Activity and Characterization of MnO_X Catalysts for Selective Catalytic Reduction of NO_X with NH_3 at Low Temperatures

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Introduction

Low-temperature catalyst for NH_3-SCR of NO has been attracted much attention in DeNOx from flue gas in stationary source because it can be placed downstream of the dust collector (or electrostatic precipitator) and desulfurizer. Mn-based catalysts show good activities for NH_3-SCR of NO at low temperatures [1-4], such as MnO_X/Al_2O_3, MnO_X/TiO_2, MnO_X/SBA-15, MnO_X/AC, and MnO_X/USY. However, the NO conversion is still low below 150 ℃. In this work, a series of unsupported amorphous MnO_X catalysts were prepared by three methods, and the catalytic activities were evaluated in the temperature range of 50-150℃. Their physical properties were characterized by BET, XRD, TEM etc, and a reaction mechanism was proposed based on in-situ DRIFTS and Raman spectroscopy results.

Materials and Methods

MnO_X catalysts were prepared by three methods, namely, Rheological phase reaction method (RP), Low temperature solid phase reaction method (SP) and Co-precipitation method (CP). For comparison, MnO_X (CA) was also prepared by the citric acid method. The samples were characterized by BET, XRD, TPD, TEM, FT-IR and Roman spectroscopy.

Catalytic activity tests were performed in a quartz tube reactor of 9 mm internal diameter in a flow of 500 ppm NO, 500 ppm NH_3, 3 % O_2, 100 ppm SO_2 (when used) and 2.8~20 % H_2O (when used). 0.5 g catalyst is used for evaluation, and the corresponding GHSV is 23,000 h^{-1} for each run. The concentrations of the NO, NO_2 and NO_x were monitored by a chemiluminescent NO/NO_x analyzer.

Results and Discussion

Table 1 summarized the physical properties of MnOx catalysts prepared with various methods. Figure 1 shows the NOx conversions over MnO_X catalysts. It is obvious that the catalytic activities of MnO_X (SP), MnO_X (RP) and MnO_X (CP) were much higher than the activity of MnO_X (CA), and more than 98 % NO_X conversion could be achieved at 80 ℃, and nearly all of the NO_X could be converted in the range of 80~150 ℃. In comparison, MnO_X (CA), was much less active. The specific surface area and morphology could be the reason that MnO_X (SP), MnO_X (RP) and MnO_X (CP) had superior low temperature catalytic activities.

The results of XPS indicated that manganese was presented on the surface in the MnO_2 state. As the results of TEM and crystal lattice analysis shown in Figure 2, it shows that the MnO_X catalyst was consisted of MnO_2 crystallite with a diameter of about 10nm. The size of the catalyst crystallite was consistent with the parameters of ε-MnO_2.

Table 1. Physical properties of the MnO_X catalysts prepared by different methods

Samples	BET surface area / ($m^2.g^{-1}$)	Pore volume / ($cm^3.g^{-1}$)	Pore diameter / (nm)
MnO_X (RP)	99.02	0.212	9.55
MnO_X (SP)	150.8	0.365	9.69
MnO_X (CP)	96.34	0.278	11.54
MnO_X (CA)	19.07	0.072	10.63

DRIFTS results revealed that NH_3 molecules were adsorbed on the Lewis acid and Brönsted acid sites to form coordinated NH_3 and NH_4^+ ion species, respectively, on unsupported MnO_X catalysts at low temperature (<150℃), and both species participated in the SCR reaction. NO molecules were also adsorbed on the MnO_X catalysts as surface adsorbed NO_2, bridging nitro-nitrito and bidentate nitrate species. The surface adsorbed NO_2 and bridging nitro-nitrito species could take part in the SCR reactions while the bidentate nitrate could not be reduced by ammonia. A probable reaction pathway of low temperature NH_3-SCR is proposed based on the experimental results. It is concluded that the adsorption and activation of NH_3 is the first step of the SCR reaction and the oxidation of NO to surface adsorbed NO_2 and bridging nitro-nitrito species is the rate-determining step of SCR.

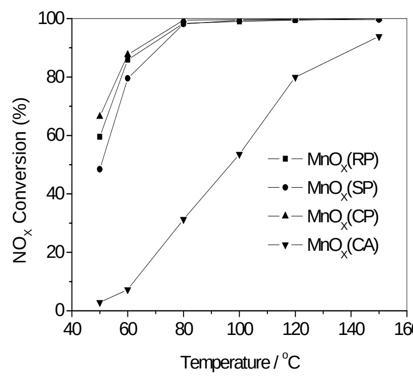

Figure 1. NO_X conversion over four MnO_X catalysts at different temperatures.

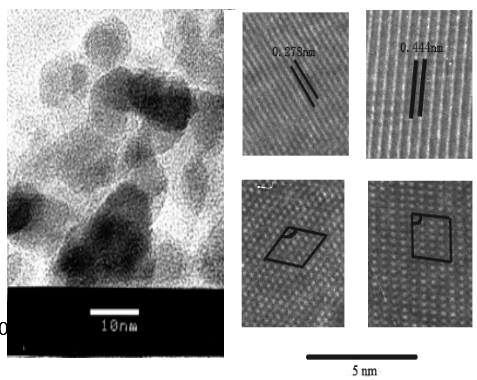

Figure 2. TEM and crystal lattice analysis of MnOx (CP)

References

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