Catalytic Oxidation of Toluene over Manganese and Cerium Complex Oxide Supported on Zeolite

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Abstract. The air pollution caused by VOCs emissions has drawn considerable attention in recent years. Many catalyst systems with excellent activity were studied for the catalytic oxidation of VOCs. In this work, using air containing toluene as the simulation of industrial emissions, MnOX-CeO2/Powder zeolite and MnOX-CeO2/Honeycomb zeolite catalyst samples prepared by the isometric impregnation method were studied for catalytic performance of toluene. The catalysts were characterized by SEM, BET, XRD, SEM, H2-TPR and O2-TPD. The research results obtained showed that MnOX-CeO2/Powder zeolite catalysts exhibited better activity than MnOX-CeO2/Honeycomb zeolite catalyst at lower temperatures, the MnOX-CeO2/Powder zeolite catalyst presented better catalytic performance with T50=223℃and T99=275℃under the condition of GHSV of 15000h⁻¹ and toluene concentration of 100ppm, which is 23℃and 47℃lower than MnOX-CeO2/Honeycomb zeolite, respectively. The characterization results also indicated that the catalytic activity was relevant closely with specific surface area, active oxygen species, catalyst morphology and valence of manganese and cerium oxides. Also, the catalyst has an excellent stability in the catalytic combustion towards toluene.

1. Introduction
Volatil Organic Compounds (VOCs) have become the main pollutants affecting the current ambient air quality in China, and it is of great significance to effectively control them. Toluene, as a typical representative of VOCs, has been widely used in various fields of industry and production and life [1,2], which has brought serious harm to human health and the environment [3, 4]. Catalytic combustion technology [5] has become one of the most widely used purification technologies for industrial VOCs in recent years due to its lower light-off temperature and higher purification efficiency. Composite oxide catalysts show higher catalyst activity and better stability under certain conditions, which is a hot topic in the field of catalysis. The effect of the carrier on the catalytic performance is also relatively large. Carriers such as cordierite, titanium dioxide, carbon nanotubes, and molecular sieves have been
successfully used as composite metal oxide catalyst carriers, which have excellent catalytic performance in the study of the catalytic degradation of many air pollutants [6-8].

There are many methods for preparing composite oxides, and the content ratio between components is one of its important influencing factors. Shi [9] et al. compared manganese-cerium catalysts prepared by co-precipitation method, ion exchange method and improved co-precipitation method to catalyze methane, and found that the catalyst prepared by improved co-precipitation method has the better low temperature activity. Delimaris et al. [10] prepared a MnOx-CeO2 composite oxide catalyst by the urea combustion method, and explored the catalytic oxidation of ethanol, ethyl acetate, and toluene. The results show that the MnOx-CeO2 composite has a larger specific surface, lower conversion temperatures and higher conversions than the pure Mn and Ce. Wang [11] et al. used a sol-gel method to prepare a MnOx-CeO2 composite catalyst, and the investigation has expressed that the relatively stable catalytic activity. When the Mn/Ce is synthesized with the ratio of MnOx (0.86)-CeO2 might have the best catalytic effect on chlorobenzene, and the conversion rate reaches 100% at 254℃.

Therefore, two manganese-cerium composite oxide supported catalysts were prepared by impregnation method in this paper, and their catalytic activities for toluene were investigated. Meanwhile, the structure was characterized by SEM, BET, XRD, H2-TPR, O2-TPD, the factors affecting the catalyst activity were analyzed systematically, and its stability was studied.

2. Materials and Methods

2.1. Catalysts

In this experiment, honeycomb zeolite was used as a carrier, and a monolithic composite catalyst was prepared by multiple equal volume impregnation methods. A part of the cellular zeolite was ground and sieved to obtain a powdered cellular zeolite carrier. In a typical method, a certain amount of cerium nitrate and manganese acetate added into an appropriate amount of ethanol, stirring well to completely dissolve, which might impregnate the obtained milky white uniform salt solution with honeycomb zeolite and powder honeycomb zeolite, and then disperse it with ultrasound for 30min, stirring at room temperature for 5h, with evaporating at 80℃ in a water bath and dry for 12h at 100℃. Finally, the powdered honeycomb zeolite supported catalyst (MnOX-CeO2/Powder zeolite) and the whole honeycomb zeolite supported catalyst (MnOX-CeO2/Honeycomb zeolite) were obtained through the calcination, with the manganese and cerium loading is 5%.

2.2. Catalyst Characterization

XRD measurements were taken on a D8 Advance diffractometer with Ni-filtered Cu Kα radiation (k = 0.15418 nm, 40 kV, 40 mA) in the 2θ range of 5-90°. The XRD phases were identified by comparison with the reference data from Joint Committee on Powder Diffraction Standards (JCPDS) data files. The specific surface area, pore volume and pore size of the samples were determined by nitrogen adsorption on an ASAP 2020 M, and the BET method was utilized to calculate the specific surface area (SBET). H2-TPR and O2-TPD experiments were performed with an Auto Chem II. The samples were pretreated in Ar at 300℃ for 30min. After that, the H2-TPR and O2-TPD experiments were carried out from 50℃ to 900℃ at a heating rate of 10℃ /min in 10% H2 /Ar and 5% O2/He (30 mL/min), respectively. The H2 and O2 consumption were determined by a TCD detector. Morphologies of the catalysts were observed by scanning electron microscopy (SEM) using a LEO-1530VP instrument operated at 1.0 kV.

2.3. Catalyst activity test

The catalyst test apparatus are composed of the valve system, the reactor and the detector, with using the toluene as target reactant. An air stream bubbling through a saturator filled with liquid toluene carried toluene vapor. The toluene destruction efficiency as a function of reaction temperature was measured in the case of space velocities of 10,000 h−1. All gases were controlled by mass flow meters. Reactants and products were analyzed by gas chromatograph (GC-7890II) with FID detector.
3. Results and Discussion

3.1. Catalyst activity evaluation
The catalytic oxidation activities of toluene, MnOX-CeO2/Honeycomb zeolite and MnOX-CeO2/Powder Zeolite, were investigated. In order to exclude the influence of material adsorption on the conversion of toluene, the CO2 selectivity was used as the evaluation index of the catalyst performance in this experiment. The space velocity was 15000h⁻¹, and the toluene inlet concentration was 100ppm. The results are shown in Fig.1.

The results show that the low-temperature catalytic activity of MnOX-CeO2/Powder Zeolite catalyst for toluene is significantly better than that of MnOX-CeO2/Honeycomb Zeolite catalyst. At a space velocity of 15000h⁻¹ and a toluene concentration of 100ppm, its CO2 selectivity to toluene is 50% achieved at 223°C (T50 = 223°C), and a conversion efficiency of 99% can be achieved at 275°C (T99 = 275°C), which is 23°C lower than the MnOX-CeO2/Honeycomb Zeolite catalyst T50, and the T99 decreased 47°C. This is mainly due to the more complete mixing of the powder carrier and the impregnating solution during the preparation of the zeolite powder, resulting in a higher loading of the active component and better binding with the carrier. In addition, in the heterogeneous reaction process, the thermodynamic equilibrium control of the reaction itself, adsorption and diffusion also play a very important role in it. If the reactant molecules are restricted in the diffusion and adsorption process, the overall catalysis will be reduced.

![Figure 1. The selectivity of CO2 for the degradation of toluene on catalysts](image)

3.2. BET analysis
Table 1 shows the specific surface area and space pore volume of various catalysts. As can be seen from the table, the manganese-cerium composite oxides on the zeolite support are significantly larger than the table BET, pore volume and pore size, but all are smaller than pure zeolite. The above results show that the introduction of manganese and cerium affects the structural characteristics of zeolite. This may be due to the fact loading of metal oxides needs to interact with the hydroxyl groups on the surface of the molecular sieve to a certain extent, so it occupies a part of the surface area. In addition, due to the agglomeration of metal oxides, it is easy to block the molecular sieve channels, which might result in a decrease in surface area. Meanwhile, it can be seen that the specific surface area of MnOX-CeO2/Honeycomb zeolite is smaller than that of MnOX-CeO2/Powder Zeolite, and the other two indicators are not much different. It shows that the dispersion effect is worse, which the manganese-cerium composite can better enter the powdery carrier during the impregnation process. This result is consistent with the carbon dioxide selectivity of the two catalysts in Fig. 1.
Table 1. The specific surface area, pore diameter and pore volume of catalysts

| Catalysts                          | BET (m²/g) | Pore Volume (m³/g) | Pore Size (nm) |
|------------------------------------|------------|--------------------|----------------|
| MnOₓ-CeO₂                          | 22.2773    | 0.009961           | 1.78672        |
| Zeolite                            | 374.3448   | 0.156615           | 3.01935        |
| MnOₓ-CeO₂ / Honeycomb Zeolite       | 292.3284   | 0.103314           | 2.76483        |
| MnOₓ-CeO₂ / Powder Zeolite          | 323.6689   | 0.110275           | 2.73264        |

3.3. SEM

The morphology of the cross section (A) and longitudinal section (B) of the monolithic honeycomb zeolite before and after loading was observed with a scanning electron microscope, and the photos are shown in Fig. 2. It can be seen that the cross section (A1) of the carrier is a porous structure composed of flake-shaped, block-shaped irregular small particles of 1 to 2 μm, and the surface is smooth. In comparison, small particles of manganese-cerium oxide appear on the cross section (A2) of the catalyst after loading the manganese-cerium oxide, indicating that the manganese-cerium oxide is supported on the surface of the molecular sieve to form a composite material with a larger specific surface area.

Compared to the longitudinal section of the honeycomb zeolite support (Fig. B1), it can be seen from the longitudinal section of the coating of the catalyst (Fig. B2) that there is no obvious separation on the inner surface of the honeycomb zeolite support after the catalyst active components are supported by the impregnation method. Layers and stacks, and the longitudinal section of the catalyst appears to form more mesoporous and macroporous structures. More mesoporous and macroporous structures can increase the activity of the catalyst, which is consistent with the conclusions obtained in Figure 1.
3.4. XRD

In order to further confirm the loading of manganese-cerium oxide on the honeycomb zeolite, the signal of the oxide was detected by XRD. The results show that only the characteristic diffraction peaks of the CeO2 cubic phase fluorite structure appear in the XRD pattern of MnOX-CeO2, and the characteristic peaks of MnOX do not appear, presumably CeO2 and MnOx formed a Mn-Ce solid solution of fluorite structure or formed Amorphous manganese oxide. Most of the diffraction peaks shown in the two supported catalyst spectra reflect the information of the cellular zeolite support. CeO2 diffraction peaks only appear at 2θ=27.3°, and Mn3O4 and MnO2 diffraction appear at 2θ=29.9° and 31.6° respectively. The peak may be due to the low loading content of the manganese-cerium oxide, which causes the signal to be too weak; Another possible reason is that Mn ions enter the CeO2 lattice to form a MnCeOx solid solution or MnOX species are highly dispersed on the catalyst surface.

![Figure 3. XRD patterns of catalysts](image)

3.5. O2-TPD

Figure 4 shows O2-TPD diagrams of various catalysts. It can be seen that the pure MnOX-CeO2 catalyst has obvious desorption peaks at four positions around 95℃, 300℃, 495℃, and 610℃. The main forms of oxygen are O2-, O- and O2-, and the order of adsorption of oxygen from weak to strong is O2→O2-→O-→O2-. Previous research [12] believes that transition metal composite oxides generally have three oxygen desorption regions: the low temperature region (50~35℃) is molecularly adsorbed oxygen (O2-); the medium temperature region (350~750℃) is adsorbed on Atoms in oxygen vacancies adsorb oxygen (O-); the high-temperature regions (> 750℃) are lattice oxygen (O2-). The analysis of the content of oxygen species and energy position of manganese cerium oxide can be inferred that the desorption peak catalyzed by MnOX-CeO2 at low temperature of 95℃ belongs to molecular adsorption oxygen, the peak appearing at 300℃ is atomic adsorption oxygen. The desorption peak of lattice oxygen is at 500-600℃, and the appearance position is obviously shifted to low temperature.

It is inferred that three oxygen desorption peaks appeared in the MnOX-CeO2/Honeycomb zeolite composite catalyst with manganese-cerium. Among them, the first major desorption peak appeared at 120~130℃, which was attributed to molecular adsorption oxygen, the secondary desorption peak appeared at 264℃, and a weak desorption peak was attributed to lattice oxygen. Comparing the two supported catalysts, the MnOX-CeO2/Powder Zeolite catalyst has a larger desorption peak than the MnOX-CeO2/Honeycomb zeolite catalyst, and it shifts towards a lower temperature. The larger the O desorption peak, the shift of the position to the low temperature direction is beneficial to improve the low temperature catalytic activity of the catalyst for toluene.
3.6. H$_2$-TPR

H$_2$-TPR can reflect the oxidation-reduction ability of the catalyst. The oxidation-reduction cycle of oxygen species accompanying the valence metal oxide is closely related to the catalytic reaction of the catalyst. The lower the reduction peak temperature, the stronger the oxidation-reduction ability of the catalyst. It can be seen from the figure that in the H$_2$-TPR diagram of MnOX-CeO$_2$, three reduction peak temperatures can be seen, of which the two peaks at low temperature (about 257°C, 350°C) are the reduction peaks of Mn, and the peak at about 710°C is the reduction peak of Ce$^{4+}$ in the bulk phase [13,14].

Both MnOX-CeO$_2$/Honeycomb Zeolite and MnOX-CeO$_2$/Powder Zeolite composite catalysts supported with manganese and cerium show a large reduction peak at about 300°C, and the size of the MnOX-CeO$_2$/Honeycomb zeolite reduction peak is smaller than that of MnOX-CeO$_2$/Powder Zeolite, the position gradually shifted to a low temperature direction, which is consistent with the activity of the catalyst.

3.7. Stability test of Catalysts

In practical industrial applications, the stability of the catalyst and its catalytic activity are both important indicators for examining the catalyst. In this experiment, the thermal stability of the catalytic oxidation
of MnOX-CeO2/Honeycomb zeolite catalyst at an anti-space velocity of 15000 h⁻¹, a toluene concentration of 130 ppm, and a temperature of 275°C for 30 hours was examined (Fig. 6). The experimental results show that the toluene conversion rate of the catalyst can be continuously maintained above 90% at a temperature of 275°C, a CO₂ selectivity of above 85%, good thermal stability, and it can be used in the process of changing the concentration of VOCs in industrial waste gas.

![Figure 6. Stability test of catalyst](image)

4. Conclusions

In this paper, two supported catalysts were prepared by the impregnation method. The catalytic oxidation activity of the catalyst for toluene was investigated. The structure was characterized by various means and the stability was studied. The main conclusions are as follows:

(1) The low-temperature catalytic activity of the prepared MnOX-CeO2/Powder Zeolite catalyst for toluene is significantly better than that of the MnOX-CeO2/Honeycomb Zeolite catalyst. At a space velocity of 15000h⁻¹ and a toluene concentration of 100ppm, its CO₂ selectivity to toluene is a 50% conversion efficiency at 223°C (T50= 223°C), a 99% conversion efficiency at 275 ° C (T99=275°C), which is lower than MnOX-CeO2/Honeycomb Zeolite catalyst.

(2) The characterization results also indicated that the catalytic activity was relevant closely with specific surface area, active oxygen species, catalyst morphology and valence of manganese and cerium oxides. Also, the catalyst has an excellent stability in the catalytic combustion towards toluene.

References

[1] M. Zimowska: Catal. Today Vol. 119 (2007), p. 322.
[2] D. Delimaris, Dimitrios, I. Theophilos: Appl. Catal. B-Environ Vol. 89 (2009), p. 295.
[3] O. Gutiérrez, I. José: Appl. Catal. B-Environ Vol. 65 (2006), p.191.
[4] X.Y. Wang, Q. Kang, D. Li: Appl. Catal. B-Environ Vol. 86 (2009), p. 166.
[5] W. B. Li: Catal. Today Vol. 93 (2004), p. 205.
[6] W. J. Ma: Ceramics International Vol. 39 (2013), p. 277.
[7] H.F. Huang: China Environ. Sci. Vol. 34 (2014), p. 2179.
[8] H.F. Lu, U.: J. Rare Earth Vol. 29 (2011), p. 855.
[9] L.M. Shi: Catalysis letters Vol. 113(2007), p. 59.
[10] D. Dimitrios, T. Ioannides: Appl. Catal. B-Environ Vol. 84 (2008), p. 303.
[11] X.Y. Wang, K. Qian, L. Dao: Appl. Catal. B-Environ Vol. 86 (2009), 166.
[12] M. Zhang, M.L. Fu, J.L. Wu, D.Q. Ye: J. Rare Earth. Vol. 29 (2011) , p.303.
[13] A. Francesco: Physical Chemistry Chemical Physics Vol. 3 (2001), p. 1911.
[14] F. Kapteijn: Appl. Catal. B-Environ Vol.3 (1994), p. 173.