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Effect of Mg²⁺ 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.

Keywords: Hydrotalcite-like compounds, magnesium ion, benzyl alcohol, Selective oxidation, Benzaldehyde

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 O_2 , H_2O_2 or tert-butylhydroperoxide (TBHP) as the oxidants, including $Co@SiO_2@[Ni(II)SBC]$ [11], NiAl-LDH [12], N-CNTs [13], CeCrO₃ [14], etc. However, few reports on the adjustment of surface basicity of catalyst and the

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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 previous report [23]. Typically, a 120 mL aqueous solution A contained 0.04 mol of $Co(NO_3)_2 \cdot 6H_2O$, 0.02 mol of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.02 mol of $Al(NO_3)_3 \cdot 9H_2O$, 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 Co_2MgAl -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 Cu-K α (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 BaSO₄ 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 (pKa = 7.6) contained 0.01 g of Bromothymol Blue in 100 mL toluene. The amount of strong basic sites (pKa = 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 Co₂Mg_xAl- LDHs samples

For LDH compounds, the M^{2+}/M^{3+} ratio has significant effect on the structure of the obtained samples. To obtain the pure HT compounds, we prepared Co₂Mg_xAl-LDHs with the (Co+Mg)/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 Co_2MgAl -LDH in Fig. 1B shows that the sample formed plate-like agglomerated crystals with a particle size of about 0.1 μ m, 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.

Figure 1

The Co₂Al-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 M^{2+}/M^{3+} exhibited lower than theoretical value, while Co/Mg ratios were almost the same as as the additions. The BET surface area of these samples decreased as the Mg/Co ratio increase, although the value of Co₂Mg_{1.5}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 (CO₂-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 shows 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.

Table 1

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 $Co_2Mg_xAl-LDHs$ with different Mg^{2+} content.

Figure 2

Inspection of the spectra reveals that, in the Co₂Al-LDH sample, the cobalt ions exist as Co²⁺ in the octahedral (Oh) surrounding, analogous to $[Co(H_2O)_6]^{2+}[29]$ and have not undergone any oxidation process. The multi-component band is centered near to 528 nm (λ_3) and can be related to transition $4T_{1g}(F) \rightarrow 4T_{1g}(P)$. The shoulder λ_2 , close to 590 nm, may be tentatively ascribed to $4T_{1g}(F) \rightarrow 4A_{2g}(F)$ transition. The shoulder at 450 nm can be attributed to spin-forbidden transitions to 2A_g (${}^2A_{1g}$ and ${}^2A_{2g}$) states [30].

Compared to the spectrum of Co₂Al-LDH, the spectra of Co₂Mg_xAl-LDHs samples demonstrate an increase of the shoulder intensities relative to the central band, indicating some changes in the ions charge and surrounding. As the increasing of the Mg²⁺ content, the darkening of the color of the Co₂Mg₂Al-LDH sample to beige supposes a partial oxidation of Co²⁺ to Co³⁺ ions. This supposition is supported by the development of a new wide band centered near to 380 nm and well defined band at 620 nm. The bands could be ascribed to d-d transitions in low spin Co³⁺ (Oh) species (${}^{1}Ag_{1g} \rightarrow {}^{1}T_{2g}$ and ${}^{1}Ag_{1g} \rightarrow {}^{1}T_{1g}$, respectively), which is accordance to the report by Gabrovska [30] and Khassin [31], where the spectra was shown versus wavenumber.

The above analysis exhibits that the partial oxidation of Co^{2+} ions is occurring during the synthesis procedure due to the thermodynamically favored oxidation of Co^{2+} to Co^{3+} ions [32]. Such an oxidation has already been reported for samples aged under hydrothermal conditions [33] and in the samples with large cobalt content [34]. In the present research, however, we found that introducing Mg²⁺ ions also could promote the oxidation process of Co^{2+} to Co^{3+} . In addition, the intensity at 380 and 620 nm increased with the Mg²⁺ content increasing, indicating that Co^{3+} content in the Co_2Mg_2Al -LDH sample is the highest. These facts drive us to suppose that M²⁺ is prone to be oxidized when M²⁺ content is high, if the ion can be oxidized. The deduction is to be further verified, however, it could be summarized that both Co^{2+} to Co^{3+} ions exist in Co_2Mg_xAl -LDHs samples, and the ratio of Co^{3+}/Co^{2+} increased with the Mg²⁺ increase.

3.2. Oxidation of benzyl alcohol catalyzed by Co₂Mg_xAl-LDHs samples

These $Co_2Mg_xAl-LDHs$ samples could smoothly catalyze benzyl alcohol oxidation under selected conditions using TBHP as the oxidant. GC-MS analysis data showed that the liquid-phase oxidation of benzyl alcohol could lead to benzaldehyde, benzoic acid and ester, while aldehyde was the predominant product.

Before discussing the effect of Mg²⁺ on the catalytic activities of these catalysts, some reaction conditions, including catalyst amount and TBHP/toluene ratio, reaction time, reaction temperature and solvent, have been optimized (the data and discussion can be found in SI). Under the optimized conditions, the results of benzyl alcohol oxidation over different catalysts are summarized in Table 2. It is clear that the introducing of Mg²⁺ into the Co₂Al-LDH samples exhibits a significant effect on the catalytic performance. When Co₂MgAl-LDH was applied in the oxidation, the conversion of benzyl alcohol significantly increased from 26.7% to 39.5% compared with Co₂Al-LDH, while the selectivity of benzaldehyde changed slightly. Concerning the effect of basic site on the oxidation, one can suppose that basic site contribute to the improvement of the catalyst's performance. To validate the fact, a controlled experiment using Co₂Al-LDH and K₂CO₃ (based on the amount of basic site of Co₂MgAl-LDH) as the catalysts, the conversion of benzyl alcohol was 26.8%, nearly the same as that without base, indicating that the base in the studied system could not affect the catalytic activity. However, the selectivity of the aldehyde was significantly influenced by the basicity, because the value increased from 91.1% to 100% when K_2CO_3 was added. The selectivity variation tendency with different catalysts with varied basicity furtherly verified the conclusion, because when the amount of basic sites increased above 1.309 mmol/g, the benzaldehyde became the only product without any other by-products. However, after reaching the highest value, the conversion of benzyl alcohol decreased as the increase of basicity, which may be mainly due to the decrease of cobalt content of these samples.

Table 2

On the other hand, TBHP is probably decomposed through a Haber-Weiss mechanism involving monoelectronic transfer in the presence of redox metals. For the redox pairs Co(III)/Co(II) involved in this case, the mixed state of cobalt ions should be benefit for the catalytic activity of the prepared samples. From the above analysis of DR UV-Vis, we have known that introducing Mg^{2+} ions can promote the oxidation process of Co^{2+} to Co^{3+} , namely that both Co^{2+} and Co^{3+} ions exist in Co_2Mg_xAI -LDHs samples (x=0.5, 1.0, 1.5, 2.0). The fact may be the reason for the higher catalytic activities of the Co_2Mg_xAI -LDH samples compared with Co_2AI -LDH. However, the conversion of alcohol decreased when the ratio of Mg/Co increased from 1/2 to 1/1, indicating that the catalytic activity might also effected by the amount of Co^{2+} and Co^{3+} . In the oxidation by TBHP over Co-composites, the formation of active radical is essential important. On the basis of above analysis, we suggest that the active radical, i.e. tert-butoxy and tert-butylperoxy radicals, were formed as a reversible Co^{2+}/Co^{3+} redox mechanism as illustrated in Fig. 3. Then these active radicals propagated the reaction to produce benzaldehyde and theyself transformed to tert-butanol [35]. The confirmation of tert-butanol by GC and GC-MS analysis, and the increasement of its concentration as the reaction proceeded further verified the reaction path.

Figure 3

In order to assess the stability of the catalysts, the catalyst was separated from the reaction mixture after each experiment by filtration, washed with the solvent (acetonitrile) and dried. From the table 2, one can observe that the catalyst could be reused at least five times with similar conversions of benzyl alcohol and selectivities for benzaldehyde, indicating that the synthesized Co₂MgAl-LDH is a stable catalyst. After reaction, the Co content of used catalyst was analyzed by ICP, and the result showed that the Co content changed from 29.03% to 28.98 %, there was almost no leaching of cobalt ion after catalytic reaction. The XRD pattern of recycled Co₂MgAl-LDH in Fig. S5 show that the structure of these catalysts did not changed in the catalytic oxidation. Although the present results do not exhibit any advantages in terms of the yield of benzaldehyde compared with the very recently reported complex catalyst Co@SiO₂@[Cu(II)SBC] [11] (the yield reached 94% using H₂O₂ as the oxidant), the study may be helpful for designing the more efficient catalysts, which can been conveniently prepared and applied in large scale.

4. Conclusions

Develop an efficient heterogeneous catalyst for the selective oxidation of benzyl alcohol without base additives has been an important topic in the research field. In this study, Co_2Mg_xAl -LDHs samples with different Mg^{2+} content by a coprecipitation method were prepared, characterized and applied to the selective oxidation of

benzyl alcohol to benzaldehyde. From the titration analysis of these catalysts, it is observed that introduction of Mg^{2+} resulted in an obvious increase of the amount of basic sites, which could contribute to high selectivity of the aldehyde in the reaction. On the other hand, the DR UV-Vis analysis indicated that Mg^{2+} ions could promote the oxidation of Co^{2+} to Co^{3+} during the process of preparation. Therefore, it can be supposed that the improved catalytic activities of the catalysts after introducing of Mg^{2+} might be ascribed to the co-existence of Co^{2+} and Co^{3+} in the structure of $Co_2Mg_xAl-LDHs$ samples. Although the efficiency in terms of the yield of products is not the best compared with some other reaction systems, the present study may be helpful for designing the more efficient catalysts. The detailed research is in progress to study the mechanism of the reaction catalyzed by $Co_2Mg_xAl-LDHs$.

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Table and figures

Fig. 1. XRD patterns and SEM image of Co₂Mg_xAl-LDH samples

Table 1 Sample notation and chemical compositions of Co₂AlMg_x-LDHs

Fig. 2. The DR UV-Vis spectra of Co₂Mg_xAl-LDHs samples

Table 2 The catalytic performance of Co₂Mg_xAl-LDHs in the selective oxidation of benzyl alcohol

Fig. 3. Suggested mechanism for the formation of active radicals over Co₂Mg_xAl-LDHs catalysts

CCC CCC



Fig. 1. XRD patterns and SEM image of Co₂Mg_xAl-LDH samples

Sample	Weight content (%)				\mathbf{S}_{BET}	Pore volume	Pore size	Basicity at H_ =
	Со	Al	Mg	- CO · Mg · Al	(m ² g ⁻¹)	(cm^2g^{-1})	(nm)	$7.6 \sim 15.0 \pmod{g^{-1}}$
Co ₂ Al-LDH	38.63	22.33	-	1.7 : 0 : 1	59	0.23	14.8	0.986
Co ₂ Mg _{0.5} Al-LDH	33.95	8.89	3.62	$1.6 \stackrel{\scriptstyle{.}}{} 0.4 \stackrel{\scriptstyle{.}}{} 1$	54	0.21	14.7	1.144
Co ₂ MgAl-LDH	29.03	8.79	5.96	$1.4 \stackrel{\scriptstyle{.}_{}}{} 0.7 \stackrel{\scriptstyle{.}_{}}{} 1$	52	0.23	16.4	1.309
Co ₂ Mg _{1.5} Al-LDH	25.78	6.35	8.03	1.7 : 1.3 : 1	57	0.27	17.2	1.408
Co ₂ Mg ₂ Al-LDH	24.77	6.43	10.11	1.6 : 1.6 : 1	47	0.20	16.8	1.983

Table 1 Sample notation and chemical compositions of Co2AlMgx-LDHs

J:1 :04:1 14:07:1 5. 17:13:1 57 .1 16:16:1 47



Fig. 2. The DR UV-Vis spectra of Co₂Mg_xAl-LDHs samples

A (x=0); B (x=0.5); C (x=1.0); D (x=1.5); E (x=2.0)

				Selectivity (%)		
Run	Catalyst	Conversion (%)	Yield ^b (%)	Benzaldehyde	Benzoic acid	
1	Co ₂ Al-LDH	26.9	24.5	91.1	8.9	
2	Co ₂ Mg _{0.5} Al-LDH	38.1	33.8	88.9	11.1	
3	Co ₂ MgAl-LDH	39.5	35.2	89.2	10.8	
4	Co ₂ Mg _{1.5} Al-LDH	33.8	31.0	92.0	8.0	
5	Co ₂ Mg ₂ Al-LDH	32.1	30.5	94.9	5.1	
6	Co ₂ Al-LDH+K ₂ CO ₃ ^c	26.8	26.8	100	0	
7	Co ₂ MgAl-LDH ^{3rd}	38.7	35.0	90.5	10.5	
8	Co ₂ MgAl-LDH ^{5th}	38.9	34.7	89.3	10.7	

Table 2 The catalytic performance of Co₂Mg_xAl-LDHs in the selective oxidation of benzyl alcohol ^a

^a Reaction conditions: benzyl alcohol 0.02 mol; solvent 8 mL; Co₂Mg_xAl-LDHs 100 mg; TBHP 0.04 mol; ^b yield of benzaldehyde; ^c Co₂Al-LDH

100 mg, K₂CO₃ 13.9 mg.



Fig. 3. Suggested mechanism for the formation of active radicals over Co₂Mg_xAl-LDHs catalysts

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



Highlights

- 1 $Co_2Mg_xAl-LDHs$ with different Mg^{2+} contents were introduced to the oxidation of benzyl alcohol.
- 2 The basicity of the catalyst could contribute to the high selectivity of aldehyde in the reaction.
- 3 Introducing Mg^{2+} ions can promote the oxidation process of Co^{2+} to Co^{3+} .
- 4 The improved catalytic activities might be ascribed to the co-existence of Co^{2+} and Co^{3+} .

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