Characterization of MgO- and TiO$_2$-Supported Pt-Ru Catalysts and Activities for Ethylene Hydrogenation and *n*-Butane Hydrogenolysis

S. Chotisuwan[a], J. Wittayakun[b]*, and B. C. Gates[c]

[a] *Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, Thailand*
[b] *School of Chemistry, Suranaree University of Technology, Nakhon Ratchasima, Thailand*
[c] *Department of Chemical Engineering and Materials Science, University of California, Davis, CA, USA*

Abstract

Bimetallic platinum-ruthenium catalyst supported on magnesia (Pt-Ru/MgO) and titania (Pt-Ru/TiO$_2$) were prepared by adsorption of Pt$_3$Ru$_6$(CO)$_{21}$(μ_3-H)(μ-H)$_3$ cluster in CH$_2$Cl$_2$ solution on MgO and TiO$_2$, and decarbonylated in helium at 300°C. Their structures were characterized by extended x-ray absorption fine structure (EXAFS) spectroscopy which indicated changes in coordination numbers and interatomic distances of metal-metal framework after decarbonylation likely caused by strong cluster-support interaction. However, both Pt-Ru/MgO and Pt-Ru/TiO$_2$ still contained Pt-Ru, Pt-Pt, and Ru-Ru bonds and small coordination number inferring good metal dispersion. Both Pt-Ru/MgO and Pt-Ru/TiO$_2$ catalysts were active for ethylene hydrogenation and *n*-butane hydrogenolysis. The temperature dependence of ethylene hydrogenation over Pt-Ru/MgO and Pt-Ru/TiO$_2$ gave apparent activation energy of 7.6 ± 0.1 and 8.1 ± 0.1 kcal/mol, respectively. The apparent activation energy of *n*-butane hydrogenolysis over Pt-Ru/MgO and Pt-Ru/TiO$_2$ were 15.5 ± 0.1 and 28.2 ± 0.1 kcal/mol, respectively. Major products were ethane and methane.

Keywords

Bimetallic catalyst, Pt-Ru, magnesia, titania, ethylene hydrogenation, n-butane hydrogenolysis

Introduction

An effective way to prepared nanosize bimetallic catalyst with bimetallic bonds is by using bimetallic cluster precursors. After ligands are removed under mild conditions, well-defined and/or highly dispersed bimetallic particles on the support could be obtained. For supported PtRu catalysts, several PtRu carbonyl clusters with various metal compositions and ligands were reported by Adams and coworkers and could serve as molecular precursors [1-3].

The goal of this work was to prepare and characterize PtRu/MgO and PtRu/TiO$_2$ catalysts from a bimetallic cluster, Pt$_3$Ru$_6$(CO)$_{21}$(μ_3-H)(μ-H)$_3$ (cluster A) containing preformed Pt-Ru bonds. The carbonyl and hydride ligands were expected to be removed easily by a thermal treatment in inert atmosphere without breaking the metal cluster core.

The prepared PtRu/MgO and PtRu/TiO$_2$ catalysts were characterized by EXAFS spectroscopy, and tested for ethylene hydrogenation and *n*-butane hydrogenolysis.

Materials and Methods

Preparation of PtRu/MgO and PtRu/TiO$_2$ catalyst. Cluster A was synthesized by a procedure described in [2], its structure was confirmed spectroscopically by IR, ^{1}H, and ^{13}C, giving evidence matching the literature report.

Supported Pt-Ru catalysts containing 1.0 wt% Pt and 1.0 wt% Ru was prepared by slurrying **A** in CH$_2$Cl$_2$ with MgO and TiO$_2$ powder for 1 day followed by evacuation for an additional day. The dry supported sample was heated in He flow at 300°C for 2 h to remove ligands.

Catalyst characterization by EXAFS spectroscopy. The obtained catalysts were characterized by EXAFS spectroscopy at X-ray beamline X-18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), Upton, NY. Each sample in sample holder was scanned at

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the Pt L_{III} edge (11564 eV) and the Ru K edge (22117 eV) in transmission mode except for supported PtRu on TiO_2 samples which were scanned at the Pt L_{III} edge in fluorescence mode. The EXAFS data processing was carried out with ATHENA software [4] and analyzed by EXAFSPAK software [5] including FEFF7.0 software [6].

Fourier transformed ranges in k (with k^3 weighting without phase correction) and r space of the EXAFS data of samples after decarbonylation scanned at the Pt L_{III} edge and the Ru K edge were summarized in Table 1.

Table 1 - Fourier transformed ranges of the EXAFS data of decarbonylated samples

Edges	Samples	Fourier Transform	
		Δk (Å^{-1})	Δr (Å)
Pt L_{III}	PtRu/MgO	3.00 – 13.40	0.00 – 4.00
	PtRu/TiO$_2$	4.10 – 12.00	0.00 – 4.00
Ru K	PtRu/MgO	4.25 – 14.35	0.00 – 4.00
	PtRu/TiO$_2$	4.00 – 14.20	0.00 – 4.25

Catalytic activities testing. The supported bimetallic clusters were tested as catalysts in once-through tubular flow reactors for ethylene hydrogenation and n-butane hydrogenolysis. Test conditions for ethylene hydrogenation included P_{H_2} = 80 Torr, $P_{C_2H_4}$ = 40 Torr, and temperature varied from -75 to -20°C. Test conditions for n-butane hydrogenolysis were as follow: P_{H_2} = 540 Torr, $P_{n-C_4H_{10}}$ = 60 Torr, and temperature varied from 190 to 260°C.

Results and Discussion

High dispersion of bimetallic particles on supports after decarbonylation. The EXAFS data analysis of the samples at the Pt L_{III} edge and the Ru K edge were summarized in Table 1. The estimated accuracies of coordination number (N), distance (R), Debye-Waller factor ($\Delta\sigma^2$), and inner potential (ΔE_o) are as follows: ± 20%, ± 1%, ± 30%, and ± 10%, respectively. The EXAFS fitting parameters of PtRu/MgO and PtRu/TiO$_2$ compared with cluster A in crystalline form are in Table 2.

Table 2   Summary of EXAFS data of samples prepared by adsorption of cluster A on MgO and TiO$_2$ after ligand removal in He flow at 300°C for 2 h

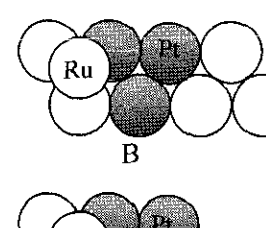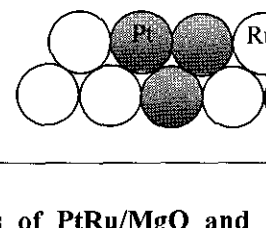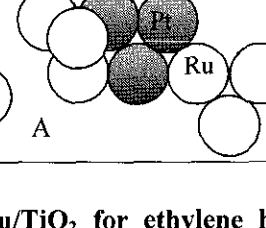| Edge	Shell	Cluster A[a]		PtRu/MgO				PtRu/TiO$_2$			
		N	R (Å)	N	R (Å)	$10^3 \times \Delta\sigma^2$ (Å^2)	ΔE_o (eV)	N	R (Å)	$10^3 \times \Delta\sigma^2$ (Å^2)	ΔE_o (eV)
Pt L_{III}	Pt-Pt	2.0	2.64	1.3	2.69	5.1	8.7	1.8	2.65	0.9	-6.8
	Pt-Ru	4.0	2.80	0.9	2.69	3.4	3.6	1.9	2.69	2.8	7.6
	Pt-CO	1.0	1.85	-	-	-	-	-	-	-	
	Pt-O$_{support}$										
	Pt-O$_s$	-	-	2.3	2.03	4.8	7.1	1.8	1.96	9.4	-0.9
	Pt-O$_l$	-	-	0.4	3.09	12.1	-3.1	0.5	3.09	-3.6	8.6
Ru K	Ru-Ru	2.0	3.04	2.6	2.63	4.8	-5.2	2.4	2.65	6.7	-7.7
	Ru-Pt	2.0	2.80	1.1	2.69	3.7	-4.0	0.9	2.69	3.0	-3.4
	Ru-CO	3.0	1.89	-	-	-	-	-	-	-	-
	Ru-O$_{support}$										
	Ru-O$_s$	-	-	1.4	2.09	12.0	7.4	2.4	2.00	10.4	-4.4
	Ru-O$_l$	-	-	0.2	2.87	-6.3	6.4	0.3	2.80	-5.5	-1.4
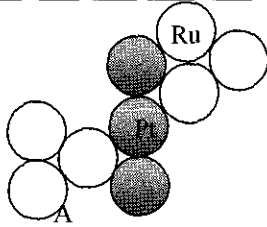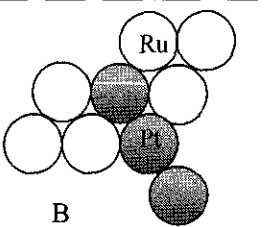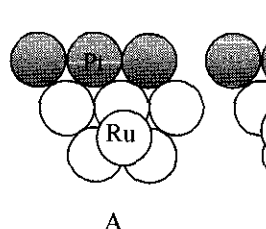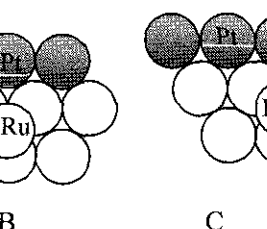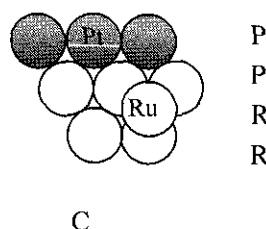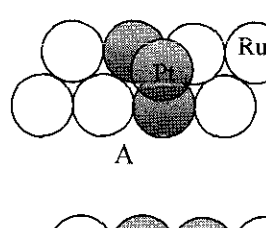
Notation: [a]XRD data of crystalline $Pt_3Ru_6(CO)_{21}(\mu_3-H)(\mu-H)_3$ [2]

Subscript s and l refer to short and long, respectively.

Pt-Ru and Ru-Pt imetallic contributions were still observed in both samples. However, both Pt and Ru coordination numbers were lower than that in the cluster precursor which were seven indicating that aggregation did not occur during decarbonylation and the size of metal core were relatively similar to the core of cluster precursor. All metal-metal distances in both catalysts changed from that in the core of the cluster precursor after ligand removal. The Pt-Pt distances of the bimetallic particles were only slightly longer than that in the core of the cluster precursor probably due to the release partially from

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Pt-Ru bonds. While the Pt-Ru and Ru-Pt increased approximately 1 Å from the precursor core, more decrease of approximately 3 Å were observed in the Ru-Ru distances probably due to the loss of hydrides during adsorption and decarbonylation. The low metal-metal coordination numbers of both metals indicated highly dispersed PtRu particles on each support were obtained. Interactions between both Pt and Ru and each support oxygen were observed. Selected models of metal particles on each support shown in Figure 1 were sketched based on EXAFS data.

Figure 1 - Selected models of metal particles on MgO and TiO$_2$ based on EXAFS data

Support	Proposed Arrangements	N
MgO	A B	Pt-Pt = 1.3 Pt-Ru =1.7 Ru-Ru = 2 Ru-Pt = 0.8
	A B C	Pt-Pt = 1.3 Pt-Ru =1.7 Ru-Ru = 3.3 Ru-Pt = 0.8
TiO$_2$	A B	Pt-Pt = 2 Pt-Ru = 2.3 Ru-Ru = 2 Ru-Pt = 1.2
	A B	Pt-Pt = 2 Pt-Ru = 2 Ru-Ru = 2 Ru-Pt = 1

Catalytic activities of PtRu/MgO and PtRu/TiO$_2$ for ethylene hydrogenation and *n*-butane hydrogenolysis. The catalysis results catalyzed by these catalysts were summarized in Table 3. The apparent activation energies of ethylene hydrogenation catalyzed by these samples are comparable to those catalyzed by Pt catalysts, and Ru catalysts consisting of metallic particles on metal oxide supports [7, 8].

Table 3   Summary of ethylene hydrogenation and *n*-butane hydrogenolysis catalyzed by PtRu/MgO and PtRu/TiO$_2$ catalysts

Catalysts	Reactions	TOF x 10^4 (s^{-1})	Temp. (K)	E_{app} (kcal mol^{-1})
PtRu/MgO	ethylene hydrogenation	3.4	198-243	7.6
	n-butane hydrogenolysis	11.7	473-533	15.5
PtRu/TiO$_2$	ethylene hydrogenation	4.9	198-238	8.1
	n-butane hydrogenolysis	1.4	473-553	28.2

Notation: TOF was measured at 198 K for ethylene hydrogenation and at 493 K for *n*-butane hydrogenolysis

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Product distribution for *n*-butane hydrogenolysis at 493 K catalyzed by PtRu/MgO was 43% methane, 52% ethane, 3% propane, and 2% *iso*-butane. *n*-Butane hydrogenolysis at 493 K catalyzed by PtRu/TiO$_2$ gave 48% methane, 32% ethane, 3% propane, and 17% *iso*-butane. The lower amount of ethane and higher amount of methan on PtRu/TiO$_2$ catalyst indicated a higher degree of multiple hydrogenolysis.

Conclusions

Highly dispersed bimetallic PtRu supported on MgO and TiO$_2$ with Pt-Ru bonds were successfully prepared from adsorption of Pt$_3$Ru$_6$(CO)$_{21}$(μ_3-H)(μ-H)$_3$. Both catalysts were active for both ethylene hydrogenation and *n*-butane hydrogenolysis.

Acknowledgements

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