

CHARACTERIZATION OF SUPPORTED PtRu CATALYSTS AND ACTIVITIES FOR ETHYLENE HYDROGENATION

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ABSTRACT Supported bimetallic PtRu catalysts were prepared by deposition a mixture solution of Pt(acac)₂ and Ru(acac)₃ (acac = acetylacetonate anion) in toluene on γ -Al₂O₃ and MgO. The organic ligand of precursors could be removed completely after heated in H₂ flow at 300°C for 2 h. The nature of metal and interaction with support was studied by temperature-programmed reductive decomposition (TPRD), infrared (IR) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The EXAFS data indicated high dispersion of Pt and Ru particles but none of Pt-Ru connections in both treated samples. Ethylene hydrogenation reaction over Pt-Ru/ γ -Al₂O₃ and Pt-Ru/MgO catalysts were carried out at -40°C and 1 atm. The temperature dependence of ethylene hydrogenation of both catalysts gave apparent activation energy of 8.1 ± 0.1 and 6.0 ± 0.1 kcal/mol, respectively.

KEYWORDS: Pt-Ru, acetylacetonate, alumina, magnesium oxide, EXAFS, ethylene hydrogenation

1. INTRODUCTION

Supported bimetallic catalysts, for instance, Pt-Re, Pt-Sn and Pt-Ir have been reported in many applications, e.g. for naphtha reforming [1], and Pt-Rh for auto exhaust conversion [2]. Supported platinum incorporating with second metal could improve the catalyst performances and stability of catalysts. In general, the simplest preparation method for bimetallic catalyst is by coimpregnation followed by high-temperature reduction. However, high temperature treatment could lead to large metal particles on support or aggregation of metal particles. In this work, a mixture of platinum and ruthenium acetylacetonate (acac) complex was employed as catalyst precursor. The acac ligands could be removed from adsorbed precursor by heat at lower temperature than chloride ligand.

The goal of this work was to prepare and characterize PtRu/ γ -Al₂O₃ and PtRu/MgO catalysts from a mixture of Pt(acac)₂ and Ru(acac)₃ in toluene. The acac ligands would be removed by thermal treatment in hydrogen atmosphere.

The catalyst characterization methods included temperature-programmed reductive decomposition (TPRD) technique [3], infrared (IR) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The catalysts were tested for ethylene hydrogenation which is simple, structural-insensitive and widely used to test catalytic activity.

2. METHODOLOGY

2.1 Chemicals and materials

The supported PtRu catalyst preparations and samples handling were performed under dry N₂ or Ar and kept in an Ar drybox to prevent contact with moisture and air. Trace of O₂ and moisture in gases [He, N₂ (Airgas, 99.99%), H₂ from H₂ generator (99.99%), and C₂H₄ (Matheson, 99.5%)] were removed by passing each gas through traps containing reduced Cu/Al₂O₃ and molecular sieve particles. Pt(acac)₂ (Aldrich, 97%) and Ru(acac)₃ (Strem, 99%) were used as received.

Prior to use as support, each of γ -Al₂O₃ (Degussa, BET surface area 100 m²/g) and MgO powder (EM Science, 97%) was added with deionized water to form paste before drying overnight at 120°C and then calcined in flowing O₂ at 400°C for 2 h and evacuated for an additional 14 h.

2.2 Preparation of supported samples

The PtRu catalysts containing approximately 1.0 wt % Pt and 1.0 wt % Ru were prepared by impregnation of a mixture solution of Pt(acac)₂ and Ru(acac)₃ in dry toluene onto γ -Al₂O₃ and MgO followed by solvent evacuation and treatment in H₂ at 300°C for 2 h.

2.3 Characterization

IR spectra of dry impregnated samples were recorded with a Bruker IFS-66v spectrometer with a resolution of 4 cm⁻¹. Each sample was scanned 64 times and the signal averaged. Reductive decomposition temperatures of Pt(acac)₂ and Ru(acac)₃ to form supported PtRu catalysts were determined with RXM-100 multifunctional catalyst testing and characterization instrument (Advanced Scientific Designs, Inc. (ASDI). Dry

impregnated sample was treated in flowing H₂ at 300°C for 2 h to remove acac ligands and then characterized by EXAFS spectroscopy at beamline X18B of the National Synchrotron Light Source (NSLS) at Brookhaven national Laboratory (BNL), New York, USA. The storage ring energy was 2.5 GeV and the ring current was in the range 110-250 mA. Self-supporting wafer was pressed from 0.3 g of sample in the Ar glovebox at the synchrotron laboratory, and placed in a special designed XAS holder [4]. After the XAS cell was evacuated, it was installed at the beamline and cooled to nearly liquid nitrogen temperature before scanning at Pt L_{III} edge (11564 eV) and Ru K edge (22117 eV) in transmission mode and integration for 1 s at each energy in the range from 200 eV below the absorption edge to 975 eV beyond the edge. A double crystal monochromator Si(111) was used.

2.4 EXAFS data analysis

The EXAFS data were collected in transmission mode at individual Pt L_{III} (11564 eV) and Ru K (22117 eV) absorption edge and analyzed with theoretical reference files. The EXAFS data processing was carried out with ATHENA software [5]. The final normalized EXAFS function from ATHENA software for each edge of each sample was obtained from the average of four scans. Phase shift and backscattering amplitudes of Pt-Pt, Pt-Ru, Pt-O_{support}, Ru-Ru, Ru-Pt, and Ru-O_{support} interactions were calculated by FEFF7.0 software [6]. The EXAFS data fittings by EXAFSPAK software [7] were accomplished with single and multiple scattering paths calculated by FEFF7.0, and the EXAFS parameters were extracted from the raw data with the EXAFSPAK software. The fitting were done in *r* space (*r* is interatomic distance from the absorber atom) and *k* space (*k* is the wave vector) with application of *k*⁰, *k*¹, and *k*³ weightings.

Raw EXAFS data obtained at Pt L_{III} edge of ligand-free PtRu/γ-Al₂O₃ and PtRu/MgO were Fourier transformed over the ranges 3.60 < *k* < 14.30, and 3.55 < *k* < 14.50 with *k*³ weighting without phase correction, respectively. The main contributions were isolated by backward Fourier transformation in the ranges 0.0 < *r* < 5.0 Å for both samples after treatment in H₂.

The raw data obtained at Ru K edge of ligand-free PtRu/γ-Al₂O₃ were analyzed over the ranges 3.25 < *k* < 14.75 and 0.0 < *r* < 4.0 Å whereas that of ligand-free PtRu/MgO were analyzed over the ranges 3.20 < *k* < 14.50 and 0.0 < *r* < 5.0 Å.

The raw data of PtRu/γ-Al₂O₃ obtained at Pt L_{III} and Ru K edge were analyzed with a maximum of 16 free parameters. The statistically justified numbers of free parameters estimated from Nyquist theorem [8], $n = (2\Delta k \Delta R / \pi) + 1$, were about 35 and 30, for data obtained at Pt L_{III} and Ru K edge, respectively. The raw data of treated PtRu/MgO obtained at Pt L_{III} and Ru K edge were analyzed with a maximum of 20 free parameters. The statistically justified numbers of free parameters estimated from Nyquist theorem were about 36 and 37, for data obtained at Pt L_{III} and Ru K edge, respectively.

2.5 Catalytic test for ethylene hydrogenation

The catalytic test for ethylene hydrogenation was carried out in a stainless steel U-tubed flow reactor at atmospheric pressure. Prior to reaction testing, catalyst sample was pretreated with H₂ at 300°C for 2 h. Typically, 10 to 20 mg of 1.0 wt% Pt and 1.0 wt% Ru catalyst was diluted with 600 mg of inert α-Al₂O₃, loaded into the reactor, and cooled to desired temperature under He flow before a gas mixture of H₂, ethylene, and balance He was flowed into reactor. The reaction condition was as follow: *P*_{ethene} = 40 Torr, *P*_{hydrogen} = 200 Torr, balanced with He, total feed flow rate = 100 ml (NTP)/min, and temperature = -50 to -9°C. The effluent gas mixture was analyzed with an on-line gas chromatograph (Hewlett-Packard HP 6890) equipped with an Al₂O₃ capillary column (50 m x 0.53 mm x 15.0 micron film thickness), and a flame ionization detector.

3. RESULTS AND DISCUSSION

3.1 Evidence of adsorbed precursor on supports from IR

The decreasing in intensity of IR peaks of isolated hydroxyl groups of γ-Al₂O₃ at 3786(w), 3728(m), and 3366(m) cm⁻¹ of dry impregnated Pt(acac)₂ and Ru(acac)₃ on γ-Al₂O₃ indicated that the hydroxyl groups on γ-Al₂O₃ involved in the interaction with the mixture of Pt(acac)₂ and Ru(acac)₃. IR broad band at 3569(m) indicates hydrogen-bonded on support [9].

After impregnation of a mixture of Pt(acac)₂ and Ru(acac)₃ in toluene onto MgO and evacuation to remove solvent, the intensity of isolated hydroxyl groups at 3764(s) cm⁻¹ decreased indicating that they were involved in precursor-support interactions.

A small IR band at 1601 cm⁻¹ of dry impregnated Pt(acac)₂ and Ru(acac)₃ on γ-Al₂O₃ and at 1608 cm⁻¹ of that on MgO were observed, each peak was assigned to the formation of Al-acac and Mg-acac species which was reported at 1590 cm⁻¹ for Al-acac imply ligand-exchange mechanism [9]. The acac ligands showed IR peaks in region of 1610-1100 cm⁻¹ [10, 11]. These ligands were removed completely after treatment in H₂ at 300°C.

3.2 Reductive decomposition temperature of supported samples by TPRD

The reductive decomposition temperature based on hydrogen consumption of dry impregnated Pt(acac)₂, Ru(acac)₃, and Pt(acac)₂ + Ru(acac)₃ on γ -Al₂O₃ and MgO are presented in Table 1. All observed peaks were broad indicating that the decomposition was a slow process. Alumina supported Pt(acac)₂ had a peak at 210°C while that of Ru(acac)₃ had a peak at 288 °C. The supported mixture of Pt(acac)₂ + Ru(acac)₃ on γ -Al₂O₃ had 3 peaks: at 124 and 199°C indicated at least two types of supported Pt on support, and at 340°C indicated reduction temperature of supported Ru. TPRD profile indicated that Pt and Ru particles were isolated from one another on γ -Al₂O₃ after treatment.

Broad H₂ consumption temperatures during reductive decomposition of Pt(acac)₂ on MgO had 3 peaks at 140, 202, and 340°C indicating that Pt had various oxidation states or various adsorption modes on MgO. On the other hand, Ru in Ru(acac)₃ supported on MgO showed decomposition temperature at 216°C indicating that only one oxidation state or one adsorption mode of Ru(acac)₃ supported on MgO. For supported PtRu sample on MgO, broad H₂ consumption was observed at 189-221°C indicating that Pt and Ru might contact to each other on MgO or change in oxidation states. The Pt-Ru connectivity could be characterized by EXAFS spectroscopy.

Table 1 Reduction temperatures of Pt(acac)₂ and Ru(acac)₃ supported on γ -Al₂O₃ and MgO

Samples	Reduction temperature (°C)
Pt(acac) ₂ / γ -Al ₂ O ₃	210 (b)
Ru(acac) ₃ / γ -Al ₂ O ₃	288 (b)
[Pt(acac) ₂ + Ru(acac) ₃]/ γ -Al ₂ O ₃	124 (sh), 199 (b), 340 (b)
Pt(acac) ₂ /MgO	140 (b), 202 (b), 340 (b)
Ru(acac) ₃ /MgO	216 (b)
[Pt(acac) ₂ + Ru(acac) ₃]/MgO	189 - 221 (b)

Notation: b = broad, sh = shoulder

3.3 Metal-metal contributions in treated samples by EXAFS

The EXAFS data of decarbonylated sample scanned at Pt L_{III} and Ru K edges at nearly liquid nitrogen temperature were processed by ATHENA software and fitted with EXAFSPAK software. The EXAFS fitting parameters of supported PtRu/ γ -Al₂O₃ and PtRu/MgO were summarized in Table 2. The estimated accuracies of coordination number (*N*), distance (*R*), Debye-Waller factor ($\Delta\sigma^2$), and inner potential correction (ΔE_0) are as follows: $\pm 20\%$, $\pm 1\%$, $\pm 30\%$, $\pm 10\%$, respectively.

Table 2 Summary of EXAFS fitting parameters of supported Pt-Ru/ γ -Al₂O₃ and Pt-Ru/MgO

Samples	Edge	Shell	<i>N</i>	<i>R</i> (Å)	10 ³ × $\Delta\sigma^2$ (Å ²)	ΔE_0 (eV)
PtRu/ γ -Al ₂ O ₃	Pt L _{III}	Pt-Pt	2.8 ± 0.1	2.77 ± 0.01	1.1 ± 0.3	7.7 ± 0.4
		Pt-Ru	-	-	-	-
		Pt-O _{support}				
	Ru K	Pt-O _s	3.4 ± 0.1	2.50 ± 0.01	0.8 ± 0.5	-5.8 ± 0.3
		Pt-O _l	1.3 ± 0.1	2.95 ± 0.01	-4.5 ± 1.0	8.7 ± 0.6
		Ru-Ru	3.3 ± 0.1	2.65 ± 0.01	3.9 ± 0.3	-7.3 ± 0.2
		Ru-Pt	-	-	-	-
Ru-O _{support}	Ru-O _s	1.7 ± 0.1	1.98 ± 0.01	14.0 ± 1.1	-3.7 ± 0.5	
	Ru-O _l	0.7 ± 0.1	2.20 ± 0.01	6.5 ± 2.6	-0.8 ± 0.8	
PtRu/MgO	Pt L _{III}	Pt-Pt	1.0 ± 0.1	3.07 ± 0.01	3.3 ± 0.5	-5.8 ± 0.6
		Pt-Ru	-	-	-	-
		Pt-O _{support}				
		Pt-O _s	0.4 ± 0.1	1.98 ± 0.01	4.9 ± 1.4	7.0 ± 0.6
		Pt-O _l	2.6 ± 0.1	2.51 ± 0.01	0.5 ± 0.2	2.1 ± 0.1
	Ru K	Pt-O _{l2}	4.3 ± 0.1	3.17 ± 0.01	-0.3 ± 0.3	-11.9 ± 0.1
		Ru-Ru	3.5 ± 0.1	2.69 ± 0.01	4.4 ± 0.3	-2.8 ± 0.2
		Ru-Pt	-	-	-	-
		Ru-O _{support}				
		Ru-O _s	2.5 ± 0.1	2.01 ± 0.01	8.6 ± 0.5	-2.8 ± 0.2
Ru-O _l	0.9 ± 0.1	2.53 ± 0.01	-3.5 ± 1.0	15.0 ± 0.4		
Ru-O _{l2}	1.1 ± 0.1	2.96 ± 0.01	1.6 ± 1.8	-3.5 ± 0.6		

Notation: the subscript s, l and l2 refer to short and long distance, respectively

The EXAFS fitting data in Table 2 included metal-metal (Pt-Pt and Ru-Ru) and metal-support (M-O_{support}: M-O_{ss} and M-O_i) contributions of supported PtRu samples on γ -Al₂O₃ and MgO. The EXAFS data showed that there were no Pt-Ru or Ru-Pt contributions on both γ -Al₂O₃ and MgO after treatment in H₂ flow at 300°C. High dispersion of Pt and Ru particles was observed by EXAFS spectroscopy. The coordination numbers of Pt-Pt on γ -Al₂O₃ was 2.8 at average distance 2.77 ± 0.01 Å, shorter than that on MgO, 3.07 ± 0.01 Å with coordination number 1.0 indicating that Pt-Pt interaction on γ -Al₂O₃ was stronger than that on MgO. Interactions of Ru-Ru contributions on both γ -Al₂O₃ and MgO were not significantly different in terms of both average distance and coordination number. After treatment in H₂ flow at 300°C to remove acac ligands, the average Pt-O_s and Ru-O_s bond distances were found at 2.50 ± 0.01 and 1.98 ± 0.01 Å with coordination numbers 3.4 ± 0.1 and 1.7 ± 0.1 , respectively for PtRu/ γ -Al₂O₃. The average Pt-O_s and Ru-O_s bond distances of PtRu/MgO were found at 1.98 ± 0.01 and 2.01 ± 0.01 Å with coordination numbers 0.4 ± 0.1 and 2.5 ± 0.1 , respectively indicating strong interaction of metal-support interactions. Normally the average M-O bond distances were observed at 2.1 - 2.2 Å for supported metal on oxide support [12].

3.4 Ethylene Hydrogenation reaction catalyzed by supported PtRu catalysts

Catalytic activity of ethylene hydrogenation catalyzed by supported PtRu/ γ -Al₂O₃ and PtRu/MgO prepared from mixed Pt and Ru compounds were carried out in stainless U-tubed reactor at atmospheric pressure under condition: $P_{\text{ethene}} = 40$ Torr, $P_{\text{hydrogen}} = 200$ Torr, balanced with He, total feed flow rate = 100 ml (NTP)/min, 10 to 20 mg of 1.0 wt% Pt and 1.0 wt% Ru catalyst, temperature ranges -50 to -9°C. Reaction temperature was kept at desired temperature with $\pm 1^\circ\text{C}$. Catalytic activities of ethylene hydrogenation catalyzed by PtRu/ γ -Al₂O₃ and PtRu/MgO prepared from the mixture solution of Pt(acac)₂ and Ru(acac)₃ were plotted as a function of time on stream (TOS) as shown in Figure 1. The activities over PtRu/MgO were much higher than that over PtRu/ γ -Al₂O₃ at temperature -50°C. The reaction reached steady-state within 20 minutes for both catalysts and deactivations was not observed during 100 minutes of the test.

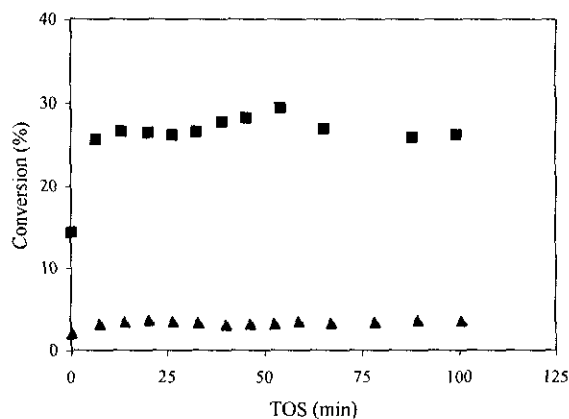


Figure 1 Activity for ethylene hydrogenation over (■) PtRu/MgO; (▲) PtRu/ γ -Al₂O₃, prepared from the mixture solution of Pt(acac)₂ and Ru(acac)₃ at temperature -50°C.

The apparent activation energy of ethylene hydrogenation over supported PtRu catalysts was collected at around 25 min TOS at this condition at temperature ranges -50 to -9°C. The catalytic activity of reaction in terms of the turnover frequency (TOF) was represented the number of molecules reacting per active sites per second [13]. It was assumed that metal particles dispersed on support accessible to reactants, so that TOF was defined as units of mole of ethylene converted to ethane per gram catalyst per second. Arrhenius plot of natural logarithm of TOF as a function of inversed temperature was in Figure 2. Due to very high activity of ethylene hydrogenation over PtRu/MgO prepared from a mixture solution of Pt(acac)₂ and Ru(acac)₃, conversion at higher temperature than -30°C was too high, thus data was collected in temperature ranges -50 to -30°C.

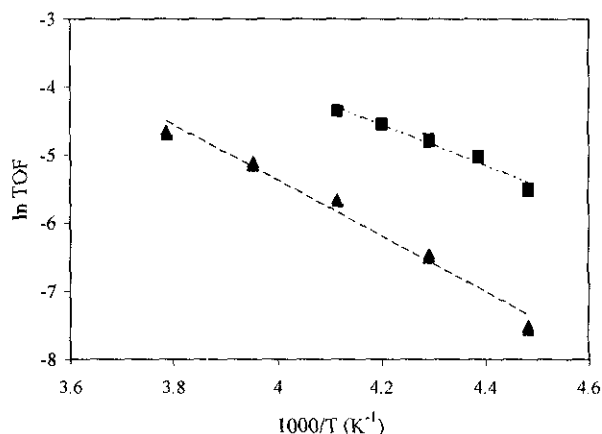


Figure 2 Arrhenius plot for ethylene hydrogenation over (■) PtRu/MgO; (▲) PtRu/ γ -Al₂O₃, prepared from the mixture solution of Pt(acac)₂ and Ru(acac)₃.

The apparent activation energy of ethylene hydrogenation catalyzed by supported PtRu catalysts could be obtained from slope of linear graph in Figure 2 and values are shown in Table 3. The apparent activation energy of supported PtRu/MgO was lower than that of PtRu/ γ -Al₂O₃ and activity (TOF) at temperature -40°C of PtRu/MgO was pretty much higher than that of PtRu/ γ -Al₂O₃ indicating that PtRu/MgO catalyst was more active than PtRu/ γ -Al₂O₃.

Table 3 Apparent activation energy for ethylene hydrogenation over PtRu catalysts prepared from mixture solution of Pt(acac)₂ and Ru(acac)₃ and treated in H₂ at 300°C for 2 h

Precursors	Supports	Activity TOF x 10 ⁴ (s ⁻¹) ^a	Apparent activation energy (kcal/mol)	Temperature (°C)
Pt(acac) ₂ + Ru(acac) ₃	γ -Al ₂ O ₃	1.5 ± 0.1	8.1 ± 0.1	-50 to -9
Pt(acac) ₂ + Ru(acac) ₃	MgO	83.9 ± 1.7	6.0 ± 0.1	-50 to -30

^a Reaction at -40°C, P_{ethene} = 40 Torr and P_{hydrogen} = 200 Torr.

4. CONCLUSIONS

TPRD, IR and EXAFS spectroscopy were used to characterize supported PtRu catalysts prepared by impregnation of the mixture of Pt(acac)₂ and Ru(acac)₃ in toluene onto γ -Al₂O₃ and MgO. The data suggested that precursors adsorbed on surface of γ -Al₂O₃ and MgO through interaction between acac ligands of precursor and surface hydroxyl group on support. The acac ligands could be removed completely in flowing H₂ at 300°C for 2 h to give PtRu/ γ -Al₂O₃ and PtRu/MgO. TPRD data showed that Pt(acac)₂ decomposed at lower temperature than Ru(acac)₃. Results from EXAFS spectroscopy indicated that there were no Pt-Ru interactions after ligand removal. Highly dispersed PtRu/ γ -Al₂O₃ and PtRu/MgO catalysts prepared from the mixture of Pt(acac)₂ and Ru(acac)₃ precursor were active for ethylene hydrogenation giving apparent activation energy 8.1 ± 0.1 and 6.0 ± 0.1 kcal/mol, respectively.

ACKNOWLEDGEMENT

S. Chotisuwan thanks for financial support from Ministry University Affair and Prince of Songkla University, Pattani campus, Thailand. We acknowledge the National Synchrotron Light Source at Brookhaven National Laboratory, Upton, NY. The EXAFS data were processed by ATHENA software developed by Bruce Raval, and analyzed with EXAFSPAK software developed by George, G. N., et al.

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