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Monolithic Pt-Au/ZnO/Al₂O₃/Cordierite Nanocatalysts for Air Pollution Control

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The catalytic activity of a monolithic catalyst with nanosized Pt and Au particles on ZnO/Al₂O₃ (Pt-Au/ZnO/Al₂O₃/M) prepared by a wash-coat method was examined, specifically for toluene oxidation. FE-SEM image showed clearly the formation of a ZnO/Al₂O₃ layer on the monolith. Nanosized Pt-Au particles on ZnO/Al₂O₃/M with different sizes could be found in the Pt-Au/ZnO/Al₂O₃/M catalyst. The conversion of toluene decreased with increasing toluene concentration and was also largely affected by the feed flow rate. The Pt-Au/ZnO/Al₂O₃/M catalysts prepared in this work have almost the same activity (molecules of toluene per second) compared with a powder Pt-Au/ZnO/Al₂O₃ catalyst with the same loadings of Pt and Au components; thus this catalyst could be used in controlling air pollution with very low concentrations and high flow rate.

Keywords: Nanosized Pt-Au Particle, ZnO/Al₂O₃, Monolithic Catalyst, Wash-coat, Toluene Oxidation.

1. INTRODUCTION

For pollution abatement applications it is common to utilize a monolithic honeycomb structured catalyst to minimize the pressure drop associated with high flow rates.^{1,2,3,4} Commercial ceramic monoliths have low surface area and large pores, so it is necessary to deposit a high surface area support, which is subsequently catalyzed, onto the channel walls. The catalyzed coating is composed of a high surface support impregnated with catalytic components. Generally, the most commonly used support is γ -Al₂O₃ due to the chemical, hydrothermal, and mechanical stability.^{5,6} This is referred to as the wash-coat. In these processes, the main problems are obtaining homogeneity with a good adhesion of the oxide layer and achieving high dispersion of the active metal on that oxide layer.

In our previous work,⁷ the bimetallic Pt and Au catalyst supported on ZnO/Al₂O₃ was used for complete volatile organic compound oxidation, and the relationship between their particle sizes and catalytic activity was investigated. It was found that nanosized gold particles greatly promoted the reduction of surface oxygen at lower temperatures. Therefore, the coexistence of Pt and Au on ZnO/Al₂O₃ shows a higher activity for toluene oxidation than either the Pt or Au alone.

In this study, the Pt-Au/ZnO/Al₂O₃ catalyst on monolith (Pt-Au/ZnO/Al₂O₃/M) was prepared by the wash-coat method. Catalytic performances for toluene oxidation over Pt-Au/ZnO/Al₂O₃/M were investigated in order to apply to the treatment of tail gas with high flow rates.

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2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

The monolithic catalyst was sequentially prepared as follows: Monolith (M) \rightarrow Al₂O₃/M \rightarrow ZnO/Al₂O₃/M \rightarrow Pt-Au/ZnO/Al₂O₃/M.

Monolithic honeycomb (400 cell/in², ORDEG, Korea) was cut into 15 mm by 50 mm cylinder, and Al(NO₃)₃ (50w/v% in DI water) was used as the Al₂O₃ precursor for monolithic catalyst. Monolith was impregnated with the Al(NO₃)₃ solution several times to get a final loading of Al₂O₃ ca. 10wt% of the weight of monolith. And dried for 24 h in a dry oven of 100 °C, and calcined in air at 600 °C for 5 h. Afterward, the monolith was impregnated with Zn(NO₃)₂ solution in order to correspond to 4wt% of ZnO, and dried for 24 h in a dry oven of 100 °C, and calcined in air at 500 °C for 5 h. Finally, 20 mL of aqueous solution of H₂PtCl₆ (1.95 x 10⁻² M) and HAuCl₄ (2.47 x 10⁻² M) as the precursors of Pt and Au was added slowly dropwise with continuous stirring at room temperature. Immediately afterwards, the resulting monolith was dried for 24 h in a dry oven of 100 °C, and calcined in air at 500 °C for 5 h. The relative loading of ZnO to Al₂O₃ was 4wt%, and Pt and Au were loaded at 2.13wt% and 2.10wt% (molar ratio: Pt/Au = 1), respectively. In addition, a powder Pt-Au/ZnO/Al₂O₃ catalyst was also prepared by co-impregnation with same loading contents of Pt and Au in order to compare with Pt-Au/ZnO/Al₂O₃/M catalyst.

2.2. Characterization

The surface morphology and composition of the Pt-Au/ZnO/Al₂O₃/M catalyst was characterized by high-resolution field emission-scanning electron microscope (FE-SEM, JSM-7001F, Jeol or S-4800, Hitachi) using 15-20 kV accelerating voltage. Secondary electron (SE) images and backscattered electron (BSE) images, whose contrast is mainly sensitive to morphology and composition, were recorded. The chemical composition of representative surface particles was analyzed by energy dispersive spectroscopy (EDS). The size of the Pt and Au particles were observed using transmission electron microscopy (TEM) as well as scanning TEM (STEM, 2010F,

Jeol) operating at 200 kV. Histograms of the particle size distribution were obtained in the micrographs, and the average particle diameter (d_M) was calculated using the formula $d_M = \sum di \cdot ni / \sum ni$, where ni was the number of particles of diameter di .

2.3. Activity Test

The experimental setup used to investigate the catalytic oxidation characteristics of toluene was a continuous flow type under atmospheric pressure. To investigate the catalytic activity, toluene (ACS grade, Aldrich) mixed with high purity air (99.999%) was used as a model gas, and an air flow was added to dilute the concentration of the model gas. The concentration of toluene for catalytic oxidation was controlled by vaporizing toluene in a saturator with air with a constant temperature vessel. A U-shaped pyrex tube with an inner diameter of 7 mm was used as the reactor. A thermocouple (Al-Cr) was inserted into the catalyst bed to control the reaction temperature. The temperature of the stream line was maintained at 100 °C by using a heating band and insulating material, and adjusted by an on/off temperature controller. The catalyst was pretreated with helium (30 mL/min) for 1 h at 300 °C. The effect of space velocity at different temperatures and reproducibility were also tested. The reactants (air and toluene) and products (CO₂ and H₂O) were analyzed by using the thermal conductivity detector of a gas chromatograph (HP-6890) equipped with a 6-way valve for on-line sampling.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

Fig. 1 shows FE-SEM images of the as-prepared Pt-Au/ZnO/Al₂O₃/M catalyst by wash-coat. The cross-sectional FE-SEM images (Figs. 1a and 1b) show a formation of a ZnO/Al₂O₃ layer (dotted line) near the surface, which is irregularly coated in the corners of the channels. ZnO/Al₂O₃ layer was well coated by wash-coat using precursor solution as Al(NO₃)₃ and Zn(NO₃)₂, respectively.

More detail at higher magnification of Pt-Au

particles on ZnO/Al₂O₃ layer is shown in Fig. 1c. It consists of many Al₂O₃ crystallites of irregular shape and size. It was thought that this was attributable to the thermal expansion coefficient of the monolith support being different from the oxide layer. The location of the Pt-Au particles, which shows as bright contrast, is seen on ZnO/Al₂O₃/M (Fig. 1c). The Pt-Au particles could be highly dispersed on monolith like on powder supports such as ZnO/Al₂O₃.

Fig. 1d shows a magnified image of a specific site in order to see the metal compositions of the particles in Pt-Au/ZnO/Al₂O₃/M catalyst. It can be seen that spherically nanosized particles in area 1 (A1) were obtained on Al₂O₃/M, and very homogeneously coated in the range from 25 to 30 nm. However, the Pt-Au particles were presented in larger sizes on ZnO/Al₂O₃/M surfaces. Furthermore, the results for elementary analyses of A1-3 in Fig. 1d were summarized in Table 1. From the EDS result, it can be confirmed that the Pt was detected in A2, while Au particles were observed in both A2 and A3, indicating that the Au particles exist on the top of Pt particles. For reference, from the XRD results, the Pt and Au were simultaneously deposited as metallic particles on the ZnO/Al₂O₃/M without forming an alloy with the Pt and Au.

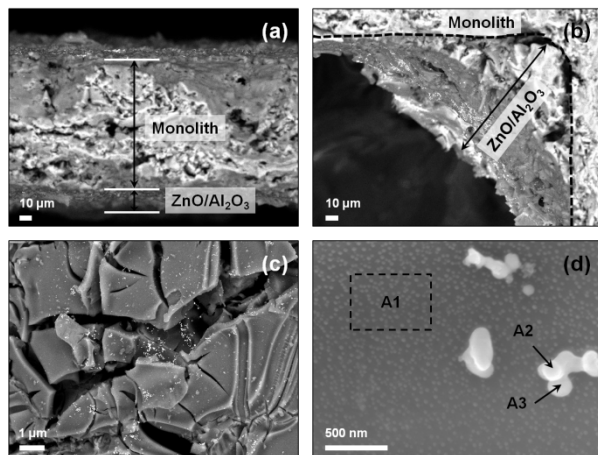


Fig. 1. FE-SEM images of Pt-Au/ZnO/Al₂O₃/M catalyst prepared by wash-coat: Cross-sectional BSE image for wall (a, x500) and edge (b, x500). The magnified front side BSE image (c, x1,000) and SE image (d, x5,000).

Table 1. Elementary analysis of areas 1-3 in Fig. 1
Elements composition (weight%)

	C	O	Al	Zn	Pt	Au
A1	1.74	49.12	45.01	4.13	ND	ND
A2	2.16	14.42	13.51	ND	ND	69.91
A3	3.30	18.35	10.94	ND	9.20	58.21

ND: Not detected.

Dispersion state of Pt and Au particles supported on ZnO/Al₂O₃/M with only Al₂O₃ layer was observed from FE-SEM images. Fig. 2a shows STEM images of the crushed Pt-Au/ZnO/Al₂O₃/M catalysts. Nanosized particles could be found in the Pt-Au/ZnO/Al₂O₃/M catalyst with varying sizes. It was found that the sizes of Pt-Au particles were in the range from 2 nm to 38 nm, mainly 2 nm to 18 nm. Unfortunately, the STEM image for the Pt and Au particles on ZnO/Al₂O₃/M could not be used to distinguish directly between the two due to the similar contrast and very small difference in the *d* spacing. According to EDS analysis (data not shown), large particles have abundant Au content compared to small particles. In addition, more Pt particles were detected in areas that contained Au particles. This result indicate the Au particles were aggregated relatively more large size than Pt particles on ZnO/Al₂O₃/M by wash-coat method.

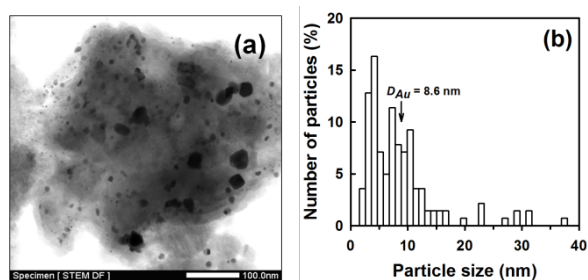


Fig. 2. STEM image (a, x250,000) and particle size histogram (b) of the crushed Pt-Au/ZnO/Al₂O₃/M catalyst.

3.2. Catalytic Activity for Toluene Oxidation

The catalytic activity of Pt-Au/ZnO/Al₂O₃/M catalyst was compared with that of powder catalyst, Pt-Au/ZnO/Al₂O₃. Fig. 3 shows the

catalytic activity for toluene oxidation of Pt-Au/ZnO/Al₂O₃ and Pt-Au/ZnO/Al₂O₃/M catalysts at the same weight hourly space velocity (WHSV = 24,000 cm³ g⁻¹ h⁻¹). The Pt-Au/ZnO/Al₂O₃/M catalyst has a similar activity compared with the powder Pt-Au/ZnO/Al₂O₃ catalyst even if same WHSV, which implies the existence of a strong mass-transfer in the channels of the Pt-Au/ZnO/Al₂O₃/M catalyst.⁸

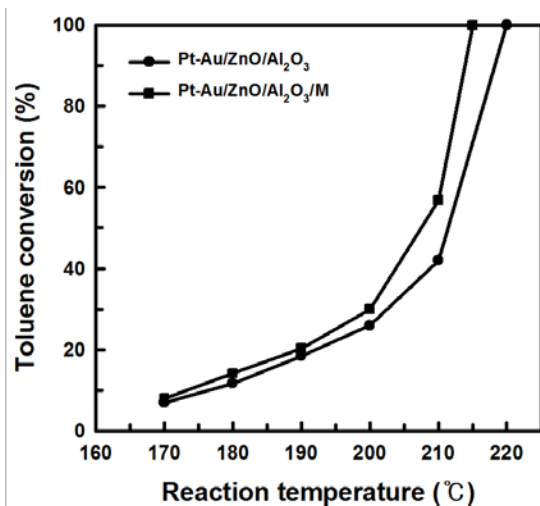


Fig. 3. Catalytic activity for toluene conversion with reaction temperatures over Pt-Au/ZnO/Al₂O₃ and Pt-Au/ZnO/Al₂O₃/M catalysts (WHSV : 24,000 cm³ g⁻¹ h⁻¹, Concentration : 1.8 mol%).

Furthermore, catalytic activity of the Pt-Au/ZnO/Al₂O₃/M catalyst was investigated for various concentrations and flow rates of toluene. The effect of the concentration of toluene on the catalyst activity with reaction temperature was shown in Fig. 4. The conversion is decreased when increasing the toluene concentration, which was due to the strongly adsorbed toluene covering the active sites; in other words self poisoning.⁹ The deficiency of oxygen adsorption can decrease the oxidation rate of the catalyst. It is therefore expected in controlling VOC emissions with very low concentrations and high flow rate.

Fig. 5 shows effect of GHSV in the range of 272 - 815 h⁻¹ on toluene conversion over the Pt-Au/ZnO/Al₂O₃/M catalyst, which can minimize the pressure drop associated with high flow rates. Activity in toluene oxidation was decreased as

flow velocity is increased at the reaction temperature of 190 °C and 210 °C. This fact suggests that the Pt-Au/ZnO/Al₂O₃/M catalyst was strongly affected by feed flow rate.

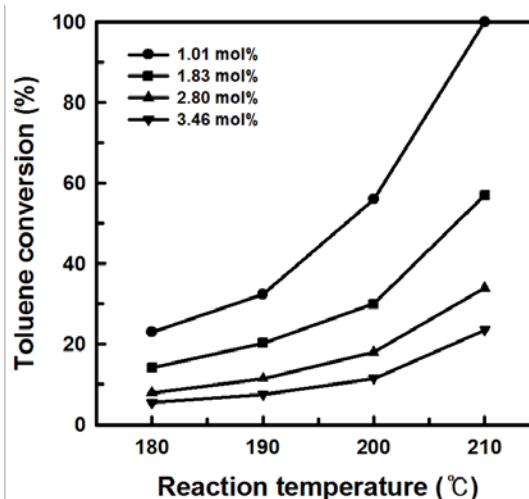


Fig. 4. The effect of toluene concentration on conversion with reaction temperatures over Pt-Au/ZnO/Al₂O₃/M catalyst (GHSV : 679 h⁻¹).

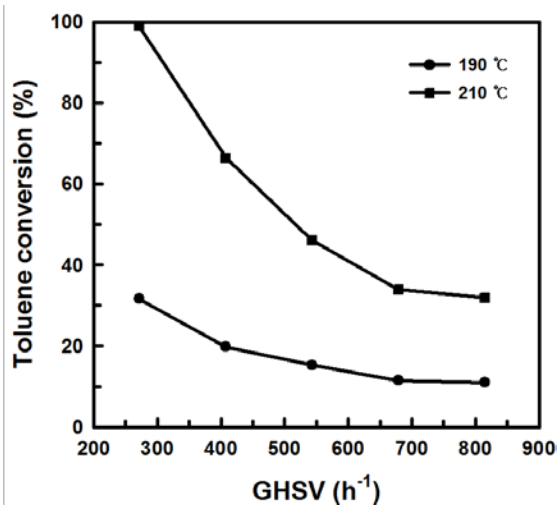


Fig. 5. Effect of GHSV of toluene on conversion over Pt-Au/ZnO/Al₂O₃/M catalyst prepared by wash-coat (Concentration: 2.8 mol%).

The stability test was performed at 210 °C during 40 h with 408 h⁻¹ of GHSV and 2.8 mol% of concentration over Pt-Au/ZnO/Al₂O₃/M in toluene oxidation activity (Fig. 6). It was

confirmed that the Pt-Au/ZnO/Al₂O₃/M has a good stability with 65.3 ± 2.3 % of conversion, which means the Pt-Au/ZnO/Al₂O₃/M catalyst using wash-coat could be an effective monolithic catalyst applicable to an environmental catalyst system.

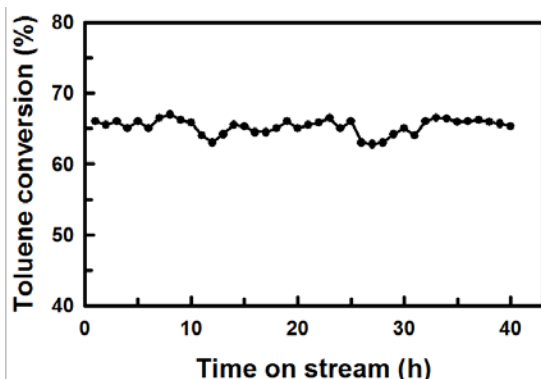


Fig. 6. Stability test on toluene conversion over Pt-Au/ZnO/Al₂O₃/M (Reaction temperature: 210 °C, Concentration: 2.8 mol%, GHSV: 408 h⁻¹).

4. CONCLUSION

FE-SEM imaging showed clearly the formation of ZnO/Al₂O₃ layer, and confirmed the presence of Pt-Au particles on ZnO/Al₂O₃/M. Spherical ZnO particles were obtained on Al₂O₃/M, and were very homogeneously dispersed. Nanosized Pt-Au particles with different sizes could be found in the Pt-Au/ZnO/Al₂O₃/M catalyst. The Pt-Au/ZnO/Al₂O₃/M catalyst showed a decreasing trend for toluene conversion when the concentration of toluene is increased. The Pt-Au/ZnO/Al₂O₃/M catalyst also has good long term stability for toluene oxidation, although the toluene conversion is decreased with increasing space velocity. As a result, the Pt-

Au/ZnO/Al₂O₃/M catalyst is likely to efficiently treat large volume of exhaust gas containing VOCs.

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