the second point, the ring-opening–ring-closing reaction of **3** gave **4**, which contains the aromatic 1,2,4-oxadiazole (as formed heterocyclic ring). Accordingly, **1** would have given **5**, containing the non-aromatic 1,2,4-oxadiazole ring, through a nucleophilic addition (A_N) to the carbonyl carbon of the thiazolone intermediate **7**. Perhaps **5** is only an unstable intermediate which collapses to **8** or alternatively **7** gives directly **8** by an acylic nucleophilic substitution (S_NAc) at the same atom with the cleavage of the feeble carbonyl–sulfur bond.[6] The thiol group of **8** in turn gives 2 by addition to the ketonic carbonyl carbon[7] and formation of a six-membered cyclic hemithioacetal.

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

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Supported ruthenium carbido-cluster catalysts ($[Ru_6C(CO)_{16}Me]^-$/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 {$[Ru_6(CO)_{18}]^{2-}$/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.

$[btma]^+[Ru_6C(CO)_{16}Me]^-$ **1** (btma = $C_6H_5CH_2NMe_3$)[3] was supported on inorganic oxides by adsorption at 290 K for 1 h in purified CH_2Cl_2 and the subsequent removal of CH_2Cl_2 under vacuum. TiO_2 (Degussa P25; surface area: 60 m² g⁻¹), ZrO_2 (Soekawa, 99.9%; 12 m² g⁻¹), Al_2O_3 (Degussa Alon C; 100 m² g⁻¹), and SiO_2 (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 La_2O_3 (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 SiO_2, 2.0 wt% for La_2O_3, 1.8 wt% for MgO, 1.5 wt% for TiO_2 and Al_2O_3, and 1.0 wt% for ZnO and ZrO_2. The supported ruthenium carbido-clusters are denoted as $[Ru_6C]$/oxide.

$[btma]^+_2[Ru_6(CO)_{18}]^{2-}$ **2**[4,5] was supported on La_2O_3, TiO_2 and Al_2O_3 in acetone in a similar procedure to the case of **1**. The supported ruthenium clusters are denoted as $[Ru_6]$/oxide. Conventional Ru catalysts were prepared by a usual impregnation method using an aqueous solution of $Ru(NO)(NO_3)_3$ (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 $[Ru_6C]$/oxides than those for $[Ru_6]$/oxides or the conventional impregnated catalysts. Those TOFs for $[Ru_6C]$/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 $[Ru_6C]$/TiO_2 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 $TiO_2 > Al_2O_3 \gtrsim ZrO_2 > La_2O_3 > SiO_2 \simeq MgO > ZnO$. Supported $[Ru_6C]$ clusters also exhibited higher selectivities to oxygenated compounds as compared with $[Ru_6]$/oxides and impregnated catalysts as shown in Table 1. $[Ru_6C]$/La_2O_3 was most selective (92% at 473 K). The order of the selectivity for support was $La_2O_3 > MgO \simeq TiO_2 \simeq ZrO_2 > Al_2O_3 > SiO_2 \gtrsim$ ZnO.

The dependency of the activity and selectivity of the $[Ru_6C]$/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_{react}/K	$[Ru_6C(CO)_{16}Me]^-$				$[Ru_6(CO)_{18}]^{2-}$				$Ru(NO)(NO_3)_3$			
	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), H$_2$ (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 [Ru$_6$C]/MgO with H$_2$ at 623 K the catalytic activities for the formation of the oxygenates decreased to 0 (473 K)–35% (523 K) of those before H$_2$ treatment. The thermal desorption experiments in D$_2$ revealed the formation of equimolar CD$_4$ to the amount of [Ru$_6$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 + H$_2$ was introduced into the [Ru$_6$C]/TiO$_2$ catalyst at 523 K, methanol was readily converted into formaldehyde and dimethyl ether. In CO + H$_2$ reactions, formaldehyde may be produced *via* methanol/methoxyl intermediates rather than directly from CO + H$_2$.

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 [Ru$_6$C]/MgO, [Ru$_6$C]/La$_2$O$_3$, [Ru$_6$C]/TiO$_2$ and [Ru$_6$C]/Al$_2$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 [Ru$_6$C]/MgO catalyst was treated in CO–H$_2$ 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 Ru$_6$ unit and a carbide atom by activation at 623 K in vacuum.

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

nm (N = 1.9), R$_{Ru-O}$ = 0.206 nm (N = 1.8), R$_{Ru-C}$ = 0.191 nm (N = 0.9), and R$_{Ru(-C-)O}$ = 0.299 nm (N = 0.8), similarly to the case of the Ru$_3$(CO)$_{12}$-derived sample.[6] The [Ru$_6$]/Al$_2$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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Intercalation of Polyethers into the MPS$_3$ (M = Mn, Cd) Host Lattice

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Polyethylene oxide and polyethylene glycols can be inserted into MPS$_3$ layered materials preintercalated with hydrated metallic cations.

Insertion of polymers into inorganic low-dimensional materials is a topic of recent interest and only a few examples have been described so far.[1–5] Among the layered transition metal chalcogenides, the MPS$_3$ materials possess a unique intercalation chemistry based on the ability of the lattice to

exchange a fraction of the M^{2+} intralayer cations.[6,7] Air-stable intercalates can thus be obtained, which in some cases have physical properties very different from those of the pure host lattices.[8,9] In order to obtain new organo-mineral composite host lattices and possible 'supported' solid electrolytes, we