J Mater Sci (2008) 43:237–243
DOI 10.1007/s10853-007-2167-8

Copper-containing mixed metal oxides derived from layered precursors: control of their compositions and catalytic properties

L. H. Zhang · C. Zheng · F. Li · D. G. Evans · X. Duan

Received: 24 July 2007 / Accepted: 13 September 2007 / Published online: 17 October 2007

Abstract In this article, a series of Cu-containing mixed metal oxides were obtained by calcination of layered double hydroxides (LDHs) precursors with Cu/Zn/Al atomic ratios ranging from 1:3:1 to 3:1:1 in synthesis mixture at 773 K. The materials were characterized by means of powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR), nitrogen sorption experiments, and X-ray photoelectron spectroscopy (XPS). The results indicate that Cu/Zn/Al cationic ratios in precursors could control the compositions of surface species on the resultant calcined LDHs. Furthermore, The catalytic activities of phenol oxidation in aqueous solutions by hydrogen peroxide over the calcined LDHs as catalysts were also tested. It is found that the high catalytic activity is relative to the high amount and dispersion of composite metal oxides containing active Cu^{2+} reaction centers on the surface of calcined samples, and the lattice oxygen species on the surface are beneficial to the deep oxidation of phenol.

Introduction

Layered double hydroxides (LDHs), $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, also known as hydrotalcite(HT)-like anionic clay materials, are a family of materials consisting of brucite-like layers, where a fraction of the divalent cations is replaced by trivalent cations. The positively charged layers are separated by the charge-balancing anions and some water molecules [1]. In past two decades, the flexibility in composition of LDHs has led to an increase in interest in these materials. As a result of their relative ease of syntheses, LDHs represent an inexpensive, versatile, and potentially recyclable source of a variety of catalyst supports [2, 3], catalyst precursors [4–6] or actual catalysts [7, 8]. In particular, mixed metal oxides obtained by controlled thermal decomposition of LDHs have large specific surface areas (100–300 m^2/g), basic properties, homogeneous and thermally stable fine dispersion of M^{2+} and M^{3+} (also known as 'non-stoichiometric spinels') at an atomic level, and synergetic effects between the elements [9, 10]. Furthermore, the intrinsic properties of the resulting catalysts, like texture, acido-basicity, thermal stability, and catalytic properties depend on the starting LDH precursors [11] and might be tuned through controlling the cationic composition of LDH precursors [12, 13].

Using as catalysts, LDHs and their derived materials have been widely applied in the synthesis of chemicals (including intermediates), environmental catalysis, energy exploitation (such as hydrogen production), and carbon nanomaterials preparation etc. Thereinto, industrial wastewater more and more represents an important class of environment pollutants that have been considered in the world. There have been many solutions for the treatment of various wastewaters; however, catalytic wet oxidation (CWO, i.e., catalytic oxidation of organic compounds by air, oxygen, hydrogen

L. H. Zhang (✉) · C. Zheng · F. Li · D. G. Evans · X. Duan
State Key Laboratory of Chemical Resource Engineering,
Beijing University of Chemical Technology, Beijing 100029,
P.R. China
e-mail: zlh_224@163.com

L. H. Zhang
Department of Catalysis Science and Technology and Tianjin
Key Laboratory of Applied Catalysis Science & Technology,
School of Chemical Engineering, Tianjin University, Tianjin
300072, P.R. China

peroxide or ozone) has been playing an important role. Transition metal oxides, especially those containing copper, have indicated good catalytic properties in CWO for phenol [14, 15]. In this article, we focus on a detailed study of a series of Cu-containing mixed metal oxides catalysts, which are prepared by calcination of layered double hydroxides precursors with Cu/Zn/Al atomic ratios ranging from 1:3:1 to 3:1:1 in synthesis mixture at 773 K. It shows that the structure, composition, and catalytic oxidation activity for aqueous phenol solutions by hydrogen peroxide of calcined LDHs could be controlled by turning cationic Cu/Zn/Al ratios in precursors.

Experimental

Sample preparation

A solution of NaOH and Na_2CO_3 ($[CO_3^{2-}] = 2[M^{3+}]$, $[OH^-] = 2\{2[M^{2+}] + 3[M^{3+}]\}$) was added dropwise with vigorous stirring to 100 ml of an aqueous solution of Cu^{2+}, Zn^{2+}, and Al^{3+} nitrates (total cation concentration of 1.2 M) with Cu/Zn/Al atomic ratios from 1:3:1 to 3:1:1. The addition was monitored by a pH regulator via a pH electrode immersed in the reagent solution and ended at a desired value of pH in the reaction mixture. The resulting precipitate was aged for a fixed period of time at 333 K with stirring, and then recovered by four dispersion and centrifugation cycles in deionized water, and the resulting gelatinous precipitate was finally dried at 333 K overnight. As-synthesized samples were denoted LDH–M/N (M/N means the Cu/Zn atomic ratio in synthesis mixture), and corresponding calcined samples at 773 K for 3 h were denoted CLDH–M/N.

Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, Cu Kα radiation. The samples, as unoriented powders, were step-scanned in steps of 0.04° (2θ) in the range from 3° to 70° using a count time of 10 s/step.

Fourier transform infrared spectra (FT-IR) were obtained in the range 4,000–400 cm^{-1} using the KBr pellet technique on a Bruker Vector-22 Fourier transform spectrometer.

Elemental analysis was performed on a Shimadzu ICPS-7500 model inductively coupled plasma emission spectrometer (ICP-ES). Samples were dried at 373 K for 24 h prior to analysis, and solutions were prepared by dissolving the samples in dilute hydrochloric acid (1:1).

Surface areas of samples were determined from N_2 adsorption–desorption measurements in a Sorptomatic1990 automatic gas adsorption instrument using the BET equation for surface area. Prior to the measurement, the samples were outgassed at 473 K under vacuum for 2 h.

The XPS results were carried out with a V.G. Scientific ESCALAB Mark II system. A Mg Kα ($h\nu$ = 1,253.6 eV) was used as X-ray source. The base pressure in the apparatus was about 2×10^{-6} Pa during analysis. Due to the rather high conductivity of the samples, the spectra were recorded at room temperature without further sample treatment and in about 20 min to avoid X-ray induced reduction of the Cu^{2+} species. All binding energy (BE) values were charge-corrected to the C1s signal which set at 284.6 eV of the carbon overlayer and the standard deviation of the peak position was within ±0.1 eV. This reference gave BE values within an accuracy of ±0.2 eV. Samples were analyzed as powders dusted onto double-sided sticky tape. The hemispherical analyzer functioned with constant pass energy of 50 eV for high-resolution spectra. The experimental bands were fitted with a combination of Gaussian–Lorentzian lines using linear baseline.

Catalytic reactions

The catalytic oxidation process was carried out in a 250 ml three-neck glass flask. Hydrogen peroxide solution (30% w/v, 1 ml) was added to an aqueous phenol solution (100 mg/l, 100 ml) containing 0.2 g of catalyst. The mixture was kept at room temperature for 60 min. The phenol conversion and product distribution were determined by HPLC. Aliquots of 5 μl were injected into a reverse-phase C-18 column, with a mixture of 30% methanol and 70% of redistilled water as a mobile phase at a total flow rate of 0.8 ml/min. The absorbance at 280 nm was used to measure the concentration of phenol.

Results and discussion

Structural properties of LDHs and resultant calcined products

Power XRD patterns of LDHs with Cu/Zn/Al atomic ratios ranging from 1/3/1 to 3/1/1 in the synthesis mixture are shown in Fig. 1a. Obviously, hydrotalcite (HT)-like layered double hydroxides were observed as the major phase in all samples [16]. In each case, XRD patterns exhibit characteristic reflections of LDH materials with a series of (00*l*) peaks appearing as narrow symmetric lines at low angle, corresponding to the basal spacing and higher order reflections. As anticipated, only LDH phase is obtained for samples with Cu/Zn ratios of 2/1 and 1/1. However, other phases such as copper–zinc carbonate hydroxide ($(Cu,Zn)_2CO_3(OH)_2$) (CZH; JCPDS 18-1059) at 2θ(values of 14.67° [17] and malachite ($Cu_2(CO_3)(OH)_2$) (MT; JCPDS 41-1390) at 17.60° [18] are formed in LDH-3/1. This is because Jahn–Teller effect of coordination environment around Cu^{2+} ions can influence the stability of brucite-like layers, which leads to segregation of some Cu^{2+} ions into non-LDH phases in the samples with higher Cu content. In addition, a small amount of zinc carbonate hydroxide ($Zn_5(CO_3)_2(OH)_6$) (ZCH; JCPDS 19-1458) at 13.07° appears in LDH-1/2 and LDH-1/3, due to higher Zn content in synthesis mixture. The result clearly indicates that the purity of precursors depends on the Cu/Zn/Al atomic ratio in synthesis mixture.

The FT-IR spectra of samples are shown in Fig. 1b. Every spectrum is similar to those of HT-like compounds reported in the literature [19, 20]. The strong and broad band observed at 3,445 cm^{-1} corresponds to O–H stretching vibration of surface and interlayer water molecules, $\nu(OH)$. The absorption at 1,640 cm^{-1} is assigned to bending vibration of water, $\delta(H_2O)$. In each case, there are two IR active absorption bands around 1,350–1,410 cm^{-1} and 800–890 cm^{-1}, arising from the ν_3 (symmetric stretching) and ν_2 (out-of-plane deformation) vibrations of the interlayer carbonate anion. In addition, a splitting band of ν_3 mode located around 1,500 cm^{-1} is observed due to the disordered nature of the interlayer or a lowering of the symmetry of the carbonate anions from D_{3h} to C_{2v} in the interlayer, which lifts the degeneracy of the ν_3 mode. On the other hand, the absorption of splitting band shifts to higher frequency with (Cu + Zn)/Al ratios, which is indicative of a strong decrease in symmetry of carbonate anion, down to C_{2v} or lower. Additionally, the appearance of the shoulder peaks near 1,408 cm^{-1} in LDH-1/2 and LDH-1/3, and the ν_1 mode around 1,050 cm^{-1}, and the apparent splitting of ν_2 mode in LDH-2/1 and LDH-3/1 also suggests a lowering of the symmetry of the carbonate anion and an increase in those impurities containing carbonates (CZH, MT, and ZCH phases) with the (Cu + Zn)/Al ratios in samples.

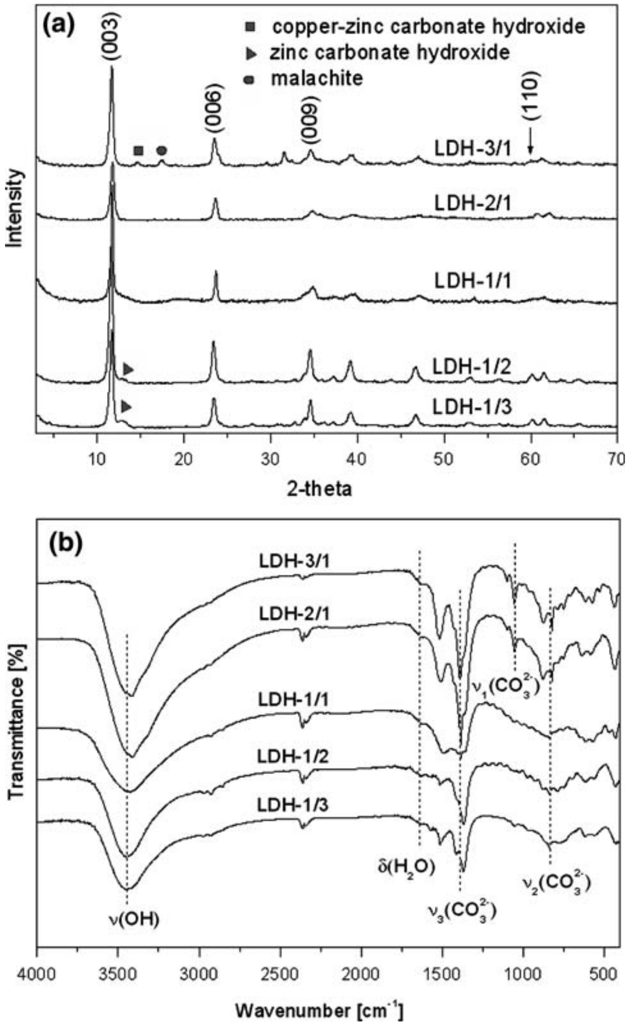

Fig. 1 XRD patterns (**a**) and FT-IR spectra (**b**) of LDHs

Figure 2 shows the XRD patterns of calcined LDHs obtained at 773 K. Clearly, calcination has destroyed the layered structure since no characteristic reflections of LDHs are present in the XRD patterns, but a broad diffraction peak at about 36° of 2θ that is obviously different from that of single metal oxide phases such as zinc oxide (JCPDS 36-1451) and copper oxide (JCPDS 05-0661) is detectable in the XRD patterns, although other amorphous phases may also be present. It indicates that after calcinations, composite metal oxide phase such as Cu^{2+}, Zn^{2+}, and Al^{3+} cation have developed. Composite metal oxide is a type of metal oxide compound composed of two or above kinds of metal cations, where different kinds of metal cations can interact and are identically situated on the structural units. Note that with the (Cu + Zn)/Al ratio, the amount of CuO or ZnO increase gradually. Furthermore, an apparent poorly crystallized phase appears in the XRD pattern of sample CLDH-1/1, indicative of formation of the highest amount of composite oxide phase. As a result, the Cu/Zn ratio in LDHs precursors can influence the composition and distribution of calcined LDHs.

Study of surface composition of calcined samples

The chemical compositions of calcined LDH samples are given in Table 1. The Cu/Zn/Al ratios in the calcined LDHs are similar to those employed in synthesis mixture of LDH precursors, indicating essentially complete precipitation of the metal ions. XPS data can provide information

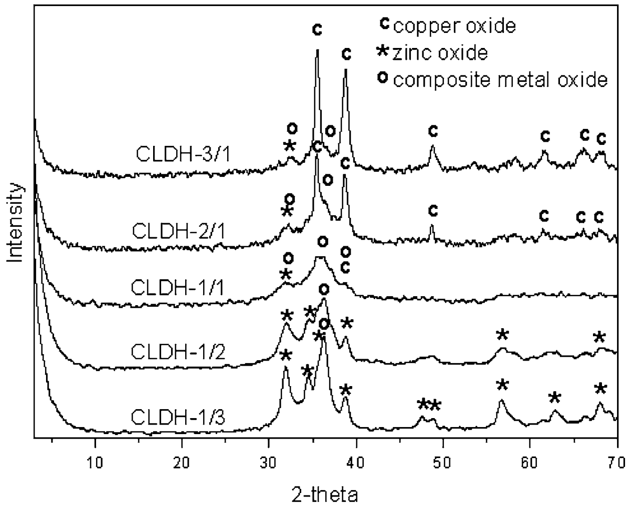

Fig. 2 XRD patterns of the calcined LDHs

about surface composition, obtained from core photoemission intensity data, and information about the chemical state of the elements in the near-surface region. However, the difference in the composition between the surface and bulk of calcined LDH samples can be observed from Table 1. Many XPS studies on metal oxides have shown the segregation or depletion of some elements at the surface [21–24], which is ascribed to surface relaxation by energetic and steric (ionic radius) considerations, and synthesis conditions, particularly the atmosphere [25]. In our case, the surface segregation or enrichment of Al^{3+} cations on the surface of calcined Cu/Zn/Al–LDHs systems is ascribed to the stronger Al–O bond than Cu–O and Zn–O bonds. Similar enrichment of the surface by Al was observed recently in the case of calcined Cu/Mg/Al LDHs [26]. Furthermore, Fig. 3 also presents the obvious surface enrichment of zinc at higher Cu/Zn ratio between Cu^{2+} and Zn^{2+} ions, which can be explained by the greatly decreasing delocalization of Zn^{2+} (*vide post* Fig. 4b).

To obtain the chemical state of surface species on calcined LDHs, XPS measurements were carried out to obtain the M2p (where M stands for Cu, Zn and Al) and O1s spectra in Fig. 4 and their corresponding XPS characteristics are listed in Table 2. In each case, the $Cu2p_{3/2}$ region in Fig. 4a shows the presence of four peaks in the range from 930 to 945 eV. The binding energy (BE) range found in the literature [27, 28] for the main $Cu2p_{3/2}$ peak of the sole CuO, generally with shake-up satellite line between 940 and 945 eV, is close to 934.0 eV. However, various studies [29–31] have showed that the position of these peaks depends on the chemical composition of the sample and particularly on the near environment of the Cu^{2+}, and it also depends of the materials in terms of crystalline structure, and content of substituent cations. In our system, it is possible to distinguish between copper species present in composite metal oxide phase (Cu_A^{2+}) and copper species in CuO phase (Cu_B^{2+}). Even bearing in mind the semi-quantitative XPS determination, clear trends can be seen from Table 2 showing the proportions of two chemical states of the Cu^{2+} as determined from the $Cu2p_{3/2}$ core level. While the proportion of Cu_A^{2+} initially increases with the value of Cu/Zn ratio, reaches maximum at a value of

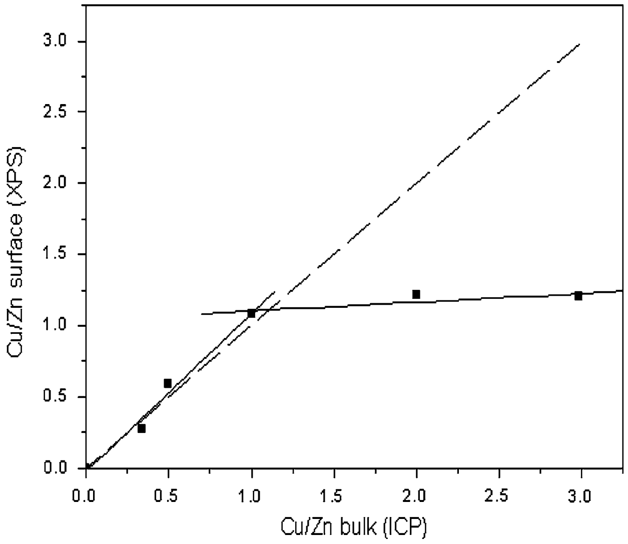

Fig. 3 Comparison of the surface and bulk Cu/Zn ratios for the calcined LDHs

Table 1 Texture and composition in the surface and bulk phases for calcined LDHs samples

Sample	Cu/Zn/Al ratio		BET surface area (m^2/g)
	Bulk[a]	Surface[b]	
CLDH-3/1	2.83:0.95:1.00	0.30:0.25:1.00	36
CLDH-2/1	1.92:0.96:1.00	0.23:0.19:1.00	47
CLDH-1/1	1.03:1.03:1.00	0.28:0.26:1.00	72
CLDH-1/2	1.02:2.02:1.00	0.40:0.68:1.00	49
CLDH-1/3	1.01:3.01:1.00	0.20:0.73:1.00	48

[a] These values were determined from peak intensities measured by use of ICP

[b] These values were determined from peak areas measured by use of XPS

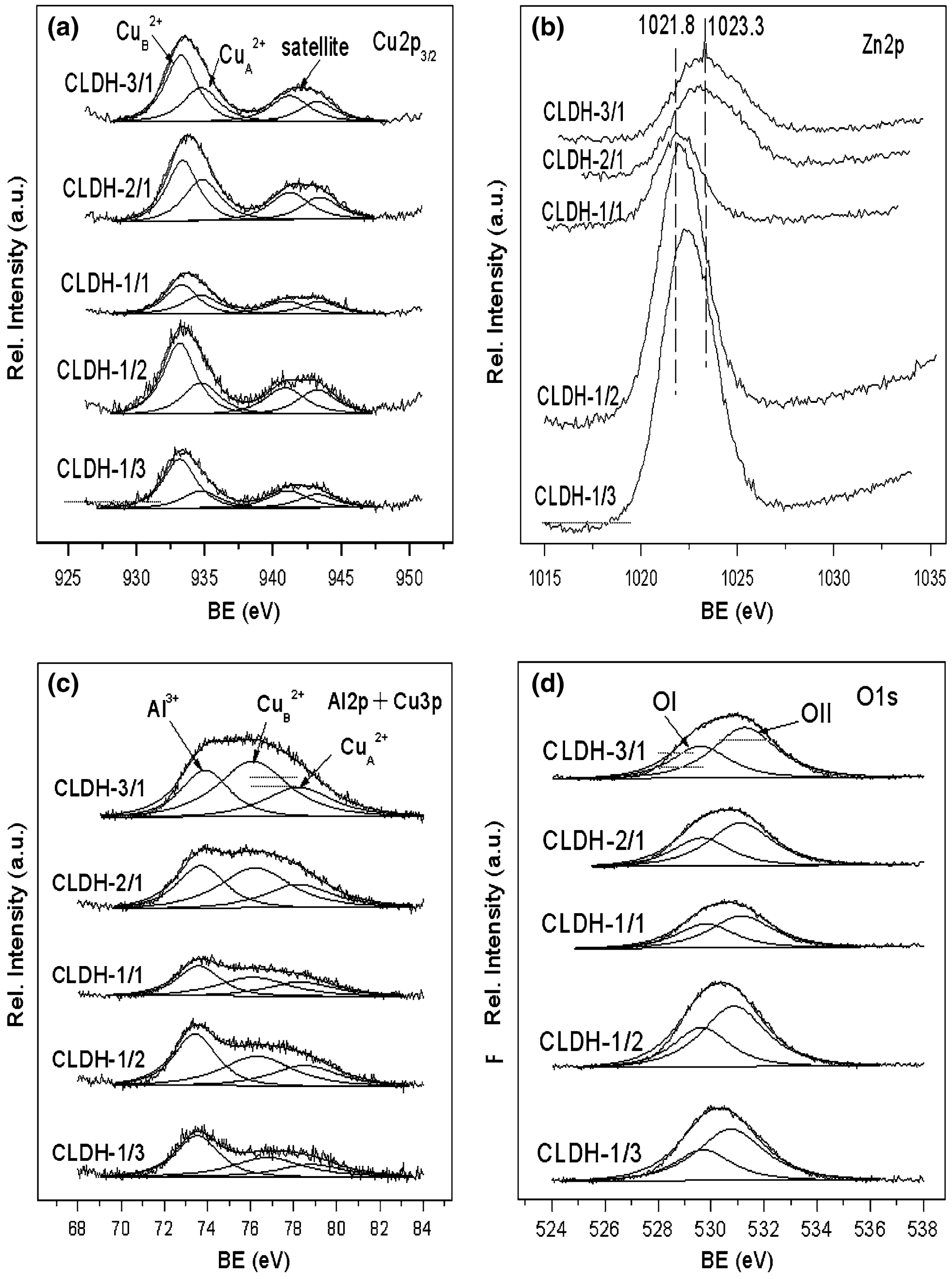

Fig. 4 XPS of $Cu2p_{3/2}$ (**a**), Zn2p (**b**), Al2p (**c**), and O1s (**d**) regions in the calcined LDHs

Cu/Zn ratio around 1, which is related to the greatly intensive surface interaction between Cu^{2+} and other metal cations, and then decreases. This is in accord with the XRD results of calcined LDHs.

Normally, the Al2p core levels are overlapped with Cu3p region peaks [31], as shown in Fig. 4c. After deconvolution, the main peak at 73.4 eV is attributed to Al^{3+}–O group due to Al2p, and the other peaks at 76.1 and 78.2 eV are assigned to $Cu_A^{2+}$and Cu_B^{2+} in Cu3p region, respectively. According to relative intensities of the two peaks located in the Cu3p regions, the change in the percentage of $Cu_A^{2+}$and Cu_B^{2+} obtained (Table 2), has the same trends as that in the Cu2p region. It is well-known that ZnO with Zn^{2+} partially replaced by Al^{3+} formed n-type semiconductor oxide catalyst and then became the acceptor of electrons, which results in the decrease in BE of Zn^{2+} [32]. From XPS spectra of Zn2p regions of the calcined samples (Fig. 4b), it can be noted that the BE of Zn2p decreases gradually with Cu/Zn ratios from 3:1 to 1:1 and from 1:3 to 1:1, indicative of the increase in the degree of delocalization of Zn^{2+}. This mainly results from the increase in the proportion of Zn^{2+} in composite metal oxide on the surface, such as $Cu_xZn_{1-x}Al_2O_4$ spinels, consistent with the XRD results of calcined samples. Figure 4d illustrates the O1s

Table 2 XPS characteristics of M2p and O1s regions for calcined LDHs samples

	Sample				
	CLDH-3/1	CLDH-2/1	CLDH-1/1	CLDH-1/2	CLDH-1/3
Binding energy (eV)					
$Cu2p_{3/2}$					
Cu_B^{2+}	933.2 (2.7)[a]	933.4 (2.7)	933.3 (2.7)	933.2 (2.8)	933.2 (2.8)
Cu_A^{2+}	934.7 (3.1)	934.8 (3.1)	934.7 (3.1)	934.7 (3.1)	934.7 (3.1)
Cu_B^{2+} sat.	941.2 (3.3)	941.2 (3.4)	941.0 (3.4)	940.9 (3.4)	941.1 (3.4)
Cu_A^{2+} sat.	943.2 (3.0)	943.4 (3.2)	943.4 (3.2)	943.2 (3.2)	943.2 (3.2)
O1s					
O_I	529.6 (2.5)[a]	529.6 (2.5)	529.8 (2.5)	529.6 (2.5)	529.7 (2.5)
O_{II}	531.3 (2.8)	531.1 (2.8)	531.1 (2.8)	530.9 (2.8)	530.7 (2.9)
Al2p/Cu3p					
Al^{3+}	73.9 (2.6)	73.7 (2.6)	73.6 (2.3)	73.4 (2.3)	73.5 (2.3)
Cu_B^{2+}	76.1 (3.8)	76.2 (3.8)	76.1 (3.8)	76.3 (3.8)	76.8 (3.8)
Cu_A^{2+}	78.2 (3.6)	78.2 (3.6)	78.2 (3.6)	78.5 (3.6)	78.8 (3.5)
Peak intensity (%)					
$Cu2p_{3/2}$					
$I(Cu_B^{2+})$[b]	61.7	56.5	55.6	62.5	67.1
$I(Cu_A^{2+})$[b]	38.3	43.5	44.4	37.5	32.9
O1s					
$I(O_I)$[c]	36.2	36.9	40.7	63.9	66.3
$I(O_{II})$[c]	63.8	63.1	59.3	36.1	33.7
Cu3p					
$I(Cu_B^{2+})$[d]	66.6	64.7	58.8	60.4	62.8
$I(Cu_A^{2+})$[d]	33.4	35.3	41.2	39.6	37.2

[a] Number in parentheses refer to FWHM in eV

[b] Intensity of the Cu_B^{2+} or Cu_A^{2+} peaks (main peak and sat.) in % of the total $Cu2p_{3/2}$ area

[c] Intensity of the peaks in % of the total O1s area

[d] Intensity of the Cu_B^{2+} or Cu_A^{2+} peaks in % of the total Cu3p area

XPS spectra of the samples. It can be observed that oxygen is present in two chemical states in all samples, denoted as O_I and O_{II}, representing two different kinds of surface species. O_I with the lower BE at ca. 529.7 eV (Table 2) belongs to the lattice oxygen, while O_{II} with higher BE at ca. 531.0 eV can be attributed to surface oxygen, including adsorbed oxygen species and mainly hydroxyl groups [33, 34]. Note that the proportion of O_I species shows a steady increase with decreasing Cu/Zn ratio, which is probably relative to the increase in the absolute concentration of ZnO proved by the above XRD results of calcined samples.

Catalytic activity

Oxidation of aqueous phenol solution by hydrogen peroxide over calcined CuZnAl–LDHs was investigated at room temperature. Analysis of the oxidation products by HPLC indicated the presence of polyhydroxylated aromatic compounds (phloroglucinol (HHQ), hydroquinone (HQ), and catechol (CTC)) and other deep oxidation products, acetic acid, and acetone. The conversion of phenol (PhOH) and product distribution obtained with different catalysts is plotted in Fig. 5. It is seen that the phenol conversion shows a volcano-shaped curve with respect to Cu/Zn ratio, and the highest catalytic activity appears for the calcined LDH with Cu/Zn ratio of 1:1 characterized by the highest proportion of Cu_A^{2+} species. This result points to the Cu_A^{2+} species centers as active sites in the oxidation of phenol. Further, it can be noted from Table 1 that with decreasing Cu/Zn ratio, the BET surface areas present a maximum in calcined sample with Cu/Zn ratio of 1:1, suggesting active copper species can highly disperse on the surface of the sample, leading to the increase in catalytic activity. As a result, the high catalytic activity of calcined samples should be relative to the great amount and high dispersion of composite metal oxide containing

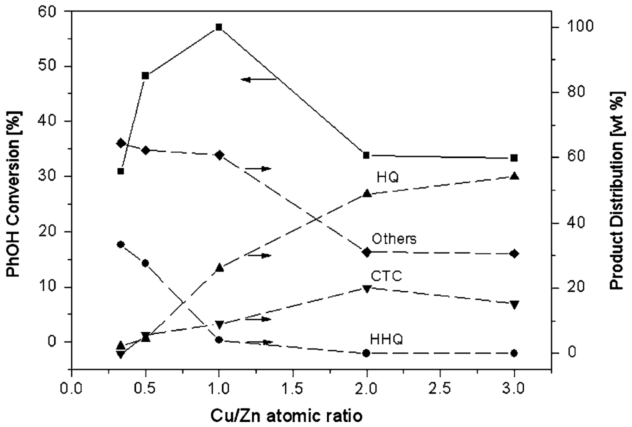

Fig. 5 The conversion of phenol and products distribution as a function of Cu/Zn ratios in the calcined LDHs

active copper centers on the surface of the calcined LDHs. On the other hand, it can be found from Table 2 and Fig. 5 that with decreasing Cu/Zn ratios from 3:1 to 1:3, the proportion of small molecule products in the reaction products increases gradually. This is because the lattice oxygen species on the surface of calcined LDHs as active oxygen centers can participate in oxidation reaction. Therefore, more the lattice oxygen species, higher the deep oxidation of phenol.

Conclusions

In summary, a series of LDHs carbonate precursors with Cu/Zn/Al atomic ratios from 1:3:1 to 3:1:1 were synthesized by conventional coprecipitation method. The cationic ratios in the synthesis mixture have a significant influence on the compositions and distributions of surface species on the resultant calcined LDHs. Calcination of the LDHs gives Cu/Zn/Al composite oxides and other metal oxides phases such as CuO and ZnO. It is confirmed that the catalytic activity for the oxidation of aqueous phenol solution is mainly relative to the amount and dispersion of composite metal oxides containing active Cu^{2+} reaction centers on the surface of calcined samples, and the lattice oxygen species on the surface of catalysts are beneficial to the deep oxidation of phenol.

Acknowledgements We gratefully acknowledge the financial support from the National Science Foundation of China (20631040, 20306003), Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT 0406) and the Program for New Century Excellent Talents in University (NCET-04-0120).

References

1. Evans DG, Slade RCT (2006) In: Duan X, Evans DG (eds) Structure and bonding, vol 119. Springer Verlag, Berlin, p 1
2. Seetharamulu P, Kumar VS, Padmasri AH, Raju BD, Rao KSR (2007) J Mol Catal A 263:253
3. Motokura K, Fujita N, Mori K, Mizugaki T, Ebitani K, Htsukawa K, Kanedar K (2006) Chem Eur J 12:8228
4. Zimowska M, Michalik-Zym A, Janik R, Machej T, Gurgul J, Socha RP, Podobinski J, Serwicka EM (2007) Catal Today 119:321
5. Obalova L, Pacultova K, Balabanova J, Jiratova K, Bastl Z, Valaskova M, Lacny Z, Kovanda F (2007) Catal Today 119:233
6. Zhao Y, Jiao QZ, Liang J, Li CH (2005) Chem Res Chin Univ 21:471
7. Hulea V, Maciuca AL, Fajula F, Dumitriu E (2006) Appl Catal A 313:200
8. Jimenez-Sanchidrian C, Hidalgo JM, Llamas R, Ruiz JR (2006) Appl Catal A 312:86
9. Belloto M, Rebours B, Clause O, Lynch J, Bazin D, Elkaïm E (1996) J Phys Chem 100:8527
10. Bellotto M, Rebours B, Clause O, Lynch J, Bazin D, Elkaïm E (1996) J Phys Chem 100:8535
11. Kooli F, Crespo I, Barriga C, Ulibarri MA, Rives V (1996) J Mater Chem 6:1199
12. Tichit D, Lhouty MH, Guida A, Chiche BH, Figueras F, Auroux A, Bartalini D, Garrone E (1995) J Catal 151:50
13. Corma A, Fornés V, Rey F (1994) J Catal 148:205
14. Christoskova StG, Stoyanova M, Georgieva M (2001) Appl Catal A 208:243
15. Pintar A, Levec J (1992) Chem Eng Sci 47:2395
16. Busetto C, Del Piero G, Mamara G, Trifirò F, Vaccari A (1984) J Catal 85:260
17. Gherardi P, Ruggeri O, Trifirò F, Vaccari A, Del piero G, Manara G, Notari B (1983) In: Poncelet G, Grange P, Jacobs PA (eds) Preparation of catalysts III. Elsevier, Amsterdam, p 723
18. Alejandre A, Medina F, Rodriguez X, Salagre P, Sueiras JE (1999) J Catal 188:311
19. Kloprogge JT, Frost RL (2001) In: Rives V (ed) Layered double hydroxides: present and future. Nova Science, New York, p 139
20. Busca G, Lorenzelli V, Escribano VS (1992) Chem Mater 4:595
21. Allen GC, Harris SJ, Jutson JA, Dyke JM (1989) Appl Surf Sci 37:111
22. Brabers VAM (1983) Mater Res Bull 18:861
23. Veprek S, Cocke DL, Kehl S, Oswald HR (1986) J Catal 100:250
24. Laine J, Brito J, Severino F, Castro G, Tacconi P, Yunes S, Cruz J (1990) Catal Lett 5:45
25. Yang BL, Chan SF, Chang WS, Chen YZ (1991) J Catal 130:52
26. Kannan S, Dubey A, Knozinger H (2005) J Catal 231:381
27. Lenglet M, D'Huysser A, Kasperek J, Bonnelle JP, Dürr J (1985) Mater Res Bull 20:745
28. Töpfer J, Feld A (1993) Solid State Ionics 59:249
29. Töpfer J, Feld A, Gräf D, Hackl B, Raupach L, Weissbrodt P (1992) Phys Status Solidi A 134:405
30. Schofield PF, Henderson CMB, Redfern SAT, Van der Laan G (1993) Phys Chem Miner 20:375
31. Tavares Figueiredo R, Martínez-Arias A, López Granados M, Fierro JLG (1998) J Catal 178:146
32. Huang WH (1998) J Tianjin Univ Commerce 13
33. Yoon C, Cocke DL (1988) J Catal 113:267
34. Muhler M, Schlogl R, Ertl G (1992) J Catal 138:413