

Selective Synthesis of Oxygenates in the CO–H₂ Reaction on Supported Ruthenium Carbido-cluster Catalysts

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Supported ruthenium carbido-cluster catalysts ([Ru₆C(CO)₁₆Me]⁻/oxide) selectively produced methanol, dimethyl ether, and formaldehyde in CO–H₂, in contrast to the preferential formation of methane and hydrocarbons on supported ruthenium cluster catalysts {[Ru₆(CO)₁₈]²⁻/oxide} without the interstitial carbon and conventional metallic Ru catalysts.

Metal clusters are expected to have unique catalytic properties associated with multiple metal sites, which are of great interest from chemical and industrial points of view. However, there are few examples of catalysis specific to metal cluster frameworks that not observed with the usual metal catalysts.^{1,2} We report the catalytic formation of oxygenated compounds on supported ruthenium carbido-clusters.

[btma]⁺[Ru₆C(CO)₁₆Me]⁻ **1** (btma = C₆H₅CH₂NMe₃)³ was supported on inorganic oxides by adsorption at 290 K for 1 h in purified CH₂Cl₂ and the subsequent removal of CH₂Cl₂ under vacuum. TiO₂ (Degussa P25; surface area: 60 m² g⁻¹), ZrO₂ (Soekawa, 99.9%; 12 m² g⁻¹), Al₂O₃ (Degussa Alon C; 100 m² g⁻¹), and SiO₂ (Fuji-Davison, silica gel No. 952; 300 m² g⁻¹) were treated at 473 K for 2 h in vacuum before use as supports. ZnO (Kadox) was treated at 773 K for 2 h. MgO (200 m² g⁻¹) and La₂O₃ (35 m² g⁻¹) were prepared from Mg(OH)₂ (Soekawa, 99.99%) and La(OH)₃ (Soekawa, 99.9%) by treatment at 773 K for 2 h in vacuum. The loadings of Ru were fixed to 3.0 wt%–Ru for SiO₂, 2.0 wt% for La₂O₃, 1.8 wt% for MgO, 1.5 wt% for TiO₂ and Al₂O₃, and 1.0 wt% for ZnO and ZrO₂. The supported ruthenium carbido-clusters are denoted as [Ru₆C]/oxide.

[btma]⁺₂[Ru₆(CO)₁₈]²⁻ **2**^{4,5} was supported on La₂O₃, TiO₂ and Al₂O₃ in acetone in a similar procedure to the case of **1**. The supported ruthenium clusters are denoted as [Ru₆]/oxide. Conventional Ru catalysts were prepared by a usual impregnation method using an aqueous solution of Ru(NO)(NO₃)₃ (N.E. Chemcat. Co.).

CO–H₂ reactions were carried out under CO of 14.6 kPa and H₂ of 14.6 kPa in the temperature range 473–523 K in a closed circulating system (dead volume: 133 ml) with a

U-shaped liquid-nitrogen trap for oxygenated compounds. Before the catalytic reaction the fresh samples were activated by heating at 623 K in vacuum. The reaction products were analysed by gas chromatography using a 5A molecular sieve column (2 m) for methane, a VZ-10 column (2 m) for ethene, ethane and propene, and a DOS (dioctyl sebacate) column (4 m) for methanol, dimethyl ether and formaldehyde. As shown in Table 1 the turnover frequencies for the formation of oxygenates were larger on [Ru₆C]/oxides than those for [Ru₆]/oxides or the conventional impregnated catalysts. Those TOFs for [Ru₆C]/oxides are comparable or superior to those for other cluster systems in the previous literature.^{6,7} This superiority of the carbido-cluster was independent of the kind of supports. The most active [Ru₆C]/TiO₂ produced formaldehyde (20%), methanol (12%) and dimethyl ether (9.6%) at 523 K, and the activity did not decrease over 15 h. The order of the activity of oxygenate synthesis for support was TiO₂ > Al₂O₃ ≥ ZrO₂ > La₂O₃ > SiO₂ ≈ MgO > ZnO. Supported [Ru₆C] clusters also exhibited higher selectivities to oxygenated compounds as compared with [Ru₆]/oxides and impregnated catalysts as shown in Table 1. [Ru₆C]/La₂O₃ was most selective (92% at 473 K). The order of the selectivity for support was La₂O₃ > MgO ≈ TiO₂ ≈ ZrO₂ > Al₂O₃ > SiO₂ ≈ ZnO.

The dependency of the activity and selectivity of the [Ru₆C]/oxide catalysts on the kind of support is fairly different from that of the usual impregnated Ru catalysts (Table 1). It is to be noted that the ruthenium carbido-cluster-derived catalysts preferentially produced the oxygenated compounds, while the impregnated metallic ruthenium catalysts produced mainly methane and hydrocarbons. Even if various amounts

Table 1 The turnover frequencies (TOF) and selectivities for the formation of oxygenates on the Ru catalysts at 473 and 523 K

| Precursor $T_{\text{react.}}/K$ | $[\text{Ru}_6\text{C}(\text{CO})_{16}\text{Me}]^-$ | | | | $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ | | | | $\text{Ru}(\text{NO})(\text{NO}_3)_3$ | | | |
|------------------------------------|--|---------------------|------------------|---------------------|--------------------------------------|---------------------|------------------|---------------------|---------------------------------------|---------------------|------------------|---------------------|
| | 473 | | 523 | | 473 | | 523 | | 473 | | 523 | |
| | TOF ^a | Selec. ^b | TOF ^a | Selec. ^b | TOF ^a | Selec. ^b | TOF ^a | Selec. ^b | TOF ^a | Selec. ^b | TOF ^a | Selec. ^b |
| MgO | 0.055 | 48 | 0.70 | 49 | — | — | — | — | 0 | 0 | 0.16 | 3.0 |
| ZnO | 0.017 | 24 | 0.10 | 10 | — | — | — | — | — | — | — | — |
| La ₂ O ₃ | 0.43 | 92 | 2.1 | 49 | 0.23 | 37 | 0.87 | 23 | 0 | 0 | 0.36 | 17 |
| TiO ₂ | 1.4 | 53 | 11.0 | 44 | 0.15 | 27 | 2.1 | 30 | 0 | 0 | 0.30 | 13 |
| ZrO ₂ | 0.53 | 53 | 3.4 | 39 | — | — | — | — | — | — | — | — |
| Al ₂ O ₃ | 0.11 | 34 | 3.8 | 27 | 0.003 | 2.3 | 0.15 | 7.1 | 0.17 | 4.2 | 0.51 | 2.1 |
| SiO ₂ | 0.37 | 34 | 0.74 | 6.2 | — | — | — | — | — | — | — | — |

^a 10⁻³ min⁻¹, ^b mol%; CO (14.6 kPa), H₂ (14.6 kPa).

of carbide were deposited on the metallic Ru particles, the formation of the oxygenated compounds was not observed. After the reduction of $[\text{Ru}_6\text{C}]/\text{MgO}$ with H₂ at 623 K the catalytic activities for the formation of the oxygenates decreased to 0 (473 K)–35% (523 K) of those before H₂ treatment. The thermal desorption experiments in D₂ revealed the formation of equimolar CD₄ to the amount of $[\text{Ru}_6\text{C}]$ units on the supports up to 623 K, suggesting the removal of the interstitial carbon by hydrogen reduction at 623 K. When a small amount of methanol together with CO + H₂ was introduced into the $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalyst at 523 K, methanol was readily converted into formaldehyde and dimethyl ether. In CO + H₂ reactions, formaldehyde may be produced *via* methanol/methoxyl intermediates rather than directly from CO + H₂.

We measured the Ru K-edge EXAFS spectra for the catalysts thermally activated at beamline 10B of the Photon Factory in the National Laboratory for High Energy Physics (proposal No. 91012). The curve-fitting analysis showed the Ru–Ru bond distances of 0.261–0.263 nm for $[\text{Ru}_6\text{C}]/\text{MgO}$, $[\text{Ru}_6\text{C}]/\text{La}_2\text{O}_3$, $[\text{Ru}_6\text{C}]/\text{TiO}_2$ and $[\text{Ru}_6\text{C}]/\text{Al}_2\text{O}_3$. These values are close to that for Ru metal. The coordination numbers (N) for the Ru–Ru bond were 3.3–4.4 similar to that for the original cluster **1**. When the $[\text{Ru}_6\text{C}]/\text{MgO}$ catalyst was treated in CO–H₂ atmosphere, the original carbido-cluster was reproduced, showing the same bond distances and coordination numbers for Ru–Ru and Ru(–C–)Ru as those for **1** as proved by EXAFS. This reversibility of the cluster structure together with a characteristic methane thermal desorption spectrum suggests the formation of a new cluster composed of a Ru₆ unit and a carbide atom by activation at 623 K in vacuum.

In contrast to these samples $[\text{Ru}_6\text{C}]/\text{SiO}_2$ ($N_{\text{Ru–Ru}} = 6.6$) aggregated by the pretreatment at 623 K. This catalyst was much less active than the $[\text{Ru}_6\text{C}]/\text{TiO}_2$ catalyst (Table 1). $[\text{Ru}_6]/\text{Al}_2\text{O}_3$ without interstitial carbon was degraded to an oxygen-incorporated cluster which exhibits $R_{\text{Ru–Ru}} = 0.261$

nm ($N = 1.9$), $R_{\text{Ru–O}} = 0.206$ nm ($N = 1.8$), $R_{\text{Ru–C}} = 0.191$ nm ($N = 0.9$), and $R_{\text{Ru(–C–)O}} = 0.299$ nm ($N = 0.8$), similarly to the case of the Ru₃(CO)₁₂-derived sample.⁶ The $[\text{Ru}_6]/\text{Al}_2\text{O}_3$ catalyst showed negligible or low activity and selectivity for the synthesis of oxygenates under identical conditions.

Thus, the specific formation of the oxygenates, unlike the CO hydrogenation of a C–O bond-breaking type on the usual impregnated metallic Ru catalysts, may be ascribed to (i) the electron-donating effect^{8–10} of an interstitial carbon (or equivalent carbon), (ii) about six-ruthenium cluster framework, and (iii) the nature of supports.

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