Catalytic performances of Cu-Mn-Ce oxide/SiC monolithic catalyst for oxidation of toluene under microwave irradiation

Bin Guo, Xurui Hu*, Xin Wang, Shuo Zhang

School of Environmental Science and Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China

*email:huxurui5200@163.com

Keywords: Catalytic combustion; Silicon carbide (SiC); Microwave irradiation; Monolithic catalyst

Abstract. A monolithic Cu-Mn-Ce oxides supported on a ring of silicon carbide (SiC) with molar ratios 1:2:1 were prepared by the sol-gel combustion method without any binder. The catalysts were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer-Emmett-Teller method (BET). Toluene was chosen as a model compound to evaluate the catalytic activity in a conventional fix-bed quartz reactor. The results showed that the mixed oxides adhered firmly to the ring of silicon carbide surface. Compared with the conventional heating, the Cu-Mn-Ce oxides monolithic catalysts under microwave irradiation showed higher activity for the combustion of toluene in the low temperature range (350 ^{o}C<400 ^{o}C) and the 90% of toluene conversion was achieved at 350 ^{o}C.

Introduction

Toxic volatile organic compounds (VOCs) become the focus and hot spots of scientific research. Because it can cause a lot of disease such as headache, nausea, intoxication and even cancer after long exposures. What's more, it can also destruction of the ozone layer indirectly and produce photochemical smog [1]-[3].VOCs waste gas mainly comes from petroleum chemical industry, pharmaceutical, paint, motor vehicle, footwear and other industries. How to effectively control VOCs pollution has become an important task of the prevention and control of atmospheric pollution. Then many techniques have been studied and applied to treat waste VOCs, such as adsorption [4], biological process [5], and combustion method [6] etc.. Catalytic combustion has the advantages of low light-off temperature, wide application range, high efficiency and no secondary pollution. Transition metals oxides, such as copper oxide and manganese oxide, as catalytic active component increases catalytic capacity by generating more surface oxygen species and creating more active sites on catalyst [7]-[9]. However, conventional heating method may cause catalyst sintering. Therefore, there is a need for a new heating method in catalytic oxidation of VOCs to overcome this weakness.

Microwave is a type of electromagnetic wave with high thermal effect has been widely used in the treatment of solid waste [10], waste water [11]and waste gas [12] because of its low thermal inertia and dipole polarization. This helps to avoid catalyst sintering. However, microwave irradiation is selective. It only heats the materials that absorb microwave energy. It's reported that silicon carbide (SiC) [13] is excellent in absorbing microwave energy. There are few reports on the process of VOCs waste gas by a microwave irradiation method.

In this study, we focus on the advantages of microwave heating over conventional heating on Cu-Mn-Ce oxides/SiC monolithic catalyst prepared by the sol-gel method without any binder during catalytic combustion of toluene. Various characterizations including BET, SEM and XRD are applied to investigate the surface properties of the monolithic catalyst.

Experimental

Catalysts preparation

The ring of silicon carbide is φ3.5mm×7mm and 6 mm length. Copper nitrate, manganese nitrate,

and cerium nitrate were mixed in molar ratios of 1:2:1 in an appropriate volume of distilled water to obtain a transparent solution. The same moles of citric acid were added into the nitrate solution and ammonia water were added into the mixed solution to adjust pH to 6. The solution was heated to 70 ^{o}C and stirred until it became viscous. Then the rings of silicon carbide were immersed in this viscous solution for 20 min. It was then dried at 120 ^{o}C for 12 h and then calcined at 550 ^{o}C for 4 h. The coating procedure was repeated to achieve the desired loading.

Activity test

A quartz glass tube (r×L=40 mm×1100 mm) was manufactured to test the activity of the catalyst. Then the catalysts were packed in the tube about 100 mm high as shown in the Fig.1. Gaseous VOCs were generated by flowing air coming from an air pump controlled by flowmeter through liquid toluene in a glass bottle. The toluene-containing stream was mixed with the air stream introduced through another flowmeter. In the microwave-heating reactor, toluene gas entered the bed from the top of the reactor and was oxidized on the surface of the catalyst. And in the conventional heating reactor, toluene gas entered the bed from the right to the left. Inflow and outflow gas were analyzed by gas chromatography to determine the removal efficiency. The whole experimental process was shown in Fig. 2.

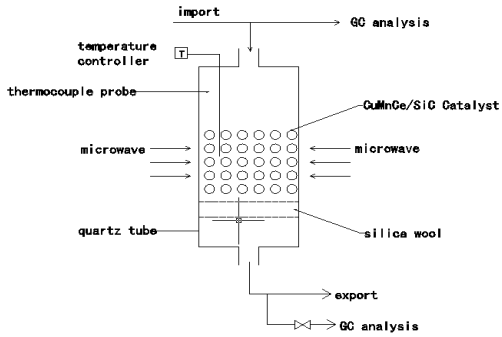

Fig.1 Diagram of microwave reactor

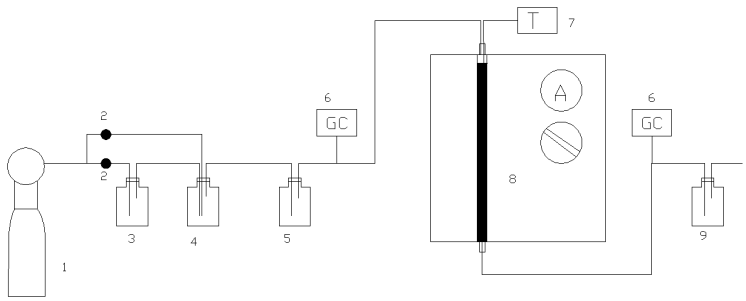

Fig.2 Schematic diagram of experimental process (1.cylinder; 2.flowmeter; 3.toluene volatilizer; 4.mixture; 5.buffer; 6.gas chromatograph; 7.temperature controller; 8.microwave reactor; 9. absorption bottle)

Catalyst characterization

The surface area (S_{BET}) was determined by BET method from N_2 adsorption isothermal at -196 ^{o}C (NOVA 2000e). X-ray diffraction (XRD) patterns were collected on an ARL SCINTAG X'TRA powder diffractometer using Cu K*a* radiation. The working voltage of the instrument was 45 kV and the current was 40 mA. The intensity data were collected at room temperature in a 2θ range from 20° to 100°. The morphology was carried out using SEM (S4800) . Samples were need to spray gold processing before the test.

Ultrasonic test was performed to evaluate the cohesive content of the active phase. The samples were subjected to ultrasonic cleaning by being immersed in water inside a glass vessel and in an

ultrasonic vibration cleaner at 40 kHz for 20 min. After ultrasonic cleaning, the samples were dried at 120 ºC for 4 h and weighed to compare with the samples before coating.

Results and discussion

Catalyst characterization

The morphology of the bare substrate (the ring of SiC) and Cu-Mn-Ce oxides/SiC catalyst is shown in Fig. 3. The surface of ring (Fig. 3 (a)) is irregular with various pore structures; this feature benefits the adhesion between the active phase and the substrate. Fig. 3 (b) shows the morphology of the Cu-Mn-Ce oxides/SiC catalysts. The comparison between the surface of the bare SiC (Fig. 3(a)) and that of Cu-Mn-Ce oxides/SiC (Fig. 3(b)) revealed the appearance of particles agglomerated in the latter. Also evident, the macroporosity of the support disappeared as consequence of the coating. This result suggested the uniform distribution of the catalyst over the SiC. Fig.3 (c) and (d) show the photos of the ring of SiC before and after coating. Ultrasonic test was employed to test content of the active phase. In order to evaluate the efficiency of the dip-coating procedure, it was carried out in consecutive steps to measure the amount of washcoating loading deposited at each step for different pieces of monoliths. The results are shown in Fig. 4. The loading obtained was increased as the number of coating increased. The oxide catalysts loading increased to 1.2% after the third coating. The BET surface areas of the powder catalyst is 17.4 m^2/g and the Cu-Mn-Ce oxides/SiC is too little to detect in the instrument.

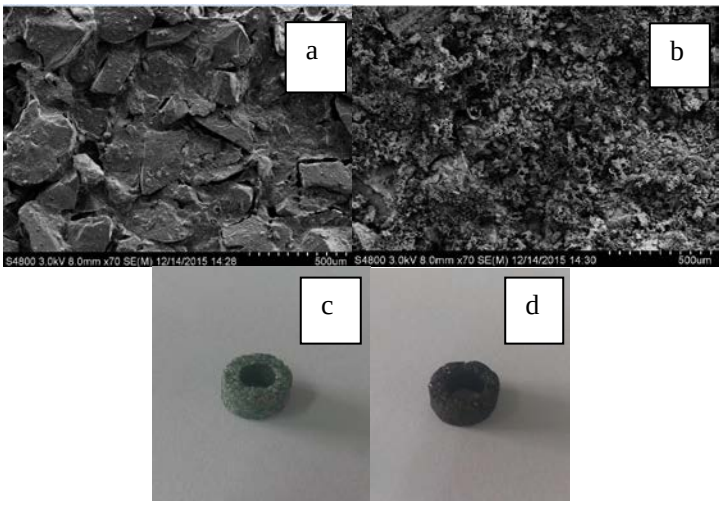

Fig.3. SEM images of the ring of SiC (a) and Cu-Mn-Ce oxides/SiC catalysts (b). The images of the ring of SiC (c) and one Cu-Mn-Ce oxides/SiC catalyst(d).

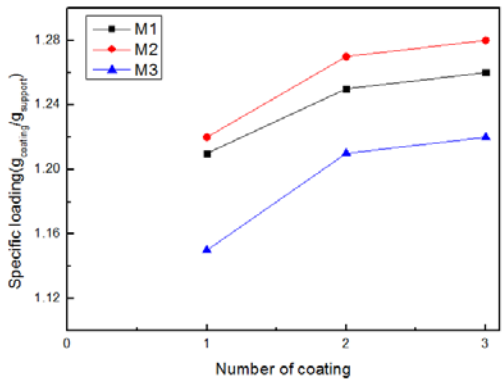

Fig.4 Cumulative specific load vs number of coating steps obtained on different batch of SiC (M1, M2, M3) coated with Cu-Mn-Ce oxides sol.

Fig.5 presents the XRD spectra of Cu-Mn-Ce oxides/SiC catalysts and Cu-Mn-Ce oxide catalysts prepared on the ring of SiC. Because of the strong presence of the diffraction lines of SiC and it is overlapped with some of the reflections of the oxide phases of the catalysts, there are few observable XRD peaks due to Cu-Mn-Ce oxide phases. The diffraction peaks of the Cu-Mn-Ce

oxides were detected corresponding mainly to CeO_2 phase and a few peaks was assigned to MnO and CuO phase, which most probably due to incorporation of the copper and manganese ions into the CeO_2 lattice.

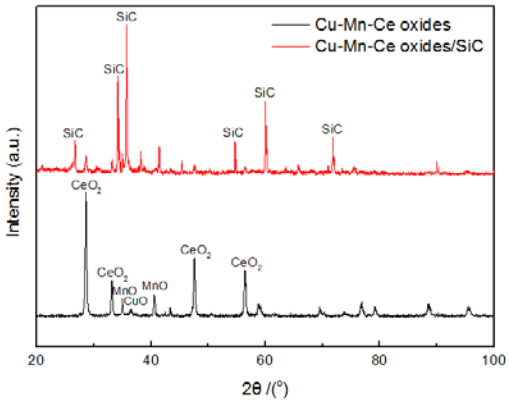

Fig. 5 XRD patterns of Cu-Mn-Ce oxides/SiC catalysts and Cu-Mn-Ce oxides catalysts

Catalytic combustion of toluene on Cu-Mn-Ce oxides/SiC catalysts under microwave heating and conventional heating

The catalytic activity of Cu-Mn-Ce oxides/SiC catalysts for the catalytic combustion of toluene is shown in Fig. 6. As shown in Fig. 6. compared to the conventional heating, the monolithic catalyst under microwave heating shows much higher activity in low temperature range. 90% of toluene conversation can be achieved at 350 ^{o}C under microwave heating, while only 40% of that can be obtained at the same temperature under conventional heating. This result shows microwave heating is a very excellent potential to process removal of VOCs.

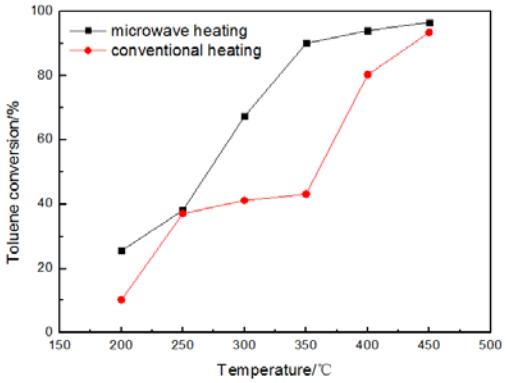

Fig.6. Comparison of toluene oxidation activity of Cu-Mn-Ce oxide/SiC monolithic catalyst under microwave heating and conventional heating.

Conclusion

In this study, a novel Cu-Mn-Ce oxide/SiC monolithic catalyst was prepared by sol-gel method, characterized and tested for catalytic toluene oxidation. Based on XRD results of Cu-Mn-Ce oxide catalyst, CeO_2 phase was the main phase in the mix-oxides, which mainly related to incorporation of the copper and manganese ions into the CeO_2 lattice. Compared with conventional heating, monolithic catalyst showed much better catalytic activity for toluene oxidation under microwave heating in the low temperature range. At 350 ^{o}C, 90% of toluene conversion was obtained under microwave heating, while only 40% under conventional heating.

Acknowledgement

This work were financially supported by the National Science-technology Support Plan Project of China (Project No.2014BAC23B04-03) and Foundation of Hebei Province (Project No.14273712D)

References

[1]Parmar G R, Rao N N. Emerging control technologies for volatile organic compounds. Critical Reviews in Environmental Science and Technology, 2009, 39(1): 41.

[2]Mitsui T, Tsutsui K, Matsui T, Kikuchi R, Eguchi K. Support effect on complete oxidation of volatile organic compounds over Ru catalysts [J]. Applied Catalysis B: Environmental, 2008, 81: 56-63.

[3]Azalim S, Brahmi R, Agunaou M, Beaurain A, Giraudon J-M, Lamonier J-F. Washcoating of cordierite honeycomb with Ce-Zr-Mn mixed oxides for VOC catalytic oxidation [J]. Chemical Engineering Jounal, 2013, 223: 536-546.

[4]Parmele C, Kovalcson T. Adsorption: carbon. In: Rafson H J, ed. Odor and VOC Control Handbook. New York: McGaw-Hill, 1998.

[5]Bielefeldt A R, Stensel H D. Treating VOC-contaminated gases in activated sludge: mechanistic model to evaluate design and performance. Environmental Science & Technology, 1999, 33(18): 3234–3240.

[6]Nedyalkova R, Ilieva L, Bernard M C, Hugot-Le Goff A, Andreeva D. Gold supported catalysts on titania and ceria, promoted by vanadia or molybdena for complete benzene oxidation. Materials Chemistry and Physics, 2009, 116(1): 214–218.

[7] Vu V H, Belkouch J, Ould-Dris A, Taouk B. Catalytic oxidation of volatile organic compounds on manganese and copper oxides supported on titania. AIChE Journal, 2008, 54(6): 1585.

[8]Tang X F, Xu Y D, Shen W J. Promoting effect of copper on the catalytic activity of MnO_x-CeO_2 mixed oxide for complete oxidation of benzene. Chemical Engineering Journal, 2008, 144(2): 175–180.

[9] Ma R, Su X, Jin L, Lu J, Luo M. Preparation and characterizations of Ce-Cu-O monolithic catalysts for ethyl acetate catalytic combustion. Journal of Rare Earths, 2010, 28(3): 383.

[10]Haili Liu, Xiaoqian Ma, Longjun Li, et al. The catalytic pyrolysis of food waste by microwave heating. Bioresource Technology, 2014, 166: 45–50.

[11]Yuan Maobiao, Ma Xiongfeng, Wang Shuping, et al.Environmental protection of chemical industry [J], 2013, 33(6): 513-517.

[12]Yet-Pole I, Liu Y C, Han K Y, She T C. Construction of a lowpressure microwave plasma reactor and its application in the treatment of volatile organic compounds. Environmental Science &Technology, 2004, 38(13): 3785–3791.

[13]Kim T H, Rupani H, Pallavkar S, Hopper J, Ho T. Destruction of toxic volatile organic compounds (VOCs) in a microwave-assisted catalyst bed. Journal of the Chinese Institute of Chemical Engineers, 2006, 37(5): 519–526.