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Carbon Grain Supported Nano-Sized Au for Low Temperature Removal of VOCs in Humid Condition: Effect of Catalyst's Synthesis Conditions

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This study reports effects of pH and PVA/Au mass ratio on properties and catalytic activity of carbon grain supported nano Au catalysts for treatment of VOC pollutants at low temperatures. The catalysts were synthesized at various pH of the sol solution and different PVA/Au mass ratios. They were characterized by specified techniques to evaluate crystallinity, surface properties, and morphology. The catalytic activity for VOCs removal has been conducted in the temperature range 100-200 °C and in the presence of water vapor. The relationship between catalyst's characterization and the low-temperature catalytic activity was evaluated, and the synergy effect in the dual functional adsorbent/catalyst was reported. Nano Au supported on granular carbon, which was synthesized with mass ratio PVA/Au = 4 at pH = 4, can removal toluene about 50.3 % from initial concentration of 314 ppmv after 60 min reaction at the reaction temperature 150 °C and high humidity (RH = 60 %). Furthermore, moisture reduces the activity only slightly due to the hydrophobicity of activated carbon, and the durability of the catalyst was also reported.

1.Introduction

Currently, chemical productions such as paint, adhesive, petrochemical industries emit huge volatile organic compounds (VOCs) as solvents or by-products. Volatile organic compounds with boiling points between room temperature and 260 °C was acknowledged as the major contributors to global air pollution. Amongst the most common and toxic non-halogenated compounds, benzene, toluene, formaldehyde, propylene, phenol, acetone, and styrene caused the major concern to scientists. Currently, many technologies have been used for VOCs treatment (adsorption (Iovino et al., 2013), hydrogenation (Zhao et al., 2019), etc.), but catalytic oxidation is considered to be the most promising method for VOCs destruction (Kamal et al., 2016). The problem that needs to be solved with oxidation catalyzed VOCs is that the reaction temperature is usually above 200 °C (Huang et al., 2015).

When the oxidation process is operated at low temperature, the catalyst can be poisoned by moisture. Reports on the effect of moisture on catalytic oxidation at low temperature are limited. Saleh-Alhamed et al. (1996) concluded that water suppresses the formation of products by blocking the most active sites. Bedia et al. (2010) used Pd catalysts supported on mesoporous carbon grains for the oxidation of toluene. Mesoporous carbon grains were obtained by chemical activation of kraft lignin with phosphoric acid (H_3PO_4) and were used as support for the preparation of carbon-based palladium (Pd) catalysts with low Pd content (0.5 %). Toluene and xylene were oxidized to carbon dioxide (CO_2) and water (H_2O) in the temperature range of from 150 to 400 °C at a space velocity of 19,000 h^{-1}, the effect of water vapor on toluene oxidation and xylene oxidation of the catalyst has not been investigated.

Among conventional noble metal catalysts, nanogold deposited on various supports presented their remarkable activity for VOCs oxidation at the low temperatures (Wang et al., 2017) due to its electronic configuration (Haruta and Daté, 2001). Long et al., (2008) researched the catalytic activity of nano-sized Au/TiO_2 catalysts for the selective catalytic reduction of NO_x by propene in the gas phase. Minh et al., (2018) synthesized nano-sized Au/Fe_2O_3/GAC and nano-sized Au/CeO_2/GAC for toluene catalytic oxidation. The

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results showed that nano Au is a promising active for the catalytic oxidation reaction. Iovino et al., (2013) reported that the granular carbon can be utilized for toluene removal by adsorption.

For the above reasons and for development of a ready-to-use catalyst, this study has focused on i) utilization of granular carbon (GC) as support in the synthesis of nano Au catalyst by a metal-sol method; ii) investigation of the VOCs removal at low temperatures using the nano Au catalysts under high humid condition; iii) synergetic effect between adsorption and catalytic oxidation and iv) catalyst stability evaluation with/without water vapor. Toluene has been selected as a VOC model for this study.

2. Materials and methods

2.1. Preparation and characterization of materials

The granular carbon with the particle size of 0.5-1 mm supplied by TRABAC Joint Stock Corporation was used as supports. Granular carbon was produced from the coconut-shell. This material is very popular in Vietnam. Other chemicals ($HAuCl_4.3H_2O$ Acros, $NaBH_4$ Acros, and polyvinyl alcohol PVA Fisher) were used in this study. A suitable amount of PVA solution (1 wt%) was added to an aqueous $HAuCl_4$ solution (0.4 mg Au/mL) under vigorous stirring. After that, a freshly prepared solution of $NaBH_4$ (molar ratio $NaBH_4$/Au = 4) was slowly added dropwise into the mixture. The GC was added after the pH of the sol solution was adjusted to about 4 using NH_4OH or HCl solution. The mixture was stirred and vacuumed at 50 °C to dry, then filtered and washed until no Cl^- was detected by $AgNO_3$ solution. After being dried at 100 °C overnight. The pH value varied from 3 to 5; the PVA/Au ratio (w/w) varied from 0 to 4 for the sample Au (0.5 wt%)/GC.

The crystalline structure of the above catalysts was analyzed by powder X-Ray diffraction using Advance D8 diffractometer, with Cu K_α radiation (λ = 1.5418 Å) operated at 40 kV and 30 mA, measurement step 0.01°, over a 2θ range from 10° to 80° at a scan rate in 2θ about 4°/min. The crystallite sizes were estimated from the line broadening of the (111) peak obtained. The crystallite size D was calculated from the Scherrer equation in Eq(1):

$$\mathrm{D} = \frac{0.9\times\lambda}{\mathrm{B}\times\cos\theta} \tag{1}$$

Where λ is the wavelength of the X-rays, θ is the diffraction angle, and B is the corrected full width, at half-maximum of the peak.

The surface area of the materials was measured by N_2 adsorption-desorption (BET) using NOVA 2200e, Quantachrome Instruments version 10.0. In order to confirm the size as well as the size distribution of Au particles, we used transmission electron microscopy (TEM) by using JEOL – JEM 1400 operated at 100 kV. Scanning electron microscopy (SEM) was used to determine the morphology of catalysts by using JEOL – JSM 5500 operated at 10 kV.

2.2. Toluene removal test

The efficiency for toluene removal of the dual functional adsorbent/catalysts in this work was processed in a packed bed reactor constituted by a U-shaped glass reactor with 12 mm internal diameter, operated in continuous mode and was performed under atmospheric pressure. The N_2 gas (99.99 %) and O_2 (99.9 %) from Phu-Thinh company and toluene (99.8 %) from Sigma Aldrich were used in the experiments. Catalysts (0.2 g) were deposited on a glass wool layer. Before using, each catalyst was pre-treated under flowing N_2 (with the flow rate of 6 L/h) at 200 °C in 1 h. The gaseous feed was obtained by passing model air (80 % N_2 and 20 % O_2) through two parallel saturators, one containing toluene in a thermostat bath and the other containing distilled water for the wet condition. Both were kept at the appropriate temperatures to ensure that the toluene concentration in the gaseous feed was 314 ppmv for humid condition, and water vapor content of 18.5 mg/L (relative humidity 60 % at 25 °C) for wet condition. The total gas flow rate was 150 mL/min, corresponding to GHSV of approximately 31,000 h^{-1}. The catalytic activity was evaluated in the temperature range from 100 °C to 200 °C. The products of oxidation reaction were monitored with an online Gas Chromatograph HP-5890plus equipped with a flame ionization detector and HP-Plot/Q (30 m x 0.53 mm) column. Notably, the 6-way valve system allows operating different processes without changing the pipeline of the system. The equation calculates the toluene removal efficiency in Eq(2):

$$\text{Toluene removal efficicency (\%)} = 100\text{-}\frac{\mathrm{S_{toluene}}}{\mathrm{S_{toluene\_o}}} \times 100 \tag{2}$$

Where $S_{toluene}$ and $S_{toluene\_o}$ are the area of the GC result's peak of the toluene at a reaction time (t) and the beginning (t=0).

3. Results and discussion

In this work, two critical parameters in the metal sol method were investigated in the preparation of nano-sized gold on carbon grain supports: (1) the pH of the sol solution and (2) the mass ratio of PVA to Au (PVA/Au). The XRD patterns of the prepared materials were shown in Figure 1 to understand the crystal structures.

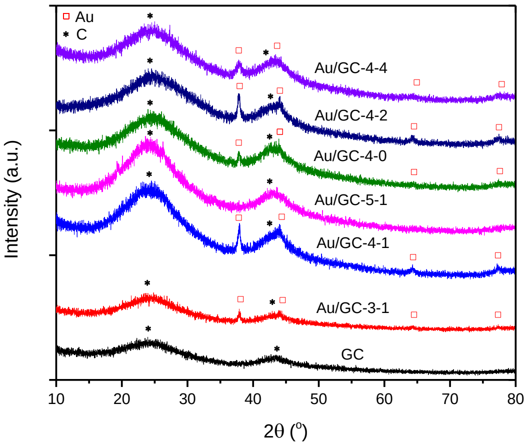

Figure 1: XRD patterns of samples

The reflection for polycrystalline Au was detected at 2θ ≈ 37.9°, 44.2°, 64.4°, 77.4°. The average size of gold crystallites, estimated from the line-width of the peak at 2θ ≈ 37.9° (111) by Scherrer equation, was less than 18 nm for samples Au/GC, this finding is in the right with recent literature result (Long et al., 2008). According to Figure 1, no characteristic diffraction peak of Au observed at pH = 5 (Au/GC-5-1), because activated carbon has pH_{PZC} = 5 (Newcombe et al., 1993). When pH = pH_{PZC} activated carbon was neutral, and gold particles negatively charged, activated carbon cannot hold Au particles on the surface. When pH = 3, pH = 4 ($pH < pH_{PZC}$) making activated carbon have a positive charge while Au nanoparticles have a negative charge, activated carbon will keep gold nanoparticles on the surface area better. The pH of the sol solution may not affect the size of the Au crystallites because the Au crystallites sizes were 14.8 nm and 14.5 nm for Au/GC-3-1 and Au/GC-4-1 (as shown in Table 1). Therefore, when changing the pH of the sol solution, the Au crystallite size was almost unchanged. This result is consistent with the previously published study (Long et al., 2008).

Table 1: Physicochemical properties of catalysts

Catalyst	pH	PVA/Au (w/w)	Crystallite size from XRD (nm)	BET surface area (m^2/g)	Pore volume (cc/g)
GC	-	-	-	728	0.016
Au/GC-3-1	3	1	14.8	-	-
Au/GC-4-1	4	1	14.5	-	-
Au/GC-5-1	5	1	-	-	-
Au/GC-4-0	4	0	17.4	-	-
Au/GC-4-2	4	2	12.5	-	-
Au/GC-4-4	4	4	8.4	675	0.015

The effect of the PVA/Au ratio on the Au crystallines size, which was calculated by Scherrer's equation, is shown in Table 1. The Au crystallines size was changed depending on the PVA/Au ratio. When the PVA/Au increased from 0 to 4, the crystallines size of Au decreased and reached 8.4 nm at PVA/Au = 4. Because the half-maximum of the characterization peak of Au (111) at 2θ ≈ 37.9° of sample Au/GC-4-4 is more extended than compared to the remaining Au/GC samples. The PVA can help dispersed Au crystallines on the surface of activated carbon, and when the crystallines disperse well, the size of the crystallines is minimal (Long et al., 2008). The BET surface area and the pore volume of the Au/GC materials decreased compared to the initial GC. The SEM images of the GC and Au/GC in Figure 2, the GC surface is porous holes; the porous GC holes are tubular. The GC image measured by this SEM is similar to the previously published research (Yan et al., 2019). After depositing the Au particle on the GC, the GC surface is still porous holes but surface the porous holes has a well-dispersed metal layer, which can be used to explain why the BET surface area and the pore volume of the catalyst decrease after adding Au.

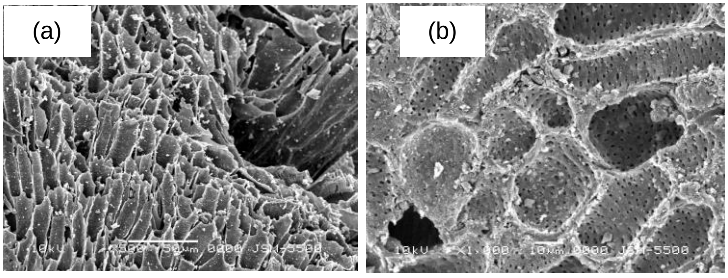

Figure 2: SEM images of (a) GC, and (b) Au/GC-4-4

The particles size of the Au was determined by the TEM analysis. Typical TEM images of Au/GC-4-1 and Au/GC-4-4 and size distribution of nano Au particles was presented in Figure 3; the mean particle sizes were obtained by measuring individuals Au particles was shown in Figure 3a and Figure 3b. The nano Au image measured by this TEM is similar to the previously published research (Minh et al., 2018). The particles size distributions were shown in Figure 3c. For the Au/GC-4-1 sample, 86 % of the Au particles had the particle diameter in the range of 10-20 nm. The Au/GC-4-4 sample had about 68 % of Au particles were in a smaller size (1-10 nm). From the above results, Au nanoparticles dispersed relatively well on GC.

Figure 3: TEM images of (a) Au/GC-4-1, (b) Au/GC-4-4 and (c) size distribution of nano Au particles

Subsequently, the materials were evaluated for catalytic activity. The toluene removal efficiency of samples GC, Au/GC-4-0, Au/GC-4-1, Au/GC-4-2, and Au/GC-4-4 under wet condition (RH = 60 %), in the temperature range 100-200 °C after 60 min reaction are shown in Figure 4.

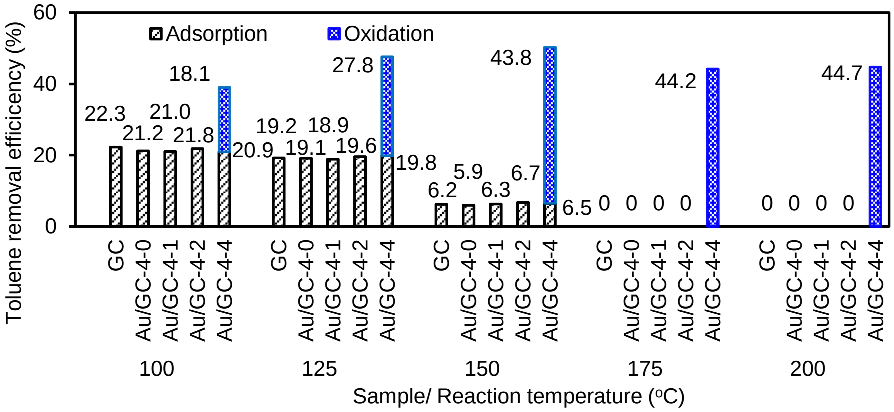

Figure 4: Toluene removal efficiency of GC, Au/GC-4-0, Au/GC-4-1, Au/GC-4-2, and Au/GC-4-4 under a humid condition at various temperatures after 60 min by adsorption–oxidation ($m_{catalyst}$ = 0.2 g, flow rate 150 mL/min, $C_{toluene}$ = 314 ppmv, RH = 60 %)

The toluene removal efficiency of the Au/GC-4-0, Au/GC-4-1, and Au/GC-4-2 samples by adsorption and oxidation is almost similar to that of the carbon grain. Thus, the toluene removal efficiency of the Au/GC-4-0, Au/GC-4-1, and Au/GC-4-2 samples may be only adsorption. Especially, the toluene removal efficiency of Au/GC-4-4 sample was 50.3 % at initial concentration of 314 ppmv at 150 °C by adsorption and oxidation. In particular, the toluene oxidation efficiency of Au/GC-4-4 sample reached 43.8 % at initial concentration of 314 ppmv after 60 min reaction. This result is consistent with the Au nanoparticle size measured by TEM as shown in Figure 3, and the Au crystallines size measured by XRD as shown in Table 1. Because Au nanoparticles may have oxidative activity when Au nanoparticle size is less than 10 nm (Haruta et al., 1989). Therefore, the toluene removal efficiency by oxidation reaction only for Au/GC-4-4 and by adsorption only for remainder materials. At 150 °C the highest slope intercept, thus the desorbed temperature of toluene is 150 °C. This result agreed with the results of Kim et al. (2006) when investigating about the adsorption-desorption characteristics of VOCs over carbon grain, maximal desorption concentrations of toluene over carbon grain was found at 150 °C. Despite high humidity condition, the material showed an effective catalytic activity.

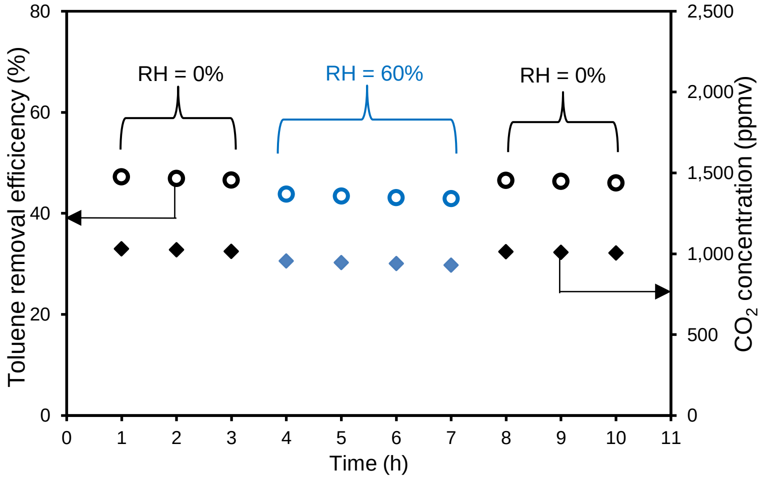

Figure 5: Catalyst's stability at two humidity condition (RH = 0 %, RH = 60 %) for oxidation activity of Au/GC-4-4 catalyst ($m_{catalyst}$ = 0.2 g, flow rate 150 mL/min, $C_{toluene}$ = 314 ppmv, $T_{reaction}$ = 150 °C)

The results of an analysis of stability, and CO_2 concentration after reaction for oxidation activity of the catalyst of Au/GC-4-4 were shown in Figure 5. The results show that despite the high humidity condition, the oxidation activity of Au/GC-4-4 has not changed significantly. The hydrophobicity of carbon grain may be the appropriate explanation for the phenomena observed in this study. This result is consistent with results reported by Wu et al. (2000) for Pt/activated carbon catalyst; water vapor reduces the activity only slightly due to the hydrophobicity of activated carbon. Furthermore, the toluene removal efficiency was almost constant for Au/GC-4-4 is good after 10 h of reaction. Finally, the carbon dioxide (CO_2) concentration in the reactor's output stream was measured by a CO_2 detector (Alphasense sensor technology company, United Kingdom) during the reaction time. It is also noted that CO was not detected by a GC (VARIAN 630, TCD detector) and no other organic compounds (except C_7H_8) have been detected by our GC (HP 5890 plus, FID detector).

As mentioned previously, the Au/GC-4-4 sample was synthesized by metal sol method, with the particle diameter mean was 8.4 nm (<10 nm), the toluene removal efficiency by combination adsorption-catalysis. According to the previous publication (Minh et al., 2018), the nano Au supported on granular activated carbon (Au/GAC) was synthesized by one-step impregnation method, with the particle diameter mean was 17.7 nm (>10 nm), the toluene removal efficiency by adsorption only. Therefore, metal sol method was found to be a suitable synthesis method to synthesize nano Au supported on granular carbon to achieve smaller Au particle size and better catalytic oxidation activity.

4. Conclusions

Nano-sized metal Au catalyst was successfully deposited by metal sol method on carbon grain. The factor's effects of the catalyst's synthesis conditions of the nano-sized Au were investigated as effect pH of the sol solution and PVA/Au mass ratio. Synthesized catalysts were characterized by XRD, BET, SEM, and TEM methods. The materials were used for toluene removal at low temperatures by oxidation and adsorption catalytic process in wet condition. The results showed that the sample Au/GC-4-4, which was synthesized with mass ratio PVA/Au = 4 at pH = 4, can removal toluene about 50.3 % at initial concentration of 314 ppmv at the reaction temperature 150 °C in high humidity (RH = 60 %) in the testing condition. Furthermore, water vapor reduces the activity only slightly due to the hydrophobicity of activated carbon, and the durability of the catalyst is excellent after 10 h of reaction. Further research work will be conducted for comprehending the reaction rate and reaction mechanism of the VOCs oxidation on the nano-sized Au supported on the carbon grain.

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