Preparation of Cu/Co/M (M=Al, Fe, Cr, NiFe) mixed metal oxides and their catalytic activity on selective catalytic reduction of NOx by hydrocarbon

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Abstract. Cu/Co/M (M=Al, Fe, Cr, NiFe) mixed metal oxides (Cu/Co/M-MMOs) were prepared by calcination of Cu/Co/M layered double hydroxide (Cu/Co/M-LDHs) precursors. Their composition, thermal stability, structure and morphology were characterized by ICP, TGA, XRD, IR, BET and SEM, respectively. The results indicated that all precursor samples show good hydrotalcite structure with carbonate inside the layer, and the carbonate is removed by calcination at 773 K. While the mixed metal oxides have spinel structure with specific areas of 20-110 m² g⁻¹. Cu/Co/M-MMOs have hexagon structure with particle size in the range of 50-100 nm. The order of catalytic activities of Cu/Co/M-MMOs on selective catalytic reduction of NOx is: Cu/Co-MMOs>Cu/Co/Ni/Fe-MMOs>Cu/Co/Fe-MMOs>Cu/Co/Al-MMOs≈Cu/Co/Cr-MMOs.

1. Introduction

With the rapid development of economy and increasing concern of environment, more and more attention has been paid to air pollution. One of the principal environmental concerns in air pollution is the minimization of NOx emissions. Research in the field of NOx abatement has grown significantly in the last two decades [1]. Several methods have been used to reduce NOx emission. One of the main methods for the removal of NOx is selective catalytic reduction of NOx with NH₃ (ammonia-SCR) [2, 3]. SCR of NOx is a highly efficient way to reduce NOx emission in the oxygen-rich exhausts [4]. Mixed metal oxides based catalysts have been widely studied in the area of catalytic removal of NOx due to their high hydrothermal stability and moderate catalytic activity [5]. But ammonia-SCR is not environment friendly. Hydrocarbon is a kind of reductant for SCR of NOx (HC-SCR) attracts more and more interest due to its low price and easy obtained as well as its formation is similar to that found in the exhaust [3, 6]. Layered double hydroxides derived mixed metal oxides catalysts have attracted much attention as potential candidates for the catalytic removal of NOx from lean-burn and diesel exhaust gases under excess oxygen conditions [7]. They have showed good catalytic activities on SCR of NOx at low temperature and in the presence of SO₂ and H₂O [8, 9]. Zhang Z. reported behavior of soot combustion with NOx/O₂ on potassium-supported Mg-Al hydrotalcite mixed oxides using in situ FTIR, the results showed that the presence of NOx in O₂ favors the soot combustion at lower temperatures (<573 K) [10]. Huang reported that MnFeO₃@TiO₂ catalyst with a core-shell structure shows excellent K tolerance on SCR of NOx by NH₃ as reductant [11]. Gao have done research on activity and SO₂ tolerance of Co- or Ni-doped MnOₓ-CeO₂ catalysts for SCR of NOx with NH₃ at low temperature, the results showed that Co/Ni-modified MnOₓ-CeO₂ catalysts showed higher SCR performance and SO₂ tolerance [12]. However only few researches on HC-SCR of NOx by using...
hydrotalcites derived mixed metal oxides catalysts. Therefore, series of Cu/Co/M-MMOs (M=Al/Fe/Cr/NiFe) were prepared in this paper and their catalytic activity of SCR of NOx using hydrocarbon as reductant was studied.

2. Experimental

2.1. Preparation of Cu/Co/M-LDHs precursor and Cu/Co/M-MMOs
Cu/Co/M-LDHs were synthesized by co-precipitation method. Metal nitrates of Cu, Co, Al, Fe, Cr, Ni and NaOH as well as Na$_2$CO$_3$ were used as raw materials. Two solutions, namely, solution (A) containing desired amount of metal nitrates were added slowly into solution (B) containing the precipitating agents (NaOH as well as Na$_2$CO$_3$). The pH value of the mixed solution was maintained constant around 9 under vigorous mechanical stirring. After aging for 24h, the obtained slurry was filtered and washed thoroughly with distilled water before being dried overnight in an oven under 373 K. The obtained Cu/Co-LDHs, Cu/Co/Al-LDHs, Cu/Co/Fe-LDHs, Cu/Co/Cr-LDHs and Cu/Co/Ni/Fe-LDHs were grinded into powder. Cu/Co/M-MMOs were prepared by calcination of Cu/Co/M-LDHs precursors in a temperature controlled muffle furnace at 773 K for 4 h. Finally, the catalysts (signed as Cu/Co-MMOs, Cu/Co/Al-MMOs, Cu/Co/Fe-MMOs, Cu/Co/Cr-MMOs and Cu/Co/Ni/Fe-MMOs, respectively) were cooled down to ambient temperature and ready for activity test.

2.2. Characterization of Cu/Co/M-LDHs precursor and Cu/Co/M-MMOs
Inductive Coupled Plasma (ICP) was used to determine the elemental composition of as prepared solid precursor sample (JY, model ULTIMA). Thermo gravimetric analysis (TGA) of the as-synthesized sample was carried out on a HCT-2 thermo balance at a heating rate of 10 Kmin$^{-1}$ from room temperature to 873 K in a flowing nitrogen atmosphere. X-ray diffraction (XRD) patterns were determined using a PANalytical X'Pert PRO MPD diffractometer equipped with Cu Kα radiation (λ=1.5406 Å) operating at 40 kV and 40 mA. Fourier Transform Infrared spectra (FT-IR) were recorded on a Brucker VECTOR22 spectrometer in 4000-450 cm$^{-1}$ using KBr pellet technique. Scanning electronic microscopy (SEM) images were taken with a Hitachi S-4800 field-emission electron microscope. The BET surface area was evaluated by N$_2$ adsorption in a constant volume adsorption apparatus (Micrometer ASAP2010).

2.3. Catalytic test of Cu/Co/M-MMOs
Cu/Co/M-MMOs catalysts were grinded to a particle size of <250 μm. The catalytic test of the sample was took place in a fixed bed reactor, which was made of quartz. 0.24–0.26g of catalysts was placed into the reactor. Prior to the tests, the catalyst was pre-treated by heating in 5% O$_2$/Ar with a total flow rate of 50 cm$^3$ min$^{-1}$ up to 573K for 1 h and then cooled down to 323K in flowing Ar. The pre-treated catalyst was introduced to the NOx reduction feed consisting of 600 ppm NO, 600 ppm C$_3$H$_6$, 12.0% O$_2$, 7.0% H$_2$O, 6.0 % CO$_2$, and He balance. The total flow rate of the NOx reduction was 200 cm$^3$ min$^{-1}$. The reaction temperature was increased with step of 50K from 323 to 823 K holding every temperature for 0.5 h. The concentrations of NO and NO$_2$ in the reactor effluent was continuously measured by a heated vacuum Chemiluminescent NOx analyzer (4000VM, SINGAL). Figure 1 show the scheme of the catalytic test of the Cu/Co/M-MMOs catalysts.

Figure 1. Scheme of the catalytic test of the Cu/Co/M-MMOs catalysts.
3. Results and discussion

3.1. Elemental composition of Cu/Co/M-LDHs

Elemental composition of the prepared Cu/Co/M-LDHs was determined by ICP. ICP results of elemental composition of Cu/Co/M-LDHs are listed in Table 1. It can be observed that all the metal contents in prepared sample solids are similar with those in solution. Cu/Co-LDHs sample has higher Cu/Co molar ratios in solid than that in solution. The fact that Cu is the only M$^{2+}$ metal leads to the hardness of LDHs formation.

| sample               | Molar ratios of n (Cu) : n (Co) : n (M) |
|----------------------|----------------------------------------|
| In solution          | In solid                               |
| Cu/Co-LDHs           | 4:1                                    | 4.88:1.00                          |
| Cu/Co/Al-LDHs        | 1:2:1                                  | 1.00:1.88:0.95                     |
| Cu/Co/Fe-LDHs        | 1:3:2                                  | 1.00:2.92:1.99                     |
| Cu/Co/Cr-LDHs        | 1:3:2                                  | 1.00:2.80:1.83                     |
| Cu/Co/Ni/Fe-LDHs     | 3:9:4:8                                | 3.24:9.04:4.00:8.32               |

3.2. Thermal stabilities of Cu/Co/M-LDHs

Thermal stabilities of Cu/Co/M-LDHs were investigated by TGA. TGA curves of Cu/Co/M-LDHs precursors are shown in Figure 2. It can be observed that different samples have different weight loss stages. Only one weight loss stage is observed for Cu/Co-LDHs. Two weight loss stages are observed for Cu/Co/Fe-LDHs and Cu/Co/Ni/Fe-LDHs samples. While three weight loss stages are observed for Cu/Co/Fe-LDHs and Cu/Co/Cr-LDHs samples. It can be concluded that the thermal decomposition of the LDHs precursors proceeded in one to three steps. The low temperature weight loss at (< 473 K) is due to the departure of weakly bonded water molecules and surface water. The second one at high temperature (473–673 K) corresponds to the dehydroxylation of the brucite–like layer as well as part of the interlayer carbonate anions. The high temperature weight loss at (> 673 K) is further dehydroxylation of the layer. The total weight loss is around 30% (by wt.). Thus, Cu/Co/M-LDHs precursors were converted into Cu/Co/M–MMOs after calcinations at 773K.

![Figure 2](image-url)
3.3. Structure of Cu/Co/M-LDHs and Cu/Co/M-MMOs

XRD was used to characterize the crystalline structure of the sample. XRD patterns for Cu/Co/M-LDHs precursors are shown in figure 3. It can be seen that all the patterns in the figure show typical LDHs structure with peaks at 2θ = 11.8 º, 23.6 º, 34.7 º. It is indicated that the samples are well crystallized with high rhombohedral symmetry layer. The first peak of Cu/Co-LDHs shifts to higher angle due to the Jahn-Teller effect of Cu. Furthermore, CuO phase was found in Cu/Co-LDHs sample. It can be also explained by the Jahn-Teller effect of Cu which leads to the hardness of Cu$^{2+}$ to introduce into the LDHs layer. Thus, the Cu$^{2+}$ formed into CuO phase and existed in the sample.

![XRD patterns for Cu/Co/M-LDHs precursors.](image1)

Figure 3. XRD patterns for Cu/Co/M-LDHs precursors.

XRD patterns for Cu/Co/M-MMOs are shown in figure 4. It can be observed that all typical peaks of LDHs are disappeared. Broad peaks at 2θ = 32 º, 37 º, 45 º, 59 º and 66 º were observed for all samples which was assigned to spinel phase. This means that Cu/Co/M-LDHs precursors are formed into spinel phase after calcination. NiO phase was seen for Cu/Co/Ni/Fe-MMOs sample. Sharp peaks of CuO phase were found for Cu/Co/Cr-MMOs sample. This drastic change in the diffract patterns reveals that thermal decomposition of the LDHs takes place via a highly disordered structure with small particle sizes.

![XRD patterns for Cu/Co/M-MMOs.](image2)

Figure 4. XRD patterns for Cu/Co/M-MMOs.
IR spectra were also taken in order to analyze the anions between layers. IR spectra are shown in figure 5. The broad peaks with low intensity at 3400, 1350 and 1480 cm\(^{-1}\) are assigned to \(-\text{OH}\) in the layer, as well as \(\text{H}_2\text{O}\) and \(\text{CO}_3^{2-}\) between the layers. For Cu/Co-LDHs and Cu/Co/Al-LDHs samples, absorption peak around 1400 cm\(^{-1}\) is appeared, which is assigned to NO\(_3^–\). It is indicated that both carbonate and nitrate are existing in the layers.

![IR spectra for Cu/Co/M-MMOs.](image)

**Figure 5.** IR spectra for Cu/Co/M-MMOs.

BET results for specific surface areas and pore diameters of Cu/Co/M-MMOs are listed in table 2. It is showed that Cu/Co-MMOs and Cu/Co/Al-MMOs have lower specific surface areas of 20~40 m\(^2\)g\(^{-1}\). Cu/Co/Fe-MMOs, Cu/Co/Cr-MMOs and Cu/Co/Ni/Fe-MMOs have higher specific surface area of 80~110 m\(^2\)g\(^{-1}\). The pore diameters are around 5~10 nm.

| Sample            | BET results          |
|-------------------|----------------------|
|                   | BET surface area(m\(^2\)g\(^{-1}\)) | Pore diameters(nm) |
| Cu/Co-MMOs        | 20.9                 | 5.73                 |
| Cu/Co/Al-MMOs     | 37.5                 | 5.44                 |
| Cu/Co/Fe-MMOs     | 85.9                 | 7.30                 |
| Cu/Co/Cr-MMOs     | 107.8                | 10.24                |
| Cu/Co/Ni/Fe-MMOs  | 94.4                 | 7.65                 |

**Table 2.** BET results for specific surface areas and pore diameters of Cu/Co/M-MMOs.

3.4. Morphology of Cu/Co/M-MMOs
Morphology of Cu/Co/M-MMOs was also investigated by SEM. SEM photos are shown in figure 6. It can be observed that Cu/Co/Fe-MMOs, Cu/Co/Al-MMOs, and Cu/Co/Ni/Fe-MMOs show hexagon flakes with particle size in the range of 50~100 nm. Cu/Co/Cr-MMOs show homogeneous regular particle with smaller size of 20~30 nm. Cu/Co-MMOs show both particles and bigger rod shape in the photo. It is not that well dispersed like the other samples. This is why Cu/Co-MMOs have lower specific surface areas than the other samples, which is in correspondence with BET results.
3.5. Catalytic activities of Cu/Co/M-MMOs

The catalytic activities of Cu/Co/M-MMOs were studied under NOx analyzer. NOx conversion rate curves catalyzed by Cu/Co/M-MMOs are shown in figure 7. It can be observed that different Cu/Co/M–MMOs samples show different NOx conversion rates. Cu/Co-MMOs sample exhibits the highest NOx conversion of 23%. It shows better NOx conversion rate than the other samples though it has the lowest specific surface areas. It also shows higher NOx conversion rate at lower temperature range. Thus it can be concluded that higher specific surface area is not necessarily corresponding to higher catalytic activity for Cu/Co/M-MMMOs catalysts. Cu/CoFe-MMMOs, Cu/Co/Al-MMMOs and Cu/Co/Cr-MMMOs have similar NOx conversion curves. SCR of NOx by using hydrocarbon as reductant show lower catalytic activities than by using NH3. The catalytic activity order is: Cu/Co-MMMOs>Cu/Co/Ni/Fe-MMMOs>Cu/Co/Fe-MMMOs>Cu/Co/Al-MMMOs≈Cu/Co/Cr-MMMOs.

![Figure 6. SEM photos for Cu/Co/M-MMMOs, (a) Cu/Co, (b) Cu/Co/Al, (c) Cu/Co/Fe, (d) Cu/Co/Cr and (e) Cu/Co/Ni/Fe-MMMOs.](image)

![Figure 7. NOx conversion curve catalyzed by Cu/Co/M-MMMOs.](image)
4. Conclusions

TGA, XRD and IR results show that Cu/Co/M-LDHs precursors and Cu/Co/M-MMOs catalysts were successfully prepared. Cu/Co/M-MMOs catalysts have spinel phase. The element compositions of catalysts are similar with those in solution. The catalysts have homogeneous distribution of hexagon flakes and particles size in the range of 20~100nm. Their specific surface areas are in the range of 20~110 m$^2$g$^{-1}$. Cu/Co/M–MMOs catalysts show some activities on SCR of NOx by hydrocarbon. Cu/Co/M–MMOs prepared with different metal show different catalytic activities. Cu/Co–MMOs sample exhibits the highest NOx conversion of 23%. The order of catalytic activity of Cu/Co/M is: Cu/Co-MMOS>Cu/Co/Ni/Fe-MMOS>Cu/Co/Fe-MMOS>Cu/Co/Al-MMOS≈Cu/Co/Cr-MMOS. SCR of NOx by using hydrocarbon as reductant show lower catalytic activities than using NH$_3$.

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