Carbon monoxide oxidation using Zn–Cu–Ti hydrotalcite-derived catalysts

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MS received 22 December 2013; revised 24 February 2014; accepted 25 February 2014

Abstract. Multioxide catalysts of zinc, copper and titanium with different ratios obtained from layered double hydroxide (LDH) precursors were used in the oxidation of carbon monoxide. The catalysts were characterized by energy-dispersive X-ray spectrometry, X-ray diffraction, thermal analyses (TG, DTG and DTA) and scanning electron microscopy. X-ray diffraction showed different phases of double hydroxide structures. On increasing the percentage of zinc, hydrotalcite structure became the main phase in these samples. SEM images confirmed the presence of layered double hydroxide as plate-like structure. Experimental results indicated a sharp increase in the catalytic activities of the calcined samples towards the oxidation of carbon monoxide at temperatures in the range of 225–275°C. High conversion of carbon monoxide (90 ~ 95%) was achieved at reaction temperature of 275°C by samples having ZnTiO₃ as a main phase. These results suggested that hydrotalcite structure of Zn–Ti has a positive catalytic effect towards carbon monoxide oxidation.

Keywords. Zn–Cu–Ti oxides; layered double hydroxide; carbon monoxide; oxidation.

1. Introduction

Conventional combustion carried out in power plants, industrial processes and on road vehicles emit many pollutants such as carbon monoxide, hydrocarbons and oxides of nitrogen. All these processes lead to severe degradation of environment. It has been reported that transportation and fuel combustion are some of the major sources of carbon monoxide release to the atmosphere. During transport, the most common cause of release of carbon monoxide is incomplete combustion due to low air-to-fuel ratios in the internal combustion engines.

Carbon monoxide reduces the oxygen-taking capacity of haemoglobin and converts it to carboxy haemoglobin and therefore causes many health problems. Any exposure to ambient air with carbon monoxide levels greater than 100 ppm is dangerous to human health. The amount of carboxy haemoglobin formed depends on the duration of exposure, concentration in air, ventilation and individual susceptibility.¹ So, oxidation of carbon monoxide to carbon dioxide is very important environmentally and industrially. A catalyst

enables the reaction to occur at much lower temperatures than required by conventional thermal oxidation. Due to the lower operating temperatures, such processes preclude the formation of toxic compounds.²

Although noble metal catalysts such as platinum and palladium^{3–9} are the best available and most active catalysts for carbon monoxide oxidation having low-poisoning and more water-tolerant action, in view of their depleting resources, base metal oxides show more promise, especially zinc oxide, titanium oxide, in addition to copper oxide.^{10–13}

Layered double hydroxides (LDHs) are promising materials for a large number of practical applications such as catalysis, adsorption, pharmaceuticals, photochemistry, and electrochemistry.^{14–17}

LDHs referred to as hydrotalcite-like compounds (HTlcs), consist of a stacking of positively charged sheets (brucite-like layers) separated by interlayer spaces containing solvated anions. The charge of the brucite-like layers is generated by the substitution of some of the divalent metal cations by trivalent ones.¹⁸ The LDHs are prepared by a number of different techniques described in the literature.¹⁹

In the case of catalysis, LDHs represent an inexpensive, versatile and potentially recyclable source of widely used catalyst supports,²⁰ catalyst precursors²¹

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or actual catalysts.²² In earlier studies, we succeeded in preparing LDHs consisting of zinc, aluminum and titanium cations (Zn-Ti LDH and Zn-Al-Ti LDH) for the first time.^{23,24} Also, the preparation of Zn-Cu-Al LDH^{25,26} and copper (II) immobilized in Zn-Al LDH²⁷ had been reported.

The present study examines the possibility of the preparation of Zn-Cu-Ti LDHs. The obtained samples were characterized by different techniques. Composite materials of zinc oxides, copper oxides and titanium oxides were obtained through thermal treatment of LDH structures. The CO catalytic oxidation of the derived oxides was also monitored.

2. Experimental

2.1 Sample preparation

Zn-Cu-Ti hydroxides were prepared by coprecipitation of Cu, Zn and Ti salts from a homogeneous solution. A solution of zinc chloride, copper chloride and titanium chloride (0.069 mol, M(II)/M(III) ratio = 5.25, and Zn/Cu ratios = 0.5, 1 and 2) was mixed with urea (0.5 mol) solution under vigorous stirring and heating. Temperature of the mixture was adjusted at 90°C for 20 h. These samples were coded Zn₃Cu₆Ti, Zn₄Cu₄Ti and Zn₆Cu₃Ti, respectively. The

precipitates were centrifuged, washed with deionized water, and dried at 90°C. The dried samples were calcined at 500°C. The calcined samples were coded Zn₃Cu₆Ti-500, Zn₄Cu₄Ti-500 and Zn₆Cu₃Ti-500, respectively.

For comparison, Zn-Al LDH was prepared by the same technique without addition of copper chloride. The dried sample was calcined at 500 and 900°C.

2.2 Characterization

Powder X-ray diffraction (XRD) spectra were recorded on Rigaku, RINT 2200 using Cu K (filtered) radiation ($\lambda = 0.154$ nm) at 40 kV and 20 mA between 1.8 and 50 degrees. Thermal analyses (TG, DTG and DTA) of powdered samples up to 800°C were carried out at a heating rate of 10°C/min in flowing nitrogen using a Seiko SSC 5200 apparatus. Energy-dispersive X-ray spectrometry measurements were carried out with a JEOL JED-2140. Scanning electron microscopy (SEM) was performed with JEOL: JSM-6330F, (15 kV/12z mA).

2.3 Oxidation reaction of carbon monoxide

The reaction of CO with oxygen was investigated in a fixed bed reactor with a continuous reactant

Figure 1. EDS spectra of Zn₄Cu₄Ti.

flow of a mixture of CO and air (CO/air volumetric ratio = 0.087) at a total flow rate of 125 mL min⁻¹. A silica tube reactor (U-shape, 20 cm long and 0.2 cm internal diameter) was used. Prior to the reaction, all the samples (100 mg of each) were pretreated at 150°C for 0.5 h in a nitrogen flow. The gas hourly space velocity (GHSV) of CO was 100 mL min⁻¹ g⁻¹. The products were analysed by a terminal GC equipped with a thermal conductivity detector (TCD).

3. Results and Discussion

3.1 Energy-dispersive X-ray spectrometry

The scanning electron microscopy and energy-dispersive X-ray spectrometry (SEM/EDS) of Zn₄Cu₄Ti revealed that zinc, copper and titanium, were clearly identified in the platelet of this sample as shown in figure 1. In addition, the presence of carbon and oxygen confirmed the presence of carbonate anions in the same structure.

3.2 X-ray diffraction

The X-ray diffraction (XRD) pattern of the prepared Zn₃Cu₆Ti sample (figure 2a) showed characteristic reflections of paratacamite, Cu_{2-x}Zn_x(OH)₃Cl (JCPDS 50-1558) at d-spacing 0.55, 0.28, 0.23 and 0.17 nm.

The XRD of Zn₄Cu₄Ti sample (figure 2b), except the characteristic reflections of paratacamite phase as described above, displayed another phase at d-spacing 0.68, 0.25, 0.27, 0.31 and 0.37 nm, which were assigned to the characteristic reflections of hydrozincite, Zn₅(CO₃)₂(OH)₆ (JCPDS 19-1458). The spacing (0.68 nm) is smaller than the spacing reported for natural LDH (hydrotalcite) and agrees with the interlayer spacing of the prepared Zn-Ti LDH which was previously published from our laboratory.²³ This means that the increase in zinc molar ratio creates mixed phase between paratacamite and Zn-Ti LDH. The intensity of Zn-Ti LDH phase increased as zinc became the major element in Zn₆Cu₃Ti sample (figure 2c).

After the calcination step, characteristic reflections of monoclinic CuO are obviously observed in the XRD pattern of Zn₃Cu₆Ti-500 sample (figure 3a), at

Figure 2. XRD patterns of (a) Zn₃Cu₆Ti, (b) Zn₄Cu₄Ti and (c) Zn₆Cu₃Ti.

Figure 3. XRD patterns of (a) $\text{Zn}_3\text{Cu}_6\text{Ti}$ -500, (b) $\text{Zn}_4\text{Cu}_4\text{Ti}$ -500 and (c) $\text{Zn}_6\text{Cu}_3\text{Ti}$ -500.

d-spacing 0.25, 0.23 and 0.19 nm (JCPDS 45-0937). Also, reflections of rhombohedral Cu_2TiO_3 may interfere with CuO reflections at d-spacing 0.25, 0.22, and 0.29 nm (JCPDS 17-0618). ZnO (JCPDS 89-1397) could be noticed as a minor phase.

Hexagonal ZnO (JCPDS 89-1397) and rhombohedral ZnTiO_3 (JCPDS 26-1500) phases appear as major phases in addition to CuO (figure 3b) due to calcination of the original sample $\text{Zn}_4\text{Cu}_4\text{Ti}$ containing both paratacamite and Zn-Ti LDH phases (figure 2b).

For $\text{Zn}_6\text{Cu}_3\text{Ti}$ -500 sample (figure 3c), hexagonal ZnO became the major phase in addition to ZnTiO_3 and CuO.

In order to study the effect of the presence of copper in the prepared samples, two structures of zinc titanate were synthesized through thermal treatment of Zn-Ti LDH. The XRD of Zn-Ti LDH (figure 4a) showed the basal peaks of planes hkl (003), (006) and (009) and non-basal peaks (100), (101), (012) and (104) with little shifting for basal peaks to higher scattering angles (2θ) compared with natural and synthetic hydrotalcites.^{23,24}

After calcination of Zn-Ti LDH at 500°C, new phases were observed (figure 4b). The pattern indicates major phase of ZnTiO_3 with characteristic reflections matching with the JCPDS file 25-0671. By thermal treatment of Zn-Ti LDH at 900°C, figure 4c shows the characteristic peaks of Zn_2TiO_4 (JCPDS 25-1164).

3.3 Thermal analysis

The TG and DTG diagrams of $\text{Zn}_4\text{Cu}_4\text{Ti}$ (figure 5) indicated the presence of five weight losses, the first is up to 265°C, the second one is up to 303°C, the third one is up to 319°C, the fourth one is up to 344°C, and the fifth one is up to 447°C. While the TG and DTG diagrams of $\text{Zn}_6\text{Cu}_3\text{Ti}$ showed three weight losses, the first is up to 258°C, the second one is up to 331°C, and the third one is up to 419°C. The corresponding DTA diagrams showed five endothermic minima for $\text{Zn}_4\text{Cu}_4\text{Ti}$ and three endothermic minima for $\text{Zn}_6\text{Cu}_3\text{Ti}$, coincident with the earlier mentioned weight losses. Endothermic minima ranged from 300° to 320°C which may be due

Figure 4. XRD patterns of Zn-Al LDH at (a) 90°C, (b) 500°C and (c) 900°C.

Figure 5. Thermal analysis (TG, DTG, and DTA) of (a) $\text{Zn}_4\text{Cu}_4\text{Ti}$ and (b) $\text{Zn}_6\text{Cu}_3\text{Ti}$.

to the loss of condensation water of paratacamite.^{28,29} Endothermic peaks that are observed in the DTA profile of $\text{Zn}_4\text{Cu}_4\text{Ti}$ at 344°C , as weak effect and in the DTA profile of $\text{Zn}_6\text{Cu}_3\text{Ti}$ at 335°C , as sharp effect, may have resulted from the conversion of hydrozincite or Zn-Ti LDH into zinc oxide.^{30,31} Endothermic effects that appear at temperatures higher than 410°C can be attributed to the loss of chlorine, very likely as HCl.^{28,29}

Thermal diagrams suggest that endothermic peaks at 265 and 258°C for $\text{Zn}_4\text{Cu}_4\text{Ti}$ and $\text{Zn}_6\text{Cu}_3\text{Ti}$, respectively, are formed due to the decomposition of carbonate anions and desorption of water produced from dehydroxylation process. These high decomposition temperatures are attributed to the strong interaction of carbonate anions with brucite layers of Zn-Ti LDH.²³ Upward shift of the decomposition temperatures in comparison to the previously prepared Zn-Ti LDH²³ could have resulted from the presence of paratacamite besides the major hydrotalcite-like phase.²⁶

3.4 Scanning electron microscope

It is known that LDH crystals possess a hexagonal plate-like morphology if they are carefully crystallized.³² A similar morphology is observed for $\text{Zn}_4\text{Cu}_4\text{Ti}$ with dimension of the plates in the order of a few micrometers in width and 100 nm in thickness as shown in figure 6. Individual plates of $\text{Zn}_4\text{Cu}_4\text{Ti}$ are flat, and the edges of the plates appeared rounded agreeing with the results reported in the literature for Zn-Al-Ti LDH.²⁴ In the case of Zn-Ti LDH, it exhibits plate-like morphology with irregular shapes as shown in figure 7a. Also, SEM images in figure 7b and c showed that Zn-Ti LDHs after thermal treatment are composed of composite structure with a diameter of about 100 nm .

3.5 Oxidation reaction of carbon monoxide

Figure 8 shows sharp increase in catalytic activities of the calcined samples towards the oxidation of carbon monoxide at temperatures in the range of $225\text{--}275^\circ\text{C}$. The CO conversion increased dramatically to 95%, 90% and 74% on using $\text{Zn}_4\text{Cu}_4\text{Ti}$ -500, $\text{Zn}_6\text{Cu}_3\text{Ti}$ -500 and $\text{Zn}_3\text{Cu}_6\text{Ti}$ -500, respectively at reaction temperature of 275°C . High catalytic activity of $\text{Zn}_4\text{Cu}_4\text{Ti}$ -500 may be attributed to the presence of ZnTiO_3 as a major phase (figure 8b).

As ZnTiO_3 is a hydrotalcite-derived phase from Zn-Ti LDH, whereas the zinc atom represents the host cation while the titanium represents the guest cation, we can replicate the catalytic activity of ZnTiO_3 phase by the activity of cationic substitutional doping of ZnO with titanium atom.

Pala *et al.*³³ showed that cationic substitutional doping of ZnO with Ti promotes adsorption of O_2 due to the high valence of titanium with respect to zinc; where, the titanium atoms, at the surface of ZnO, do not find enough lattice oxygen atoms to satisfy their valence. This drives them to adsorb gas-phase O_2 . As titanium atoms prefer to have one additional oxygen atom, rather than two, the adsorbed O_2 molecule reacts readily with CO species.

To confirm the importance of the presence of ZnTiO_3 , catalytic activities of the two structures of zinc titanate were measured towards the oxidation of carbon monoxide at the same range of temperatures and displayed in figure 8 (inset). The prepared ZnTiO_3 exhibited 90% and 95% catalytic activity at reaction temperatures of 275 and 400°C , respectively. Also, the prepared Zn_2TiO_4 showed 80% and 95% catalytic activity at the same temperatures. Agreeing with our speculation, these results confirm that ZnTiO_3 has a

Figure 6. SEM images for $\text{Zn}_4\text{Cu}_4\text{Ti}$.

Figure 7. SEM images for Zn-Al LDH at (a) 90°C, (b) 500°C and (c) 900°C.

positive effect in the structure of ZnCuTiO multi-oxide composite material towards CO oxidation.

Also, according to Pala *et al.*³³ the second relevant factor is that the Zn atoms do not adjust its valence to respond to the presence of a dopant; in the Zn–O–Ti groups present on the surface, Zn will stay divalent. CuO doped with Ti would behave differently than ZnO in this respect, because in the group Cu–O–Ti, Cu may become monovalent to give the dopant a chance

to bind more strongly to the shared oxygen atom. Such speculation may explain the relative low catalytic activity of Zn₃Cu₆Ti-500.

Figure 8. CO oxidation using (a) Zn₃Cu₆Ti-500, (b) Zn₄Cu₄Ti-500 and (c) Zn₆Cu₃Ti-500 (inset ZnTiO₃ and Zn₂TiO₄).

Figure 9. Reaction mechanism of CO oxidation in presence of air over Zn-Cu-Ti composite materials.

Relative high catalytic activities of samples contain CuO, i.e., Zn₃Cu₆Ti-500 and Zn₄Cu₄Ti-500 with respect to Zn₆Cu₃Ti-500, at reaction temperatures lower than 250°C, may have resulted from the presence of cupric oxide species having (111) surface (JCPDS 45-0937) with polar orientation, that subsequently enhance catalyst surface adsorption efficiency.³⁴ Also, the chemical state of copper species is synergistically affected both by titania and by the electron donor ZnO, which enhance low temperature adsorption of CO.³⁵

According to our results, a possible mechanism with regard to CO oxidation reaction over the prepared ZnCuTiO multi-oxide composite material is shown in figure 9. It is believed that molecularly adsorbed oxygen which is available in air, is first activated on the surface of titanium oxides because of the high valence of titanium with respect to zinc to form highly oxidative intermediates. Then, the superficial CO and intermediates react to form CO₂ and O. The adsorbed O would further react with superficial CO to produce CO₂.

4. Conclusion

In this study, ZnCuTiO multi-oxide catalysts obtained by thermal decomposition of double hydroxide structures were evaluated in the oxidation of carbon monoxide. These catalysts showed sharp increase in the catalytic activities of the calcined samples towards the oxidation of carbon monoxide at temperatures in the range of 225–275°C. The CO conversion increased dramatically to 95%, 90% and 74% by using Zn₄Cu₄Ti-500, Zn₆Cu₃Ti-500 and Zn₃Cu₆Ti-500, respectively at reaction temperature of 275°C. In addition, the prepared ZnTiO₃ and Zn₂TiO₄ exhibited 90% and 80% at the same temperature, respectively. Finally, Zn₄Cu₄Ti-500 was found to be highly active for carbon monoxide oxidation at reasonable temperature and in presence of CO₂ in the feed stream (air). High catalytic activity of Zn₄Cu₄Ti-500 may be attributed to the presence of ZnTiO₃ as a major phase in the composite material.

Acknowledgements

The authors thank the Deanship of Scientific Research in King Faisal University (Saudi Arabia) for funding and providing the facilities required for this research as a part of Annual Research Grants Program (130146).

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