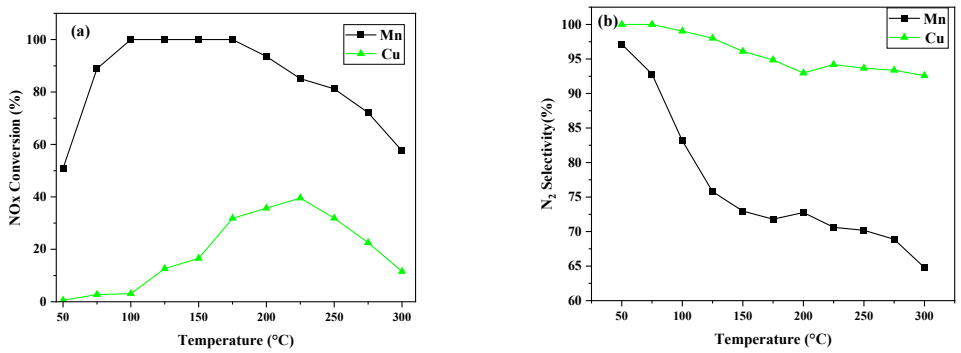


Fig. 1, The catalytic performance of transition metal oxide catalysts in NH_3-SCR, (a) conversion rate of NOx, (b) N_2 selectivity, under the reaction conditions of 500 ppm NH_3, 500 ppm NO, 5% O_2, N_2 balance; GHSV = 30,000 h^{-1}.

1. Single metal oxide NH3-SCR

Fig.1a. shows the test results of the NH_3-SCR reaction based on Mn and Cu single-metal oxide catalysts. The NOx conversion rates of all catalysts increase with temperature in the entire testing temperature range. The catalytic activity decreases in the order of Mn > Cu, and Mn oxide exhibits better low-temperature activity. At 100°C, the NOx conversion rate is close to 100%, while the Cu catalyst activity is almost zero. Even at 150 °C, the conversion rate is only 33%. Therefore, for the NH_3-SCR reaction, Mn has higher low-temperature catalytic activity.

Fig.1b shows the N_2 selectivity of the samples. Obviously, the N_2 selectivity of the catalysts decreases with the increase of reaction temperature. Among all catalysts, the metal Mn exhibits the worst N2 selectivity, with only about 96% N_2 selectivity even at 50°C, and then it

drops sharply to 65% at 300°C. This is due to the excessively strong redox properties, which result in the non-selective oxidation of NH3 and the partial reduction of NO. For Cu catalysts, although their low-temperature catalytic activity is poor, their N_2 selectivity is higher. The N_2 selectivity is not less than 90% throughout the entire testing temperature range, as most reactants do not participate in the reaction.

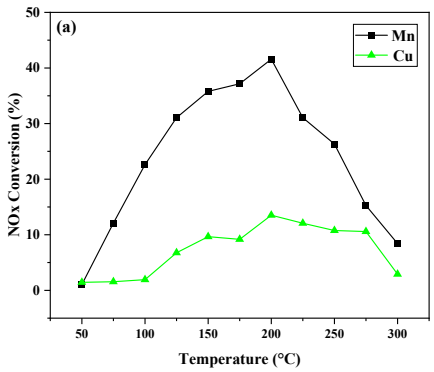
2. Single metal oxide CO-SCR reaction and CO oxidation activity.

To clarify the interaction mechanism between single-metal oxides in NO+CO+O_2, we tested the CO-SCR reaction and CO oxidation reaction under a rich oxygen atmosphere (5vol.%O_2). Fig. 2a shows the NOx conversion rate in the CO-SCR reaction. The NOx conversion rate in all samples did not exceed 50%. Even for Mn, which exhibited the highest activity in the NH_3-SCR reaction, the maximum conversion rate was only 41% at 200°C. Cu samples showed almost no NO reaction, and the NOx conversion rate throughout the temperature range was not higher than 10%. In the NO+CO+O_2 system, as shown in Fig. 2b, the CO conversion rate of the Mn sample was 45% at the initial temperature, and it was completely converted at 125 °C.

The test results of CO oxidation activity of single metal oxides under an atmosphere condition without NO participation are shown in Fig. 2c. Mn catalyst can completely convert CO at 100°C, while the effect on Cu

sample is small, with only a 3% increase at 200°C. Obviously, the participation of nitrogen oxides inhibits the CO reaction activity of Mn sample at low temperature, and this inhibition effect is in the order of Mn > Cu, which is related to the competition of NO and oxygen for adsorption on the catalyst surface. By recording the changes in N_2O concentration, the N_2 selectivity in CO-SCR reaction of all samples is 100%.

In summary, according to the results of NH_3-SCR, CO-SCR, and CO catalytic oxidation tests, sample Mn exhibits the best NH_3-SCR and CO oxidation reaction activity, while the CO-SCR reaction performance is poor, which can be attributed to the rich surface-active oxygen of Mn oxide, and the excessive active oxygen can cause non-selective reactions. In comparison, the activity of single metal Cu is the poorest.



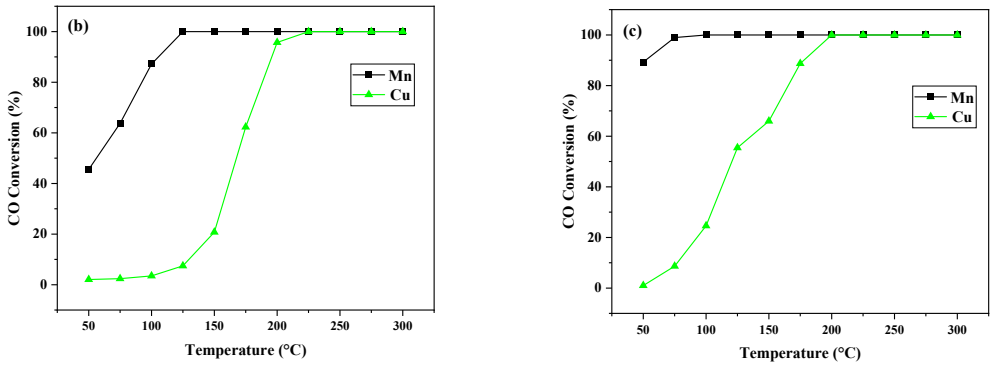


Fig. 2. (a) Conversion rate of NOx in CO-SCR reaction, reaction conditions: 1000 ppm CO, 500 ppm NO, 5% O_2, balanced N_2; GHSV = 30,000 h^{-1}. (b) Conversion rate of CO in CO-SCR reaction, reaction conditions same as (a). (c) Conversion rate of CO in CO oxidation reaction, reaction conditions: 1000 ppm CO, 5% O_2, balanced N_2; GHSV = 30,000 h^{-1}.

3. Study on surface crystal forms of single metal oxides.

Fig.3 shows the XRD patterns of single metal oxide catalysts Mn and Cu. For the Cu sample, strong diffraction peaks corresponding to (110), (-111), (111), (-202), (-113), (-311), and (220) planes of CuO (PDF#72-0629) are observed at 2θ = 32.5°, 35.6°, 38.8°, 48.8°, 61.6°, 66.3°, and 68.1°, respectively. The crystal structure is obvious with no other impurities present. Similarly, the XRD pattern of Mn oxide shows weak and broad peaks, indicating that the Mn sample exists in an amorphous state and can form multiple Mn oxides. The peaks related to (200), (201), (310), (-210), and (301) planes of MnO_2 (PDF#44-0141) are detected at 2θ = 18.1°, 21.6°, 28.7°, 36.7°, and 44.4°, as well as peaks related to Mn_5O_8 (PDF#39-1218)

at 2θ = 8.7°, 31.9°, 47.8°, 58.0°, and 66.1°.

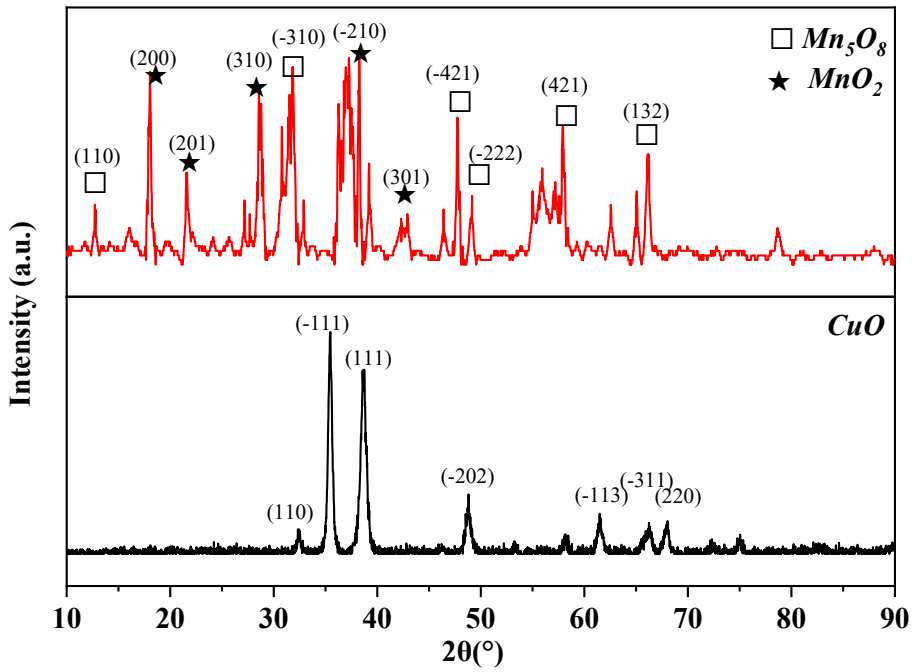
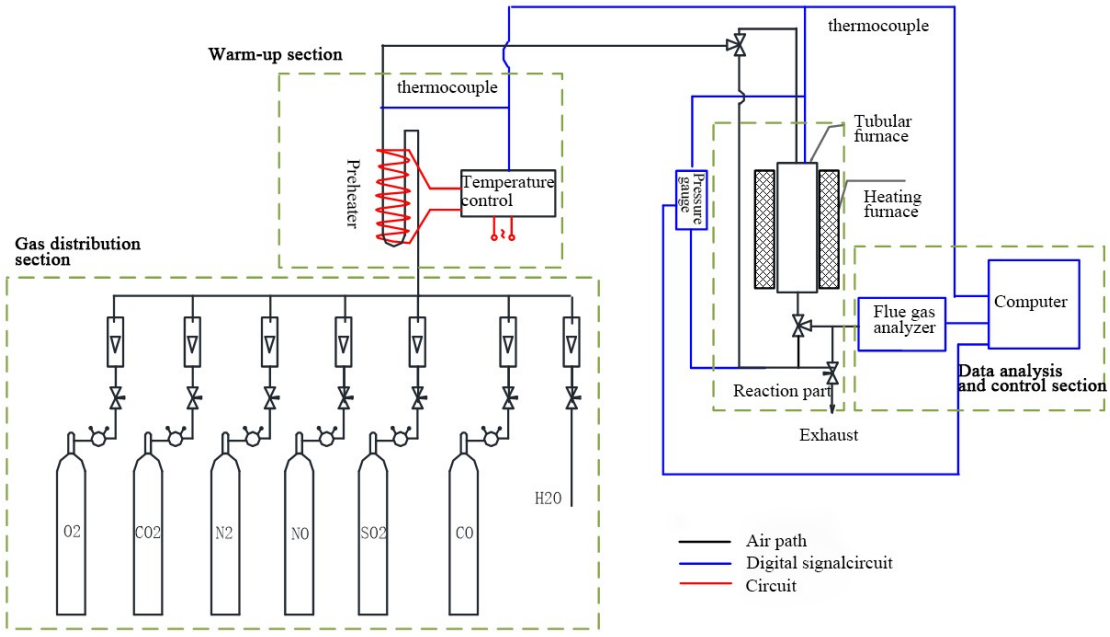


Fig. 3. XRD spectra of single metal oxide Mn and Cu catalysts.



Schematic diagram of fixed bed reaction system.