2	13	1	5	50
MgO	270	1.7	31	22	6	14	2	33	1	17	0	5	69
TiO_2	270	1.1	25	18	3	18	2	30	2	20	0	7	75
TiO_2	300	2.3	23	22	4	22	1	28	1	16	0	6	72
TiO_2	330	3.7	35	32	5	29	1	26	0	6	0	1	62
TiO_2	360	8.0	36	38	7	30	1	19	0	5	0	0	54

[a] Reaction conditions: $CO + H_2 = 400$ Torr, $H_2/CO = 2$, catalysts = 0.4 g.

[b] Rate is represented by mol CO · mol Ru^{-1} · h^{-1}.

[c] Selectivity to $CO_2 = 100 \times N(CO_2)/[\Sigma\{nN(C_n^-) + nN(C_n^{2-})\} + N(CO_2)]$.

[d] Percentage of C_n^- (paraffin) or C_n^{2-} (olefine) $= 100 \times nN(C_n^-)$ or $nN(C_n^{2-})/\Sigma\{nN(C_n^-) + nN(C_n^{2-})\}$, where $N(C_n^-)$ = molecules of paraffin with n carbon atoms, and $N(C_n^{2-})$ = molecules of olefin with n carbon atoms.

Table 1 lists the results of CO hydrogenation performed at an initial pressure of 400 Torr ($H_2/CO = 2$; 1 Torr = 133.3 N m^{-2}). The activity and selectivity at 270°C for the formation of hydrocarbons depended strongly upon the type of support used. The activity decreased in the order: $Al_2O_3 > SiO_2 > MgO > TiO_2$. Also, the selectivity toward olefinic C_2–C_5 hydrocarbons changed drastically among the supported $Na[Ru_3H(CO)_{11}]$ catalysts and decreased in the order: $TiO_2 > MgO > Al_2O_3 > SiO_2$. The $Na[Ru_3H(CO)_{11}]$ on TiO_2 and MgO exhibited a high selectivity (69 ~ 75%) for the formation of C_2–C_5 olefins at 270°C and showed a narrow product distribution which deviated from the Schulz–Flory distribution (*8*). In contrast, the ordinary Schulz–Flory product distribution was observed with the $Na[Ru_3H(CO)_{11}]$ on SiO_2 which gave a low selectivity (5%) for olefin formation. As shown in Table 1, the selectivity for the formation of C_2–C_5 olefins over the $Na[Ru_3H(CO)_{11}]/TiO_2$ somewhat decreased with rising reaction temperature from 270 to 360°C. An apparent activation energy for the rate of CO hydrogenation was determined as 16 kcal mol^{-1}.

The recent work of Pierantozzi *et al.* (*9*) has also demonstrated that the nature of metal oxide support has a significant influence on the product distribution in CO hydrogenation over the catalysts derived from $Ru_3(CO)_{12}$ on metal oxides (Al_2O_3 and MgO).

A strong support effect on the selectivity in the Fischer–Tropsch synthesis over the sodium-anionic triruthenium cluster was investigated by XPS spectroscopy. The Ru $3d_{5/2}$ peak in the XPS spectrum of $Na[Ru_3H(CO)_{11}]$ on SiO_2 shifted from 280.2 to 279.9 eV after decarbonylation. The decarbonylated $NaRu_3$ on MgO and TiO_2 gave the Ru $3d_{5/2}$ peak (279.3 eV) at lower binding energies than that (279.9 eV) on SiO_2, confirming that Ru atoms on MgO and TiO_2 are more electron-rich than those on SiO_2. Thus, the electronic structure of Ru atoms is drastically influenced by the metal oxides used as supports.

In conclusion, an electron-rich ruthenium cluster produces selectively light olefins in the C_2–C_5 range from CO and H_2. The use of $Na[Ru_3H(CO)_{11}]$ as catalyst precursor offers a simple method for the preparation of highly active and selective Fischer–Tropsch catalyst.

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