SUPPORTED PtRu CATALYSTS FROM A MIXTURE OF PLATINUM AND RUTHENIUM ACETYLACETONATE: CHARACTERIZATION AND ACTIVITY FOR ETHYLENE HYDROGENATION

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Abstract

Supported bimetallic PtRu catalysts were prepared by adsorption of a mixture of Pt(acac)$_2$ and Ru(acac)$_3$ (acac = acetylacetonate) in toluene, onto γ-Al$_2$O$_3$ and MgO and the organic ligands were removed by heat in H$_2$ flow at 300°C for 2 h. The nature of metal and interaction with each support was studied by temperature-programmed reductive decomposition (TPRD) and infrared (IR) spectroscopy. TPRD data did not indicate any contact between Pt and Ru atoms on both supports after the treatment. Ethylene hydrogenation over PtRu/γ-Al$_2$O$_3$ and PtRu/MgO catalysts were carried out at 1 atm from -50 to -9°C. The temperature dependence of ethylene hydrogenation of PtRu/γ-Al$_2$O$_3$ and PtRu/MgO prepared from acac precursors gave apparent activation energy 8.1 ± 0.1 and 6.0 ± 0.1 kcal/mol, respectively.

Keywords: Pt-Ru, acetylacetonate, alumina, magnesium oxide, ethylene hydrogenation

Introduction

Supported bimetallic platinum-based catalysts have been reported in many applications, for instance, Pt-Ir, Pt-Re and Pt-Sn for naphtha reforming (Sinfelt, 1983) and Pt-Rh for auto exhaust conversion (Shelef and Graham, 1994). Supported platinum catalysts incorporating with second metal exhibited improvement in both performance and stability. Pt-Ru catalysts have also been widely investigated. The incorporation of Ru in supported platinum catalysts could prevent the formation of strong Pt-CO or CO poisons of Pt (Braccini *et al.*, 2000). In general, the simplest preparation method for bimetallic catalyst is by coimpregnation with metal precursor salts or complexes followed by high-temperature reduction. Examples of the reported platinum and ruthenium precursors are (a) H_2PtCl_6 and $RuCl_3$, (b) $Pt(NH_3)_4(NO_3)_2$ and $Ru(NH_3)_6Cl_3$ (Alerasool and Gonzalez, 1990), (c) $Pt(NH_3)_4Cl_3$ and $Ru(NH_3)_6Cl_3$ (Martins *et al.*, 2001).

However, the conventional methods using mixture of Pt and Ru compounds containing chloride do not allow an ability to control particle

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size, structure, composition, and stoichiometry of bimetallic catalysts (Shirai *et al.*, 1999). In addition, a high-temperature reduction leads to nonuniform materials with large metal particles and broad particle size distribution. To avoid difficulties caused by such conventional precursors, supported PtRu catalysts were prepared in this work from a mixture of organometallic precursors $Pt(acac)_2$ and $Ru(acac)_3$ (acac is acetylacetonate anion, $C_5H_7O_2^-$). Because acac ligand in metal salts could be removed at relatively lower temperature than other ligands, the supported PtRu catalysts prepared from a mixture of $Pt(acac)_2$ and $Ru(acac)_3$ were expected to contain bimetallic particles on support with Pt-Ru connections and possibly high dispersion.

The goal of this work was to prepare and characterize PtRu/γ-Al_2O_3 and PtRu/MgO catalysts from a mixture of $Pt(acac)_2$ and $Ru(acac)_3$ in toluene. The acac organic ligands could be removed by thermal treatment in hydrogen atmosphere resulting in highly dispersed metal on support.

The interactions between precursors and metal oxide supports were characterized by IR spectroscopy. The reductive decomposition temperatures of supported samples were investigated by the temperature-programmed reductive decomposition (TPRD) technique. The catalysts were tested for ethylene hydrogenation which is simple, structural-insensitive and used to test catalytic activity of many catalysts.

Materials and Methods

Sample Preparation

Prior to be used as support, γ-Al_2O_3 (Degussa, BET surface area 100 m^2/g) and MgO (EM Science, BET surface area 60 m^2/g) powder supports were calcined in flowing O_2 at 400°C for 2 h and evacuated for an additional 14 h. The PtRu catalysts containing approximately 1.0 wt% Pt and 1.0 wt% Ru were prepared by adsorption of a solution mixture of $Pt(acac)_2$ (Aldrich, 97%) and $Ru(acac)_3$ (Strem, 99%) in dry toluene onto γ-Al_2O_3 and MgO followed by the solvent evacuation and the treatment in H_2 at 300°C for 2 h.

PtRu Catalyst Activation

Each fresh supported sample was heated in flowing H_2 at 300°C for 2 h to remove ligands from adsorbed precursor and reduce metal particles.

Characterization by IR Spectroscopy

IR spectra of dry supported samples were recorded with a Bruker IFS-66v spectrometer with a resolution of 4 cm^{-1}. Each sample was scanned 64 times and the signals were averaged.

Characterization by TPRD

Reductive decomposition temperatures of dry supported samples to form supported PtRu catalysts were determined with RXM-100 multifunctional catalyst testing and characterization instrument (Advanced Scientific Designs, Inc., ASDI). The diagram of TPRD apparatus is shown in Figure 1. A U-shaped quartz tube reactor containing dry supported sample (250 - 300 mg), connected to the TPRD apparatus, was evacuated to around 10^{-8} Torr and then Ar was flowed into the reactor around 20 min. The gas was then switched to 5 vol% H_2 in Ar and the temperature was increased to 400°C with a rate of 10°C/min. The TPRD signal was monitored with the thermal conductivity detector (TCD).

Catalytic Test for Ethylene Hydrogenation

The catalytic test for ethylene hydrogenation was studied in a stainless steel U-tube flow reactor at the atmospheric pressure. Each dry supported sample was pretreated with H_2 at 300°C for 2 h, and then 10 to 20 mg of the pretreated catalyst was diluted with 600 mg of inert α-Al_2O_3, and tested at the following condition: He:H_2:ethylene ratio = 13:5:1, total feed flow rate = 100 ml (NTP)/min, and temperature = -50 to -9°C. The effluent gas mixture was analyzed with an online gas chromatograph (Hewlett-Packard HP 6890) equipped with an Al_2O_3 capillary column (50 m × 0.53 nm × 15.0 micron film thickness), and a flame ionization detector (FID).

Results and Discussion

Evidence of Adsorbed Precursor on Supports from IR Spectra

The decrease in intensity of IR peaks of isolated hydroxyl groups of γ-Al_2O_3 at 3,786 (w), 3,728 (m), and 3,666 (m) cm^{-1} of dry supported $Pt(acac)_2$ and $Ru(acac)_3$ on γ-Al_2O_3 (spectrum 2 in Figure 2(a)) indicated that the hydroxyl groups on γ-Al_2O_3 involved in the interaction with $Pt(acac)_2$ and $Ru(acac)_3$. The IR broad band at 3,569 (m) indicates hydrogen-bonded on support (Alexeev *et al.*, 2002).

The IR intensity of isolated hydroxyl groups at 3,764 (s) cm^{-1} (spectrum 5 in Figure 2(a)) of dry supported $Pt(acac)_2$ and $Ru(acac)_3$ on MgO also decreased when compared with that of bare MgO indicating the hydroxyl groups involved in precursor-support interactions. The acac ligand showed the IR peaks in the region of 1,610-1,200 cm^{-1} (SADTLER Research Laboratories, 1965; The Coblentz Society, 1970).

The adsorption of metal acetylacetonate precursors could occur through interaction between acetylacetonate ligand and surface of support without loss of any acetylacetonate ligands (Kenvin and White, 1991). Several

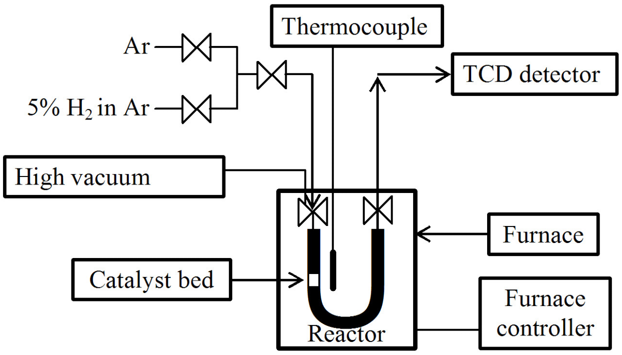

Figure 1. Temperature-programmed reductive decomposition apparatus

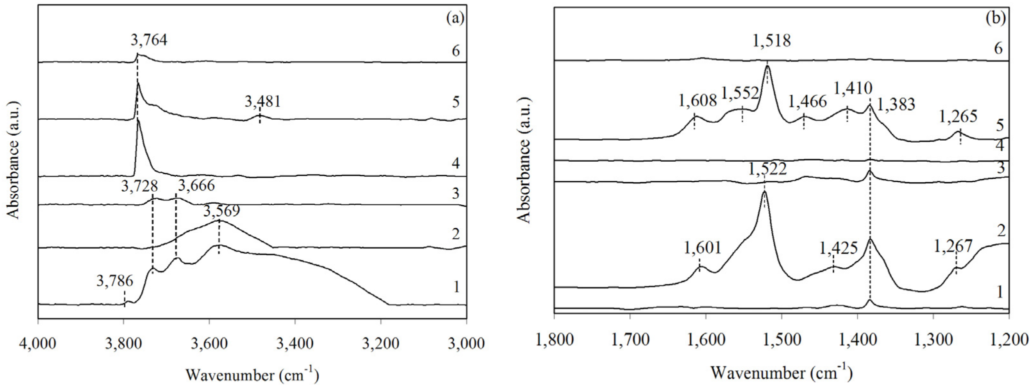

Figure 2. IR spectra in (a) ν_{OH} region and (b) $\nu_{C\text{-}H}$ region of (1) calcined γ-Al_2O_3; (2) supported sample of $Pt(acac)_2$ and $Ru(acac)_3$ on γ-Al_2O_3; (3) PtRu/γ-Al_2O_3 after the treatment at 300°C in H_2 flow for 2 h; (4) calcined MgO; (5) supported sample of $Pt(acac)_2$ and $Ru(acac)_3$ on MgO; (6) PtRu/MgO after the treatment at 300°C in H_2 flow for 2 h

researchers utilized extended X-ray absorption fine structure (EXAFS) spectroscopy to characterized the neighbor atoms of Pt in supported Pt sample prepared from $Pt(acac)_2$ (Fiddy *et al.*, 1999a; Fiddy *et al.*, 1999b; Womes *et al.*, 2003). The reported coordination number of Pt-O was approximately 4, the same as untreated supported Pt sample implying the $Pt(acac)_2$ adsorbed intact on support. Moreover, Plyuto *et al.* (1999) found by thermal study that $Ru(acac)_3$ adsorbed on Al_2O_3 without an elimination of acetylacetonate ligand.

Consequently, the adsorption process of $M^{n+}(acac)_n$ on γ-Al_2O_3 in this work could be explained with equation (1) without an elimination of acac ligand (Plyuto *et al.*, 1999; Womes *et al.*, 2003).

$$M^{n+}(acac)_{n\,(solution)} + [\text{H-O-}\S]_{surface} \longrightarrow [M^{n+}(acac)_n\text{-H-O-}\S]_{surface} \qquad (1)$$

The acac ligands were removed completely after the treatment in flowing H_2 at 300°C. This was confirmed by disappearance of ligand characteristic peaks (spectra 3 and 6 in Figure 2(b)).

Determination of Reductive Decomposition Temperature of Supported Metal Complexes by TPRD

The reductive decomposition temperature based on hydrogen consumption of dry supported samples on γ-Al_2O_3 and MgO are presented in Table 1. The reductive decomposition of supported metal acac species could be explained in equation (2) giving the metal particle on support and decomposition products such as acetylacetone (acacH), isopropanol and acetone or methane (Dossi *et al.*, 2003).

$$M^{n+}(acac)_{n\,(surface)} + H_2 \xrightarrow{\Delta} M_{(surface)} + \text{decomposition products} \qquad (2)$$

All of the observed peaks (Table 1) were broad indicating that the decomposition was a slow process. The supported mixture of $Pt(acac)_2$ and $Ru(acac)_3$ on γ-Al_2O_3 showed reductive decomposition temperature at 124 and 199°C indicating at least two types of supported $Pt(acac)_2$ structures on support, and at 340°C indicating reduction temperature of supported $Ru(acac)_3$. TPRD data of both supported samples indicated that Pt and Ru particles were isolated from one another on γ-Al_2O_3 after the treatment.

The broad reductive decomposition temperatures of $Pt(acac)_2$ on MgO indicated that Pt had various oxidation states or various adsorption modes on MgO, whereas only one oxidation state or one adsorption mode of $Ru(acac)_3$ on MgO was observed. For supported sample on MgO, broad H_2 consumption was observed at 189-221°C indicating that Pt and Ru might contact each other on MgO or change their oxidation states.

However, no Pt-Ru contributions were observed by EXAFS spectroscopy on both catalysts (Chotisuwan *et al.*, 2004a). High dispersion of metals on both supports was confirmed from EXAFS spectroscopy. The average Pt-Pt coordination numbers of PtRu/γ-Al_2O_3 and PtRu/MgO were 2.8 ± 0.1 and 1.0 ± 0.1 whereas the Ru-Ru coordination number of those catalysts were 3.3 ± 0.1 and 3.5 ± 0.1.

Table 1. Reduction temperatures of $Pt(acac)_2$ and/or $Ru(acac)_3$ supported on γ-Al_2O_3 and MgO

Samples	Reduction temperature range (°C)	Peak (°C)
$Pt(acac)_2/\gamma$-Al_2O_3	53 - 282	210
$Ru(acac)_3/\gamma$-Al_2O_3	213 - 375	288
$[Pt(acac)_2 + Ru(acac)_3]/\gamma$-$Al_2O_3$	98 - 144, 163 - 240, 295 - 400	124, 199, 340
$Pt(acac)_2$/MgO	63 - 168, 176 - 235, 250 - 391	140, 202, 340
$Ru(acac)_3$/MgO	92 - 341	216
$[Pt(acac)_2 + Ru(acac)_3]$/MgO	84 - 286	189 - 221

Ethylene Hydrogenation Reaction Catalyzed by Supported PtRu Catalysts

The apparent activation energy of ethylene hydrogenation over supported PtRu catalysts was collected at a steady state, at the temperature ranging from -50 to -10°C. The catalytic activity in terms of the turnover frequency (TOF) was represented the number of molecules reacting per active sites per second based on the assumption that all metal particles dispersed on support accessible to reactants giving a 100% metal dispersion. The Arrhenius plot of a natural logarithmic of TOF as a function of inversed temperature is shown in Figure 3.

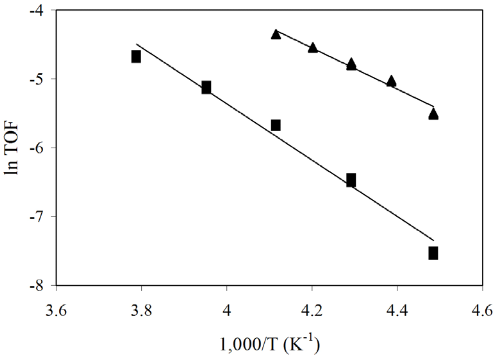

Figure 2. Arrhenius plot for ethylene hydrogenation over (▲) PtRu/MgO; (■) PtRu/γ-Al_2O_3, prepared from the solution mixture of $Pt(acac)_2$ and $Ru(acac)_3$

The supported PtRu catalysts in this work were active for ethylene hydrogenation. The apparent activation energies (E_{app}) of ethylene hydrogenation catalyzed by these catalysts and PtRu catalysts prepared from organometallics containing chloride, a mixture of $Pt(cod)Cl_2$ and $Ru(cod)Cl_2$, (cod = 1, 5-cyclooctadiene or C_8H_{12}) (Chotisuwan *et al.*, 2004b), are shown in Table 2. The supported PtRu/MgO catalyst prepared from a mixture of acac complexes was more active than other catalysts in Table 2. The E_{app} for ethylene hydrogenation of PtRu/γ-Al_2O_3 was comparable to that catalyzed by Pt catalysts supported on oxide supports, ranging from 8.6 to 11.7 kcal/mol, obtained at various conditions (Hwang *et al.*, 2003; Cortright *et al.*, 1991; Dorling *et al.*, 1969). In addition, the E_{app} obtained from this work was near the value obtained from polymer-supported Pt-Ru catalysts prepared from [$RuPt_2(CO)_5(Ph_2P$-Ⓟ$)_3$], 7.8 ± 1.2 kcal/mol obtained at $P_{hydrogen}$ = 555 Torr and $P_{ethylene}$ = 152 Torr, temperature ranges 73 to 98°C (Pierantozzi *et al.*, 1979).

Conclusions

Supported PtRu catalysts were prepared by adsorption of the mixture of $Pt(acac)_2$ and $Ru(acac)_3$ in toluene onto γ-Al_2O_3 and MgO. The

Table 2. Apparent activation energy for ethylene hydrogenation over PtRu catalysts prepared from mixture of $Pt(acac)_2$ and $Ru(acac)_3$, and mixture of $Pt(cod)Cl_2$ and $Ru(cod)Cl_2$, after the treatment in flowing H_2 at 300°C for 2 h

Precursors	Supports	Activity TOF × 10^4 (s^{-1})[a]	E_{app} (kcal/mol)	Temp. (°C)
$Pt(acac)_2 + Ru(acac)_3$	γ-Al_2O_3	1.5 ± 0.1	8.1 ± 0.1	-50 to -10
$Pt(acac)_2 + Ru(acac)_3$	MgO	83.9 ± 1.7	6.0 ± 0.1	-50 to -30
$Pt(cod)Cl_2 + Ru(cod)Cl_2$	γ-Al_2O_3	6.8 ± 0.2	6.7 ± 0.1	-50 to -10[b]
$Pt(cod)Cl_2 + Ru(cod)Cl_2$	MgO	6.9 ± 0.3	6.7 ± 0.1	-50 to -10[b]

[a] Reaction at -40°C, atmospheric pressure with $P_{ethylene}$ = 40/760 Torr and $P_{hydrogen}$ = 200/760 Torr

[b] Chotisuwan *et al.* 2004b

IR data suggested that $Pt(acac)_2$ and $Ru(acac)_3$ adsorbed on the surface of γ-Al_2O_3 and MgO through acac ligands and surface hydroxyl groups. The acac ligand could be removed from supported samples completely after the treatment in H_2 flow at 300°C for 2 h. No Pt-Ru connections were observed in both catalysts. The supported PtRu catalysts prepared in this work were active for ethylene hydrogenation.

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