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Preparation and Catalytic Property of High Surface Area Mixed Oxides from Calcination of MgCuCr- and MgCuAl-Layered Double Hydroxides

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Abstract

In this research work layered double hydroxides (LDHs) containing Mg, Cu and Cr(or Al) were prepared with starting Mg:Cu:Cr (or Al) molar ratio of 2:1:1. They were calcined at 500 ºC for 5 h to convert into corresponding mixed oxides possessing high surface area. The catalysts were characterized by chemical analysis (ICP), infrared spectroscopy (FTIR), thermal analysis (TGA/DTA), powder X-ray diffraction (XRD), surface area measurements and H_2 temperature programmed reduction (TPR). Catalytic property of these mixed oxides catalysts were tested in the oxidation of ethylbenzene using *tert*-butylhydroperoxide as an oxidant without added solvent. The experimental results show that high conversion of ethylbenzene and selectivity to acetophenone can be obtained. The MgCuAl oxide shows higher selectivity to acetophenone (95%) whereas the MgCuCr oxide displays higher activity (88% conversion). The difference in catalytic performance is due to type of metal in the material. The catalysts could be reused at least 3 times without significant loss in activity.

Key words: Mixed oxides, Layered double hydroxides, Oxidation, Ethylbenzene

Introduction

Layered double hydroxides (LDHs) are represented by the general formula: $(M(II)_{1-x}M(III)_x(OH)_2)^{x+}(A_{n-\ x/n})^{x-}\cdot mH_2O$, for which M(II) and M(III) are divalent and trivalent metal cations, and A is an anion.(1) LDH has been widely used in many fields including catalysis.(2) Calcination of LDH is known to produce spinels or mixed oxides.[3,4] Metal oxides containing transition metal cations with oxidative, or reductive properties are often used as heterogeneous catalysts for many chemical reactions including oxidation due to their unique combination of acid-base and redox properties.(5-7)

Oxidation of ethylbenzene is also important for the production of acetophenone, used as a component of perfumes and as an intermediate for the manufacture of pharmaceuticals, resins and alcohols.(8) Several heterogeneous catalysts have been reported,(9,10) including CrMCM-41 catalyst using O_2 (66% conversion and 90% selectivity in 24 hours at 95ºC)(11) and nickel substituted copper chromite spinel ($Cu_{0.5}Ni_{0.5}Cr_2O_4$) catalyzed using *tert*-butyl hydroperoxide (56% conversion and 69% selectivity of acetophenone).(12) We have recently reported high conversion (80%) and selectivity (92%) from the MgCuAl (3:1:1) oxide in oxidation of ethylbenzene.(13)

Materials and Experimental Procedures

Materials

$Mg(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Al(NO_3)_3.9H_2O$ and $Cr(NO_3)_3.9H_2O$ were purchased from Fluka and used without further purification.

Preparation of Layered Double Hydroxides

Two solutions, A and B were prepared. The solution A was an 1.5 M aqueous solution of nitrate salts: $Mg(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$ and $Cr(NO_3)_3.9H_2O$ or $Al(NO_3)_3.9H_2O$ (with Mg:Cu:Al(or Cr) molar ratio = 2:1:1) while the solution B, was 0.1 mol of Na_2CO_3 and 0.33 mol of NaOH in 150 mL of distilled water. Then, both solutions were simultaneously added to 50 mL of water at 65ºC with stirring. The pH was maintained at 10 by NaOH. The precipitate was aged at room temperature for 18 hours. The precipitate was

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filtered, washed thoroughly with distilled water until pH 7 and dried at 110ºC for 12 hours. The synthesized LDHs were calcined at 500ºC for 5 hours to obtain the corresponding mixed oxides.

Characterization techniques

The metal content in the sample was determined by ICP-AES analysis using a LIBERTY 200-VARIAN instrument. Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku RINT 2200 spectrometer using filtered CuKα radiation. The crystallite size was calculated using Scherrer equation:

$$D = B\lambda/\beta_{1/2} \cos \theta$$

where D is the average crystallite size, B is the Scherrer constant (0.89), λ is wavelength of the X-ray beam, $\beta_{1/2}$ is the full-width at half-maximum (FWHM) of diffraction peak and is the diffraction angle. The total surface area, S_{BET}, was calculated by applying the Brunauer-Emmett-Teller (BET) equation using a Quantachrome Autosorb-IC-VP Analyzer. Pore size distribution over the mesopore range was determined by the Barrett-Joyner-Halenda (BJH) analysis of the desorption branches, and values of the average pore size were calculated. Prior to the measurements, the samples were degassed at 100ºC for 2 hours. FT-IR spectra (KBr discs) were recorded on a Nicolet FT-IR Impact 410 Spectrophotometer. Thermogravimetric and differential thermal analysis (TGA-DTA) was carried out in air using a SDTQ600 comprehensive thermal analyzer with a heating rate of 10ºC/min. Temperature programmed reduction (TPR) measurements were carried out on a TPR MODEL BEL-CAT instrument equipped with a thermoconductivity detector (TCD). The sample (50 mg) was placed in a quartz reactor and reduced in a stream (flow rate 50 ml/min) of H_2 (3% H_2+ 97% He) with a heating rate of 15ºC/min over the range 25-900ºC and held at this temperature for 20 minute.

Catalytic oxidation

The reaction was performed in a magnetically stirred stainless steel reactor. Ethylbenzene (1.2 ml, 10 mmol), catalyst (0.2 g) and TBHP (70% aqueous) were added successively. The reaction was heated at 80 and 110ºC for 12 hours and stirred at 300 rpm. The catalyst was filtered and the products were analyzed by GC (Agilent Technologies 6890N Network GC System with FID, a DB-1 capillary column) equipped with a flame ionization detector using the internal standard method. Quantification was done by determining the response factors of the reagents and products obtained using standard mixtures. The spent catalysts were washed with acetone, and calcined at 500ºC for 5 hours. Fresh ethylbenzene was then employed in the repeated testing.

Results and Discussion

Characterization

The chemical composition, surface area and XRD phase of the samples are given in Table 1. In both MgCuAl- and MgCuCr-LDHs Mg:Cu:Cr(or Al) ratio is close to ratio of the starting solutions. Thermal decomposition of LDH precursors at 500ºC for 5 hours led to the formation of mixed oxides possessing higher surface area, pore volume and pore size. N_2 physisorption experiments were carried out to examine the adsorption isotherm of different LDHs materials. Both MgCuAl- and MgCuCr-LDHs display type IV isotherms (in Figure 1) according to IUPAC classification, characteristic of mesoporous materials.[14] The mixed oxides also show type IV isotherms with H3-type hysteresis loops with a broad pore sizes distribution. The H3 type hysteresis loop does not exhibit any limiting adsorption at high P/P_o. This is commonly observed for those aggregates of plate-like particles giving rise to slit-shaped pored, indicating that the plate morphology of the LDH.

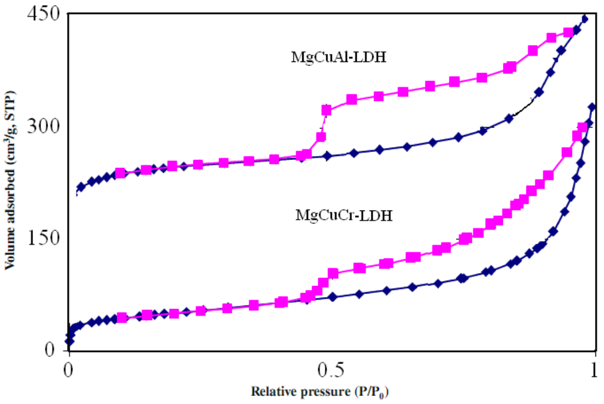

Figure 1. N_2 physisorption isotherms of MgCuAl-LDH and MgCuCr-LDH.

Table 1. Characteristics of LDHs and oxides

Catalyst	Atomic ratio Mg/Cu/Al(or Cr)		As-syn.			Calcined		
	Starting	Analyzed	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
MgCuAl	2:1:1	2.1:1:0.9	120	0.3	10	131	0.5	11
MgCuCr	2:1:1	2.2:1:0.8	107	0.4	11	115	0.6	14

The phase transformation of LDHs during the calcination treatment was evaluated by TGA/DTA. As shown in Figure 2, the first weight loss (~100-150ºC) corresponds to the removal of physically adsorbed water and interlayer structural water. The weight loss at 150-200ºC is due to the dehydroxylation of the brucite-like sheets and one at 250-440ºC is due to the decomposition of the carbonate anions. Therefore the calcination temperature for all samples was 500ºC to ensure the complete conversion of the LDHs to mixed oxides.

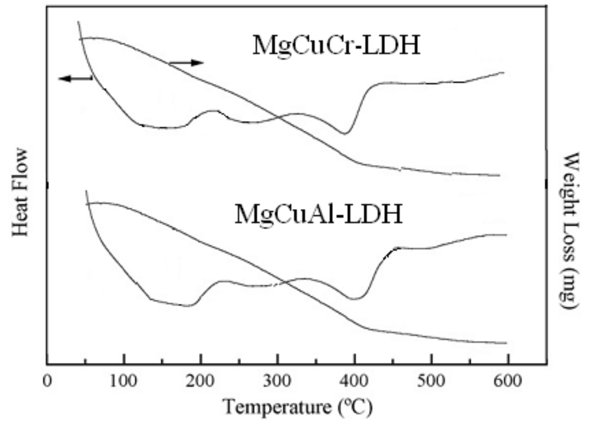

Figure 2. TGA/DTA curves for MgCuAl-LDH and MgCuCr-LDH.

Figure 3 shows XRD patterns of the LDHs (A) and their corresponding mixed oxides (B). The XRD patterns (A) exhibit the characteristic diffractions of a layered double hydroxide material (JCPDS 37-0630). Cr occupies a similar position to that of Al in layered double hydroxides. The diffraction peaks become less intense in the MgCuCr-LDH sample. This effect can be originated by the difference in the ionic radii of Cr^{3+} (0.64 Å) and Al^{3+} (0.57 Å). Inclusion of large cations in the brucite-like layers will give rise to distortion of these layers. The average crystallite sizes were estimated from Scherrer equation using the FWHM of the basal reflection plane (006). The obtained crystallite size was around 15 and 17 nm for MgCuAl-LDH and MgCuCr-LDH, respectively. The lattice *a* parameter ($a = 2d_{110}$) of the MgCuAl-LDH and MgCuCr-LDH was calculated to be 0.305 and 0.308 nm. The calculated *c* parameter ($c = 3d_{003}$) was 2.270 and 2.275 nm for MgCuAl-LDH and MgCuCr-LDH, respectively. The slight increase of lattice parameters agrees with the larger ionic radius of Cr^{3+}.

Upon calcination at 500ºC the layered structure of the LDH was destroyed and transformed into spinel phase ($(Mg_xCu_{1-x}Cr(\text{or }Al)_2O_4$ spinel solid solutions) together with CuO.(15) The MgCuAl sample shows lower crystallinity (broader peaks) and contains higher amount of CuO than the MgCuCr sample. In the MgCuCr sample in which Al was replaced with Cr ions, little amount of $CuCrO_4$ was also detected. The crystallite size of mixed oxide was around 19 and 22 nm for MgCuAl- and MgCuCr-oxide, respectively.

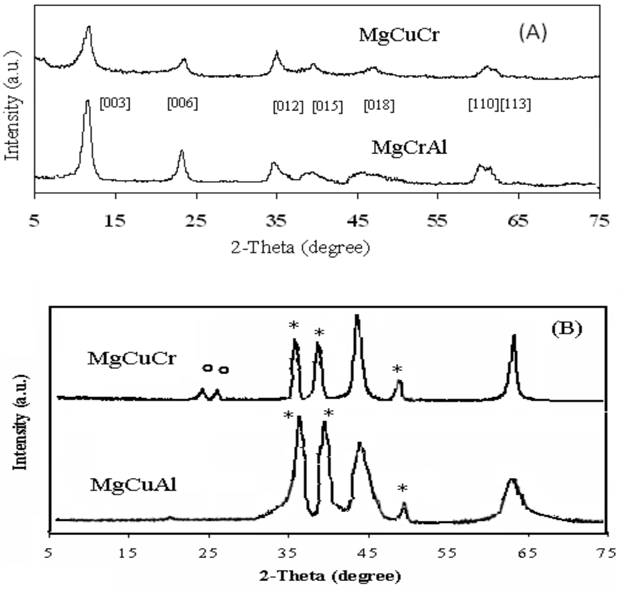

Figure 3. XRD patterns of (A) LDHs and (B) mixed oxides.(*) CuO, (o) $CuCrO_4$

Figure 4 shows the FTIR spectra of the LDHs and their corresponding oxides. In the LDHs (A), a strong absorption band in the range 3500-3400 cm^{-1} is attributed to the O-H stretching. A little shoulder around 3020 cm^{-1} is due to OH stretching of hydroxyl groups hydrogen-bonded to carbonate anions. A band at 1625 cm^{-1} may be ascribed to the bending mode of interlayer water molecules. The sharp absorption appeared around 1356 cm^{-1} is due to anti-symmetric stretching of carbonate at interlayer vibrations. The bands observed below 810 cm^{-1} correspond to metal-oxygen (M-O) vibrations. In the mixed oxides (B), both samples show bands in 550-800 cm^{-1} which are attributed to metal-oxygen. The minor remaining carbonate band arises from the adsorption of carbon dioxide from air on the surface of the metal oxide.

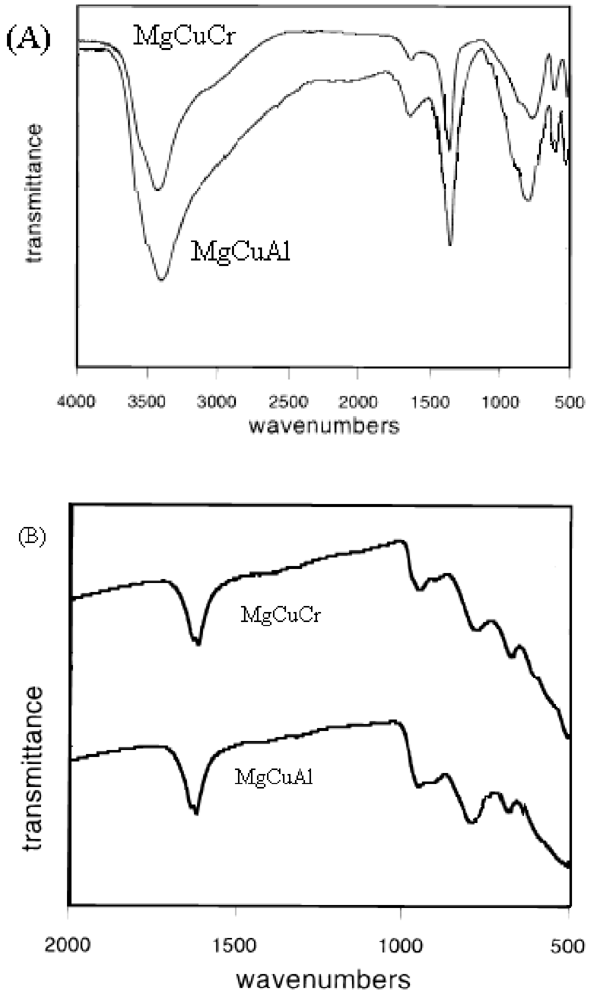

Figure 4. FTIR spectra of (A) LDHs and (B) mixed oxides.

The incorporation of transition metals in the prepared samples was confirmed by diffuse reflectance technique, the UV-vis spectra are shown in Figure 5. The MgCuAl-LDH shows a single broad band at 400-500 nm. For the MgCuCr-LDH, band at 320-395 nm is due to Cr^{3+} (d^3) ions in an octahedral environment.(16) The band in the 550-630 nm range corresponds to d-d transitions of Cu^{2+} in an octahedral configuration more or less tetragonally distorted.(17)

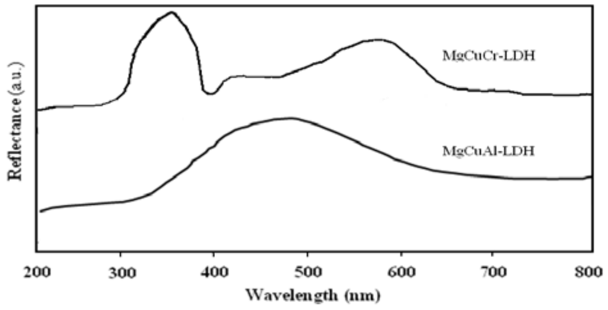

Figure 5. UV-vis diffuse reflectance spectra of Mg CuAl-LDH and MgCuCr-LDH.

The reducibility of the mixed oxides was studied by TPR experiments (Figure 6). In the MgCuCr oxide there appeared three reduction peaks. The peak at the low temperature 200-230ºC, attributed to the reduction of Cu oxide whereas other two peaks at 290-350 ºC and 420-510ºC are due to reduction of Cr oxide in which Cr ions are in different oxidation states. For the MgCuAl oxide, only one peak was observed in the low temperature region around 190-220ºC which can be ascribed to the reduction of the Cu^{2+} species in spinel and CuO to Cu.

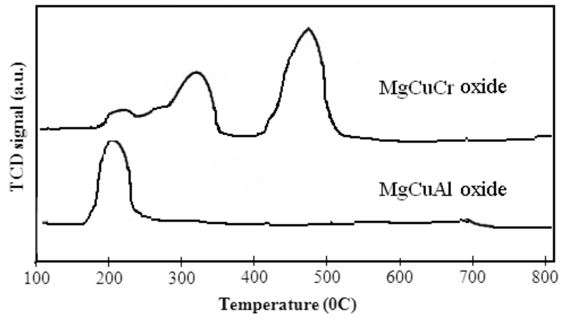

Figure 6. TPR of mixed oxides.

Catalytic activity

Oxidation of ethylbenzene was performed using TBHP as oxidant without the need of any added solvent. The result is shown in Table 2. The blank experiment shows that ethylbenzene oxidation does not occur in the absence of the catalyst. The oxidation of ethylbenzene gives rise to acetophenone as the main product with small amount of 1-phenylethanol.

Table 2. Oxidation of ethylbenzene over mixed oxides using TBHP (ethylbenzene 10 mmol, catalyst 0.2 g)

Catalyst	Ethylbenzene:TBHP molar ratio	Temp. (°C)	Time (h)	Conv. (%)	Sel. (%)[a]
MgCuAl	1:3	110	12	84	95
	1:2	110	12	80	95
	1:2	80	12	65	92
MgCuCr	1:3	110	12	88	90
	1:2	110	12	82	89
	1:2	80	12	67	88
CuCr[b]	1:2	70	8	33	14

[a] Selectivity to acetophenone, other products: 1-phenylethanol, benzaldehyde and benzoic acid.

[b] 0.1 g catalyst, 10 mL acetonitrile. 83.4% selectivity to 1-phenylethanol [12]

The MgCuCr oxide shows higher activity than the MgCuAl oxide, this demonstrates that combination of Cu and Cr can enhance the catalytic activity. This might be due to reductions of both Cu and Cr ions, as shown in TPR result (Figure 6). However, the selectivity to acetophenone was lower than that from the MgCuAl oxide.

The MgCuAl oxide (Mg:Cu:Al = 2:1:1) shows higher performance than the previously reported MgCuAl oxide (Mg:Cu:Al = 3:1:1), 80% conversion and 92% selectivity,[3] this is due to higher percentage of Cu in this MgCuAl oxide (Mg:Cu:Al = 2:1:1). The reaction using ethylbenzene /TBHP molar ratio of 1:3 yielded higher conversion than that using ratio of 1:2, however the selectivity was unchanged. When reaction was conducted at lower temperature (80°C), the conversion decreased. Compared to the CuCr oxide catalyst, it should be noted that Mg influences product selectivity to acetophenone, due to its basicity.(18) It should be mentioned that the mixed oxides in this work can be prepared easily without need to complex metal with any ligand as reported in other work.(19)

After the reaction, the catalyst was filtered and washed with acetone and reused. It was found that the catalyst shows a slight drop in activity after the third run (2%). In addition the filtrate was also analyzed by ICP. The result shows the absence of metal ions leach-out.

Conclusions

MgCuAl and MgCuCr mixed oxides possessing high surface area were easily prepared from their LDHs by calcination at 500°C. These mixed oxides were shown to be efficient catalyst for selective oxidation of ethylbenzene with *t*-butyl hydroperoxide to acetophenone (95 %selectivity). The advantage of this system is the oxidation can be performed under solvent free condition and the catalyst can be reused.

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