Preparation Copper/Manganese Catalyst by Sol–Gel Process for Catalytic Incineration of VOCs

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ABSTRACT

Molecular sieve was utilized as a carrier of active metals copper and manganese to determine the effectiveness of removing toluene using a catalytic incineration. Catalysts with various metal ratios and weight loadings were produced by sol-gel to treat toluene. This investigation selected the most effective catalyst, based on the conversion rate of toluene and CO₂ yield. The influences of operating parameters of toluene oxidation on the conversion rate and long-term variations in catalytic activity were investigated, and the physical properties of catalysts were determined by Scanning Electron Microscopy (SEM). The conversion rate for toluene reached 50% and 95% (T₅₀ and T₉₅) when the Cu/Mn catalyst was used with a metal ratio of 1:1 and 20% loading at 263°C (T₅₀) and 400°C (T₉₅), respectively, an influent toluene concentration of 1000 ppm, oxygen concentration of 21%, a gas hourly space velocity (GHSV) of 12000/hr, and relative humidity (R.H.) of 26%. The stability of the Cu/Mn catalyst structure was assessed. This catalyst is a high-oxidation catalyst, yielding nearly 95% CO₂ at 400°C. Differences between fresh and aged catalysts were analyzed using analytical instruments, such as SEM. No obvious deactivation of the catalytic surface was detected.

Keywords: Molecular sieve; Cu/Mn catalyst; Sol-gel; Toluene; Operational parameters.

INTRODUCTION

Volatile organic compounds (VOCs) are recognized as major air pollutants, because of their toxic properties and their participation in the formation of photochemical smog (Kumar et al., 2008). They have high vapor pressure and are easily vaporized at ambient temperature and pressure. VOCs are carcinogenic and cause risk to skin, neural systems, eyes and other organs. Thermal incineration and catalytic incineration are the most efficient techniques for destroying VOCs (Wang and Lin, 2004; Wang et al., 2006). Cooling condensation, adsorption and absorption also convert VOCs, as activated carbon (Cheng, 2008) and zeolite are used to adsorb low concentrations of VOCs, and cooling condensation is used to adsorb high concentrations of VOCs. However, thermal incineration requires a high temperature of 800-900°C, a long retention time and a higher fuel cost than catalytic incineration. Catalytic incineration requires a much lower temperature, in the range 200-500°C (Wang et al., 2006), which can significantly reduce the formation of harmful by-products, such as dioxins from chlorinated compounds and nitrogen oxides.

Catalytic incineration involves supported noble metals and metal oxides as catalysts. The most common catalysts used in VOCs abatement are noble metals (Pt, Pd and Rh) and transition metal oxides (Mn₃O₄, NiO, Cr₂O₃, V₂O₅) dispersed on supports with high surface areas, such as alumina, silica and titania (Noordally et al., 1993; Zwinkels et al., 1993; Gandia et al., 2002; Alvarez-Galván et al., 2004). This study adopted a mixed ceramic honeycomb Pt/Pd catalyst to treat toluene, an important aromatic compound found in gasoline, and found a conversion rate of 95% at 230°C with an inflow toluene concentration of 2000 ppm, and a space flow speed of 40000/hr (Li et al., 1997), the Ptγ-Al₂O₃ catalysts prepared by sol-gel method showed higher thermal stability of metal particles than the conventional impregnation catalyst, because the exposed Pt metal particles strongly anchored onto the alumina support by metal–support oxygen bonding (Cho et al., 1998). It has been reported that Pt/HAUF causes methyl-isobutyl-ketone (MIBK) conversion to increase with oxygen concentration at low MIBK concentrations, and to increase at higher concentrations (Tsou et al., 2005). Chou et al. tested the influences of both MLSS (mixed liquor suspended solids) and diffuser type on VOC removal efficiency. Results showed that higher MLSS, such as 10,000-40,000 mg/L in mixed liquor, did not greatly enhance the transfer and removal of the introduced toluene (2009).

This study considered non-noble, metal-oxide catalysts, such as manganese-containing catalysts, which are low cost, environmentally friendly and relatively highly active in the combustion of VOCs (Li et al., 2004). Several investigations have shown that VOC oxidation is affected by the species of metal oxide, metal loading and preparation (Alvarez-Galván et al., 2003; Abdullah et al., 2006; Wyrwalski et al., 2007). Liu et al. utilized the TiO₂ carrier-supported active metal manganese, with an excellent conversion rate of chlorobenzene (2001). Results of using copper-on-silica catalysts prepared by sol-gel and impregnation methods showed that the distribution of copper species differed in the catalysts prepared by the two methods (Wang et al., 2002). Aluminum oxide was utilized as a carrier of active metals copper and manganese.

Catalysts with various metal ratios and weight loadings were produced by incipient impregnation to treat toluene (Lin and Lou, 2007). Wang adopted a CuOγ-Al₂O₃ catalyst to treat toluene and found that it performed best because it converted all of the toluene and yielded nearly 100% CO₂ at the lowest temperature (Wang et al. 2004). Aleksandra adopted nickel catalysts (8 wt% of NiO) that contained ZSM-5 and aluminum hydroxide (1:1) and tested them for activity in the hydrogenation of toluene, and found a high conversion rate at high temperature (Aleksandra,
Wang et al. adopted a CeO$_2$ catalyst in the catalytic incineration of aromatic hydrocarbons, and found a conversion rate of 95% at 280°C with an inflow toluene concentration of 4000 ppm and a space flow speed of 7200/hr (2004). Kim adopted a Cu/Al$_2$O$_3$ catalyst to treat toluene, and found a conversion rate of 95% at 340°C with an inflow toluene concentration of 1400 ppm, and a space flow speed of 40 cm$^3$/min (2002). The main purposes of this study were to produce catalysts and measure their properties, then compare their activities in oxidizing toluene and determine operational parameters.

Larsson and Andersson noted excellent performance in catalytic combustion of CuO$_x$/Al$_2$O$_3$ and CuO$_x$–CeO$_2$/Al$_2$O$_3$ (Larsson and Andersson, 2000). Tseng et al. reported excellent metal-oxide catalyst activity (MnO/Fe$_2$O$_3$) in the catalytic oxidation of styrene (2001). García treated naphthalene with CeO$_2$, and found that a higher temperature (250°C) required for complete oxidation of naphthalene increased with the gas hourly space velocity (GHSV) (García et al., 2006). It was found that increasing the GHSV reduced toluene conversion when CuO/CeO$_2$ catalyst was used to treat toluene (Wang et al., 2006).

MATERIALS AND METHOD

Experimental Instruments

Fig. 1 displays the catalytic incineration system in this experiment. It includes a high-temperature catalytic reaction system comprised of: a high-temperature furnace 30 cm in length, with an inner diameter (ID) of 3.5 cm; a K-type thermocouple 45 cm long, with an ID of 0.35 cm, and a tubular catalytic-bed quartz reactor 30 cm long and an ID of 2.54 cm. The system also included a gaseous toluene-manipulating system with a reaction system that included three independent lines to feed N$_2$, O$_2$ and toluene (C$_7$H$_8$), as well as a sampling and analyzing system. The tubular catalytic-bed quartz reactor was filled to 2.5 cm with catalyst. The toluene was carried in air into the catalytic-bed quartz reactor. All gases were filtered to remove moisture and impurities before they entered into the flow meter. Toluene concentrations were determined using a gas chromatograph with a flame ionization detector (GC-FID, Shimadzu GC-14A). The amount of CO$_2$ product in the effluent gas was measured using a gas chromatograph with a thermal conductivity detector (GC-TCD, Shimadzu GC-14).

Catalyst Preparation

In this study, a molecular sieve was utilized as a carrier of copper and manganese by sol-gel method. Table 1 shows the physical and chemical properties of the molecular sieve. Catalysts with various ratios (wt/wt) of metals (Cu, Mn, Cu/Mn = 1), and different loadings (10 wt% and 20 wt%) were produced to neutralize toluene. The molecular sieves were treated with deionized water; dried in a vacuum oven at 105°C for 24 hr., and cooled to room temperature. A known amount of aluminum isopropoxide (AlIP) in deionized water was shocked for 30 min at 80°C, after which 65% HNO$_3$ was added and shocked for 30 min. A known amount of metal salt (Cu, Mn) aqueous solution was added to the solution and shocked for 30 min at 80°C. The molecular sieve in solution was then shocked at 85°C for 30 min, then dried in an oven at 105°C for 24 hr, and finally calcined in an oven with air supplied (0.2 L/min) at 600°C for 4 hr.

Activity Measurements

Activity measurements were made in a tubular catalytic-bed quartz reactor at nearly atmospheric pressure. The activity of the catalyst was measured as follows. About 1g of powdered quartz was placed under the catalyst (10g) to reduce the temperature gradient in the catalytic bed. The catalysts were pretreated at 100-500°C, with an influent toluene concentration of 1000 ppm, an oxygen concentration of 21%, a space velocity of 12000/hr and a humidity of 26%. The temperature was increased from 200°C to prevent the adsorption of toluene in the initial stages of the test, and then increased stepwise 50°C until 500°C. In each step, the temperature was held at 20 min and the gases were analyzed in the steady state. Toluene conversion rates with various catalysts were compared to choose the most active catalyst to measure the incineration efficiency of toluene, as described below.

Incineration Efficiency with Various Operation Parameters

Table 2 shows various operating parameters including reaction temperature, influent toluene concentration, space velocity and oxygen concentration. The reaction was performed at 100-500°C,
Table 1. Physical and chemical properties of molecular sieve.

<table>
<thead>
<tr>
<th>DETERMINATIONS</th>
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<tbody>
<tr>
<td>Pore Diameter</td>
<td>10 Å</td>
</tr>
<tr>
<td>Packing Density</td>
<td>640 kg/m²</td>
</tr>
<tr>
<td>Particle Diameter</td>
<td>3.92~4.11 mm</td>
</tr>
<tr>
<td>Crush Strength</td>
<td>82 N</td>
</tr>
<tr>
<td>Moisture Content</td>
<td>&lt; 1%</td>
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Table 2. Various operating parameters and range.

<table>
<thead>
<tr>
<th>Operating parameters</th>
<th>Operating range</th>
</tr>
</thead>
<tbody>
<tr>
<td>reaction temperature</td>
<td>100°C–500°C</td>
</tr>
<tr>
<td>influent toluene concentration</td>
<td>350 ppm–1,600 ppm</td>
</tr>
<tr>
<td>space velocity</td>
<td>3750/hr–12,000/hr</td>
</tr>
<tr>
<td>oxygen concentration</td>
<td>21%–40%</td>
</tr>
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with an inlet toluene concentration of 350 ppm-1,600 ppm, a space velocity of 3750/hr-12000/hr, an oxygen concentration of 21%-40%. The temperature was increased from 100°C in steps of 50°C until 500°C.

RESULTS AND DISCUSSION

Screening catalytic Activity
Sol-gel was adopted to prepare the catalyst using molecular sieve carrier-supported active metals, copper and manganese. Various ratios of metals (Cu, Mn, and Cu/Mn = 1) were prepared with different loadings (10 wt%, 20 wt%) under the same reaction conditions (toluene conc. = 1000 ppm, GHSV = 12000/hr, O₂ = 21%, R.H. = 26%). Fig. 2 shows a strip chart of the toluene conversion rate for simplex Cu or Mn and various weight ratios of metal catalysts at 100-500°C. The simplex Mn (10 wt%) metal catalyst was the least active, with Tₕ₀ of the toluene at 389°C, unable to remove T₉₅ of the toluene. The Cu/Mn (20 wt%) catalyst was the most active, because Tₕ₀ and T₉₅ of the toluene at 263°C and 400°C respectively, yielding almost 95% of CO₂. The Cu/Mn (10 wt%) catalyst was the next most active, with Tₕ₀ of toluene at 268°C and T₉₅ of toluene at 425°C. The toluene conversions increased with the loading.

Fig. 3 plots the toluene conversion for different weight loadings at various temperatures (Inlet Conc. = 1000 ppm, GHSV = 12000/hr, O₂ = 21%, R.H. = 26%). Various Cu/Mn weight loadings (10 wt%, 20 wt%, and 30 wt%) were utilized to elucidate the effect of Cu/Mn weight loading on toluene conversion. The three conversions followed in the order of: 20 wt% Cu/Mn, 30 wt% Cu/Mn and 10 wt% Cu/Mn. Results were: Cu/Mn (20 wt%) removed T₉₅ of the toluene at 400°C. The 10 wt% Cu/Mn and 30 wt% Cu/Mn removed T₉₅ of the toluene at 425°C. Therefore, the Cu/Mn (20 wt%) catalyst almost covered the molecular sieve carrier to saturation, and the optimal Cu/Mn weight loading was 20 wt%. The cost was low and the performance favorable, as well. Accordingly, the Cu/Mn (20 wt%) catalyst was used in the following experiments.

Catalytic Incineration System Test
Blank test
“Blank” refers to the absence of catalyst on the catalytic bed, with the catalyst replaced by quartz. “Molecular sieve carrier blank” refers to molecular sieve on the catalytic bed. Fig. 4 displays the effect of toluene conversion on the blank, molecular sieve carrier blank and Cu/Mn (20 wt%) catalyst at various temperatures. The blank test toluene converted as the temperature rose, regardless of whether molecular sieve carrier and metal catalyst were present in the catalytic bed. However, the conversion was limited; the blank exhibited about 16% conversion at 400°C and the molecular sieve carrier blank exhibited around 24% conversion at 400°C. Adding the Cu/Mn (20 wt%) catalyst significantly increased the conversion to 95% at 400°C, indicating that a true Cu/Mn catalyst can lower the reaction temperature of toluene, most of which was removed catalytically. Accordingly, the catalyst in this study was very effective in eliminating toluene.

Effect of Toluene Inlet Concentration
The test utilized various toluene inlet concentrations (350 ppm, 600 ppm, 1000 ppm, 1,200 ppm and 1,600 ppm) at various temperatures (GHSV = 12000/hr, O₂ = 21%, R.H. = 26%). Fig. 5 displays the toluene concentrations of 1,200 ppm and 1,600 ppm at temperatures of 300-400°C; the toluene conversion rate decreases slightly as the toluene concentration increases. Nonetheless, the toluene inlet conversions were approximately 95% at all toluene concentrations at 450°C. This result demonstrated that the conversion did not vary significantly with the toluene concentration.

Space Velocity
Space velocity is defined as the inverse of residence time: as the space velocity decreases, the residence time increases. A
Fig. 4. Effect of toluene conversion on blank, carrier blank and Cu/Mn (20 wt%) catalyst at various temperatures (Inlet Conc. = 1000 ppm, GHSV = 12000/hr, O2 = 21%, R.H. = 26%).

Fig. 5. Effect of toluene conversion under various toluene inlet concentrations at various temperatures (GHSV = 12000/hr, O2 = 21%, R.H. = 26%).

longer residence time normally increases the reaction rate, such that the conversion should increase as the space velocity decreases. This phenomenon was noted as early as 1976 (Pope et al.). The test involved various space velocities (3750/hr, 5600/hr, 7500/hr, 9350/hr and 12000/hr), and various reaction temperatures and toluene conversion were observed. Fig. 6 shows that toluene conversion fell as the space velocity increased at a given reaction temperature. When the space velocity was less than 7500/hr, the decrease in the toluene conversion rate was obvious: T95 of toluene at 300°C and a space velocity of 7500/hr. Nevertheless, T95 of toluene converted at 400°C at all space velocities. It declined to 5% as the space velocity increased to 9350/hr and 12000/hr at 400°C, but the toluene conversion rate still reached 95%. The conversion truly decreased as the space velocity increased in the experimental operating range. Moreover, the space velocity clearly influenced the conversion, but at a temperature of 400°C, the conversion did not vary significantly with space velocity. This parameter was not important at high temperatures.

**Effect of Oxygen Concentration**

In this study, toluene conversion was observed at various oxygen concentrations (21%, 30%, and 40%) and temperatures.

Fig. 7 reveals that the conversion of toluene increased with oxygen concentration. For example, the toluene conversion rate was 62% and 87% at oxygen concentrations of 21% and 30%, respectively, at 300°C. The oxidation of toluene depends on oxygen, and toluene may have reacted with oxygen on the catalyst. Therefore, an oxygen concentration of close to the saturation concentration of dissolved oxygen is advantageous to toluene conversion. However, oxygen concentration surpasses the saturation of dissolved oxygen, perhaps because of sintering of the catalyst surface, thus reducing the toluene conversion rate. For example, the toluene conversion rate was 87% and 56% at oxygen concentrations of 30% and 40%, respectively, at 300°C.

**Test of Extended Decay of Catalyst**

The decayed catalyst is poisonous, dirty; it breaks and loses activity. The long-period decay test was performed five days (with one analysis every 12 hr) to elucidate the variation of toluene conversion at 350°C (Inlet Conc. = 1000 ppm, GHSV = 7500/hr, O2 = 21%, R.H. = 26%). Fig. 8 depicts the use of the Cu/Mn (20 wt%) catalyst to treat the toluene, and the toluene conversion rate was 88-93% at a reaction temperature of 350°C. The results indicated that the conditions of toluene conversion decay did not clearly vary at 350°C, also indicating that the Cu/Mn catalyst was quite stable.

Fig. 6. Effect of toluene conversion on various space velocities at various temperatures (Inlet Conc. = 1000 ppm, O2 = 21%, R.H. = 26%).

Fig. 7. Effect of toluene conversion under various oxygen concentration at various temperatures (Inlet Conc. = 1000 ppm, GHSV = 12000/hr, R.H. = 26%).
Fig. 8. Toluene conversion at different reaction times (Inlet Conc. = 1000 ppm, GHSV = 7500/hr, O2 = 21%, R.H. = 26%, catalyst: Cu/Mn 20%).

The SEM demonstrates that the original particle sintering or any destruction of spherical particles was observed. This figure demonstrates that the catalyst show a morphology, consisting of conglomerates of spherical particles and the particle size of the catalyst was nearly 50-100 nm.

The characteristics of the products of catalytic incineration were usually related to those of the catalysts and the reactants. Eq. (1) describes the general complete oxidation of toluene.

\[
C_7H_8CH_3 + 8O_2 \rightarrow 6CO_2 + 4H_2O
\]  

(1)

The experimental results demonstrated that the gaseous end product of toluene oxidation was CO2 after the Cu/Mn (20 wt%) catalyst was incinerated. Fig. 9 depicts that this catalyst is a high-oxidation catalyst, yielding nearly 95% CO2 at 400°C.

CONCLUSIONS

Toluene gas was catalytically treated with various metals at various weight ratios with the following important conclusions being drawn.

1. The simplex Mn metal catalyst was the least active because it was unable to convert 95% of toluene.
2. The Cu/Mn (20 wt%) catalyst was the most active, because it converted 95% of toluene at 400°C and yielded nearly 95% CO2. The Cu/Mn (10 wt%) catalyst was the second most active, because it converted 95% of toluene at 425°C.
3. The Cu/Mn (20 wt%) catalyst almost covered the aluminum oxide carrier to saturation, and the optimal Cu/Mn weight loading was 20 wt% because the cost was low and the performance favorable.
4. The Cu/Mn catalyst can reduce the reaction temperature of toluene and most of the toluene was removed catalytically.
5. The result demonstrated that the conversion did not vary significantly with the toluene concentration. The space velocity clearly influenced the conversion, but at a temperature of 450°C, the conversion did not vary significantly with space velocity.
6. The conversion of toluene increased with oxygen concentration. However, if the oxygen concentration exceeds the saturation concentration, then sintering of the catalyst surface may occur, and the toluene conversion rate will be reduced.

ACKNOWLEDGMENTS

The authors would like to thank the National Science Council of the Republic of China, Taiwan for financially supporting this research under Contract Number NSC 97-2221-E-110-042-MY2. Ted Knoy is appreciated for his editorial assistance.

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Received for review, May 7, 2009
Accepted, June 3, 2009