Catalytic oxidation of benzene using nano-CuO/γ-Al₂O₃ and commercial catalysts

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Abstract. Volatile organic compounds (VOCs) such as benzene are among the most dangerous air pollutants emitted by chemical industry stacks, as they may contribute to environment and health issues. Lean catalytic oxidation of benzene has been considered as most proper method to abate it from the flue gas. This work developed nano-based copper oxide catalysts for lean oxidation of benzene. The aim of this study was to evaluate the activity performance of the nano-based copper oxide catalyst and compare to commercial catalyst. On the basis of the commercial catalyst, this study was also aimed to determine the reaction rate and its kinetic parameter. The oxidation of benzene was conducted in a fixed bed reactor at 300°C, 1 atm, and GHSV of 15,000 h⁻¹. The concentration of benzene in the feed and product were measured using online gas detector (Cosmos Gas Detector). The catalyst activity of nano-based copper oxide catalysts showed 20-30% conversion of benzene, while for commercial catalyst showed 86%. The reaction rate determination for first order reaction of benzene indicated that the activation energy was 48 kJ/mol with Arrhenius constant of 3x10⁴ s⁻¹.

1. Introduction

Volatile Organic Compounds (VOCs) have been widely recognized as one of the most dangerous air pollutants that may contribute to environment and health issues. VOCs may cause the photochemical smogs formation, ozone layer depletion, and global warming as greenhouse gases [1]. VOCs are frequently emitted by various sources such as vehicle emissions, industrial emissions, and household emissions [2]. Benzene is one of VOCs that has carcinogenic properties and very harmful to human health. Benzene is generally emitted from chemical industry such as petrochemical and oil refinery [3]. There are many methods to convert VOCs into harmless substance, such as adsorption, absorption, thermal oxidation, and catalytic oxidation [4]. The catalytic oxidation is well recognized as one of the most appropriate methods for treating VOCs due to its catalytic performance, large capacity, and moderate operating cost [4,5]. In addition, the catalytic oxidation can efficiently treat VOCs at very dilute concentration (below 1%) with operating temperature much lower than thermal oxidation [6].

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In general, there are two types of catalyst used in VOCs catalytic oxidation, i.e. noble metal catalyst and metal oxide catalyst. Noble metal catalysts, such as platinum and palladium, have high catalyst activity but they are quite expensive and can be easily poisoned. Metal oxide catalysts, such as CuO, FeO, NiO, and MnO, have high thermal resistance, not expensive, and not easily poisoned [7,8,9,10], although the catalyst activity is much lower than noble metal catalyst [11]. In recent years, many researchers have shown that metal oxide catalyst with the highest catalyst activity are copper-based metal oxide catalyst (CuO) [6,10,11,12]. Addition of ceria and mangan oxide as catalyst support also increases catalyst activity [11].

In recent years, nanomaterial has been used as catalyst and called as nanocatalyst. Nanocatalysts have very active site and high surface area, thus the activity of nanocatalysts are much larger than the conventional catalysts [13]. In addition to high surface area, nanocatalysts also have high selectivity and good stability [14]. Copper based nanocatalyst has been developed by many researches and has been shown a high catalyst activity property [13]. Nano-CuO catalyst has been developed in previous research [15] by impregnating copper into alumina mesoporous which is made by urea combustion method. The aim of this work was to investigate the activity of nanocatalyst that has been developed in previous research, compare the result with commercial CuO catalyst, and determined kinetic parameter for nanocatalyst.

2. Materials and methods

2.1. Catalyst preparation
The details of the preparation of nano-CuO /γAl₂O₃ catalyst using urea nitrate combustion and Cu impregnation have been described in the previous work [15]. Gamma alumina was prepared by mixing specific ammounts of aluminium nitrate nonahydrate [Al(NO₃)₃.9H₂O] and urea at specific ratio, in water under vigorous stirring for 1 hour. The mixture was then dried in an oven at 120°C for 5 h and at 250°C for 3 h. The sample was calcined in air atmospheric at 500°C for 6 h. The resulted powder was then added into copper nitrate solution at specific concentration while vigorously stirred for 45 minute. The sample was subsequently dried in oven at 120°C until water content was removed. Then the sample was calcined at 700°C or 800°C for 6 h.

2.2. Experimental setup
The experimental runs for catalysts activity test were performed in a quarts tubular fixed bed reactor (Ø-10 mm) operated at atmospheric pressure. The reaction mixture was composed of nitrogen, oxygen (+21%), and 5,000 ppm of benzene. For catalyst activity test, 200 mg of catalyst was diluted with glass bead to give porosity around 0.4 and loaded into the fixed-bed reactor. The reaction temperature and GHSV were kept constant at 300°C and 15,000 h⁻¹. The benzene concentration in gas stream was measured by an online gas detector (Cosmos XP3160 type). The schematic view of the experimental set up is shown in figure 1. The activity test was conducted for 9 variations of nanocatalyst, 1 commercial catalyst, 2 types of alumina mesoporous support without impregnated Cu, and 1 commercial alumina, which are shown in table 1.
Table 1. Variations of catalyst in activity test.

| Catalyst no. | Variation | Al : Urea | Calcination Temperature (°C) | Cu loading |
|--------------|-----------|-----------|-----------------------------|------------|
| 1            | 1:2       |           | 800                         | 30%-w      |
| 2            | 1:2       |           | 800                         | 10%-w      |
| 3            | 1:2       |           | 800                         | 5%-w       |
| 4            | 1:2       |           | 700                         | 30%-w      |
| 5            | 1:2       |           | 700                         | 5%-w       |
| 6            | 1:3:5     |           | 700                         | 5%-w       |
| 7            | 1:3:5     |           | 800                         | 30%-w      |
| 8            | Alumina Commercial | 1:2 | 800                         | 10%-w Ni  |
| 9            |           |           | 800                         | 30%-w      |
| 10           |           |           |                             |            |
| 11           |           |           |                             |            |
| 12           |           |           |                             |            |
| 13           |           |           |                             | Alumina commercial |

3. Results and discussion

3.1. Activity test

The results of activity test for 13 types of catalysts are shown in figure 2. The activity of catalyst is measured as benzene conversion for benzene oxidation reaction. From figure 2, the highest benzene conversion is 86% obtained from the commercial catalyst. Nanocatalysts resulted in benzene conversion much lower, in the range of 16%-27%. The alumina mesoporous gave benzene conversion in the range of 20%-40% with the highest conversion coming from alumina mesoporous with Al:urea 1:2, and the lowest was from commercial alumina. The commercial catalyst indicated higher activity than nanocatalyst because of the existence of other components in the commercial catalyst instead of CuO which acted as promoter.

Table 2 shows the surface area for alumina mesoporous before and after impregnation. Before impregnation, the alumina mesoporous had surface area around 150 – 200 m²/g. After impregnation, the alumina mesoporous had surface area around 40 m²/g. The decrease in the surface area indicated that there was a failure in the method of making nanocatalysts. One possible cause of failure was the higher calcination temperature, which was in the range of 700 – 800°C. The high calcination temperature might cause several failures in making nanocatalyst. There might be sintering of the copper that caused blockage or agglomeration in catalyst pore which reduced surface area greatly.
There might be a change of alumina phase from gamma alumina, which had high surface area to alpha alumina, which had lower surface area. It could also cause a chemical reaction between alumina solids with copper to produce inactive component, which lowered catalyst activity.

![Figure 2. Benzene Conversion for each type of catalysts.](image)

**Table 2.** Surface area of Al₂O₃ before and after impregnation with 30%-Cu and calcined at 800°C.

| Alumina type                              | Surface area before impregnation | Surface area after impregnation |
|-------------------------------------------|---------------------------------|---------------------------------|
| Alumina mesoporous with Al:urea = 1:2    | 213                             | 44                              |
| Alumina mesoporous with Al:urea = 1:3.5  | 126                             | 44                              |
| Alumina commercial                        | 150                             | 44                              |

From XRD data at figure 3, there were other components beside CuO in nanocatalyst. The copper oxide (CuO) components acted as active phase in nanocatalysts [6,10,11,12]. The other component formed was CuAl₂O₄ or copper aluminat. The copper aluminat was formed at high calcination temperature at 700 and 800°C. This also indicated that at calcination temperature higher than 700°C, copper would react with alumina to produce copper aluminat, which was inactive component.

Figure 2 also showed that alumina mesoporous before impregnation (catalyst number 11 and 12) has higher activity than after impregnation. This indicates that the calcination temperature was too high. Several researches usually calcined the catalyst at 500 – 600°C [6,10,11]. The effect of copper loading in catalyst also had bigger role in decreasing catalyst activity. Figure 2 shows that the higher the copper loading in catalyst, the lower the benzene conversion. This indicated that at high amount of copper loading, the agglomeration in surface area became more significant thus lowered the activity. Other research [6] indicated that copper loading above 7%-weight would lower the activity.
3.2. Determination of kinetics rate equation

Kinetics rate determination was performed for catalyst 3, which had highest activity among nanocatalyst. The power law model was used as kinetic equation for benzene oxidation. The catalytic oxidation of benzene operated in the excess of oxygen can be described by a first-order kinetic equation (1):

$$ r_{bz} = k \cdot C_{bz} = A \cdot \exp \left( -\frac{E_a}{RT} \right) \cdot C_{bz} $$

where $r_{bz}$ is kinetic rate, $A$ is Arrhenius constant, $E_a$ is activation energy, and $C_{bz}$ is benzene concentration. The reactor was assumed as plug flow reactor, which has reactor model as written in equation (2) with $\tau$ is gas retention time.

$$ \frac{dC_{bz}}{d\tau} = -r_{bz} $$

At GHSV 15,000 h$^{-1}$, experiment was conducted by varying reaction temperature from 300 to 400°C. The data treatment resulted in conversion and reaction rate constant ($k$) as presented in Table 3. The reaction rate constant was obtained by combining equation (1) and (2). The activation energy and Arrhenius constant were calculated from the plots of ln $k$ versus $1/T$, where $E_a$ was obtained from the slope of the resulting linear plots, and $A$ was obtained from the intercept. From the calculation, $E_a$ for benzene oxidation with nanocatalyst was 48 kJ/mol and $A$ was $3 \times 10^4$ s$^{-1}$. From this kinetic parameter, the conversion of benzene at several temperatures were calculated and shown in figure 4.

![Figure 3. Diffraction patterns of Al$_2$O$_3$ mesoporous with Al:urea = 1:2 after Cu impregnation and calcined at (a) 600°C, (b) 700°C, (c) 800°C. The insert shows a magnification of the diffraction pattern of the sample calcined at 600°C.](image)

![Figure 4. Benzene conversions at GHSV 15,000 h$^{-1}$ and varied reaction tempearature using nano-catalyst. Line (·) shows data from simulation and Dots (o) shows data from experiment.](image)
Table 3. Benzene conversion of varied reaction temperature at GHSV 15,000 h\(^{-1}\)

| Temperature (°C) | Benzene Conversion | \(k\) (s\(^{-1}\)) |
|-----------------|--------------------|------------------|
| 300             | 27.0%              | 1.31             |
| 350             | 48.6%              | 2.77             |
| 400             | 75.8%              | 5.91             |

4. Conclusion
The activity of nano-CuO/\(\gamma\)-Al\(_2\)O\(_3\) and commercial catalyst has been tested in the fixed bed reactor. The result shows that nanocatalyst has much lower catalyst activity than commercial catalyst. There has also been done for determining the kinetic rate parameter of the nanocatalyst.

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6. References
[1] Kamal M S, Razzak S A and Hossain M M 2016 *Atmospheric Environment* **140** 117-134
[2] Liotta L F 2010 *Applied Catalysis B: Environmental* **100** 403-412
[3] Özçelik Z, Soylu G S P and Boz I 2009 *Chem. Eng. J.* **155** 94-100
[4] Santos V P 2010 Catalytic Oxidation of Volatile Organic Compounds *Phd dissertation from University of Porto* 9 – 12
[5] Kim H S, Kim T W, Koh H L, Lee S H and Min B R 2005 *Applied Catalysis A: General* **280** 125-131
[6] Yang J S, Jung W Y, Lee G D, Park S S, Jeong E U, Kim H G and Hong S S 2008 *J. of Industrial and Eng. Chemistry* **14** 779-784
[7] Wu H, Wang L, Zhang J and Shen Z 2011 *Catalysis Communications* **12** 859-865
[8] Zeng J, Liu X, Wang J, Lv H and Zhu T 2015 *J. of Molecular Catalysis* **408** 221-227
[9] Mu Z, Li J J, Duan M H, Hao Z P and Qiao S Z 2008 *Catalysis Communications* **9** 1874-1877
[10] Li S, Wang H, Li W, Wu X, Tang W and Chen Y 2015 *Applied Catalysis B: Environmental* **166-167** 260-269
[11] Li T Y, Chiang S J, Liaw B J and Chen Y Z 2011 *Applied Catalysis B: Environmental* **103** 143-148
[12] Tang X, Xu Y and Shen W 2008 *Chemical Engineering J.* **144** 175-180
[13] Hu C, Zhu Q and Jiang Z 2008 *Powder Technol.* **194** 109-114
[14] Singh B S and Tandon P K 2014 *J. of Energy and Chem. Eng.* **2** 106-115
[15] Maharsi R, Septianto R D, Rohman F, Iskandar F, Devianto H and Budhi Y W 2017 *Material Research Express* **4** 044002
[16] Xing T, Wan H, Shao Y, Han Y, Xu Z and Zheng S 2013 *Applied Catalysis A: General* **468** 269-275