Noble metal exchange of tunnel structured manganese oxides for NO reduction by CO in presence of excess O₂

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Abstract: In this work, the tunnel structured manganese oxides with different pore size had been successfully synthesized. Then the ion-exchange method was employed for the deposition of the noble metal components for the activity test of NO reduction by CO. Results reveal that complete NO conversion was obtained in 200 °C for 5Pt-MnO2×2 sample. While, with the introduction of oxygen in the feeding gas, 5Pd-MnO2×2 sample showed the 100% CO conversion at 50 °C with 80% conversions of NO, and maintained the crystal phase of the catalyst in the presence of excess oxygen. It can be seen clearly from HAADF-STEM image that the MnO2×2 revealed straight tunnel structure with Pd nanoparticles well-dispersed in it.

Keywords: NO+CO+O₂, Manganese catalyst, Noble metal.

1. Introduction

The selective catalytic reduction of NO in an oxidizing atmosphere has recently received extensive attention, since it has potential as a practical strategy for removing NOx emitted from diesel engines, lean-burn engines, and combustors. Numerous efforts have been taken for developing the advanced catalysts. Among them, considerable attentions have been paid to the tunnel structure manganese oxides due to their excellent catalytic performances1. Here, we synthesized manganese oxides with different pore size and exchanged by various metal components and investigated the catalytic performance of NO reduction by CO in the presence of excess oxygen.

2. Experimental

The tunnel structured manganese oxides with different pore sizes (denoted as MnO1×1, MnO2×2, and MnO3×3, respectively) were synthesized according to the reported literature2.

The parent manganese support was subsequently doped with different metals (nominal loading = 5 wt.%) using the ion exchange procedure. A diluted aqueous solution of the corresponding metal precursor was refluxed with the manganese oxides at 80 °C for 24 h.3

3. Results and discussion

Firstly, activity tests of NO+CO over the Pt exchanged different type of manganese oxides was shown in Figure 1. Results revealed that platinum exchanged 2×2 structured manganese oxide has the best activity for completely conversion of NO at 200 °C, and CO conversion maintains the similar pace with NO at the same time. Theoretically, however, CO conversion should reach to 50% when NO was completely converted since the CO concentration was 2 times of NO in inlet gas flow. From the XRD patterns of 5Pt-MnO2×2 before and after used (embedded in Figure 1), it can be seen that the main phase of sample transformed from MnO2 to Mn₂O₃ during the reaction, suggesting that the excessive CO was oxidized by lattice oxygen of MnO₂. After 7% O₂ introducing, as presented in Figure 2, the conversions of NO and CO showed distinct differences over the different catalysts. The oxidation of CO increased dramatically with the elevated temperature, meanwhile NO conversion almost constant at about 80%. Specifically, Pd-MnO2×2 showed the lowest Tₜ₀₀ (temperature required to reach 100% conversion) of CO at 50 °C. Moreover, the
main crystal phases of all samples were maintained in this condition. While, the Pd nanoparticles confined in the straight tunnel of MnO2×2 may lead to the best activities (the HAADF-STEM image in Figure2).

![Figure 1](image1.png)

**Figure 1.** NO+CO activities of Pt exchanged different type of manganese oxides.

![Figure 2](image2.png)

**Figure 2.** NO+CO+O activities of various noble metal exchanged MnO2×2 and HAADF-STEM of 5Pd-MnO2x2 sample.

4. Conclusions

Herein, the tunnel structured manganese oxides with different pore sizes were synthesized and exchanged with various noble metal components, both NO and CO could be completely abated at 200 °C by Pt exchanged MnO2×2 catalyst but simultaneously with the reduction of catalyst. In the presence of excess oxygen, 5Pd-MnO2×2 indicated the best catalytic activities with the lowest 100% conversion temperature and maintained 80% NO conversion at 50 °C, which may be due to the confined Pd nanoparticles in the tunnel of MnO2×2.

References