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Catalytic Decomposition of Ozone by CuO/MnO_2-Performance, Kinetics and Application Analysis

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Abstract

Ozone as a major ambient gas pollutant needs to be removed for many indoor environments due to its adverse health effect. The objective of this study is to investigate the ozone removal performance of a Hopcalite catalyst CuO/MnO_2 under different operation conditions. The effect of relative humidity (15-80%), temperature (30-160°C) and ozone concentration (200-2000ppb) was experimentally tested. Then the catalyst was coated on fiberglass media for application. The influence of preparation method was also investigated. Finally, the application analysis of such material is discussed for building environment control situation.

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Keywords:

1. Introduction

The ground-level ozone concentration keeps increasing due to photochemical effect and has also become an important ambient air pollutant during the past several decades [1]. Ozone concentration in urban ground air is usually below 100ppb, but can reach to over 200 ppb in some megacities (e.g., Beijing, Shanghai) in polluted season [2]. Ozone is also a major gaseous pollutant in aircraft cabin environment, which can cause comfort, and health problems for crewmembers and passengers. Ozone can cause dry skin, dry eyes, sore throat and other respiratory symptoms. Long-term exposure to high concentrations of ozone may result in serious damage to human health; even

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cause cancer [3]. Therefore it is necessarily to remove the ozone from the air to be delivered to human occupied space.

Various metal oxides and carriers-supported noble metal catalysts have been studied for gas ozone removal, including MnO_2, Fe_2O_3, Ag_2O, CuO, and NiO_2 [4,5]. The Hopcalite catalyst, which is a mixture of MnO_2 and CuO was studied for ozone removal performance in current study. For ambient ozone pollutant control, the operation temperature should also not be much higher than ambient temperature. The traditional catalytic ozone converters work at the temperature of 150~250°C [6], but the operation temperature will decrease to lower than 120°C in the emerging electric air system, which is already used in Boeing 787 [7]. Therefore the purpose is to investigate the performance of CuO/MnO_2 catalyst at the lower temperature range, mainly lower than 100°C. The tests temperature range is 25~160°C in current study. Relative humidity is an important factor that affects the performance of Hopcalite when it is used to convert CO to CO_2.However, the effect of relative humidity is not clear when used for ozone removal. To explore the catalyst performance within ppb-ppm concentration range, the target concentration level in this study is designed to be 100~2000 ppb.

For practical application, many structural forms, including packed bed, fibrous materials [8], and catalysts carried on monolith [9] or metal foam [10], were used. For the removal of ozone in the makeup air supplied to buildings, fibrous materials or even packed bed may be feasible because of the affordable pressure drop. In current study, the MnO_2/CuO catalyst was coated on fibrous material, the performance was tested and its application for building environment control is analyzed.

2. Methods

The commercially Hopcalite catalyst CuO/MnO_2 with 50~60 mesh size was studied (mass ratio of CuO and MnO_2 is about 1:3, from Xinhua Chemical Co., China). The ozone removal performance of the catalyst was evaluated with a single pass test system. The experiments were performed in a fixed bed reactor with a quartz tube (i.d.= 3 mm). The reactor was equipped with a tubular heater and the temperature can be controlled in the range of 20~250±1°C. The relative humidity was controlled by adjusting the flow ratio between bypass and water bubbling bottle, and could be controlled in the range of 5~80±3% at 25°C. The flow rate through the packed column was 1.5 LPM, of which 1.2 LPM was used for humidity control and dilution, and the other 0.3 LPM was used as carrier gas of ozone generation by an ultraviolet ozone generator (UVP SOG-2). The ozone generation rate was controllable. An ultraviolet ozone analyser (API T400) was used for concentration measurement.

About 8.1 mg catalyst was used in each test, which will generate a bed depth of about 2.1 mm, a gas hourly space velocity (GHSV) of 6.10×10^6 h^{-1}, and a residence time of 5.90×10^{-4} s. The test temperature was 25 to 160 °C with the interval of 10 or15 °C. During each test, the downstream concentration was continuously measured with constant upstream concentration. The temperature was kept at the lowest level for at least 2 hours to allow a steady –state to be reached. Then the temperature was adjusted to higher levels gradually and the measured was kept for 20min for each temperature. The average of downstream concentration at the last 10 min of each reaction temperature was taken as the outlet concentration C_{out}. Example downstream concentration profile was shown in Figure 1. The tests were conducted for 7 concentration levels, namely 107, 157, 320, 495, 822, 1148 and 1530 ppb. All the tests were repeated at three relative humidity levels, namely 15±2%RH, 50±3%RH and 85±3%RH.

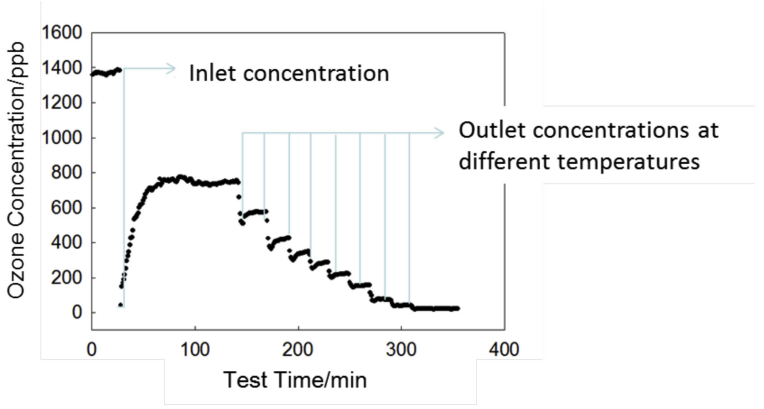


Fig. 1. *An example of downstream concentration profile during the test at changing reaction temperatures*

3. Results

3.1. The decomposition rate at different temperature and concentration

The ozone decomposition rate(r, s^{-1}) was defined as the mass of removed ozone by per unit mass of catalyst during unit time, and was calculated as Equation (1).

$$r = \frac{G(C_{in} - C_{out})}{M} \tag{1}$$

Where C_{in} and C_{out} are the inlet and outlet ozone concentration; G is the airflow rate, M was the catalyst mass.

Table 1. *The decomposition rate at different reaction temperature and concentration (10^{-6} s^{-1})*

Ozone/ ppb / Temp./°C	1498	1116	820	495	Ozone/ ppb / Temp./°C	320	157	107
160	9.919	7.354	5.401	3.232	130	1.983	0.978	0.689
145	9.645	7.046	5.260	3.161	120	1.904	0.944	0.675
130	9.270	6.610	5.010	3.048	110	1.842	0.910	0.658
115	8.774	6.136	4.643	2.906	100	1.812	0.892	0.640
100	8.199	5.663	4.250	2.756	90	1.753	0.876	0.621
85	7.684	5.247	3.851	2.598	80	1.686	0.839	0.601
70	7.061	4.822	3.521	2.444	70	1.649	0.792	0.580
55	6.590	4.401	3.344	2.237	60	1.613	0.754	0.555
40	6.008	4.025	3.025	2.036	50	1.536	0.689	0.532
25	5.621	3.740	2.699	1.856	40	1.448	0.627	0.508
					30	1.324	0.571	0.495

The calculated decomposition rate at different temperatures and concentrations (15%RH) are listed in Table 1. The decomposition rate at 40, 70, 100 and 130°C are also plotted with concentration in Figure 2. A linear relation was found.

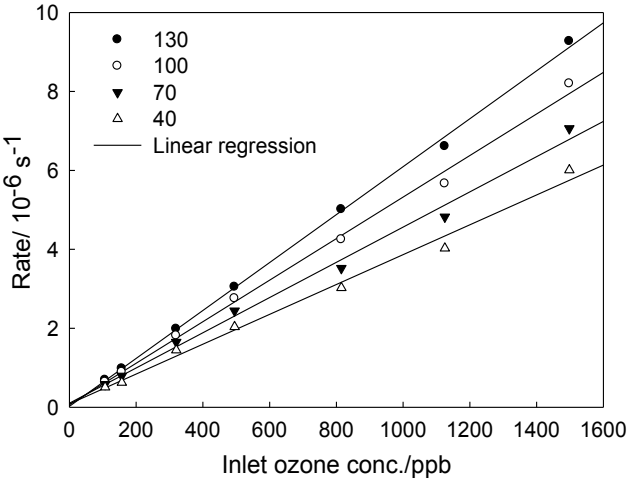


Fig. 2. The decomposition rate versus concentration at four different temperature levels

Radhakrishnan consider the ozone decomposition rate on MnOx can be expressed as following at the steady state [11]:

$$r_{ss} = A_{app} \exp\left(-\frac{E_{app}}{RT}\right) O_3^n \tag{2}$$

Where A_{app} is frequency factors for the specific reaction coefficient, E_{app} is the activation energy ($Jmol^{-1}$), $T$is the absolute temperature (K), and $R$is the universal gas constant ($J\ mol^{-1}\ K^{-1}$). And the ozone decomposition order, n, on MnO_X supported by Al_2O_3, ZrO_2, TiO_2 and SiO_2 was found to be 0.99, 0.98, 0.85 and 0.92 respectively. The reaction order in current tests was also fitted with the Equation (3) with a MATLAB program, and n is 0.987, 0.993, 0.991 and 1.002 for the temperature of 40, 70, 100, and 130°C respectively, which are all close to 1.Therefore the reaction of ozone on this catalyst can be considered as first order approximately.

Then at each concentration level, the plots of reaction rate r vs $1/T$ are presented in Figure 3. Therefore the kinetic parameters can be obtained through exponential fitting for each concentration, and the average is: A_{app}=49.7±1.93 $m^3 \cdot g^{-1} \cdot h^{-1}$, E_{app}=5362±118 $kJ \cdot mol^{-1}$, and the relation index R^2=0.998.

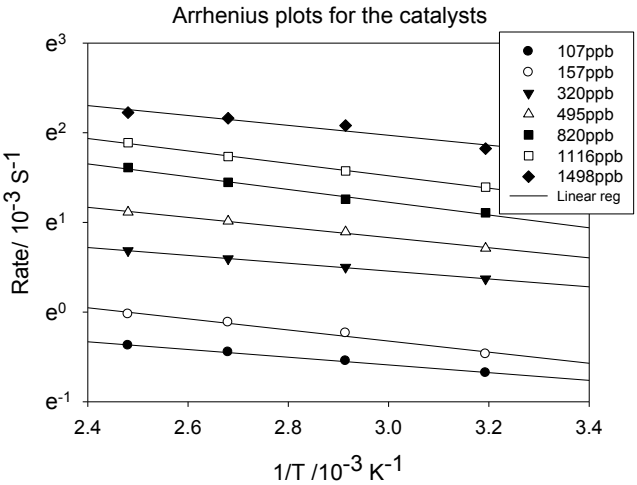
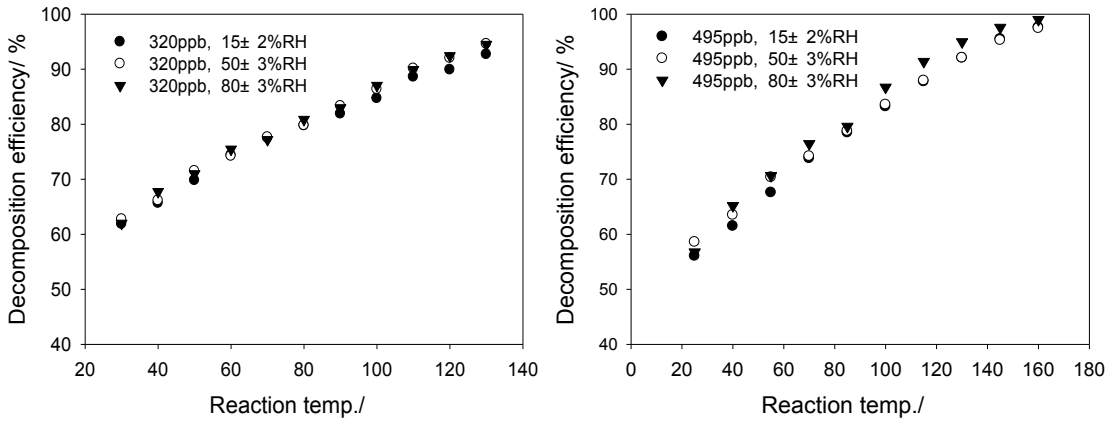


Fig. 3 Arrhenius plots of reaction rate at different inlet ozone concentrations

3.2. Effect of relative humidity

The effect of relative humidity on the decomposition efficiency was presented for four concentration levels in Figure 3. The maximum difference on efficiency was 11% during all the tested temperature-concentration points, which occurs at 882 ppb and 85°C point. Then one could consider that RH has little impact on ozone decomposition by Hopcalite catalyst at the tested concentration and temperature levels.



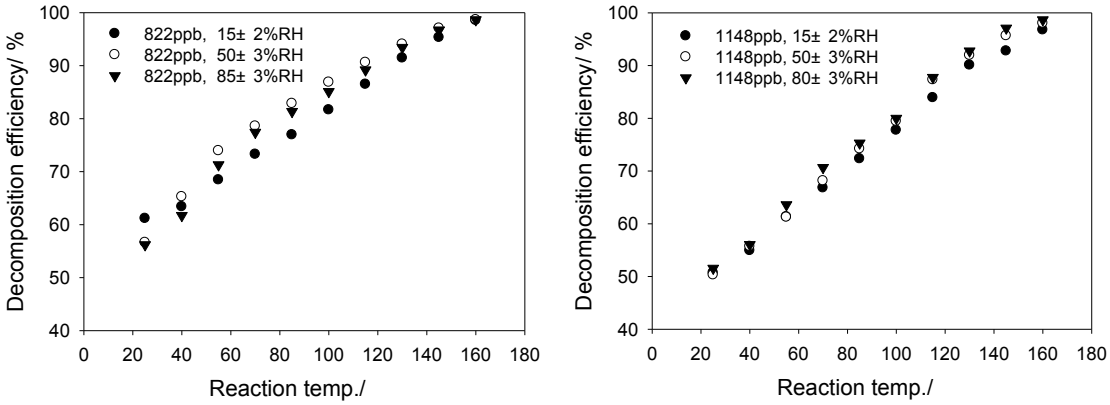


Fig. 4. The effect of RH on ozone removal at different temperature and concentration

The results agree with prior studies. Vol'Fson et al. reported that MnO2 and Ag-promoted catalysts show unchanged activity at relative humidity levels of 10% and 85%RH [12]. Mehandjiev and Naidenov tested the ozone decomposition on α-Fe2O3 at 10% and 85%RH, and found that the ozone decomposition efficiency curves are almost the same. Sullivan et al. reported the Al2O3 activity would not be affected by the water vapour [13]. And Spasova et al. tested the aluminium-supported copper oxide, manganese and copper-manganese catalysts at 10% and 85%RH, and the catalysts activity also remain almost the same with the difference of relative humidity [14].

3.3. Performance of catalyst loaded fibrous material

Ozone decomposition materials, catalyst or sorbent, all need to be incorporated into filter material type for real application. The most common types are V-bank filter bed, fibrous material or coated monolith honeycomb. For application as ozone catalytic converter in aircraft cabin, the catalysts are coated onto monolith honeycomb. The V-bank filter bed can hold large amount of sorbent media, therefore has large ozone removal capacity, but also leads to higher pressure resistance. The sorbent activated carbon can also be sandwiched into two layers of fibrous material, and then can be made into pleated filter. This is often used in building environment control, and can also be used for other gas contaminant control. The catalyst/sorbent particles sandwiched between fibrous layers need to be large enough for enough capacity. The manufacture process normally need to use glues to keep the particles uniformly between the fibrous covers, and therefore may block some surface area of the catalyst and decrease the active site availability. In current study, the catalyst was coated onto glass fiber material using impregnation method. The catalyst particles are much smaller, and therefore decrease the internal diffusion time in catalyst particles. Also, the fibrous material owns the benefit of large porosity and therefore less pressure resistance

The glass fiber filter media was impregnated with HCL solution (0.5%, 1% and 3%) to form microspores on the surface and to increase the internal surface of the fiber. Then the fiber was dried and impregnated in the mixture solution of $Cu(NO_3)_2$ and $Mn(NO_3)_2$ (1:3, 1:1, and 3:1) for several hours (3h, 5h and 6h). The impregnated fiber was drained and dried at different temperatures (50℃, 70℃ and 90℃) and roasted at different temperatures (150℃,200℃ and 250℃.The material preparation matrix is listed in Table 2.

The prepared media was then tested for ozone removal performance. A stainless steel column reactor (9mm I.D.) with a fibrous media holder was used for single pass efficiency test. The reaction temperature was set as 26° C, face velocity as 1.0m/s, and relative humidity as 15%. The challenge ozone concentration is 150ppb. Three layers of coated glass fiber media was installed in the system, which gives a media depth of 6mm, and a residence time of 6ms. The weight of the material is 0.22g, and the active catalyst mass loaded was calculated to be 0.13g.

Table 2. *Fibrous material preparation parameter and its ozone decomposition performance (η : single pass efficiency at steady state, r: decomposition rate)*

Material*	η /%	r/$10^{-6}s^{-1}$	Material*	η /%	r/$10^{-6}s^{-1}$
#1:0.5%, 1:3, 3h, 50° C, 150° C	54.1	0.149	#15: 1%, 1:1, 6h, 50° C, 250° C	48.5	0.134
#2: 0.5%, 1:3, 3h, 50° C, 200° C	54.3	0.150	#16: 1%, 3:1, 3h, 70° C, 150° C	44.4	0.122
#3: 0.5%, 1:3, 3h, 50° C, 250° C	49.3	0.136	#17: 1%, 3:1, 3h, 70° C, 200° C	45.0	0.124
#4: 0.5%, 1:1, 5h, 70° C, 150° C	44.0	0.121	#18: 1%, 3:1, 3h, 70° C, 250° C	45.3	0.125
#5: 0.5%, 1:1, 5h, 70° C, 200° C	44.3	0.122	#19: 3%, 1:3,6h, 70° C, 150° C	48.0	0.132
#6: 0.5%, 1:1, 5h, 70° C, 250° C	43.4	0.120	#20: 3%, 1:3,6h, 70° C, 200° C	61.2	0.169
#7: 0.5%, 3:1, 6h, 90° C, 150° C	54.4	0.150	#21: 3%, 1:3,6h, 70° C, 250° C	54.6	0.150
#8: 0.5%, 3:1, 6h, 90° C, 200° C	54.8	0.151	#22: 3%, 1:1,3h, 90° C, 150° C	49.6	0.137
#9: 0.5%, 3:1, 6h, 90° C, 250° C	48.0	0.132	#23: 3%, 1:1,3h, 90° C, 200° C	45.8	0.126
#10:1%, 1:3, 5h, 90° C, 150° C	45.3	0.125	#24: 3%, 1:1,3h, 90° C, 250° C	45.1	0.124
#11:1%, 1:3, 5h, 90° C, 200° C	47.1	0.130	#25: 3%, 3:1,5h, 50° C, 150° C	47.3	0.130
#12: 1%, 1:3, 5h, 90° C, 250° C	45.1	0.124	#26: 3%, 3:1,5h, 50° C, 200° C	51.5	0.142
#13: 1%, 1:1, 6h, 50° C, 150° C	54.3	0.150	#27: 3%, 3:1,5h, 50° C, 250° C	48.4	0.133
#14: 1%, 1:1, 6h, 50° C, 200° C	51.1	0.141			

Note*: the parameters for material preparation are HCL solution concentration, Cu/Mn ratio, impregnation time, dry temperature and sintering temperature, respectively.

Similar as the raw pellet material, the initial ozone decomposition efficiency is high over 90%, then it decreased over time, and reach a quasi steady state after about 10 hours. The efficiency and corresponding reaction rate was calculated with the data at quasi steady state. The performance of the 27 impregnated fibrous media was compared in Table 2. Although the performance of the media prepared according to different parameters was not significantly different, with the efficiency in the range of 40~60%, the #20 material prepared with 3% HCL solution, Cu/Mn ratio as 1:3, impregnated for 6hours, dry at 70° C, and sintered at 200° C presents the best performance. The range analysis of the results shows that the order of the parameter influence significance are Cu/Mn ratio > sintering temperature> HCL solution concentration> dry temperature > impregnation time.

4. Discussions

For application in building environment ozone control, the Cu/Mn catalyst coated fiberglass media can be used as a filter material in building Air Handling Unit. To demonstrate, a typical office building was used as an example for feasibility analysis. Consider a three-floor office building with a volume of 20000m^3, and total supply airflow rate (Q) of 20000m^3/h, if the make up air ratio is 30%, the fresh airflow rate (Q_o) would be 6000m^3/h. The outdoor ozone concentration was assumed to be 0.25mg/m^3(about 128 ppb) as a representation of a high ozone pollution case. The indoor target ozone concentration was set to be 0.08mg/m^3 (about 41 ppb). Ozone can be adsorbed by or react with many building environment surface and related material. The average deposition of ozone on old building materials was found to be 13% (Klen et al. 2010), and this value was taken as the ozone deposition percentage η_d during indoor stay. So the ozone concentration at return air Cr can be calculated with supply air concentration as Cr =(1-0.13) Cs.

To reach the target indoor concentration, the required ozone removal rate can be calculated through mass balance equation as follows:

$$Q_o C_o - Q_e C_r - Q C_s \eta_d - E = 0 \quad (3)$$

where the Q_o is the fresh air flow rate (m^3/h), which is equal to the exhaust air flow rate Q_e (m^3/h) , C_o, C_r and $C_s$are the ozone concentration (mg/m^3)of outdoor air, return air, and supply air respectively. E is the ozone removal rate by the air-cleaning unit (g/h).

With serious outdoor ozone pollution ($\mathbf{C_o}$=0.25mg/m^3), the supply air ozone concentration was calculated to be 0.20mg/m^3 without ozone removal unit (i.e. E=0), which is still higher than the standard requirement, and the indoor concentration can be even higher with higher ventilation rate. If the supply air concentration is set to be the target concentration 0.08mg/m^3, the required ozone removal rate E can be calculated to be about 0.9g/h, and the corresponding removal efficiency is 56.5%.

The required catalyst mass to reach this efficiency can be calculated according to the performance data above. The decomposition rate at test condition 150ppb (0.3mg/m^3) is $0.169\times10^{-6}s^{-1}$. As the reaction can be considered to be a first order one, the decomposition rate at target level (0.25mg/m^3) is calculated to be $0.141\times10^{-6}s^{-1}$. Then the required catalyst mass according to equation (1) is 1.8kg. Such a filter is normally achievable to be installed in the AHU.

5. Conclusions

The performance of CuO/MnO_2 catalyst for ozone contaminant removal was experimentally investigated at different temperature, relative humidity, and concentration levels. The relative humidity has negligible effect on the performance of this catalyst. The temperature effect can be described by Arrhenius equation, and the reaction can be considered as a first order reaction with challenge concentration. The catalyst was then impregnated on glass fiber material with the optimized preparation method found through orthogonal test, and the single pass efficiency can reach about 56% under typical environment condition. An application analysis using such material shows that its feasibility in building environmental ozone control.

Acknowledgements

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