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Carbon supported nano-sized Au catalysts for toluene removal in humid condition

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ABSTRACT

In this study,one-step impregnation methodwas successfully used in preparation of gold nanoparticles supporting on granular carbon. By this method, in the presence of $Fe_2O_3$the size of Au particles was 10÷15 nm which was smaller than that in the absence of Fe_2O_3. Thecatalysts were characterized to evaluate crystalline structure, surface properties and morphology.These materials are then used for catalytic oxidation of toluene under various conditions such as temperature, moisture content and gas hourly space velocity (GHSV).Results showed that the catalyst exhibited catalytic oxidationactivity even at low temperatures (at 75°C). Inverse effects of moisture were observed between low temperature reaction (75°C) and high temperature reaction (200°C).

Introduction

Volatile organic compounds (VOCs) are one of the major causes of air pollution. In fact, Increased VOCs emissions not only directly threaten people through their toxicity, can cause cancer,but also indirectly result in photochemical smog and ozone pollution[1].Therefore, the development of effective methods and materials for the abatement of VOCs is of great significance. Catalytic oxidation is considered to be the most promising method for VOCs destruction. Unlike adsorption, in which VOCs are just transferred from gas phase to the adsorbent and the adsorbent needs frequent regeneration, catalytic oxidation can destruct VOCs and convert them into harmless CO_2 and water [2-3].

However, some problems remain to be solved with VOCs catalytic oxidation.Reaction temperatures are generally much higher than 200°C [4-6].It hasthe risk of explosion and the formation of NO_x byproduct for heating the entire gasstream to a high temperature [3, 7]. Furthermore, The deactivation of the catalyst may be due to the presence of water in almost all of the emissions and formation in the oxidation reaction. However, the effect of moisture on oxidation of VOCs was studied by only a few research groups. Huang et al. reported that the catalytic deactivation of benzene using nanoparticles MnO_2 carrying on the zeolite was due to the occupation of the active part and the adsorption centers by steam [8].Recently, Soares et al. reported in 2016 that the negative effects of steam on the oxidative reactions of ethyl acetate and butyl acetate on the cryptomelane catalyst (MnO_2) have been observed [9].However, Wu et al. reported that for Pt/activated carbon catalysts, moisture content was reduced significantly due to hydrophobic properties of activated carbon [10].

In recent years, scientists have focused on developing efficient catalysts for reducing the temperature for oxidation of VOCs. Generally,there are two major types of efficient catalysts developed for total VOCs oxidationand they are: supported noble metals and transition metal oxides. Owing to theunremitting efforts after so many years, highly efficient catalysts have beensuccessfully developed for catalytic oxidation of VOC at low temperatures, even atroom temperature in some cases [11-12].

For these reasons, we focus on the synthesis of gold nanoparticles on activated carbon carriers, using the Fe_2O_3 promoter to oxidize VOC at low temperatures. This study reports experimental information from synthesis, characterization to catalytic activity test of the nano Au supporting on granular carbon catalyst.

Experimental

Gold (III) chloride trihydrate ($HAuCl_4.3H_2O$) was purchased from Acros, Granular coconut shell active carbon with the size of 1÷2 mm was purchase from TRABAC Joint Stock Company referred as "GAC", Iron (III) nitrate $Fe(NO_3)_3.9H_2O$ was purchased from Sigma Aldrich, Ethanol 99.5%wt was purchased from VN – Chemsol Co., Ltd. All the chemicals were used as received without further purification.A series of highly dispersed Nano materials $Au/Fe_2O_3/GAC$ were synthesized by one – step – impregnation – method. An appropriate of GAC used as support was stirred in 100 mL of ethanol at room temperature in 15 minutes in a Schlenk flask to wet the surface. The appropriate amounts of $Fe(NO_3)_3.9H_2O$ was dissolved in C_2H_5OH was added slowly with to the above reaction vessel containing the wetted GAC. The mixture was stirred under vacuum condition at 100°C to remove the partial excess solvent until the total volume reached 60 mL. Then, $HAuCl_4.3H_2O$was diluted in 40 mL of H_2O, was added slowly to the previous reaction vessel to obtain 0.2 wt. % of Au. After that, all the solvent was removed in the same vacuum condition above. Finally, the solid was dried at 80°C under air atmosphere overnight. The solid was calcined at 400°C for 4hours with the ramp of 6°C/min under flowing of N_2at 6L/hour to obtain the catalyst structure $Au/Fe_2O_3/GAC$. The sake of comparison, material Au/GAC was prepared by the same synthesizing procedure above but without nitrate salt solutions.

Crystalline structure of four above catalysts was analyzed by powder X-Ray diffraction using Bruker D2 diffractometer, with Cu Kα radiation (λ = 1.54184Å) operated at 30 kV and 10 mA, over a 2θ range from 10˚ to 80˚. Phases of each catalyst were identified by matching experimentally patterns to the JCPDS powder diffraction file.The morphology and microstructure of each catalyst and GAC were observed by the scanning electron microscopy (SEM) using Keyence VE8800, 5 kV and transmission electron microscopy (TEM) using JEM – 1400, 100 kV.

The efficiency for toluene removal in this work were carried out in a packed bed reactor constituted by a U-shaped glass reactor with 12 mm internal diameter, operated in continuous mode and 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 gram) are deposited on a glass wool layer. Before using, each catalyst was pre-treated under flowing N_2(with the flow rate of 6.0 L/hour) at 200 ˚C in 1 hour. 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 humid condition. Both of them were kept at appropriate temperature to ensure that the toluene concentration in the gaseous feed was 630 ppm for dry and humid condition.In dry and humid condition, the catalytic activity was measured in the temperature range from 75˚C to 200˚C.The products of oxidation reaction were monitored with an on-line gas chromatograph HP-5890plus equipped with a flame ionization detector and HP-Plot/Q (30 m x 0.53 mm) column.

Results and discussion

The XRD patterns of prepared materials were shown in Fig1 for understanding the crystal structures. In the first pattern representing for $Au/Fe_2O_3/GAC$, the characteristic peaks of Fe_2O_3 were detected at 2θ ≈ 24˚, 34˚, 38˚, and 55˚(JCPDS no. 86-2368). The reflections for polycrystalline gold are expected at 2θ ≈ 38.2˚, 44.4˚, 64.6˚, 77.4˚ (JCPDS no. 04-0784).However,only a small broad peak at 2θ ≈ 38.2˚ (111) was detected by XRD pattern of material Au/GAC, suggesting the presence of metallic gold). There are no diffraction peaks at 2θ ≈ 38.2˚ for gold(111) in the XRD patterns of $Au/Fe_2O_3/GAC$ suggesting the presence of highly dispersed gold crystallites at low concentration (0.2 wt.% Au).

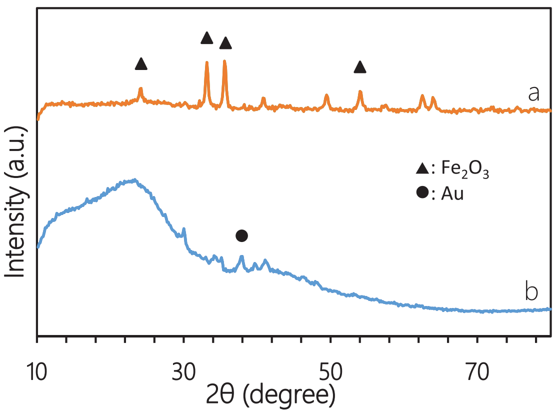

Fig 1. XRD patterns of Au/Fe_2O_3/GAC (a) and Au/GAC(b).

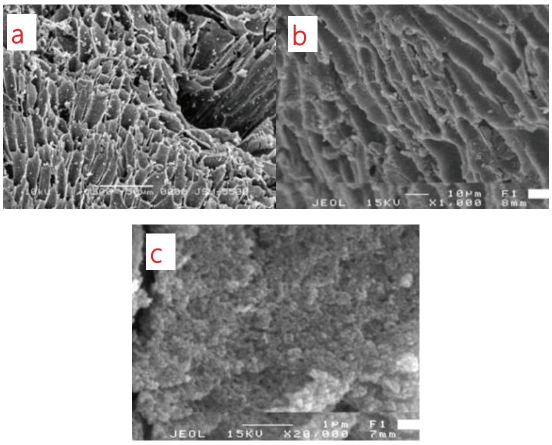

Fig 2. SEM image of AC (a), Au/Fe_2O_3/GAC (b, c)

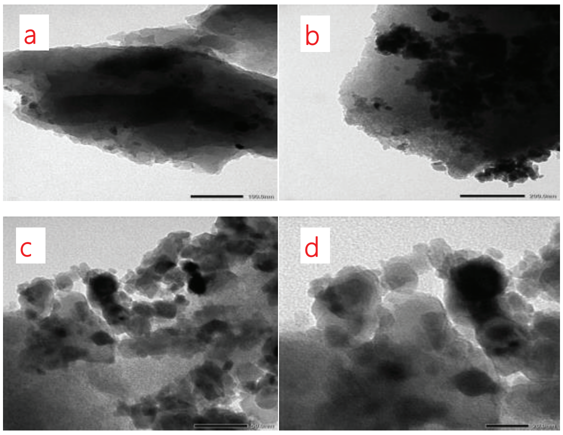

Fig 3. TEM image of Au/GAC (a), Au/Fe_2O_3/GAC (b,c,d)

The distribution of nano gold and metal oxides on GAC was observed with scanning electron microscopy (SEM) and showed in Fig 2. From Fig 3a, the pores on the surface of GAC were observed. In contrast, the surface Au/Fe_2O_3/GAC (b, c) are cover by multiple layer of iron oxide, and this metal are distributed evenly on the surface of GAC support.

The particle size of three materials Au/GAC, Au/Fe_2O_3/GAC is showed in Fig 3. With material Au/GAC (a), diameter of gold particle varied from 20÷25 nm. However, from TEM image of Au/20Fe_2O_3/GAC (b, c, d), with the presence of iron oxide, the Au particles were smaller(10÷15 nm).

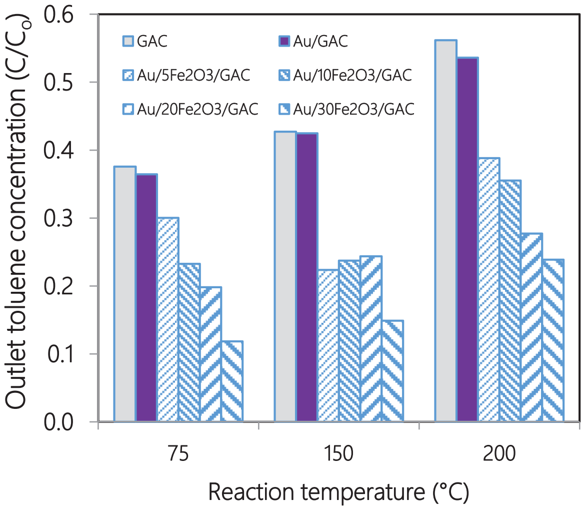

Fig 4. Toluene removal efficiencyof catalysts at different temperatures(reaction time = 30 minutes).

Effect of iron oxide contain on the removal efficiency of toluene wereinvestigated and reported in Fig.4 .The data were obtained at reaction period of 30 minutes for each materials with the temperature range 75–200°C and GHSV=10500h^{-1}. For comparing between adsorption and oxidizing reaction, the outlet toluene concentration in the case ofGAC was also measured in the same condition (Fig 4). The results indicated thatthe presence of individual gold particle did not improve the toluene removalof Au/GAC.The C/C_o ratio in the cases of GAC and Au/GAC were almost the same at 75°C (0.38 and 0.37, respectively), and there was toluene adsorption only.However, as reflected from Fig.4, at reaction temperature of 75 °C and 200 °C increases of toluene removal efficiency was observed when the iron oxide contain was increased.With the presence of iron oxide, the toluene removal efficiency is significantly higher than that of GAC and Au/GAC. These results predicted that the presence of Nano gold reduced the strength of the Fe – O bond near the Au atoms. This enhanced the mobility of oxygen in the crystal lattice, because of the formation defect of Au nanoparticles. According to previous studied [13-14], Mars – Van Kreveken (MVK) mechanism was used to explain this process, the oxygen atoms in the crystal lattice are seen as radical active oxygen, which is the main agent for VOCs oxidation reaction on metal – based catalyst.

It can be seen that, when the reaction temperature was increased, the outlet toluene concentration was increased. when the outlet toluene concentration was increased, the toluene removal efficiency was decreased. Because:

$$\text{Toluene removal}\,(\%) = 100 - \frac{C}{C_o} \times 100$$

Where C and $C_o$are the area of the GC result's peak of the toluene at a reaction time (t) and at the beginning (t=0), respectively. At 200°C, the outlet toluene concentrationof Au/20Fe_2O_3/GAC and Au/30Fe_2O_3/GAC higherthan that at 75°C (0.08 and 0.12, respectively).

Simona and co-work demonstrated that Iron (III) oxide only exhibited the catalytic activity in toluene oxidation at the reaction temperature above 250°C. This suggested the role of nano particles of Au/Fe_2O_3 in catalytic activity and GAC supported for toluene adsorption. However, in heterogeneous catalyst reaction, the adsorption of the reactant(s) in gaseous phase on the catalyst surface is the first and a required step in the reaction.Therefore, in the case of Au/Fe_2O_3/GAC, when the temperature was increased, the toluene conversion was decreased due to desorption of adsorbed toluene molecules.

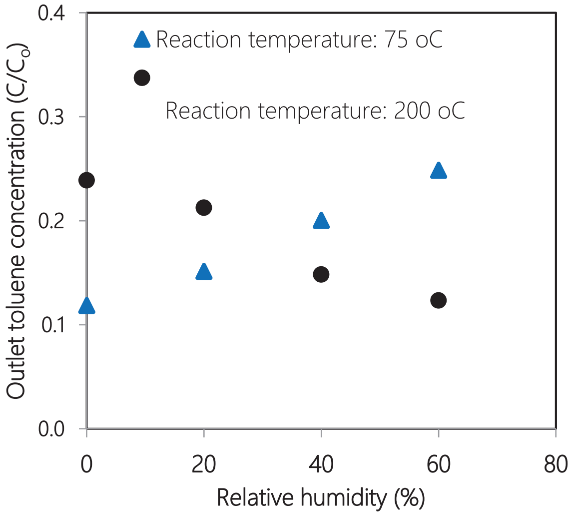

Fig 5.Toluene removal efficiency of Au/30Fe_2O_3/GAC in various humidity conditions(reaction time = 30 minutes).

To investigate the effect of humidity on catalytic activity of Au/30Fe_2O_3/GACcatalyst, different water vapor (RH: 0%; 25%; 40%; 60%) was introduced into the gaseous feed. The reaction time was 30 minutes and GHSV = 10500 h^{-1}.

The result is shown in Fig 5, the results in dry condition (RH: 0%) were also shown for reference. As we can see, at 75°C the outlet toluene concentration increased when the vapor water presence in gaseous feed was increased, the outlet toluene concentration is 0.12 at RH: 0% and 0.25 at RH: 60%. However, when the reaction temperature was at 200°C, the humidity was increased, but the outlet toluene concentration was decreased. This demonstrated that when the temperature reached 200°C, the humidity contributed to the increase of the catalytic activity. Interestingly, at 75°C and 150°C the humidity leaded to decrease the catalyst activity. These results were similar with Bing – bing Chen and co – worker [15]. The presence of water vapor led to a decrease of the activated energy of reaction and interacted with the mobility lattice oxygen in catalyst crystal atoms to create co – catalyst mixture.

Based on these results, it can be seen that, when both water vapor and oxygen presence in gaseous feed, water vapor contributed to create oxygen free and OH groups according to this equation: $O_2 + H_2O \rightarrow O^* + 2OH$ [16]. These OH groups were created on the surface of the catalyst, then oxidized absorbed reactants[17,18]. Besides that, according to MVK mechanism, Nano Au weakened the Fe – O bond, thus, the more Fe_3O_4 was formed the more mobility Oxygen was created.Moreover, Andreeva's group reported thatwater vapor decreased the activated energy of $Fe_2O_3 \rightarrow Fe_3O_4$, and Nano Au distributed as a promoter enhancing the reaction rate constant of this process [19-20].As a result the catalytic oxidation activity was promoted at the high temperatureby the presence of water vapor.

Fig6 showed the effect of GHSV on the catalytic activity of the nano Au supporting on granular carbon for toluene removal. It is clearly seen that, when increasing the GHSV (h^{-1}) values, the outlet toluene concentrationwas increased at all the temperatures. This can be explained that, the increase of GHSV led to the decrease of interactive time between catalysts and reaction agents. Thus, the catalytic activity was decreased.

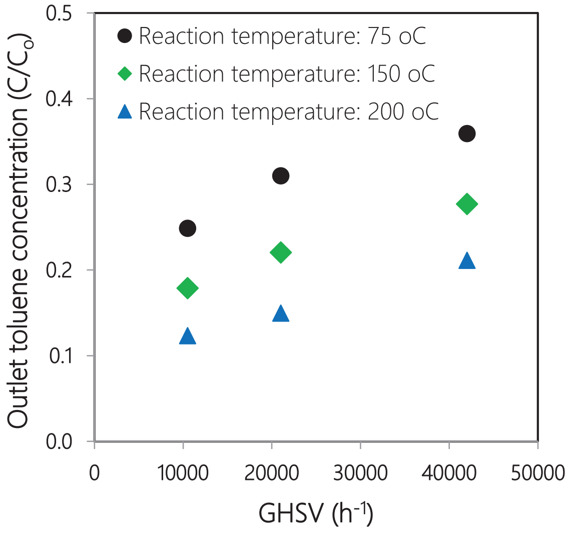

Fig 6. Influence of GHSV on toluene removal efficiencyof Au/30Fe_2O_3/GAC in highly humid condition (RH 60%)(reaction time = 30 minutes)

Conclusions

Nano Au/Fe_2O_3/GAC has been prepared by one – step impregnation method. The results indicated that, the Au particles became smaller (10–15 nm) with presence of iron (III) oxide.Toluene can be removed at low temperatureby using nano Au dispersed on Fe_2O_3/GAC materials. By testing the influences of temperature, Fe_2O_3 content, humidity and GHSV on the toluene removal efficiency, it was found thatthe nano Au/Fe_2O_3/GAC catalyst exhibited catalytic activity for toluene removal even at75°C. The negative effect of water vapor on the toluene removal efficiency was observed at 75°C. However, at 200°C the presence of moisture improved the catalytic oxidation activity of the nano Au catalyst.

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