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Catalytic combustion of toluene over Fe–Mn mixed oxides supported on cordierite

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Abstract

The catalytic combustion of toluene over Fe–Mn mixed oxides supported on cordierite was investigated. The catalysts were synthesized by the impregnation method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and BET specific surface area measurement. The effects of the mole ratio of Fe to Mn, the loading of Fe–Mn mixed oxides on the catalyst support and the calcination temperature were all investigated. The results indicate that Fe–Mn/cordierite catalysts with a 4 mol ratio of Fe to Mn, used with 10 wt% loading, and calcined at 500 °C showed the highest catalytic activities as measured by the oxidation of toluene. Compared to unsupported powder catalysts of Fe–Mn mixed oxides, the Fe–Mn/cordierite catalyst showed higher activity for the catalytic combustion of toluene with less active component.

Keywords: D. Cordierite; Fe–Mn mixed oxides; Catalytic combustion; Catalysts

1. Introduction

Volatile organic compounds (VOCs) are important air pollutants because they are toxic and can lead to environmental problems such as photochemical ozone formation, global warming and stratospheric ozone depletion [1,2]. The production and use of automobiles are the main sources of VOC emissions [3]. For these reasons, the treatment of VOCs has become an important component of environment protection.

Physical, chemical, biochemical and photocatalytic techniques have been developed to aid in the elimination of VOCs [1]. Because catalytic combustion can operate with dilute VOC effluent streams ($<1\%$ VOCs) at much lower temperatures than conventional thermal incineration methods, it is an effective and economical method for VOC elimination [2]. Because the choice of catalyst is the key factor in this treatment, much attention has been paid to the development of novel catalysts with improved activities [4].

Catalysts using noble metals, transition metal oxides or complex oxides, with or without supports, have been widely reported for catalytic combustion of VOCs [5–12]. Although noble metal catalysts have shown higher activity than base metal oxides, they are less economical due to their high costs [13]. Transition metal oxides of iron and manganese are potential activity promoters for the catalytic combustion of toluene. Fe–Mn mixed oxides have been prepared with the citrate [14] and the reverse microemulsion methods [5], but all of these catalysts were powders and showed deactivation towards VOC conversion. In order to obtain more suitable and economical catalysts, the activity of Fe–Mn mixed oxides supported on cordierite was investigated, and the results are reported in this paper. These samples were characterized by XRD, SEM and BET, and the effects of the mole ratio of Fe to Mn, the loading of the Fe–Mn mixed oxides on the cordierite support and the calcination temperature on the activity of these catalysts were investigated.

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2. Experimental

2.1. Catalyst preparations

A series of Fe–Mn mixed oxides catalysts with different molar ratios of iron to manganese were prepared by the impregnation method. An aqueous solution containing appropriate amounts of $Fe(NO_3)_3 \cdot 9H_2O$ and $Mn(NO_3)_2$ was prepared, cordierite (5 g) was added to the solution, and the mixture was stirred for 20 h. The impregnated samples were dried at 80 °C for 5 h and then calcined at 500 °C for 5 h. Other catalysts were also prepared using this method for the purpose of comparison.

2.2. Catalyst characterization

The X-ray diffraction (XRD) ($2\theta = 5° - 80°$) of the catalyst powders were obtained using an AXS D8 advance diffractometer equipped with a graphite monochromator and a CuKα radiation source with a wavelength of 0.154 nm. The BET specific surface area of each catalyst was determined by nitrogen adsorption at 77 K using an ASAP-2020 analyzer. Scanning electron microscopy (SEM) was performed on a JSM-6301F instrument after pre-coating of the samples with gold.

2.3. Catalytic activity measurements

Catalytic activity tests were carried out in a fixed-bed flow reactor under atmospheric pressure. The reactor was set in an electric heating furnace with a diameter of 0.7 cm and a length of 81.3 cm, which provided uniform heating of the catalyst bed [16]. The reactant gas was a mixture of gases containing toluene vapor and air, and the catalyst (5 g) was loaded in layers of quartz wool. The temperature of the catalyst bed was monitored with a thermocouple and controlled by a temperature controller in the range of 150–450 °C. A toluene concentration of 1000 ppm and a GHSV of 10,000 h^{-1} were used. The reactants and reaction products were analyzed by an on-line gas chromatograph (GC-2014, Shimadzu Corp) equipped with an FID detector and using a Restek Rtx-1 column [16].

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD

X-ray diffraction was used to determine the crystalline phases of these catalysts. Fig. 1 shows the XRD patterns of Fe–Mn mixed oxide catalysts prepared with different molar ratios and calcined at 500 °C. XRD for the pure oxides MnO_x and FeO_x exhibited typical patterns for Mn_2O_3 and Fe_2O_3 [14]. With increasing content of iron oxide, the significant diffraction peaks for Mn_2O_3 gradually disappeared and were replaced with increasingly intense diffraction peaks corresponding to Fe_2O_3. There were no diffraction peaks of manganese oxide detected on samples with molar ratios of 1.5 or 4 of Fe to Mn. The Fe–Mn/cordierite catalyst prepared with a 4 M ratio of Fe to Mn showed the highest activity, indicating that Fe_2O_3 was the main active component for the catalytic combustion of toluene.

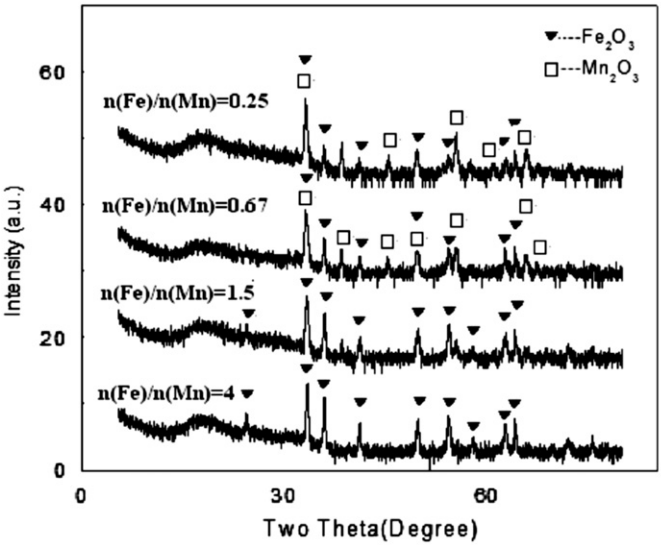

Fig. 1. XRD pattern of Fe–Mn/cordierite catalysts.

3.1.2. Bet

The BET surface area, pore volume and pore size of the Fe–Mn/cordierite catalysts, after calcination at 500 °C, are shown in Table 1. The surface areas of Fe–Mn mixed oxides supported on cordierite with different molar ratios were as follows: $S_{Fe/Mn=1/4} = 5.53\ m^2/g < S_{Fe/Mn=2/3} = 7.97\ m^2/g < S_{Fe/Mn=3/2} = 8.32\ m^2/g < S_{Fe/Mn=4/1} = 8.57\ m^2/g$. It was clear that the pore size decreased with increasing iron oxide content. These results were consistent with increasing surface areas of the catalysts. Although the surface areas of these catalysts did not change drastically, it is believed that the activities were likely influenced by the surface areas [16–18], and the catalyst ($n(Fe)/n(Mn) = 4$) showed the highest activity for toluene combustion.

3.1.3. SEM

Fig. 2 shows the SEM images of the Fe–Mn/cordierite catalysts calcined at 500 °C with different Fe/Mn molar ratios. As shown in Fig. 2 (a), pure cordierite showed a smooth surface with few pores on the surface and smaller surface area, consistent with other reports. Fig. 2 (b) shows the SEM image of the catalyst with a Fe/Mn molar ratio of 0.25, indicating few activated particles that have an uneven distribution on the surface of cordierite. Fig. 2 (c) and (d) show the surface images of samples ($n(Fe)/n(Mn) = 0.67$ and 1.5), indicating that some large activated particles were found on the surface. The smooth surface of the cordierite could be observed, which is believed to be unfavorable for the enhancement of activity. However, the SEM image of the ($n(Fe)/n(Mn) = 4$) catalyst of mixed oxides (Fig. 2 (e))

Table 1
Textural properties of Fe–Mn oxides loaded on cordierite support with different molar ratios at a calcination temperature of 500 °C.

Materials	BET surface area (m^2/g)	Pore volume ($\times 10^{-8} m^3/g$)	Pore size (nm)
Fe/Mn=1/4	5.53	2.30	1666.7
Fe/Mn=2/3	7.97	2.98	1494.3
Fe/Mn=3/2	8.32	2.87	1379.6
Fe/Mn=4/1	8.57	2.77	1289.4

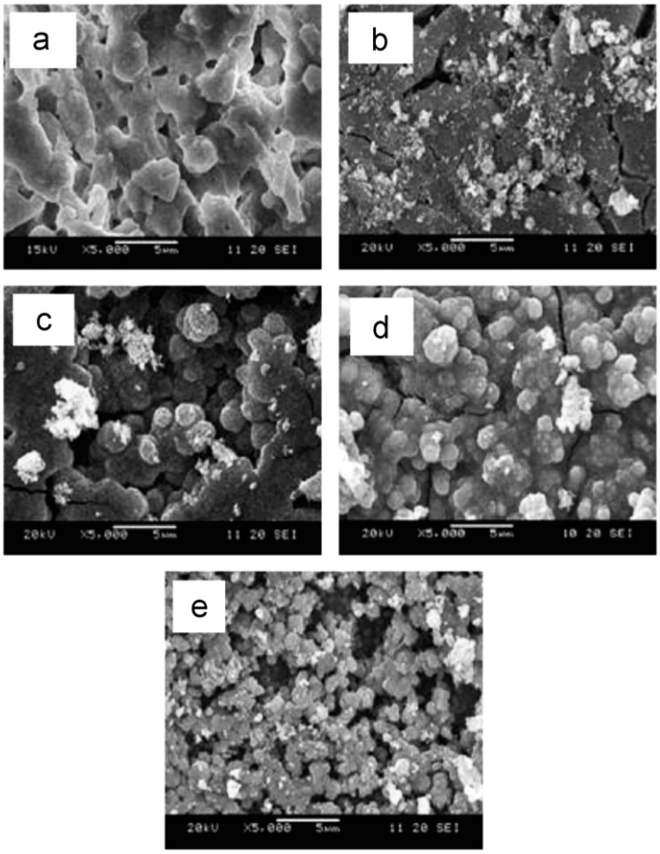

Fig. 2. SEM images of Fe–Mn/cordierite catalysts: (a) cordierite, (b) n(Fe)/n(Mn)=0.25, (c) n(Fe)/n(Mn)=0.67, (d) n(Fe)/n(Mn)=1. 5 and (e) n(Fe)/n(Mn)=4.

shows a multitude of active components that are uniform in particles size and are supported evenly on the surface of the cordierite. This finding is in agreement with the highest surface area analyzed by BET and is believed to be important for the increased activity observed for toluene oxidation by this catalyst [5].

3.2. *Activities of Fe–Mn mixed oxides catalysts*

3.2.1. *The activities of Fe or Mn oxides catalysts*

The conversion of toluene with iron oxide or manganese oxide supported on cordierite is shown in Fig. 3. As can be observed, cordierite showed the lowest activity for toluene oxidation. The manganese oxide catalyst showed higher activity than the iron oxide catalyst. Manganese oxides have a higher capacity for oxygen storage than iron oxides, which may possibly have provided more lattice oxygen to oxidize toluene. However, the mixed Fe–Mn oxides showed higher activities than the single metal oxide catalysts, and the combustion of toluene reached as high as 90.4% at 300 °C. In addition, the ignition temperature decreased from 260 °C to 180 °C. These results indicate that the mixed oxides enhanced activities for the catalytic combustion of toluene.

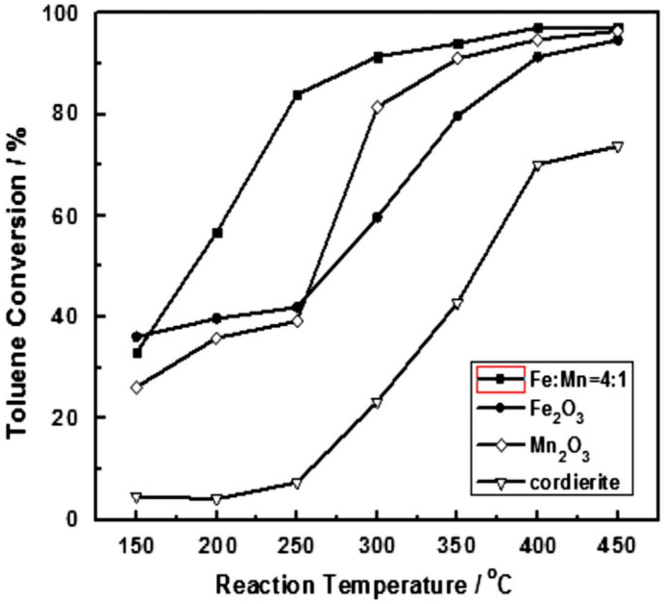

Fig. 3. Toluene conversion vs. reaction temperature over the Fe–Mn/cordierite catalysts.

3.2.2. *Effect of the Fe/Mn molar ratios*

The toluene combustion activities were measured as a function of reaction temperature with a series of Fe–Mn mixed oxides catalysts supported on cordierite, and the results are presented in Fig. 4 and Fig. 5. It can be seen that the catalyst with a Fe/Mn molar ratio of 4 exhibited the highest activity for toluene oxidation, with conversion reaching 90.4% at 300 °C. Meanwhile, the conversions with different molar ratios, n(Fe)/n(Mn)=0.25, n(Fe)/n(Mn)=0.67 and n(Fe)/n(Mn)=1.5, were 80.2, 85.6 and 80.3%, respectively. These catalytic activities are higher than for Fe–Mn oxides catalysts previously reported [14], and these results are attributed to the higher dispersion of activated particles on the surface of the cordierite. It was

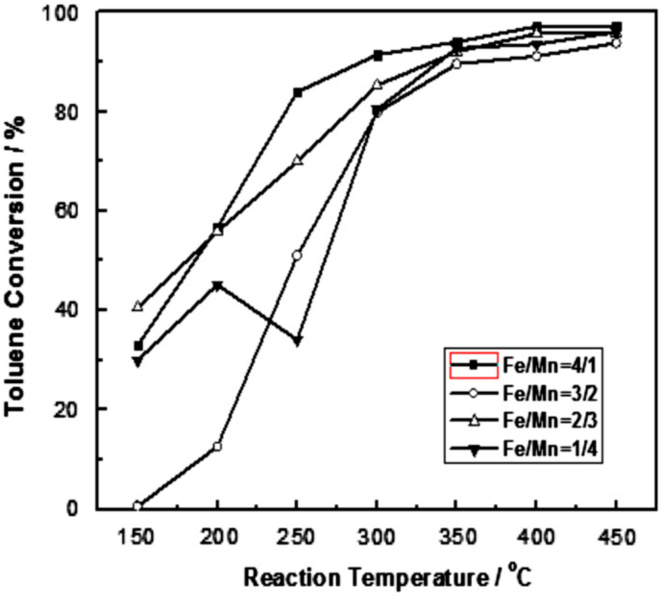

Fig. 4. Toluene conversion vs. reaction temperature over the Fe–Mn/cordierite catalysts with different Fe/Mn molar ratios.

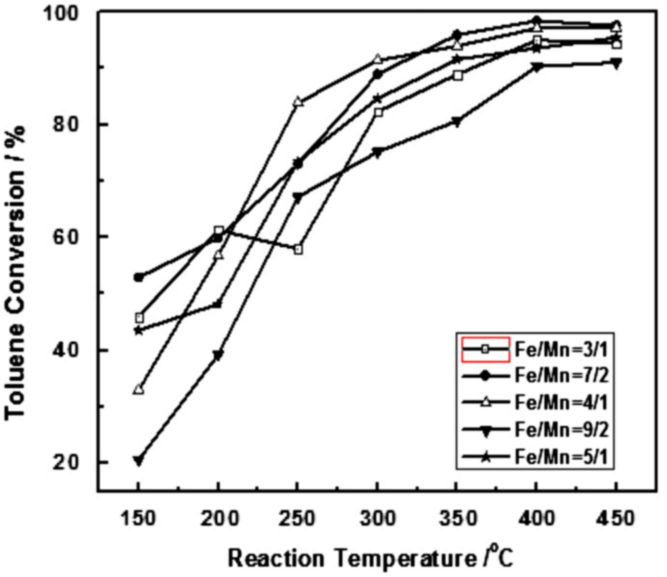

Fig. 5. Toluene conversion vs. reaction temperature over the Fe–Mn/cordierite catalysts with additional different Fe/Mn molar ratios.

anticipated that the catalysts with the highest surface areas would show the best activity and that the activity would increase as the amount of iron increased. As shown in Fig. 5, the samples with the Fe/Mn molar ratios of 3.5 and 4 exhibited similar high activities. As expected, the results indicated that the iron and manganese oxides at the correct molar ratio could exhibit a higher activity than other mixed oxide catalysts. The results may correlate with the provision or and removal of lattice oxygen.

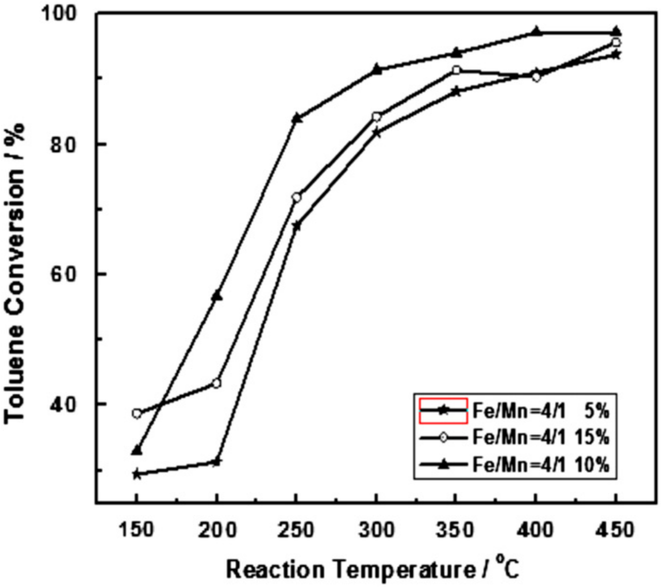

Fig. 6. Toluene conversion vs. reaction temperature over the Fe–Mn/cordierite catalysts with different Fe/Mn molar ratios with different loadings.

3.2.3. *Effect of the amount of active particles*

To analyze the effect of the loading of active particles, three different loadings with the same Fe/Mn molar ratio were prepared. Fig. 6 shows toluene conversion versus reaction temperature of a series of Fe–Mn/cordierite catalysts with (5, 10 and 15 wt%, respectively). The order of activity was 10 wt% > 15 wt% > 5 wt%. The activity increased from 5% to 10% loading. However, when the Fe–Mn loadings reached 15 wt%, a lower activity relative to the 10 wt% loadings resulted at reaction temperatures between 200 °C and 450 °C. It is believed that that the catalyst with 10 wt% loading performed with a higher activity than the catalyst with 15 wt% loading due to a higher dispersion of the Fe–Mn oxides species on the surface of the cordierite, which is consistent with the SEM results previously reported [19].

3.2.4. *Effect of calcination temperature*

Because the calcination of the catalysts at high temperatures might lead to sintering of manganese oxide, the effect of the calcination temperature could be an important factor in the activity of the catalysts. The activities of catalysts calcined at temperature ranges of 300–700 °C are shown in Fig. 7. The samples calcined at high temperature led to a decrease of catalytic activity, as expected [5]. When the temperature was increased from 300 °C to 700 °C, the toluene oxidation conversion decreased from 85% to 15% at 250 °C, while the catalysts calcinated at 500 °C showed 90.6% conversion. These results implied that a high calcination temperature could result in an increase in the size of active particles on the surface due to sintering while also increasing the interaction between metal oxides and cordierite [17].

4. Conclusions

In this study, mixed Fe–Mn oxides on cordierite support were investigated and characterized with XRD, BET and SEM. The mixed Fe–Mn oxides showed higher activity for

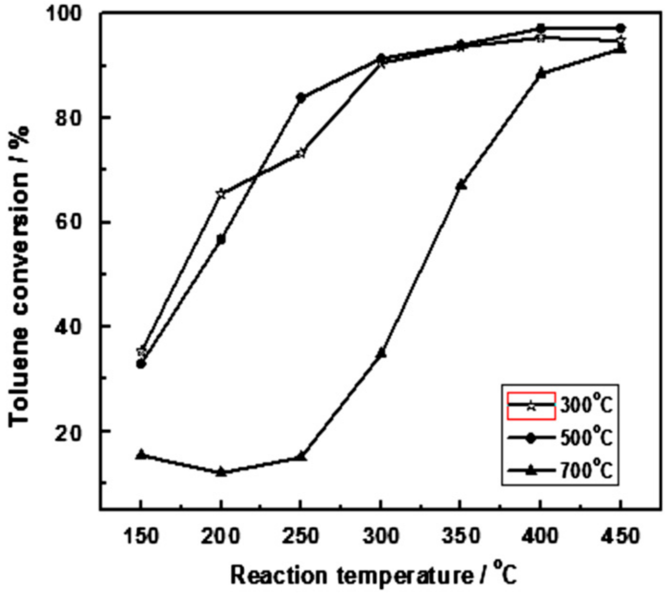

Fig. 7. Toluene conversion vs. reaction temperature over the Fe–Mn/cordierite catalysts with different calcination temperatures.

combustion of toluene than the simple Fe or Mn oxides. The catalyst with a Fe/Mn molar ratio of 4, a 10 wt% loading and calcined at 500 °C showed the highest activity and achieved 90% conversion at 300 °C. High dispersion of the mixed oxides on the surface of the cordierite support was the most important factor for the catalytic combustion of VOCs, as indicated by SEM. In conclusion, it was shown that the iron oxides were the main active components. These active catalysts were all prepared on cordierite and could prove to be more economical than other catalysts.

Acknowledgments

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