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Combination of adsorption – desorption with complete oxidation on the MnCoCe oxide based catalyst for toluene treatment

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ABSTRACT

The Adsorption – desorption is considered as one of the most promising VOCs treatment technologies due to its cheap operational cost and low energy consumption. However, there are a huge amount of adsorbed VOCs released in desorption process. That is the reason why this study focused on the combination of adsorption-desorption with catalytic oxidation to treat completely VOCs as toluene. The adsorption catalyst MnCoCe/AC (metal oxide catalyst MnO_2-Co_3O_4-CeO_3 on Actived carbon) and oxidation catalyst Au/MnCoCe (Au supported on metal oxide catalyst MnO_2-Co_3O_4-CeO_3) were investigated and characterized by SEM - EDX, BET. The catalytic activity test were carried out on a micro-flow reactor system connected with GC online using a TCD detector.The results shown that Au/MnCoCe is a potential catalyst for the complete oxidation of toluene with the temperature for 100% toluene conversion of 300°C. The combination of adsorption-desorption with catalytic oxidation decreased the temperature for 100% toluene conversion to 250 °C.

Introduction

atile organic compounds (VOCs) are one kind of air pollutants with the boiling points ranging from 50 to 260 °C under atmospheric pressure [1]. Emission of atile organic compounds is one of the major contributors to air pollution. The main sources of VOCs are petroleum refineries, fuel combustions, chemical industries, decomposition in the biosphere and biomass, pharmaceutical plants, automobile industries, textile manufacturers, solvents processes, cleaning products, printing presses, insulating materials, office supplies etc [2]. The most common VOCs are halogenated compounds, aldehydes, alcohols, ketones, aromatic compounds, and ethers [3].

Toluen is one of the most frequently occurred VOCs species due to its wide usage in industry, accounting for 7.5% of total VOCs. It is not only toxic and carcinogenic but also cause severe damage to ozone layer, produce photochemical smog, and posed multagenic hazards [4] . In enclosed spaces, toluene causes irritation to eye, nose and throat, and more severly cause dizziness, headache, memory and visual impairment and even death [1].

Until now, a variety of toluene treatment technologies have emerged, such as incineration, biodegradation, absorption, adsorption and catalytic oxidation. Among these methods, adsorption and catalytic oxidation are two types of potential technologies for toluene abatement. Catalytic oxidation is the preferred because this method completely oxidize toluene into CO_2 and H_2O [5÷7]. Meanwhile, adsorption is more popular in industry than catalytic oxidation because of its cheap

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operation cost and low energy consumption [2]. The key of adsorption technology is adsorption materials which have high adsorption capacity such as actived carbon, zeolite, MOFs, ...But in the desorption process, these marterials release absorbed toluene gas. That is the reason why it needs one more step to completely treat toluene. Moreover, from the viewpoint of fundamental science, adsorption is the essential and first step of catalytic oxidation, followed by catalytic transformation and desorption, thus adsorption and catalytic oxidation are closely correlated [1].

Therefore, the aim of this work is to combine adsorption/desorption with catalytic oxidation to treat completely toluene. We synthezised adsorption material base on metal oxide system MnO_2-Co_3O_4-CeO_3 (which was known as an effective catalyst for complete oxidation of CO, NO_x, propylene in our previous studies [8-10]), while actived carbon was used as the support. The oxidation catalyst is gold supported on metal oxide system MnO_2-Co_3O_4-CeO_3.

Experimental

Preparation of the catalysts

MnCoCe/AC

3.8849 grams $Co(NO_3)_2.6H_2O$, 0.1545 grams $(NH_4)_2Ce(NO_3)_6$ and 0.531 grams $Mn(NO_3)_2$ 50 % solution were diluted with 20 mL of distilled water to obtain a solution of mixed salts. About 3÷5 drops of nitric acid were added into the mixture to prevent metal salt hydrolysis during the preparation. 2 grams of actived carbon were also added into the solution. after 8 hours, the mixture was dried at 100 °C for 8 hours before calcinated at 300 °C for 3 hours with the rate of 3 °C/minute.

Au/MnCoCe

Meanwhile, the catalyst for the oxidation process (2 % Au/MnCoCe) was synthesized base on co-precipitation method. 20 mL of $HAuCl_4$ 0.01016 M was added to the precursor solution including 0.7478 grams 50 % $Mn(NO_3)_2$, 0.8589 grams $(NH_4)_2Ce(NO_3)_6$, 5.4709 grams $Co(NO_3)_2.6H_2O$ in 100 mL of distilled water. Then drops of Na_2CO_3 solution (which is prepared from 11.66 gram Na_2CO_3 dissolved in 100 mL of distilled water) was added with the rate of 10 mL/min at room temperature. After 3 hours, the precipitate was filtered and washed with distilled water at 60 °C to remove Cl^- ions. Finally, the precipitate was dried at 50 °C for 48 hours before calcined at 300 °C for 3 hours at a heating rate of 2 °C/min.

The synthesis of 1.5 %Au/MnCoCe and 1 %Au/MnCoCe were completely similar to 2 %Au/MnCoCe. The only point which different is that the amount of $HAuCl_4$ - solution used is 15 mL and 10 mL.

Characterization of catalyst

The morphology and microstructure of the catalysts were examined by scanning electron microscope (SEM) on a Hitachi S-4800 (Japan). The chemical compositions and metal content of the catalysts were also analyzed by a Hitachi system (S-4800 model) scanning electron microscope equipped with a energy-dispersive X-ray (EDS) spectrometer. The specific surface area were determinded at 77 K by the BET method based on Nirtogen adsorption – desorption isotherms using a Micromeritics Gemini VII 2390 device. The catalyst was also characterized by powder X-ray diffraction (XRD) on D8 Advance Bruker instrument.

Measurement of catalytic activity

Complete oxidation experiment

The treatment of toluene was carried out in a fixed-bed reactor systems. The Schematic diagram is shown in Fig 1. Gaseous toluene was prepared by bubbling N_2 into liquid toluene. Then toluene was mixed with N_2 and O_2. The total flow rate was seted up at 50 mL/min. When the inlet concentration of toluene reached a steady state at 9000 ppm, it was treated in the fixed bed reactor. 0.1 grams of each catalyst 1 %Au/MnCoCe, 1.5 %Au/MnCoCe, 2 %AuMnCoCe were loaded into the middle of the ¼ inch reactor which was 60 cm length. Analysis of the reactants and products (CO_2 and toluene) was performed using an on-line Focus-Thermo Scientific gas chromatograph with a thermal conductivity detector (TCD).

Adsorption – desorption and oxidation experiment

In this experiment, the treatment of toluen was divided into three steps: (1) the adsorption of toluene on MnCoCe/AC, (2) The oxidized desorption of previous adsorbed toluene from the catalyst MnCoCe/AC, (3) the complete oxidation of the remained toluene on the catalyst MnCoCe using Au/MnCoCe. The micro-reactor was set up with 2 reactors connecected in series. While 9000 ppm toluene was in balance, 0.05 grams of adsorption material (MnCoCe/AC) was added into the first reactor. At this time, the adsorption process was taking place at room temparature. After the satured adsorption, the temperature of the first reactor was changed to 180 °C in order to come up desorption process. The outlet flow released form the first reactor was leaded to the second reactor which was added 0.1 grams of the oxidation catalyst (Au/MnCoCe) into the internal diameter tube at 250 °C. The outlet flow was detected by an online Gas chromatograph (GC) with a Thermal Conductivity Detector (TCD).

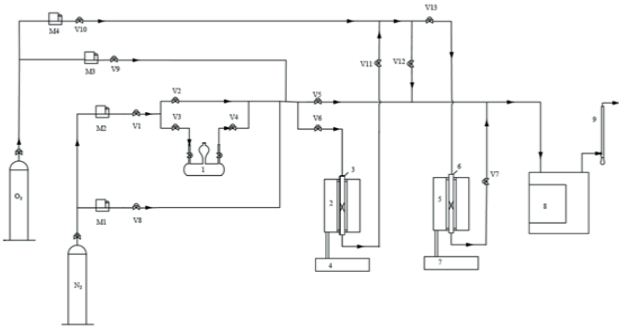

Figure 1: Schematic diagram of toluen Adsorption and Oxidation experiment

1.Toluene tank
2, 5. Heating furnace
3,6. Internal diameter tube
4,7. The temperature controller of the furnace
8. GC with TCD detector
9. Soap bubbler flow meters
V1÷V13. Valse
M_1÷M_3. Mass flow controller

Results and discussions

Catalyst characterization

Figure 2 illustrates XRD pattern of 2% Au/MnCoCe catalyst. The XRD pattern of this catalyst showed the typical peak of Co_3O_4 appeared at 2-theta of 36.88°, 65.3° while that of MnO_2 is 38.4°. In addition, the baseline of pattern was quite high proving the presence of amorphous phase and/or small particle sizes of synthesized sample.

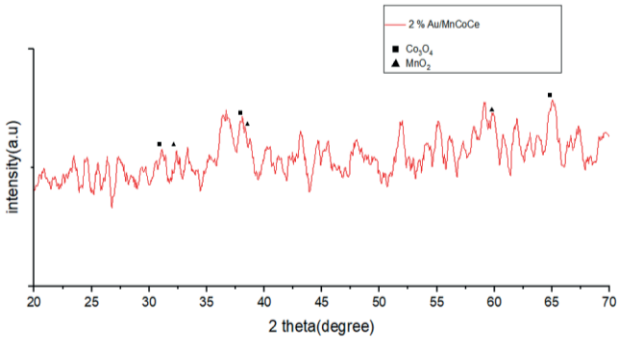

Figure 2: XRD pattern of 2 %Au/MnCoCe.

Table 1 shows the specific surface area and porous structure of all catalysts. The results indicated that when actived carbon acts as a support, the catalyst may have high surface area. The BET surface area of MnCoCe/AC was high (537 m^2/g), it is very suitable for the adsorption process because it is generally believed that adsorption capacity increases as specific surface area increase. Meanwhile the catalysts without activated carbon support which contain Au on mixed metal oxides, possessed the much lower surface area.

Table 1. BET surface area, pore size of synthesized sample

Sample	S_{BET} (m^2/g)	D_{pore} (Å)
MnCoCe/AC	537.0	35.6
1 %Au/MnCoCe	121.3	135.7
1.5 %Au/MnCoCe	112.3	78.6
2 %AU/MnCoCe	113.7	179.2

The results are illustrated by the data in the figure 3. The figure presents N_2 adsorption-desorption of synthesized samples showing type IV isotherms according to the UIPAC classification, indicating that all of the samples contained mesoporous structure.

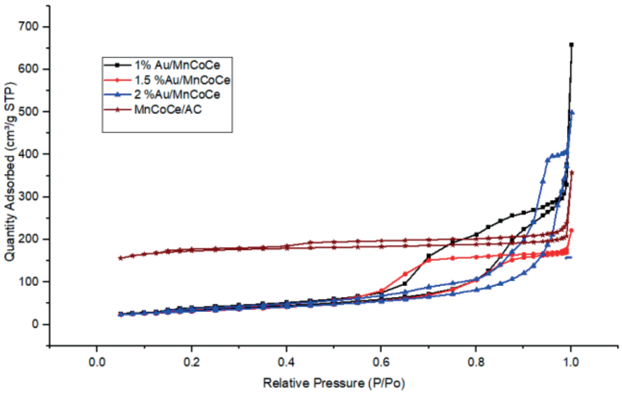

Figure 3: Nitrogen adsorption-desorption isotherm of the synthesized samples

The morphology of all samples was investigated (figure 4 and figure 5) to observe the differences of each one. The SEM image of MnCoCe/AC (figure 4) had shown that this sample has porous structure. The particle size of the catalyst were not uniform.

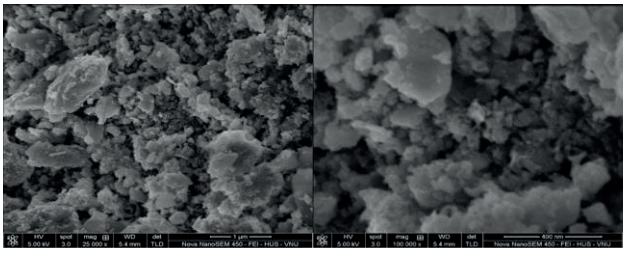

Figure 4: SEM images of MnCoCe/AC

Meanwhile, as shown figure 5, the catalyst which contains Au on mixed oxide had fairly uniform particle size distribution.

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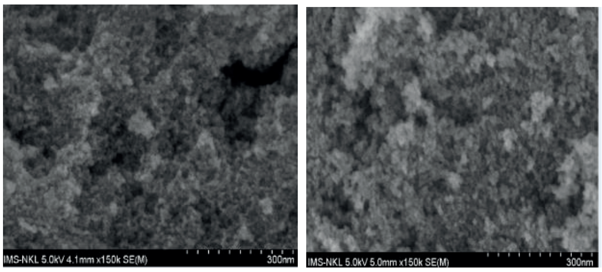
The SEM image of 1 %Au/MnCoCe sample synthesized by the co- precipatiation method is shown in figure 5a. The particles were distributed evenly and concentrated mainly at 10 nm.

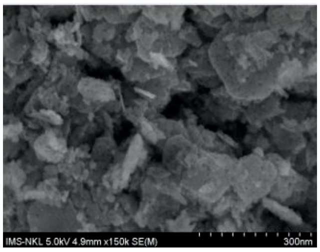
The uniform distribution between the particles of sample 1.5 %Au/MnCoCe was maintained as that of 1 %Au/MnCoCe (Figure 5b). However, on closer inspection, it could be seen that the appearance of clustering of small particles into larger particles which were 50-150 nm.

The SEM images of the catalyst had shown that there were the apperances of bright point of unusual indensity. This could be a sign of gold paricles being on the catalytic surface. To further investigate this issue, the EDX measurement were performed.



a, 1 %Au/MnCoCoCe.

b, 1.5 %Au/MnCoCe.



c, 2 %Au/MnCoCe.

Figure 5: SEM images of Au/MnCoCe samples.

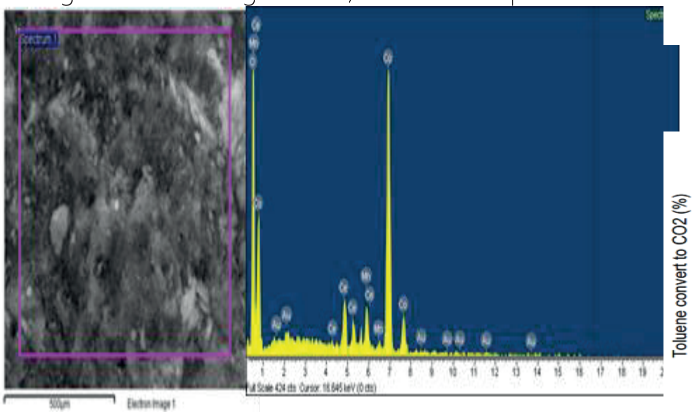


Figure 6. SEM-EDX analysis images of 1 %Au/MnCoCe samples

Figure 6 showed representative EDX spectra of 1 %Au/MnCoCe. The descriptive statstics of the percentages of the major elements in that sample detected by EDX were complied in Tab 2. For 1 %Au/MnCoCe, the means of element precentages were in the descending order of: O > Co > Ce > Mn >Au. This The result reflexed that the major components were O and Co. The percentage of Au was 1.2 % which quite close to the theory.

Table 2: SEM-EDX anlysis of 1 %Au/MnCoCe.

Element	Weight percent	Atomic percent
O	42.83	75.7
Mn	4.04	2.08
Co	41.59	19.96
Ce	10.34	2.09
Au	1.2	0.17
Total	100	

Catalytic activity

The treatment of toluene using complete oxidation method

Catalytic activity of the catalyst (1 % Au/MnCoCe, 1.5 %Au/MnCoce, 2 %Au/MnCoCe) for the oxidation of toluene into CO_2 and H_2O are presented in Fig 7 and Fig 8. In general, in the low temperature range form 100 to 200 °C, the toluene conversion of the catalyst system (Au/MnCoCe) and the percentage of toluene converted to CO_2 was still low.

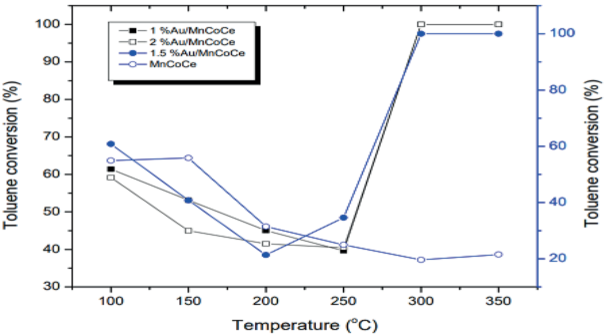


Figure 7: Toluen conversion of complete oxidation experiment at different temperatures

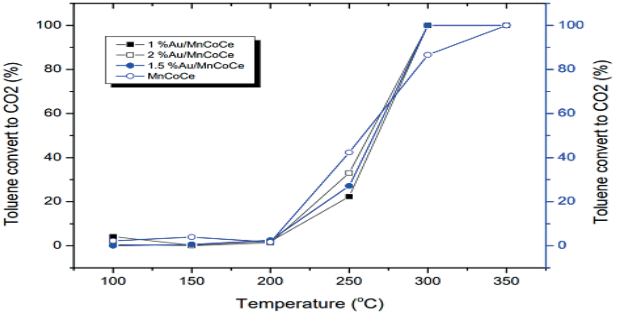


Figure 8: Percentage of toluene convert to CO_2 of complete oxidation experiment at different temperatures

Because all three catalysts possessed high BET surface area (roughly 120 m^2/g) and the adsorption precess takes place mainly at low temperature. Meanwhile, in the temperature range from 250 to 350 °C, the toluene treatment capacity of all three catalysts which contained gold is quite similar and superior to the MnCoCe catalyst. Especially, the Au/ MnCoCe catalysts gave complete treatment of toluene at 300 °C. Thus, the presence of Au increased the ability to completely oxidize toluene of the MnCoCe.

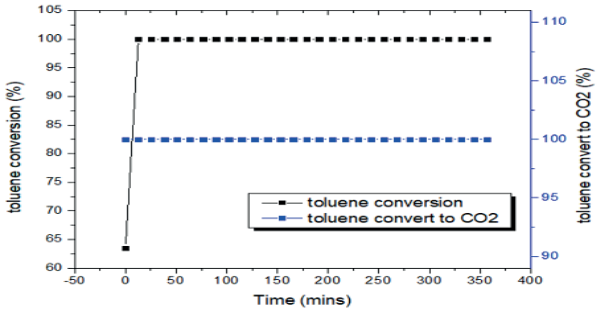


Figure 9: Toluen conversion of complete oxidation experiment at 300 °C

Among these three catalysts containing gold, 1 %Au/MnCoCe not only gave the best toluene treatment ability but also gave the greatest economic efficiency when containing the smallest Au content. Therefore, research on the durability over time at 300 °C of this catalyst was carried out. The results shown in Fig 9. During the first 25 minutes, there is a stabilization of the treatment process, so the toluene conversion did not reach 100%. Once stability had been reached, both toluene conversion and the percent of toluene covered to CO_2 kept at 100%. Even after 6 hour, toluene is still completely converted to CO_2.

The treatment of toluene using adsorption – desorption and oxidation method.

With the aim to treat almost completely toluene and convert it to CO_2 in the lowest cost way, the combination of adsorption with complete oxidaiton was carried out. At first, toluene was adsorbed on the catalyst MnCoCe/AC. After the saturated adsorbtion at room temperature, the reactor temperature was increased to 180 °C for toluene desorption process with the presence of oxygen. The outlet flow from the first reactor was lead into the second reactor which contain oxidation catalyst Au/MnCoCe. At the same time, a flow of oxygen was injected to the second reactor. With the presence of oxygen and the high temperature which was adjusted at 250 °C, the remain desorbed toluene will be oxidized. The results showed that toluen conversion, percentage of toluene convert to CO_2 of MnCoCe/AC + 1 %Au/MnCoCe catalyst systems at 250°C are 100%, which means that toluene has been completely oxidized to CO_2.

Thus, we can see that the combination of 2 kinds of catalyst completely treated toluene to CO2 at lower temperature than the oxidation method (temperature for the complete oxidation of toluene is 300°C).

Conclusion

The supported Au catalyst on mixed oxide MnO_2-Co_3O_4-CeO_2 system is a potential catalyst for complete oxidation of toluene. Especially, 1 %Au/MnCoCe completely converted toluene to CO_2 at 300 °C. The combination of adsorption – desorption with complete oxidation is a effective way to treat toluene. It not only the ablility to adsorb large amounts of toluene but also completely convert toluene CO_2 at lower temperature (250°C). The results from the catalyst system which contained MnCoCe/AC and 1 %Au/MnCoCe proved that.

Acknowledgement

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