



Short communication

Effect of Mg^{2+} on the catalytic activities of CoMgAl hydrotalcites in the selective oxidation of benzyl alcohol to benzaldehyde



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ABSTRACT

With the knowledge the significant effect of basic site on the catalytic performance of heterogeneous catalysts in the selective oxidation of alcohol, a series of Co_2Mg_xAl -LDHs ($x = 0, 0.5, 1.0, 1.5,$ and 2.0) compounds with different Mg^{2+} contents have been prepared, characterized and introduced into the selective oxidation of benzyl alcohol with TBHP as the oxidant. The results showed that introducing Mg^{2+} ions can not only influence the amount of basic site, but also promote the oxidation process of Co^{2+} to Co^{3+} . These facts must contribute to the markedly improved catalytic activities of Co_2Mg_xAl -LDH samples.

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1. Introduction

Benzaldehyde is an important raw material in perfumery and pharmaceutical industries. Selective oxidation of benzyl alcohol to benzaldehyde under efficient catalyst is an industrially important reaction as it avoids large amounts of highly toxic heavy metal wastes, generating from traditional production process [1,2]. Therefore, various catalysts have been developed for the reaction. Although noble metal catalysts are known to be effective catalysts for liquid-phase aerobic oxidation of benzyl alcohol, the base additives are always needed [3,4]. To avoid the using of soluble base, basic supports, such as MgO, $Mg(OH)_2$, hydrotalcite (HT), etc., has been widely applied as the support for noble metal catalysts, such as Pd [5], Au [6], Pt [7] and Ru [8]. It has been demonstrated that the Au/HT catalysts can be more active in the absence of base additives than other commonly used gold catalysts such as Au/TiO₂, Au/CeO₂ and Au/Al₂O₃. Under the optimized conditions, the conversion of benzyl alcohol reached to 96% with a selectivity of >99%, suggesting synergy between AuNPs and basic sites of the HT [9,10]. However, from the viewpoint of economy and sustainable chemistry, it is especially important to develop economically catalysts for the selective oxidation of benzyl alcohol, because noble metal catalysts are highly expensive and scarce.

Actually, some catalytic systems based on transition metals have been reported using O₂, H₂O₂ or tert-butylhydroperoxide (TBHP) as the oxidants, including Co@SiO₂@[Ni(II)SBC] [11], NiAl-LDH [12], N-CNTs [13], CeCrO₃ [14], etc. However, few reports on the adjustment

of surface basicity of catalyst and the effect of basicity on the catalytic performance, although much research proved that the surface basicity of supports play an important role in affecting the catalytic activity.

Layered double hydroxides (LDHs) or synthetic anionic clays, having a hydrotalcite-like structure, are composed of positively charged, tri-octahedral hydroxide layers with interlayer anions, and represented by the general formula of $[M(II)_{(1-x)}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$ [15, 16]. Since these compounds vary in their composition as well as the properties with the substitution of cation in the brucite layer, LDHs have been widely applied as catalysts in oxidations [17,18] and the reactions catalyzed by base [19,20]. The properties of hydrotalcites can be finetuned because of the adjustability of the cations and anions in the brucite layer and interlayer [21,22]. These particular properties of LDHs should provide us a new method of designing bifunctional catalyst possessing both basicity and the redox functionality.

With this knowledge and background, in the present study, Co_2Mg_xAl -LDHs ($x = 0, 0.5, 1.0, 1.5,$ and 2.0) compounds with different basic properties tuned by Mg contents have been prepared, characterized and introduced into the selective oxidation of benzyl alcohol in liquid phase with TBHP as the oxidant. The effect of Mg^{2+} content on the basic properties of the catalysts and their catalytic properties were investigated.

2. Experimental

2.1. Preparation of catalysts

Co_2Mg_xAl LDHs with different Mg contents ($x = 0, 0.5, 1.0, 1.5$ and 2.0) were synthesized by a coprecipitation method according to

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previous report [23]. Typically, a 120 mL aqueous solution A contained 0.04 mol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.02 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.02 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and a 120 mL aqueous solution B contained 0.067 mol of Na_2CO_3 and 0.2 mol of NaOH . The two solutions were added dropwise with stirring to 120 mL deionized water at 60 °C while the pH was maintained 10.0 ± 0.5 , followed by stirring for another 30 min. The resulting slurry was digested at 80 °C for 24 h. The precipitate was washed with deionized water until the pH of the filtrate was around 7.0. And then dried in an oven at 100 °C for 12 h. The solids obtained were named $\text{Co}_2\text{Mg}_x\text{Al-LDH}$.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) patterns of the as-synthesized samples were obtained using a Rigaku D/max 2500 PC X-ray diffractometers with $\text{Cu-K}\alpha$ (1.5402 Å) radiation at 10 min^{-1} . The compositions of samples were analyzed by inductively coupled plasma analysis (ICP) using a Varian Vista-AX device. Diffuse reflectance ultraviolet visible spectra (DR UV-Vis) were recorded in a Perkin-Elmer Lambda 35 spectrophotometer, using BaSO_4 as a reference. For the scanning electron microscopy (SEM) study of the samples, a JEOL JSM-6360LA scanning electron microscope was used. The specific surface areas of samples were determined by the BET method using a micromeritics ASAP2010C apparatus, and the gas adsorbed at -196 °C was pure nitrogen. The basic properties were determined by titration with 0.01 M benzoic acid solution in toluene using 0.15 g of vacuum dried solid sample suspended in 2 mL of indicator solution [24]. The indicator solution for the determination of weak basic sites ($\text{pK}_a = 7.6$) contained 0.01 g of Bromothymol Blue in 100 mL toluene. The amount of strong basic sites ($\text{pK}_a = 15.0$) was determined in the presence of an indicator solution containing 0.01 g of 2, 4-dinitroaniline in 100 mL toluene.

2.3. Reaction procedure for benzyl alcohol oxidation

Liquid-phase catalytic oxidation of benzyl alcohol was carried out in a 50 mL four-neck-flask with reflux condenser and magnetically stirred autoclave heated in an oil bath under atmospheric pressure. Acetonitrile (solvent, 10 mL), catalyst (0.1 g) and 0.02 mol benzyl alcohol were magnetically stirred at 60 °C, followed by dropwise addition of 0.04 mol of TBHP (70%) in 30 min. The product samples were drawn at regular time intervals and analyzed with a gas chromatography (Shimadzu GC-2010AF) having Chromopak capillary column and FID detector. The products were further confirmed using GC-MS (Shimadzu GCMS-2010). After the reaction, the resulting mixture was cooled with ice bath and the catalyst was separated by centrifugation and washed with solvent. After drying at room temperature in vacuum, the recycled catalyst can be reused in the next run under the same conditions. The conversion, yield of benzaldehyde and selectivity presented here are

based on the GC calculations using cyclohexane as the internal standard reference compound.

3. Results and discussion

3.1. Characterization of $\text{Co}_2\text{Mg}_x\text{Al-LDHs}$ samples

For LDH compounds, the $\text{M}^{2+}/\text{M}^{3+}$ ratio has significant effect on the structure of the obtained samples. To obtain the pure HT compounds, we prepared $\text{Co}_2\text{Mg}_x\text{Al-LDHs}$ with the $(\text{Co} + \text{Mg})/\text{Al}$ ratio between 2.0 to 4.0, and layered structure of the samples was confirmed by XRD measurements (Fig. 1A).

The diagrams are vertically displaced and the same scale is used for an easier comparison. The patterns show common features, with reflections located at the angles typical of a hydrotalcite-like phase, containing carbonate anions in the interlayer space: sharp and symmetrical for (003), (006), (110) and (113), and broad and asymmetrical for (009), (015) and (018), respectively [25,26]. These results indicate that Co was incorporated into the HT structures and the cations were well dispersed. All the samples showed the similar morphologies, and the SEM image of $\text{Co}_2\text{MgAl-LDH}$ in Fig. 1B shows that the sample formed plate-like agglomerated crystals with a particle size of about 0.1 μm , representing the character of layered materials [27,28]. The FTIR (Fig. S1) and TG/DTA (Fig. S2) spectra also verified the formation of hydrotalcite phase.

The $\text{Co}_2\text{Al-LDH}$ and the samples with varied Mg^{2+} content were also examined by the nitrogen adsorption–desorption method. The data of ICP analysis, the surface areas, pore volumes and pore sizes of these samples are summarized in Table 1. The ratios of $\text{M}^{2+}/\text{M}^{3+}$ exhibited lower than theoretical value, while Co/Mg ratios were almost the same as the additions. The BET surface area of these samples decreased as the Mg/Co ratio increase, although the value of $\text{Co}_2\text{Mg}_{1.5}\text{Al-LDH}$ exhibited exceptional. However, the pore volumes and pore sizes of these samples didn't show markedly different. Temperature-programmed desorption of carbon dioxide ($\text{CO}_2\text{-TPD}$) is an efficient method for measuring the basicity of samples, but the high temperature needed during the pretreatment must destroy the structure of LDHs samples. Therefore, the amount of the basic sites in the catalysts was analyzed qualitatively using Hammett indicators. The results in Table 1 show that the total basic sites on the surface of these samples increased with the magnesium content increase, indicating that changing the magnesium content is an efficient method for adjusting the basicity of these samples.

DR UV-Vis spectroscopy is proved to be a sensitive technique that is widely used to detect coordination states of incorporated cobalt species in various materials. Fig. 2 shows the DR UV-Vis spectra of the prepared $\text{Co}_2\text{Mg}_x\text{Al-LDHs}$ with different Mg^{2+} content.

Inspection of the spectra reveals that, in the $\text{Co}_2\text{Al-LDH}$ sample, the cobalt ions exist as Co^{2+} in the octahedral (Oh) surrounding, analogous

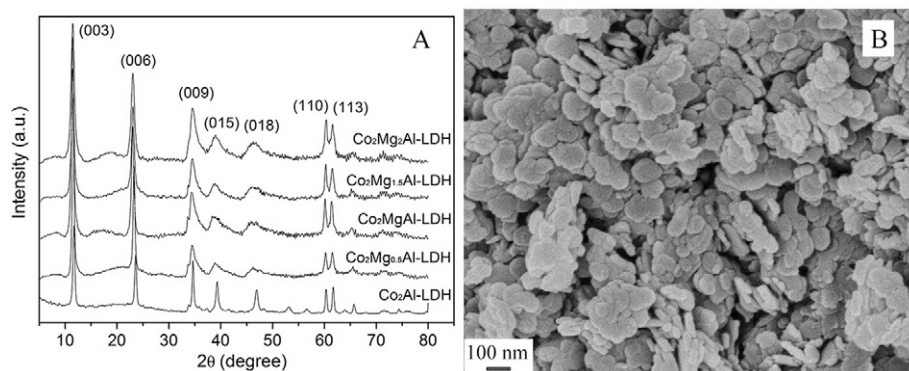


Fig. 1. XRD patterns and SEM image of $\text{Co}_2\text{Mg}_x\text{Al-LDH}$ samples.

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