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Cu–Mn mixed oxides for low temperature NO reduction with NH_3

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Abstract

Cu–Mn mixed oxides were prepared by a co-precipitation method and applied for low temperature NO reduction with NH_3 in the presence of excess oxygen. Effects of [Cu]/[Mn] ratio and calcination temperatures on NOx conversions were investigated. Cu–Mn oxide catalysts containing small amounts of copper showed the complete NOx conversion in a wide range of reaction temperature from 323 to 473 K. This catalyst showed a reversible deactivation due to the presence of water vapor and SO_2. Different catalytic activities of Cu–Mn mixed oxides could be attributed mainly to surface areas and the crystalline nature.

Keywords: NH_3-SCR; Cu–Mn oxides; Precipitation method; H_2O; SO_2

1. Introduction

The emission control of nitric oxides (NO, NO_2 and N_2O) from various combustion processes has been a major environmental concern related to the air quality because these cause the photochemical smog, acid rain, ozone depletion and greenhouse effects. The selective catalytic reduction (SCR) is one of effective post-treatments for the abatement of NOx emission to the atmosphere. Although a number of reducing agents can be utilized in SCR, ammonia has been adopted in general, which is called NH_3-SCR, for stationary sources such as power plants and nitric acid plants [1]. In this process, NO contained in flue gases is reduced to N_2 and H_2O by injected NH_3:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

Many catalysts have been reported to be active for the NH_3-SCR technology [2–4]. Commercially available catalysts are based on V_2O_5/TiO_2 [5]. Because these catalysts exhibit high conversions in the temperature range of 573–673 K, the SCR should be applied before units for particle removal and desulphurization where the gas temperature decreases [6]. However, when the flue gas has high concentrations of particles and other contaminants, which are deleterious for the catalyst, proper units should be located at the upstream of the catalyst bed to resolve above problems, which causes the decrease of the exit gas temperature. Therefore, there is a great interest in the development of SCR catalysts active at low temperatures (<573 K).

A number of catalysts consisted of various transition metal (V, Cr, Mn, Fe, Co, Ni and Cu) oxides on different commercial supports such as silica and alumina have been studied. Among these catalysts, manganese oxides such as $MnOx/Al_2O_3$ [7], MnOx/NaY [8] and $MnOx/TiO_2$ [9,10] have attracted much interest due to their high catalytic activities. These catalysts were prepared by the solution impregnation method on supports using manganese nitrate or acetate. Unsupported MnOx catalysts generally showed less NOx conversion than did supported MnOx catalysts because of its low surface area.

A number of factors have been claimed to affect the low-temperature selective reduction of NO with ammonia over manganese oxide catalysts. Singoredjo et al. [7] studied alumina supported manganese oxides from different manganese precursors and found that manganese acetate resulted in a

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better dispersion of the manganese oxide on the support and a higher specific catalyst activity than manganese nitrate as precursor. Kapteijn et al. [11] compared manganese oxides of different crystallinity, oxidation state and specific surface, and suggested that a highly dispersed amorphous Mn_2O_3 should be optimum for this reaction. To increase the catalytic activity of manganese oxides, various transition metal oxides were incorporated as a promoter. Long et al. [12] prepared Fe–Mn based catalyst by a co-precipitation method and found a high catalytic activity at 373–453 K. MnOx–CeO_2 catalyst was also reported to be active for low-temperature SCR of NO with NH_3 [13,14].

Mixed oxides containing Cu and Mn as main metal element have been reported to be very active for complete oxidation reaction at low temperatures [15]. This can help the facile formation of NO_2 and promote the NO reduction with ammonia at low temperatures [16]. In this report, various Cu–Mn oxide catalysts were prepared by a co-precipitation method and were applied to low temperature NO reduction with NH_3. The effect of molar ratio of Cu/Mn and calcination temperature on NOx conversions was studied. The surface area and the crystalline structure were measured to explain different catalytic activities over Cu–Mn oxide catalysts.

2. Experimental

2.1. Catalyst preparation

All the catalysts tested in this study were prepared by a co-precipitation method. After aqueous solutions of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, Aldrich, 98+%) and manganese nitrate ($Mn(NO_3)_2 \cdot xH_2O$, Aldrich, 98.0+%) with different concentrations were pre-mixed, aqueous sodium carbonate (SHINYO, 99.0%) solution was continuously added to the mixed nitrate solution until the pH of the solution reached 8. The resulting precipitate was aged at 298 K for 1 h, filtered and washed several times with distilled water. The cake was dried in air at 393 K for 12 h and calcined at various temperatures in static air. The catalysts is denoted as Cu*x*Mn*y*(*z*), where *x* and *y* represent the molar concentration of copper and manganese and *z* denotes the calcination temperature (K), e.g. Cu0.01Mn0.50(623).

2.2. Catalyst characterization

Bulk crystalline structures of catalysts were determined with an X-ray diffraction (XRD) technique. XRD patterns were obtained by using Cu Kα radiation using a Rigaku D/MAC-III instrument at room temperature. Surface areas were determined by N_2 adsorption using the BET method. The XAFS spectra were taken in a transmission mode for the K-edge of Mn and Cu at beamline 3C1 of the Pohang Light Source (PAL) operating at 2.5 GeV with ca. 100–150 mA of stored current. The detector gas was N_2 for the incident beam and the transmitted beam. In addition to catalyst samples, XAFS data were also obtained for Cu foil, Cu_2O, CuO, Mn foil, MnO, Mn_2O_3, Mn_3O_4 and MnO_2 as references. They were analyzed by using ATHENA [17].

2.3. Activity measurements

Catalytic activities were measured over a fixed bed of catalysts in a tubular flow reactor of 8 mm i.d. Reactant gases were fed to the reactor by means of electronic mass flow controller (MKS). The reactant gas typically consisted of 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, 11 vol.% H_2O, 100 ppm SO_2 and N_2. The NOx concentration in the inlet and outlet gas was analyzed by means of a NO/NO_2 combustion gas analyzer (Euroton). The steady-state NOx conversion was measured at each reaction temperature.

3. Results and discussion

Fig. 1 shows NOx conversions in NO reduction with NH_3 at a different reaction temperature over various Cu–Mn oxide catalysts. These catalysts were composed of different molar ratios of Cu/Mn and were all calcined at 623 K before a reaction. The gradual increase in NOx conversion with a

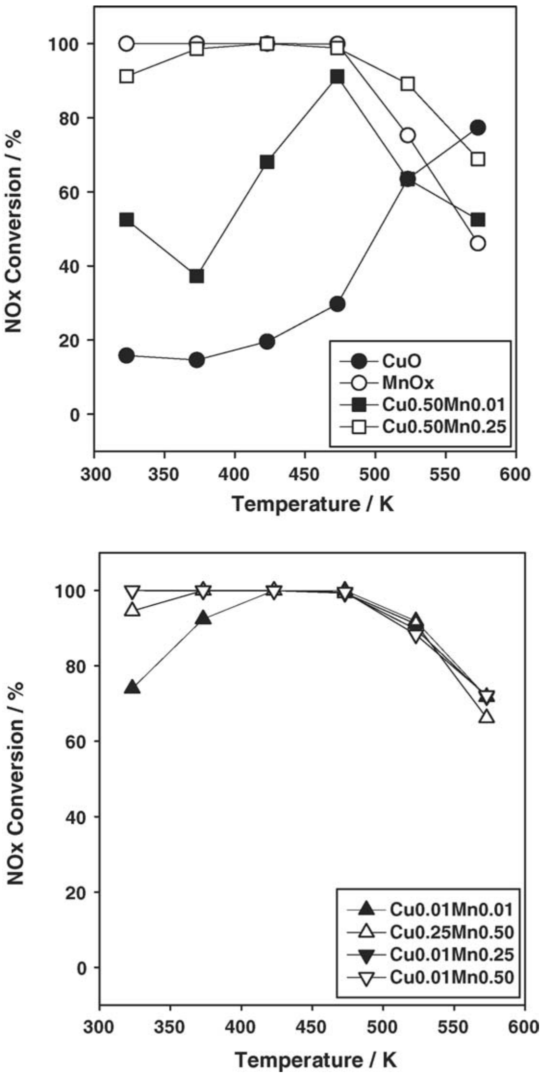

Fig. 1. NOx conversions over Cu–Mn oxide catalysts calcined at 623 K with a different molar ratio Cu to Mn. Reactants: 500 ppm NO, 500 ppm NH_3 and 5 vol.% O_2 in N_2. The gas hourly space velocity (GHSV) was 30,000 h^{-1}.

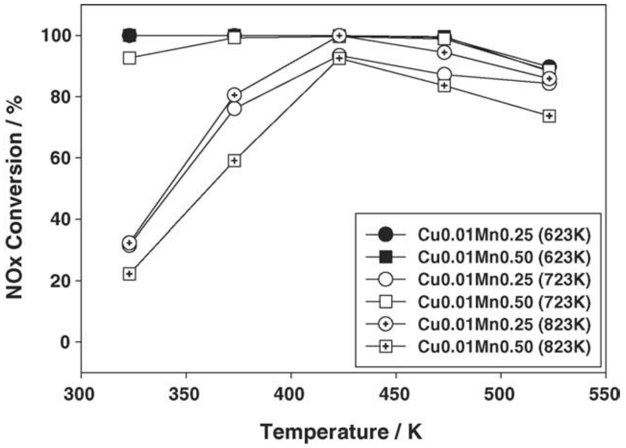

Fig. 2. NOx conversions over Cu0.01Mn0.25 and Cu0.01Mn0.50 catalysts calcined at 623, 723 and 823 K. Reactants: 500 ppm NO, 500 ppm NH_3 and 5 vol.% O_2 in N_2. The gas hourly space velocity (GHSV) was 30,000 h^{-1}.

reaction temperature was observed over pure CuO. This catalyst gave the lowest NOx conversion below 523 K among the tested catalysts. When a small amount of Mn was incorporated into CuO (Cu0.50Mn0.01(623)), catalytic activities at low temperatures increased. As the molar ratio of Mn/Cu increased, the NOx conversion at low temperatures also increased until a molar ratio of Mn/Cu reached 25. 100% NOx conversion was obtained below 473 K as long as a molar ratio of Mn/Cu was more than 25. MnOx also gave complete NOx conversion at low temperatures. However, Cu–Mn oxide catalysts containing small amounts of Cu showed higher NOx conversions than did pure MnOx catalyst when a reaction temperature was higher than 473 K. Therefore, there was a wide temperature range showing more than 90% in NOx conversion from 323 to 523 K over Cu–Mn oxide catalysts containing small amounts of Cu.

Fig. 2 presents NOx conversion over Cu–Mn oxide catalysts, in which a molar ratio of Mn/Cu was 25 and 50, calcined at different temperatures. As the calcination temperature increased, the NOx conversion decreased over both catalysts.

Table 1
Textural properties of Cu–Mn oxide catalysts

Sample	Calcination temperature (K)	S_{BET} (m^2/g)
CuO	623	21.4
MnOx	623	131.0
Cu0.50Mn0.01	623	27.7
Cu0.50Mn0.25	623	86.5
Cu0.01Mn0.01	623	61.5
Cu0.25Mn0.50	623	97.3
Cu0.01Mn0.25	623	175.5
	723	41.7
	823	35.5
Cu0.01Mn0.50	623	108.9
	723	86.2
	823	19.2

The higher NOx conversion was obtained over Cu0.01Mn0.50 compared with Cu0.01Mn0.25 when both catalysts were calcined at 723 K. However, almost same NOx conversion was observed over both catalysts when they were calcined at 823 K.

To find out changes in a surface area of Cu–Mn oxide catalysts with different molar ratios of Mn/Cu and at different calcinations temperatures, N_2-adsorption experiment was conducted. Table 1 shows the surface area for each catalyst examined in this work. There is no correlation between the BET surface area and the molar ratio of Mn/Cu in mixed metal oxide catalysts. However, the NOx conversion at low temperatures appeared to increase with increasing BET surface area. As usual, the BET surface area decreased with increasing calcination temperature.

XRD was conducted to determine crystalline structure of Cu–Mn oxide catalysts with different molar ratios of Mn/Cu and at different calcinations temperatures. Fig. 3 shows XRD pattern of Cu–Mn oxide catalysts with different compositions. XRD patterns of CuO and MnOx were also shown for comparison. Manifest peaks representing CuO were observed in catalysts with high molar ratio of Cu/Mn. The peak intensity decreased as the molar ratio of Cu/Mn decreased. When the

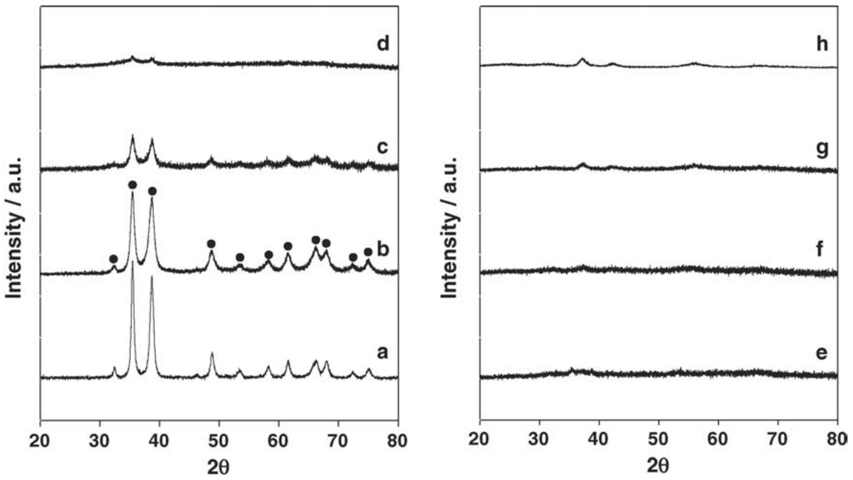

Fig. 3. XRD patterns of CuO, Cu–Mn oxide catalysts prepared by a co-precipitation method and calcined at 623 K and MnOx. (a) CuO, (b) Cu0.50Mn0.01 (c) Cu0.50Mn0.25, (d) Cu0.01Mn0.01, (e) Cu0.25Mn0.50, (f) Cu0.01Mn0.25, (g) Cu0.01Mn0.50 and (h) MnOx. The symbol (●) represents CuO.

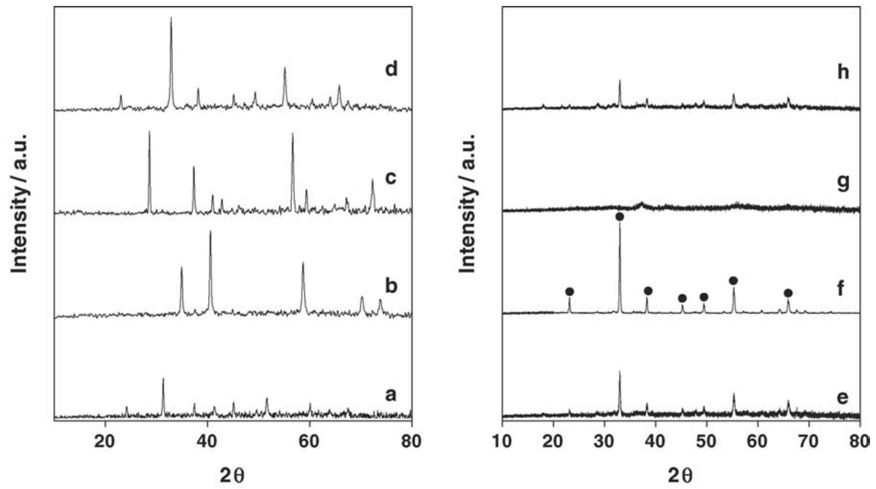

Fig. 4. XRD patterns of reference manganese oxides, Cu0.01Mn0.25 and Cu0.01Mn0.50 calcined at 723 and 823 K. (a) MnO, (b) MnO_2, (c) Mn_2O_3, (d) Mn_3O_4, (e) Cu0.01Mn0.25(723), (f) Cu0.01Mn0.25(823), (g) Cu0.01Mn0.50(723) and (h) Cu0.01Mn0.50(823). The symbol (●) represents Mn_2O_3.

molar ratio of Cu/Mn is less than 0.5, no crystalline phase can be determined from XRD. However, crystalline phase appeared when these catalysts were calcined at a higher temperature than 623 K as shown in Fig. 4. Manifest peaks representing Mn_2O_3 were observed and strengthened with increasing calcinations temperatures.

To determine the structural and electronic information of Cu–Mn oxide catalysts, which are amorphous from XRD data, Mn K-edge and Cu K-edge XANES spectra were obtained. Fig. 5 presents Mn K-edge XANES spectra of Cu0.01Mn0.25 calcined at 623 and 823 K and Mn reference compounds of Mn foil, MnO, Mn_3O_4, Mn_2O_3 and MnO_2. Easily discernible features of XANES spectra were observed for Mn reference samples and the edge energy shift toward a higher energy was an expected result with the increase in the oxidation state of Mn from metallic Mn foil to Mn(IV)O_2. Mn K-edge XANES spectra of Cu0.01Mn0.25 calcined at 623 K appeared to be different from any XANES spectra of Mn reference samples measured. However, Mn K-edge XANES spectra of Cu0.01Mn0.25 calcined at 823 K was similar to that of Mn_2O_3, which is consistent with the fact that crystalline Mn_2O_3 phase was observed from XRD. To determine the quantitative amount of each manganese oxides, a linear XANES fitting was conducted for Cu0.01Mn0.25 calcined at 623 and 823 K. Different weight fraction of manganese oxides appeared to be present in these catalysts (Table 2). In Cu0.01Mn0.25 calcined at 623 K, Mn_2O_3 and Mn_3O_4 were determined to be dominant manganese oxides and small amounts of MnO_2 were also calculated. When this catalyst calcined at 823 K, large amounts of Mn_2O_3 and small amounts of Mn_3O_4 and MnO_2 were determined to be present.

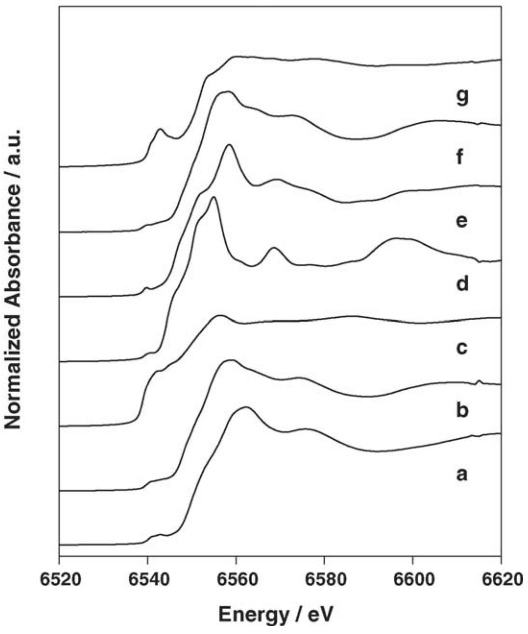

Fig. 5. Mn K-edge XANES spectra for Cu0.01Mn0.25 calcined at 623 K (a) and 823 K (b) and some reference manganese oxides such as Mn foil (c), MnO (d), Mn_3O_4 (e), Mn_2O_3 (f) and MnO_2 (g).

Fig. 6 presents Cu K-edge XANES spectra of Cu0.01Mn0.25 calcined at 623 K and Cu reference compounds of Cu foil, Cu_2O and CuO. Easily discernible features of XANES spectra were observed for Cu reference samples and the edge energy shift toward a higher energy was an expected result with the increase in the oxidation state of Cu from

Table 2
The linear combination fitting result for Cu0.01Mn0.25 calcined at different temperatures

Temperature (K)	E_o (eV)	Standard sample	Weight fraction	E_o shift	R-factor[a]
623	6549.727	MnO	0.0	–	0.02109
		Mn_3O_4	0.479	3.295	
		Mn_2O_3	0.363	3.651	
		MnO_2	0.158	−1.861	
823	6548.484	MnO	0.041	−2.092	0.00512
		Mn_3O_4	0.139	2.662	
		Mn_2O_3	0.708	0.896	
		MnO_2	0.111	−2.524	

[a] R-factor is defined as follows: $R = \text{sum}(\text{data-fit})^2/\text{sum}(\text{data}^2)$.

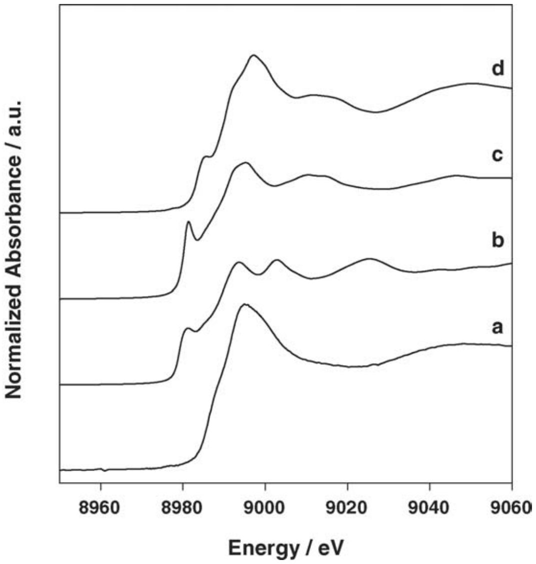

Fig. 6. Cu K-edge XANES spectra for Cu0.01Mn0.25 calcined at 623 K (a) and some reference copper compounds such as Cu foil (b), Cu_2O (c) and CuO (d).

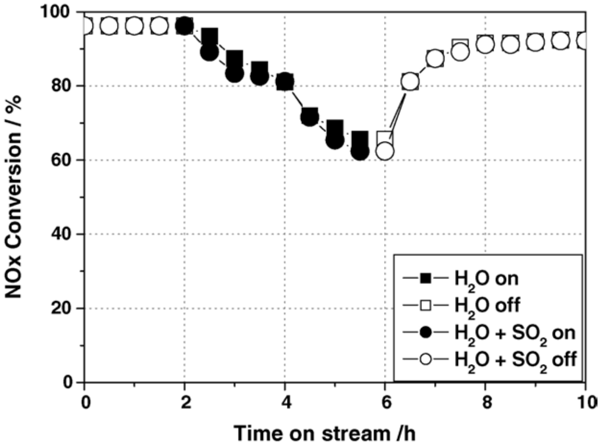

Fig. 7. Effects of H_2O and SO_2 on NOx conversions over Mn–Cu oxides at 398 K. Reactants: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, 11% H_2O and 100 ppm SO_2 in N_2. The gas hourly space velocity (GHSV) was 50,000 h^{-1}.

metallic Cu foil to Cu(II)O. Cu K-edge XANES spectra of Cu0.01Mn0.25 calcined at 623 K appeared to be different from any XANES spectra of Cu reference samples measured. However, the oxidation state of copper was determined to be +2 from the shift of edge energy.

Because the catalyst is usually deactivated mainly by water vapor and SO_2 in the combustion gases, the resistance of de-NOx catalysts to water vapor and SO_2 is very important for industrial applications. The combined effect of both SO_2 and H_2O on NOx conversions over Mn–Cu oxides at 398 K with a space velocity of 50,000 h^{-1} is shown in Fig. 7. When 100 ppm SO_2 and 11 vol.% H_2O were added to the reaction gas mixture, the NOx conversion over Cu–Mn oxides decreased from 95 to 64% at 398 K after 4 h. However, the activity was gradually recovered after stopping the supply of SO_2 and H_2O.

From these results, the most active catalyst for low temperature NO reduction with NH_3 should be amorphous manganese oxides containing small amounts of copper oxide with a high surface area. The promotional effect of copper oxide can be interpreted that NO could be oxidized into NO_2 easily at low temperatures. This can help the formation of ammonium nitrite. The anomalous promotion of Cu–Mn mixed oxides has been ascribed to the formation of the copper manganese spinel $CuMn_2O_4$, precisely to an electronic transfer between copper and manganese cations within the spinel lattice [15]:

$$Cu^{2+} + Mn^{3+} \leftrightarrow Cu^{+} + Mn^{4+}$$

Similarly to CO oxidation, an oxidation mechanism for NO oxidation can be described by following reactions:

$$NO + Mn^{4+} \rightarrow NO_{ads}{}^{+} + Mn^{3+}$$

$$1/2O_2 + Cu^{+} \rightarrow Cu^{2+} + O_{ads}{}^{-}$$

$$NO_{ads}{}^{+} + O_{ads}{}^{-} \rightarrow NO_2$$

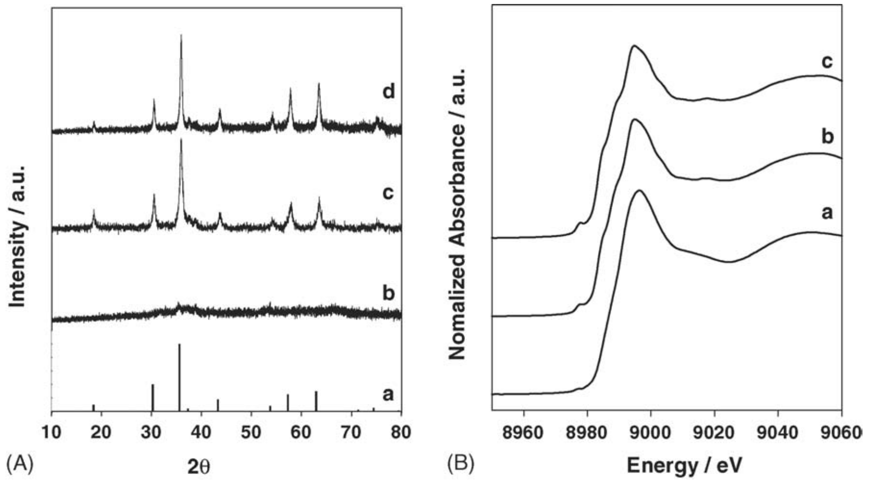

Fig. 8. (A) XRD patterns of $CuMn_2O_4$ (a) in JCPDS card and Cu0.25Mn0.50 calcined at 623 K (b), 723 K (c) and 823 K (d). (B) Cu K-edge XANES spectra for Cu0.25Mn0.50 calcined at 623 K (a), 723 K (b) and 823 K (c).

From Cu K-edge XANES spectra for Cu0.01Mn0.25(623) in Fig. 6, it can be concluded that Cu(II) species must be different from CuO. Fig. 8 shows XRD patterns and Cu K-edge XANES spectra of Cu0.25Mn0.50 calcined at different temperatures. Cu–Mn oxide catalyst calcined at 623 K showed no crystalline phase in XRD, but almost same Cu K-edge XANES spectra with that of Cu0.01Mn0.25(623) was observed. When Cu0.25Mn0.50 was calcined above 723 K, manifest peaks representing $CuMn_2O4$ were observed in XRD pattern. Therefore, we can postulate that amorphous $CuMn_2O_4$ was dominantly present in Cu0.01Mn0.25(623). This can contribute the additional promotional effect on NOx conversions at low temperatures.

4. Conclusions

Cu–Mn mixed oxides prepared by a co-precipitation method using sodium carbonate were highly active for the selective catalytic reduction of NOx with NH_3 in the presence of excess oxygen at low temperatures. The presence of small amounts of copper oxide gave the wide temperature window showing 100% NOx conversion compared with single metal oxide catalysts such as CuO and MnOx. Amorphous manganese oxides were determined to be present in active Cu–Mn mixed oxide catalysts. The oxidation state of copper was determined to be +2. The addition of SO_2 with H_2O in the feeding gas has a reversible adverse effect on the NOx conversion.

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