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SURFACE-GRAFTED TRIRUTHENIUM KETENYLIDENE CLUSTERS AND THEIR CATALYTIC ACTIVITY IN CO EXCHANGE AND HYDROFORMYLATION OF ETHYLENE

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A triruthenium ketenylidene cluster $[PPN]_2[Ru_3(CO)_9(CCO)]$ was deposited on MgO, SiO_2, and SiO_2-Al_2O_3, and the nature of surface species on the oxides were studied by an IR spectroscopic study along with catalytic performances in ^{13}CO exchange reaction and hydroformylation of ethylene. The IR study suggested the stoichiometric protonation of $[Ru_3(CO)_9(CCO)]^{2-}$ with surface hydroxyl groups on SiO_2 and SiO_2-Al_2O_3 to give $[HRu_3(CO)_9(CCO)]^-$ and $H_2Ru_3(CO)_9(CCO)$, respectively. $H_2Ru_3(CO)_9(CCO)/SiO_2$-Al_2O_3 was active for ^{13}CO exchange reaction, while $[Ru_3(CO)_9(CCO)]^{2-}/MgO$ showed high activity and selectivity toward propanol in hydroformylation of ethylene.

1. Introduction

Molecular metal clusters are useful precursors for the design of active metal centers in heterogeneous catalysis, because they have small sizes and definite compositions of metal frameworks [1–3]. Metal clusters grafted on oxide supports offer promises for understanding of the elementary steps of heterogeneous catalytic reactions and the metal-support interaction in terms of surface organometallic chemistry. In particular, a number of metal carbonyl clusters on oxides have been used as the catalytic precursors in CO-based reactions such as CO hydrogenation, water-gas shift reaction, and hydroformylation of olefin, since the transformation of CO on the metal clusters may result in unique reactivities and selectivities that have not been observed on conventional metal catalysts [3,4].

Product distribution in CO hydrogenation by supported metal catalysts is

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markedly influenced by the nature of oxide supports. Rh catalysts, prepared by the deposition of $Rh_4(CO)_{12}$ on TiO_2, ZrO_2, and La_2O_2 give ethanol and acetaldehyde as C_2-oxygenates [5]. Methanol is produced over the Rh cluster catalysts supported on ZnO and MgO, while methane is a major product on SiO_2 and Al_2O_3 [6,7].

Ketenylidene ligands in trinuclear clusters $[PPN]_2[M_3(CO)_9(CCO)]$ (M = Fe, Ru, Os) are possible intermediates in CO hydrogenation over supported-metal catalysts, and transformation of the ketenylidene cluster by the reaction with nucleophiles and electrophiles has been extensively investigated [8].

In this letter, the trinuclear ketenylidene cluster $[PPN]_2[Ru_3(CO)_9(CCO)]$ is deposited on MgO, SiO_2, and SiO_2-Al_2O_3, which have different surface acid-base properties. The cluster-support interaction results in the formation of various ketenylidene clusters on the surfaces. FTIR spectroscopy was conducted to monitor the transformation of the surface-grafted clusters. The ^{13}CO isotopic exchange reaction of the surface-grafted clusters and the catalytic performance in ethylene hydroformylation have been studied.

2. Experimental

$[PPN]_2[Ru_3(CO)_9(CCO)]$ (PPN = bis(triphenylphosphine)nitrogen(1 +)) was synthesized according to previous reports [9]. CH_2Cl_2, used as a solvent, was stored under N_2 after being refluxed with and distilled from P_4O_{10}. Aerosil 300 (Nippon Aerosil Co.), Silica Alumina Catalyst (Davison, Grade 135), and MgO (Merck, GR) were used as supports of SiO_2, SiO_2-Al_2O_3, and MgO, respectively. The small amount of Na^+ ions present in the SiO_2-Al_2O_3 were exchanged with H^+ by treatment of an aqueous solution of NH_4Cl at 368 K. After removing water, the SiO_2-Al_2O_3 was calcined in air at 823 K for 2 h. This exchange-calcination was repeated three times to complete the ion-exchange, giving the H-type SiO_2-Al_2O_3.

Powders of the oxides were pressed into disks (30–35 mg, diameter 20 mm), and mounted in JR cells with CaF_2 or KBr windows. The disk was dried at 573 K for 2 h, and cooled to room temperature. $[PPN]_2[Ru_3(CO)_9(CCO)]$ (2 mg) was dissolved in 0.2 ml of CH_2Cl_2 under N_2, the solution was dropped onto the disks through the injection part of the cell without air contamination, then the CH_2Cl_2 was removed under vacuum. IR spectra were recorded in transmission mode on a double-beam Fourier-transform infrared spectrometer (Shimadzu FTIR-4100) at a resolution of 2 cm^{-1}. CO (purity 99.9995 vol%) and H_2 (99.95 vol%) were purchased from Takachiho Trading Co., and ^{13}CO (isotopic purity 99.3%) from MSD Isotopes. The gases were used without further purification.

Hydroformylation of ethylene was carried out in the vapor phase at atmospheric pressure with a flow-mode Pyrex glass reactor, charged with 1 g of the surface-grafted cluster catalyst (1 wt% of Ru loading). The catalyst was reduced in flowing H_2 (1 atm, 60 ml/min) at 573 K for 2 h. A mixture of C_2H_4, CO, and H_2 (1 : 1 : 1 molar ratio, 1 atm of total pressure) was introduced into the reactor at a flow rate of 60 ml/min and a space velocity of 670 h^{-1}. Gaseous products were quantitatively analyzed by TCD-gas chromatography with active carbon and DMF/Al_2O_3 columns. The propanal and 1-propanol produced were collected by bubbling the off-gas into a water trap, and analyzed by FID-gas chromatography with a Chromosorb 101 column.

3. Results and discussion

3.1. DEPOSITION OF RUTHENIUM KETENYLIDENE CLUSTER ON VARIOUS METAL OXIDES

$[PPN]_2[Ru_3(CO)_9(CCO)]$ was deposited on a SiO_2 disk at room temperature from the CH_2Cl_2 solution in an in situ IR cell under N_2, and CH_2Cl_2 was

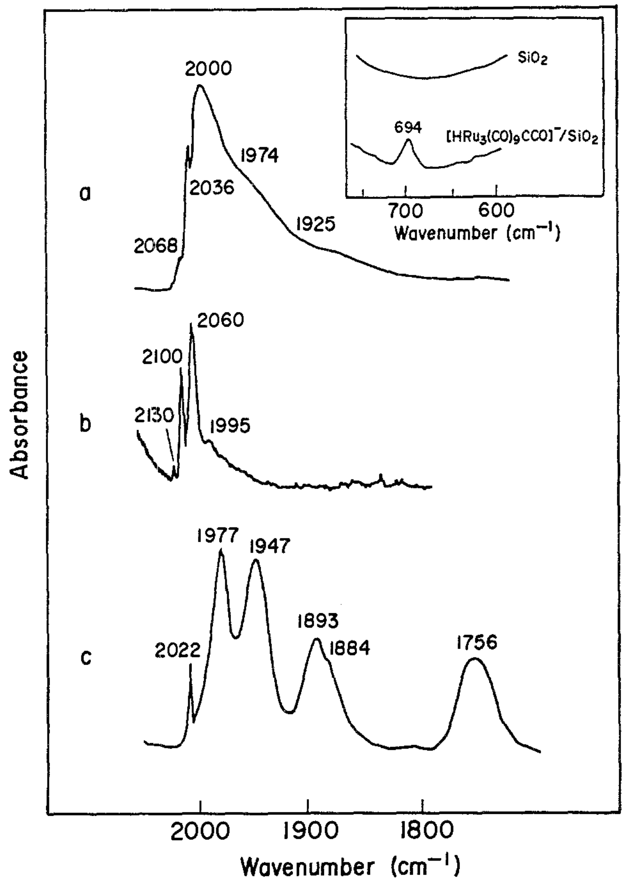
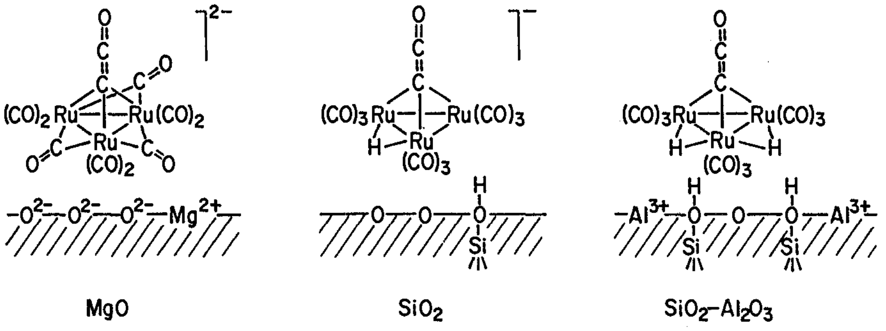


Fig. 1. IR spectra of carbonyl bands of Ru ketenylidene clusters on SiO_2 (a), SiO_2-Al_2O_3 (b) and MgO (c).



Scheme 1

removed under vacuum. The resulting sample gave carbonyl bands in the IR region at 2068, 2036, 2000, 1974, and 1925 cm^{-1} (fig. 1a), which were in good agreement with those of $[HRu_3(CO)_9(CCO)]^-$ in CH_2Cl_2 [9]. The band of bridging CO in $[PPN]_2[Ru_3(CO)_9(CCO)]$ was not observed in the IR spectrum, suggesting the complete transformation of $[Ru_3(CO)_9(CCO)]^{2-}$ into $[HRu_3(CO)_9(CCO)]^-$. Also the sample showed a new band at 694 cm^{-1}, which is likely associated with out-of-plane bending of Ru-H-Ru. It is reported that $[HRu_3(CO)_{11}]^-/SiO_2$ prepared by the deposition of $Ru_3(CO)_{12}$ on SiO_2 has the out-of-plane bending of Ru-H-Ru at 682 cm^{-1} [10]. Presumably, the starting dianion cluster was mono-protonated by the surface silyl OH, where the band of SiOH at 3740 cm^{-1} was substantially reduced with formation of the monohydride cluster.

Addition of a CH_2Cl_2 solution of $[PPN]_2[Ru_3(CO)_9(CCO)]$ on SiO_2-Al_2O_3 as a strong Brönsted acid resulted in further protonation of the starting dianion cluster; the sample before evacuation of CH_2Cl_2 had carbonyl bands in the IR region at 2124, 2088, 2040, and 2010 cm^{-1} similar to those of $H_2Ru_3(CO)_9(CCO)$ in CH_2Cl_2 [9] (fig. 1b). The band intensity of Al-SiOH at 3620 cm^{-1} was greatly decreased with the formation of $H_2Ru_3(CO)_9(CCO)$, while the band of SiOH at 3640 cm^{-1} was unchanged. Accordingly, the starting dianion cluster might be protonated by the more acidic OH of Al-SiOH than that of SiOH to form the dihydride ketenylidene cluster.

In contrast to the Brönsted acidic oxides such as SiO_2 and SiO_2-Al_2O_3, $[PPN]_2[Ru_3(CO)_9(CCO)]$ was simply adsorbed as a dianion ketenylidene cluster on basic MgO; the sample gave IR bands at 2024, 1977, 1947, 1893, and 1756 cm^{-1} (fig. 1c), which were at the same positions as those of $[PPN]_2[Ru_3(CO)_9(CCO)]$ in CH_2Cl_2. Three different ketenylidene species are grafted on SiO_2-Al_2O_3, SiO_2, and MgO, as represented in scheme 1.

3.2. ^{13}CO EXCHANGE REACTION

^{13}CO exchange reactions were performed to study the reactivity of oxide-grafted triruthenium ketenylidene clusters.

$[HRu_3(CO)_9(CCO)]^-/SiO_2$ was exposed to 15 Torr of ^{13}CO at room temperature for 2 h, where the ligand carbonyl bands at 2036 and 2000 cm^{-1} were reduced, and a strong band appeared at 1996 cm^{-1} due to ^{13}CO isotopic exchange reaction. The intensity of the carbonyl band at 1974 cm^{-1}, which was assigned to CCO [11], did not change in the presence of ^{13}CO at room temperature, but the ^{13}CO exchange reaction was pronounced at 430 K. The difference IR spectra showed that the 1974 cm^{-1} band was shifted to 1940 cm^{-1} at 430 K. When $[PPN]_2[Ru_3(^{13}CO)_9(C^{13}CO)]$ (30% enriched) was deposited on SiO_2, the band of $C^{13}CO$ in $[HRu_3(CO)_9(CCO)]^-/SiO_2$ appeared at 1939 cm^{-1}.

^{13}CO exchange reaction proceeded with a higher rate on $H_2Ru_3(CO)_9(CCO)/SiO_2\text{-}Al_2O_3$ than on $[HRu_3(CO)_9(CCO)]^-/SiO_2$. The admission of ^{13}CO at 300–373 K on $H_2Ru_3(CO)_9(CCO)/SiO_2\text{-}Al_2O_3$ led to the facile exchange of the carbonyl bands. In contrast, $[Ru_3(CO)_9(CCO)]^{2-}/MgO$ showed a negligible or lowest activity even at 500 K.

The order of the activity in ^{13}CO exchange reaction is as follows: $H_2Ru_3(CO)_9(CCO)/SiO_2\text{-}Al_2O_3 \gg [HRu_3(CO)_9(CCO)]^-/SiO_2 > [Ru_3(CO)_9(CCO)]$ which is likely to depend on the formal charges of the oxide-grafted ketenylidene clusters.

3.3. REACTION WITH CH_3I

Although $[Ru_3(CO)_9(CCO)]^{2-}/MgO$ is inactive for ^{13}CO exchange reaction, it reacts with CH_3I in vapor phase to form an acetyl cluster $[Ru_3(CO)_9CC(O)CH_3]^-MgO$, as was expected from the chemistry in solution [9]. When CH_3I (80 Torr) and CO (80 Torr) were admitted onto the sample disk of $[Ru_3(CO)_9(CCO)]^{2-}/MgO$ in the IR cell at room temperature, the bands at 1977,

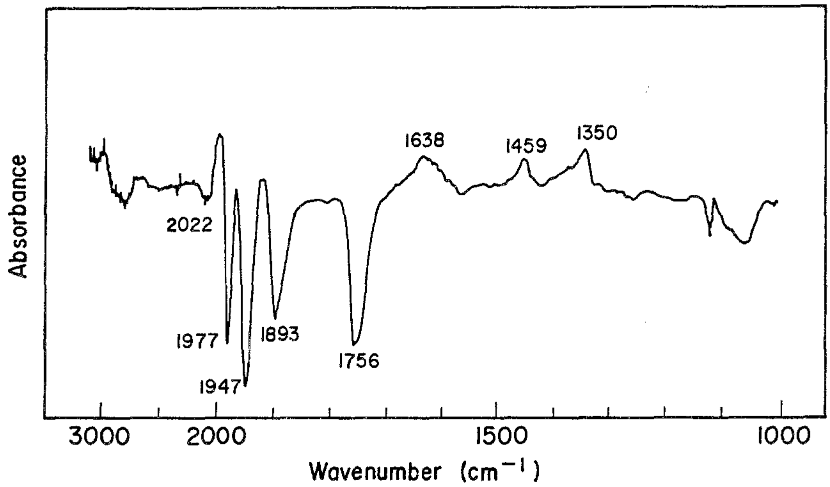


Fig. 2. A differential spectrum after admission of 80 Torr of CH_3I and 80 Torr of CO onto $[Ru_3(CO)_9(CCO)]^{2-}/MgO$ at 300 K for 2 h.

1943, 1894, and 1756 cm^{-1} diminished and new bands appeared at 2022,1952, and 1896 cm^{-1} in the carbonyl region (fig. 2). In addition, three bands were observed at 1638, 1459, and 1350 cm^{-1}; the 1638 cm^{-1} band is assigned to the $C=O$ stretching of the acyl moiety and the others to the deformation of C-H in $C(O)CH_3$.

Reaction of $[HRu_3(CO)_9(CCO)]^-/SiO_2$ with CH_3I at room temperature proceeded very slowly, but $[Ru_3(CO)_9C(O)CH_3]^-$ was formed at 470 K, giving the characteristic IR bands due to the acyl complex. By contrast, $H_2Ru_3(CO)_9(CCO)/SiO_2$-Al_2O_3 was completely inactive for the reaction with CH_3I up to 570 K.

3.4. HYDROFORMYLATION OF ETHYLENE

The results of hydroformylation of ethylene on the oxide-bound ketenylidene clusters ($C_2H_4 : CO : H_2 = 20 : 20 : 20$ ml/min, 1 atm, 445 K) are summarized in table 1. In all runs, the activity reached steady state after 5 h on stream and remained constant for subsequent 55 h. The rates were evaluated at steady state of the reaction. Higher rates for propanal and 1-propanol were observed on MgO-supported Ru ketenylidene dianion cluster-derived catalyst than on SiO_2- or SiO_2-Al_2O_3-supported ones. The rate for ethane was effectively suppressed on the MgO support. The orders of activity and selectivity for ethane and oxygenates (propanal and 1-propanol) in the hydroformylation of ethylene depending on various oxides used are as follows;

Activity for oxygenates: $MgO > SiO_2 > SiO_2$-Al_2O_3
Selectivity for alcohol: $MgO \gg SiO_2$, SiO_2-Al_2O_3
Activity for ethane: SiO_2-$Al_2O_3 > SiO_2 > MgO$

It is shown that the Ru catalyst on the basic oxide such as MgO gives higher activity to produce oxygenated products, which is the reverse of the reactivity in the ^{13}CO exchange reaction. The orders of activity toward oxygenates in the

Table 1
Hydroformylation of ethylene on surface-deposited Ru ketenylidene cluster catalysts [a]

precursor/support	Rate of formation at 445 K [b]		Selectivity for oxygenates (mol %) [c]	Selectivity for alcohol (mol %) [d]
	C_2H_6	$C_2H_5CHO + C_3H_7OH$		
$[Ru_3(CO)_9(CCO)]^{2-}/MgO$	0.030	0.011	27	46
$[Ru_3(CO)_9(CCO)]^-/SiO_2$	0.055	0.0035	6	0
$H_2Ru_3(CO)_9(CCO)/SiO_2$-Al_2O_3	0.12	0.0020	2	0

[a] Flow rate $C_2H_4 : CO : H_2 = 20 : 20 : 20$ ml/min, total pressure 1 atm.
[b] $mol/mol_{Ru}/min$.
[c] $(C_2H_5CHO + C_3H_7OH)/(C_2H_6 + C_2H_5OH + C_3H_7OH)$ 100%.
[d] $C_3H_7OH/(C_3H_7OH + C_2H_5CHO)$ 100%.

hydroformylation of ethylene were in good accordance with those for the reactivity of CH_3I with ketenylidene species impregnated on the different metal oxides.

It was found by the TPD (temperature-programmed desorption) coupled with FTIR spectroscopy that $[HRu_3(CO)_9(CCO)]^-$ on SiO_2 was considerably stable up to 400 K, and was gradually decarbonylated at above 450 K to give the surface species having a ketenylidene group characteristic of a $C=C=O$ band at 1970 cm^{-1}. Alter the H_2 reduction of the resulting catalysts at 573 K for 2 h, they chemisorbed CO, showing the $C=C=O$ IR band at 1970 cm^{-1} as well as CO IR band at 2100–2000 cm^{-1}. Although the catalytic active species for olefin hydroformylation have not yet been completely characterized, the basic groups OH^- and O^{2-} on MgO are likely to promote the catalytic CO insertion by the Ru clusters to produce the oxygenates in olefin hydroformylation and CO hydrogenation, similarly as it has been reported [12] on the catalysts derived from $Rh_{4-x}Co_x(CO)_{12}$ ($x = 0$–4) impregnated on the basic oxides, e.g., MgO, ZnO, TiO_2, and ZrO_2.

4. Conclusion

1. Deposition of $[PPN]_2[Ru_3(CO)_9(CCO)]$ on SiO_2, SiO_2-Al_2O_3, and MgO results in the formation of $[HRu_3(CO)_9(CCO)]^-/SiO_2$, $H_2Ru_3(CO)_9(CCO)/SiO_2$-Al_2O_3, and $[Ru_3(CO)_9(CCO)]^{2-}/MgO$, respectively.

2. In ^{13}CO exchange reaction, the order of the reactivity is as follows: $H_2Ru_3(CO)_9(CCO)/SiO_2$-$Al_2O_3 > [HRu_3(CO)_9(CCO)]^-/SiO_2 >$ $[Ru_3(CO)_9(CCO)]^{2-}/MgO$.

3. $[Ru_3(CO)_9(CCO)]^{2-}/MgO$ reacts with CH_3I to form the acetyl cluster $[Ru_3(CO)_9CC(O)CH_3]^{2-}/MgO$, whereas $[HRu_3(CO)_9(CCO)]^-/SiO_2$ and $H_2Ru_3(CO)_9(CCO)/SiO_2$-Al_2O_3 are inactive in the reaction with CH_3I.

4. Hydroformylation of ethylene proceeded with higher rates on the catalyst derived from MgO-supported Ru ketenylidene to give propanal and 1-propanol than on SiO_2- or SiO_2-Al_2O_3-supported catalysts, but the rates for ethane production on the MgO-supported catalyst are lower.

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