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Preparation and characterization of the bimetallic Pt–Au/ZnO/Al_2O_3 catalysts: Influence of Pt–Au molar ratio on the catalytic activity for toluene oxidation

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ABSTRACT

The bimetallic Pt–Au catalysts supported on ZnO/Al_2O_3 with different Pt/Au molar ratios were prepared by impregnation (IMP) method using a mixed solution of Pt and Au precursor. These were characterized by X-ray diffraction (XRD), CO chemisorption, temperature programmed reduction (TPR), and transmission electron microscopy (TEM) equipped energy dispersive spectroscopy (EDS). Catalytic activity for complete oxidation of toluene was measured using a flow reactor under atmospheric pressure. In the results, the aggregation of Au particles depended on the molar ratio in the bimetallic Pt–Au catalyst, and Pt particles was well dispersed homogeneously even by the IMP method. The $Pt_{75}Au_{25}$ and $Pt_{67}Au_{33}$ catalysts concurrently coated with Pt and Au precursors by IMP method showed higher activity than monometallic Pt and Au catalyst for toluene oxidation. Also, in order of the catalytic activity for toluene was very good agreement compare with the TPR results. The Au particles might promote the toluene oxidation over the bimetallic catalyst concurrently coated with Pt and Au particles. Therefore, the size of Pt and Au particles and catalytic activity were confirmed to be correlated to molar ratio of Pt and Au loaded.

1. Introduction

Volatile organic compounds are one of the most common pollutants emitted by the chemical process industries, which include most solvents such as thinner, degreasers, cleaners, lubricants, and liquid fuels. VOCs are pollutants because they almost always contribute to ozone formation, and in addition are odorous and sometimes toxic. In other words, they react in sunlight with other pollutants such as nitrogen oxides to form ozone and the other compounds (known as photochemical oxidants), which make up photochemical smog [1–3]. VOCs, such as, toluene is suspected endocrine disrupting chemicals, and is many used in making paints, paint thinner, fingernail polish, lacquers, adhesives, and rubber and in some printing and leather tanning processes.

Several techniques for VOCs have been investigated such as thermal incineration, catalytic oxidation, condensation, absorption, bio-filtration, adsorption, and membrane separation [4]. Among these methods, catalytic combustion has advantageous features for VOCs removal, due to complete combustion of dilute fuel proceeds stably at low temperatures [5]. The main advantages of catalytic combustion compared with other decontamination technologies can be summarized as follows: high efficiency at very low pollutants concentration, low energy consumption, small size of the depuration unit, and very low production of secondary pollutants (NO_x).

The bimetallic catalysts are particularly attractive because of their ability to improve the catalytic properties of metals [6–8]. They are widely used for many industrial processes because they can improve the activity and selectivity of the single metal catalyst in a given chemical reaction [9]. However, it is difficult to thoroughly understand their surface characteristics, i.e., changes in surface atomic structure depending on the preparation of the bimetallic catalysts [10]. Therefore, many efforts have been made to investigate the chemical characteristics of the bimetallic catalysts.

Platinum catalysts are known to be catalytically very active for the oxidation of hydrocarbons [11]. And it has been reported that nanosized gold particles on metal oxides such as Al_2O_3, Co_3O_4, NiO and Fe_2O_3 have been reported to oxidize CO or H_2 actively, even at low temperatures [12], selective catalytic reduction (SCR) of NO_x [13], and to facilitate the oxidation process. In addition, nanosized gold supported on ZnO/Al_2O_3 increased the catalytic activity for complete methanol oxidation [14]. The bimetallic formed between platinum and gold changes the catalytic behavior compared to the single metal phase, thereby increasing the

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selectivity toward certain products while also decreasing the deactivation rate [15].

The oxidation mechanism of toluene is highly exothermic reaction ($C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$, $\Delta H = -93.98$ kcal/mol), and hence its equilibrium constant decreases with the temperature, and high conversions are favored by low temperatures. So far, the reaction mechanism of toluene was not clearly, but it was expressed Langmuir–Hinshelwood model; the oxygen is dissociated and adsorbed on the metal particle, the adsorbed oxygen reacts with toluene that was adsorbed on support to form the reaction products carbon monoxide and water [16]. Furthermore, catalytic activity is strongly dependent on the particle size of metal, and the combination of metal and support is indeed a superior catalyst for complete toluene oxidation. Consequently, it is worthy to investigate the factors influencing the activity of toluene complete oxidation over the bimetallic Pt–Au catalysts. The purpose of this study was to investigate the physical characteristics of Pt and Au particles on ZnO/Al_2O_3 prepared with different molar ratios, and their catalytic activity for toluene oxidation.

2. Experimental

2.1. Preparation of catalysts

The catalysts were prepared by loading Pt and Au particles on ZnO/Al_2O_3. Zinc oxide with 4 wt% loading supported on alumina (γ-Al_2O_3, 177 m^2/g, <120 mesh, JRC-ALO-4) was prepared by the conventional IMP method, and the statistical method was similar to that reported elsewhere [13]. Aqueous solutions of $H_2PtCl_6 \cdot 5H_2O$ (Aldrich) and $HAuCl_4 \cdot 3.7H_2O$ (Kojima) were used as the precursor of Pt and Au, respectively. The bimetallic Pt and Au catalyst of various molar ratios (Pt:Au = 0:1, 1:1, 1:2, 1:3, 2:1, 3:1 and 1:0) were prepared on ZnO/Al_2O_3 by IMP method. Loading contents of Pt and Au with molar ratios were calculated for ZnO/Al_2O_3 (Table 1). The ZnO/Al_2O_3 powder was put into the precursor solution of Pt and Au, and the water was evaporated in a water bath. The remaining powder was dried for 24 h in a dry oven of 100 °C, and calcined in air at 500 °C for 5 h.

2.2. Characterization of bimetallic catalyst

Instrumental analyses were carried out to investigate the physical characteristics of the prepared catalysts. A nitrogen gas adsorption analyzer (ASAP 2010, Micromeritics) was used to observe change in specific surface area at −196 °C. Before analysis, the catalyst was preheated in He for 3 h at 250 °C. Specific surface values were computed using the BET equation from the amount of N_2 physisorbed at different relative pressures.

Temperature-programmed reduction (TPR) measurements were performed using a commercial TPR apparatus (neo-TPD) from Mirae Scientific Instruments. Moisture trap (−77 °C, dry ice-acetone) for removing the water formed during reduction was mounted in the gas line prior to the thermal conductivity detector. The sample (100 mg) in a quartz reactor was pretreated with 50 ml/min of Ar during 1 h at 300 °C to eliminate possible contaminants, and then cooled to room temperature in Ar gas flow before reduction was performed. A gaseous mixture of 1%-H_2/in Ar was fed to the reactor at 50 ml/min. The temperature was raised to 500 °C at a heating rate of 10 °C/min. The amount of consumed hydrogen was measured by a thermal conductivity detector (TCD).

The crystalline phases were identified by X-ray diffraction (XRD) in a D/Max 2200 instrument (Rigaku) operating at a 40 kV and a current of 30 mA with Cu $K\alpha_1$ radiation in the 2θ scan range from 10° to 100° with a step size of 0.04°. Measured XRD patterns were compared with JCPDS file. Scherrer's equation was applied to the major (1 1 1) peak in the corresponding diffraction pattern [17]:

$$d_{Au}(\mathrm{nm}) = \frac{k \cdot \lambda}{FWHM \cdot \cos\theta}$$

where k is a shape factor of the average crystallite (0.9), and λ and θ are the wavelength (0.154059 nm for Cu $K\alpha_1$) and incident angle of the X-rays, respectively. FWHM is the full width at half maximum of the peak in radians.

CO chemisorption was performed using the pulse method [18]. For reference, it was verified that pure $Au/ZnO/Al_2O_3$ does not chemisorb CO at 25 °C. Therefore, CO chemisorption applied to only Pt particle determination. The Before chemisorption, the following pretreatment procedure was applied: the sample (0.1 g) was reduced in H_2 flow rate of 15 ml/min for 2 h at 400 °C, purged in He at 400 °C for 1hr and then cooled to room temperature. Gas mixture of 10%-CO/He was used as a probe gas. Injection of the gas mixture into a He carrier gas stream flowing at 30 ml/min was done at 5 min interval. The amounts of CO chemisobed was measured by using a gas chromatograph (GC-14B, Shimadzu) with thermal conductivity detector (TCD).

The dispersion (D) and mean particle size (d_{Pt}) of Pt can be calculated from the total amount of CO adsorbed. The Pt dispersion and mean particle size are determined by assuming an adsorption of 1 CO per surface Pt site:

$$D(\%) = \frac{X \cdot MW_M}{W_M} \times 100$$

$$d_{Pt}(\mathrm{nm}) = \frac{6 \cdot W_M}{X \cdot 6.02 \times 10^{23} \cdot \rho_M \cdot S_M}$$

Table 1

The nomenclature, the metal loadings, the BET surface area, CO chemisorption and X-ray diffraction data of the bimetallic Pt–Au catalysts with various molar ratios.

Nomenclature	Molar ratio (Pt:Au)	Pt loading[a] (wt%)	Au loading[a] (wt%)	BET surface area (m^2/g)	Pt			Au	
					CO uptake (μmol/g)	Dispersion (%)	Mean diameter[b] (nm)	FWHM[c]	Mean diameter[d] (nm)
$Pt_{100}Au_0$	1:0	3.75	0	177.2	78	41	2.8	–	–
$Pt_{75}Au_{25}$	3:1	2.98	1.03	176.5	81	54	2.1	0.299	28.1
$Pt_{67}Au_{33}$	2:1	2.69	1.38	168.7	89	65	1.7	0.275	30.6
$Pt_{50}Au_{50}$	1:1	2.10	2.13	166.6	47	44	2.6	0.197	42.7
$Pt_{33}Au_{67}$	1:2	1.46	2.90	175.4	46	63	1.8	0.183	45.9
$Pt_{25}Au_{75}$	1:3	1.12	3.33	173.3	34	61	1.9	0.176	47.8
Pt_0Au_{100}	0:1	0	4.64	168.0	–	–	–	0.125	67.3

[a] Loading content of Pt and Au was calculated on the assumption that none loss of catalyst during the preparation process by IMP.

[b] Caculated from the CO chemisorption.

[c] Full width at half maximum of the peak in radians.

[d] Mean diameter of gold estimated by line broadening of powder XRD peak at $2\theta = 38.2°$ using the Scherrer equation.