Short Communication

Selective oxidation of styrene over Mg–Co–Al hydrotalcite like-catalysts using air as oxidant

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ABSTRACT

A set of synthesized Mg/Co/Al hydrotalcites was synthesized and characterized by XRD, XPS, BET, SEM, TEM, and FT-IR physical techniques. The partial substitution of Mg^{2+} by Co^{2+} in brucite layers has not significantly affected the layered double hydroxide structure, but plays a crucial role in the oxidation of styrene in the presence of air. The prepared Mg/Co/Al hydrotalcite-like compounds express a good activity and stability in the oxidation of styrene in the free-solvent condition. Both styrene conversion and desired product selectivities are strongly dependent on the cobalt substitution content. The intra-hydrotalcite lattice Co^{2+} ions are active sites for the epoxidation of styrene.

1. Introduction

Oxidation of styrene is a reaction of great interest because its products act as versatile and useful intermediates [1]. Conventionally, this process has been usually carried out by homogeneous catalysts and resulted in a huge amount of toxically corrosive chemical wastes. Recently, there has been much interest in solid catalysts and uses of environmentally friendly cheap oxidants [2,3]. Several transition metal-containing catalysts based on Ru, Cu, Fe, Mn, V, Ti… have been used in the liquid phase oxidation of olefinic compounds to oxygenates [3–6]. Among those, Ru- and Cu-based heterogeneous solids are restricted only to doubly activated alkylaromatics while Fe- and Ni-containing catalysts usually give a rather low yield of oxygenated products [3–7]. Therefore, the synthesis of novel easily recyclable catalyst for the oxidation of alkylbenzenes is still a great challenging goal of fine chemical industry.

Hydrotalcite-like compound is known as a layered double hydroxide (LDH) mineral with the general formula of $[A^{2+}_{(1-x)}B^{3+}_{x}(OH)_{2}(CO_{3})_{0.5x}\cdot nH_{2}O]$. Cations are usually located in coplanar $[M(OH)_{6}]$ octahedra sharing vertices and forming $M(OH)_{2}$ layers with the brucite structure [8]. Partial substitution of divalent cations by trivalent cations leads to the appearance of positive layers which is usually compensated by anions between layers. Thus, the complexity of chemical composition in hydrotalcite-like compound makes it be able to act as basic solids and oxidation–reduction catalysts [9–11]. For example, Ni-containing basic hydrotalcites were used for the selective oxidation of benzylic C–H bonds of ethyl benzene [11]. Mn–MgAl and MoO_{4}^{-}/MgAl

hydrotalcite-like catalysts present a good activity in the oxidation of alkylbenzenes [9,12]. Cobalt-containing hydrotalcites have been used for the steam reforming of ethanol [13] and synthesis of benzoin methyl ether [14]. In these cases, transition metal ions in layered structure are the key for the catalytic activity. This article provides a novel applicability of Mg–Al hydrotalcites partially substituted by cobalt ions as effective catalyst for the oxidation of styrene under milder conditions.

2. Experimental

2.1. Preparation and characterization of the catalysts

Mg/Co/Al hydrotalcite-like compounds were prepared by the coprecipitation method. The detailed procedure was described in our previous publication [15]. In brief, 150 mL-mixed aqueous solution of $Mg(NO_{3})_{2}\cdot6H_{2}O$ (99%), $Co(NO_{3})_{2}\cdot6H_{2}O$ (98%) and $Al(NO_{3})_{3}\cdot9H_{2}O$ (>98%) with $Co^{2+}/(Mg^{2+} + Al^{3+})$ molar ratios ranging from 0 to 0.44 was added dropwise to 25 mL of 0.6 M $Na_{2}CO_{3}$ under vigorous stirring. The exact amounts of starting materials for each catalyst are given in Supporting information (Table 1S). The solution pH was adjusted to 9.50 using 1.5 M NaOH and was kept for 24 h. Then, the resulting gel-like material was aged at 65 °C for 24 h. The resultant slurry was then cooled to room temperature and separated by filtration, washed with hot distilled water several times, and then dried at 80 °C for 24 h in air. The prepared catalysts are denoted as Mg/Co/Al-1, -2, and -3 (Table 1).

The elemental composition (Mg, Co, Al) of catalyst was measured using an ICP-MS Elan 9000 (PerkinElmer, USA) and carbon content instrument PE 240 (USA). Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using CuK_{α} radiation

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Table 1
Physical properties of the prepared Mg/Co/Al hydrotalcite-like compounds.

Catalyst batch	Molar ratio of $Co^{2+}/(Mg^{2+}+Al^{3+})$	Elemental analysis (wt.%)				BET surface area (m^2/g)	Pore volume (cm^3/g)
		Mg	Co	Al	C		
Mg/Al-0	0	24.74	–	11.93	2.39	83.4	0.62
Mg/Co/Al-1	0.10	21.34	8.16	12.30	1.98	78.9	0.60
Mg/Co/Al-2	0.24	14.20	12.72	8.14	1.87	74.6	0.58
Mg/Co/Al-3	0.44	9.18	17.89	8.10	1.89	74.5	0.58
Mg/Co/Al-2 reacted	0.24	10.13	9.71	7.24	2.11	44.2	0.49

(λ = 0.1549 nm). Fourier transform infrared (FT-IR) spectra were obtained in 4000–400 cm^{-1} range on a FT/IR spectrometer (DX-PerkinElmer, USA). TEM images were collected on a Japan JEOL JEM-1010. The nitrogen physisorption was run on an Autochem II 2920 (USA). The X-ray photoelectron spectra (XPS) of catalysts were recorded with a Thermo K-Alpha.

The catalytic oxidation of styrene in the absence of solvent was carried out in a 100 mL three-neck glass flask fitted with a reflux condenser. For a typical run, 87.28 mmol of styrene and 0.2 g of catalyst were loaded into the flask unless some particular tests were indicated. After the reaction mixture was magnetically stirred and heated to the desired temperature, the flow of air (5 mL/min) was bubbled through the vigorously stirred reaction mixture and the reaction time starts recorded. After the reaction, the mixture was quenched to room temperature and then catalyst was filtered off. The filtrate was analyzed by a GC–MS (HP-6890 Plus) and a frame ionization detector (FID) is used as a detector.

3. Results

3.1. Catalyst characteristics

The prepared catalyst characteristics and chemical composition are summarized in Table 1. Fig. 1 displays the powder X-ray diffraction patterns for all synthesized Mg–Co–Al hydrotalcite-like materials. Overall, all samples present a set of reflection lines matching to those characteristics of layered double hydroxide structure [8,10,13,15]. Indeed, two sharp and intense peaks at low diffraction angles of 23.2 and 34.4° are ascribed to the diffraction by basal planes (006) and (102), respectively [10,15]. Furthermore, broad, less intense peaks at higher angles around 38, 46, and 60° indexed to (105), (108), and (110) planes also confirm the hydrotalcite structure [14,15]. The positions of these reflection lines are slightly changed but the signal to noise ratio and full width at
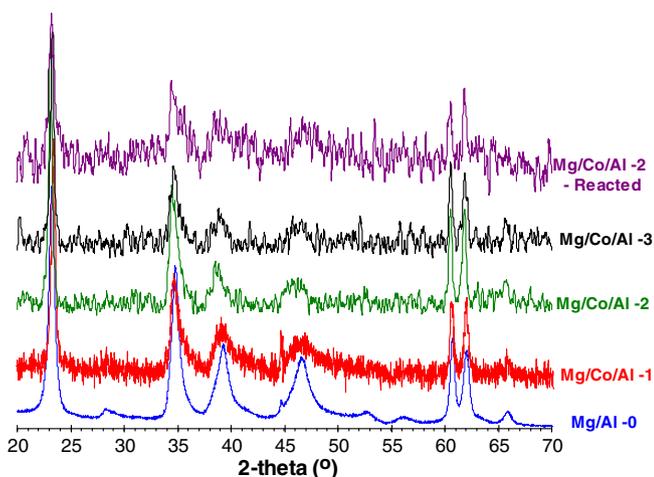
half maximum peaks vary with increased cobalt content. The latter could possibly be explained by only subtle differences in the octahedral ionic radii of Co^{2+} (0.74 Å) and Mg^{2+} (0.72 Å) [13]. The XRD patterns (Fig. 1) reveal that the cobalt rich-samples are somewhat poorer crystallinity because the affinity of CO$_3^{2-}$ to Co^{2+} is less than that to Mg^{2+} [10,13]. No reflection lines corresponding to cobalt oxides are observed, suggesting that cobalt ions are present in LDH structure [13,14].

The major photoelectron lines of the elements in a representative Mg/Co–Al-1 are reported in Fig. 2A. Clearly, magnesium, cobalt, oxygen, carbon and aluminum have photoelectron lines at 1s (1303.93 eV), 2s (88,08); 2p (781.08 eV); 2p (531.90 eV); 2p (289.08 eV) and 2p (74.34 eV), respectively [13]. To investigate the oxidation state in the near-surface region, the spectrum corresponding to the Co 2p core level is represented in Fig. 2B while Mg 1s and Al 2p scans are elucidated in Supporting information. XPS spectrum of Co 2p in Mg/Co/Al sample shows two clear peaks positioned at binding energy values of 781.1 (Co 2p$_{3/2}$) and 797.1 eV (Co 2p$_{1/2}$), along with shake-up satellites. These binding energy values and the peak separation are essentially ascribed to Co^{2+} species. Furthermore, the high intensities of the satellites are typical characteristics for the cobalt containing layered double hydroxide structure. Thus, it is suggested that Co^{2+} ions locate at octahedral sites in brucite-like layers [13,16].

FT-IR spectra of Mg/Co/Al hydrotalcite-like materials present the main band around 3454 cm^{-1} assigning to the OH stretching mode of water molecules and hydroxyls in the layers [10,12]. This band shows a prominent shoulder around 2950 cm^{-1} ascribed to hydrogen bonding of OHs of layered lattice and/or water molecules with interlayer carbonate anions (see Fig. 1S in Supporting information). A sharp band at 1365 cm^{-1} is firmly assigned to the asymmetric stretching vibration of the CO$_3^{2-}$ in the hydrotalcite layers. A set of bands at 437, 663, 742, and 927 cm^{-1} is associated to Al–O, Co–O, Al–OH translation, and doublet Al–OH deformation modes, respectively [13,17].

The textural properties of nominal Mg/Co/Al hydrotalcite-like compounds were insignificantly changed with molar ratios of Mg/Co/Al.
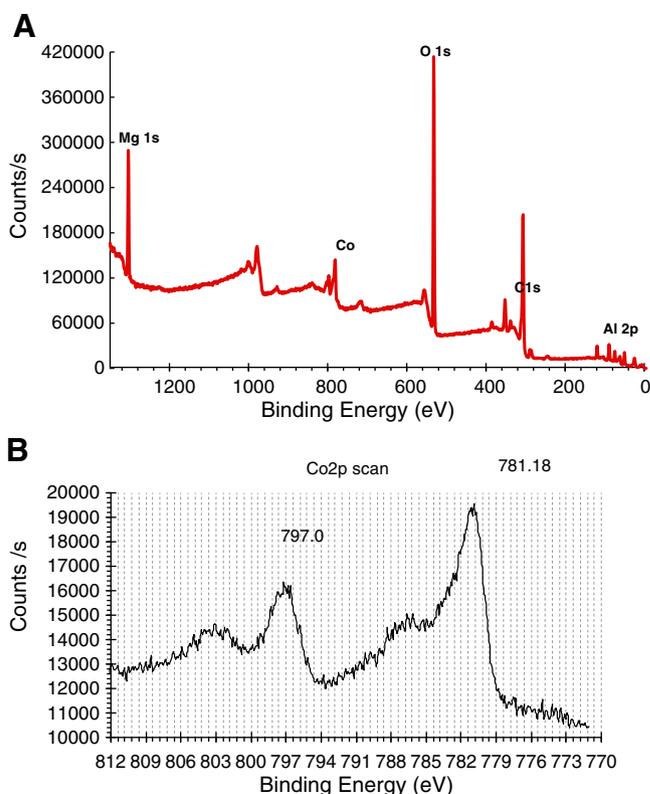
Fig. 2. Survey scan (A) and Co 2p XPS spectrum (B) of as-synthesized Mg/Co/Al-2 hydrotalcite-like material.

Fig. 1. XRD patterns of as-synthesized hydrotalcite-like compounds and the used sample.