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Synthesis of Nanosize Supported Hydrotalcite-like Compounds $CoAl_x(OH)_{2+2x}(CO_3)_y(NO_3)_{x-2y}\cdot nH_2O$ on γ-Al_2O_3

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Nanosize (5−7 nm) supported Co^{II}Al-hydrotalcite-like compounds (Co^{II}Al-HTlcs) on γ-Al_2O_3 have been synthesized with a coprecipitation method in which the γ-Al_2O_3 acts as a source of aluminum for coprecipitation and a support for the compound formation. The synthesis parameters identified are initial concentrations of metal and base, aging time, and more importantly, the addition sequence of the metal or base solution. Using multiple characterization methods, the supported Co^{II}Al-HTlcs have been investigated for their structural phase and chemical composition. The chemical formula determined for these samples is $CoAl_x(OH)_{2+2x}(CO_3)_y(NO_3)_{x-2y}\cdot nH_2O/\gamma$-$Al_2O_3$, where $x = 0.25-0.40$, $y = 0.02-0.07$, and $n = 1.3-1.7$, and the distance of inter-brucite-like sheets (d_{003}) is in the range of 7.65−7.79 Å. Because of the formation of nanosize crystallites, decomposition of the supported Co^{II}Al-HTlcs occurs at ≈211−217 °C, which is markedly lower than that of unsupported pure Co^{II}Al-HTlcs. After calcination in air, the supported Co^{II}Al-HTlcs are transformed into cubic spinel oxides $Co^{II}Co_{2-x}{}^{III}Al_xO_4/\gamma$-$Al_2O_3$ and high catalytic activity for the N_2O decomposition reaction is observed for these supported spinel catalysts.

Introduction

In recent years, research on layered double hydroxides (LDHs) has become an active field in materials research of layered solids.[1−10] Among these interesting layered materials, hydrotalcite-like compounds (HTlcs), in particular, have attracted great attention because of their intercalation ability and other important physicochemical properties for technological applications as anion adsorbents, medicine stabilizers, and ion exchangers.[1,5−7,9]

In the hydrotalcite-like compound, a divalent metal cation is located in the center of an oxygen octahedron constructed by six hydroxyl groups. The resultant octahedrons then share their edges to form two-dimensional infinite sheets (C_6-type), which is similar to the basic structure of brucite $Mg(OH)_2$.[1] The brucite-like sheets can stack upon one another to form a three-dimensional solid, owing to various chemical interactions between the sheets. Nonetheless, if some of the divalent cations in the octahedrons are substituted by trivalent cations, organic or inorganic anions including oxometalates (from preparative solution) will be intercalated into the inter-brucite-like sheet space (or interlayer space) to compensate extra charges possessed by the trivalent cations in substitution. This anion intercalation process therefore leads to the formation of a hydrotalcite-like structure, which is named after the natural hydrotalcite compound, $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$.[1]

Calcined HTlcs are often used as catalysts in heterogeneous catalysis. In particular, various transition metal cations (mainly divalent and trivalent) have been introduced into the brucite-like sheets of HTlcs. In addition to common anions such as nitrate and/or carbonate in the interlayer space, oxometalates (from low to high nuclearity), complexes of macrocyclic ligands, and polymeric anions have also been intercalated into the interlayer space of the HTlcs.[10−13] Recent research development has shown great flexibility of HTlcs in tailoring catalytic properties and photophysical properties of the materials to meet a specific application.[10]

For practical catalytic applications, it is desirable to use supported catalysts instead of unsupported types to increase metal utilization. Furthermore, if the support-type catalysts are used, mechanical strength and thermal stability of the catalysts can be enhanced to withstand harsher industrial reaction conditions. The research on synthesis of supported HTlcs, therefore, is

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an important area for both fundamental interest and practical usage of the layered materials. Although the supported HTlcs had been prepared as early as the 1970s,[1] detailed fundamental investigations on the preparation method and resultant compounds were only started recently, and the information revealed is still very limited. Since only 1995, for example, the investigation on supported $Ni^{II}Al$- and $Co^{II}Al$-hydrotalcite-type coprecipitates on γ-alumina (γ-Al_2O_3) support has been carried out, aiming at a fundamental understanding of dissolution and reprecipitation of the alumina support in a neutral or near neutral pH range.[14,15] It is noted that the actual chemical composition and structural data (such as distance of inter-brucite-like sheets and crystallite size) of these supported HTlcs have not yet been available.[14,15] Other important investigations of the general issues of the impregnation method for solid catalytic materials at the molecular level have been conducted in recent years. Such examples include an investigation of ligand-promoted alumina dissolution in preparation of MoO_x/γ-Al_2O_3 catalysts and interfacial coordination chemistry of Ni^{II} complexes and surface interaction.[16-18]

In this paper, we report an investigation of the synthesis of nanocrystalline supported $Co^{II}Al$-HTlcs on γ-Al_2O_3. More specifically, our effort is focused on obtaining the chemical composition and structural information of the supported compounds using multiple characterization techniques, concerning the scarcity of these data in the literature.[1] The as-prepared $Co^{II}Al$-HTlcs/γ-Al_2O_3 are also thermally converted into supported catalytic oxides CoAl-spinels/γ-Al_2O_3 for a model catalytic test using N_2O decomposition as a probe reaction, noting that the N_2O gas is one of the six prime greenhouse gases under today's environmental concern.[4] Several important synthetic parameters for this type of HTlc preparation have been identified and examined in the present work.

Experimental Section

Materials Preparation. The as-received γ-Al_2O_3 pellet support (Alfa, 99% metal basis, 90 $m^2\ g^{-1}$, $\phi = 3.2$ mm, $h = 3.4$ mm) was grinded into small particles. The size between 45 and 16 mesh (aperture: 345−1000 μm) was selected as the support for synthesis. Two preparation methods for the supported $Co^{II}Al$-HTlcs can be described as the following (see also Table 1 and Figure 1): (A) 3.0 g of the above-prepared γ-Al_2O_3 particles was soaked in a three-necked round-bottom flask that contained 50.0 mL of ammoniacal solution (Merck) for 1 day, after which 20.0 mL of cobalt solution ($Co(NO_3)_2 \cdot 6H_2O$, >99.0%, Fluka) was added dropwise to the above solution−solid system; (B) 3.0 g of the γ-Al_2O_3 particles was added to the reaction flask containing 20.0 mL of cobalt nitrate solution for 5 h, followed by an addition of 50.0 mL of ammoniacal solution. In both cases, stirring of the solution−solid mixture was done manually, after which an aging treatment was followed. During the course of precipitation and aging, purified nitrogen (Soxal, 99.9995%) at a rate of 50 mL min^{-1} was flowed through the reaction flask to ensure a nonoxidative atmosphere. After aging, the final supported products were separated from the solution and as-formed precipitates (which were not supported on γ-Al_2O_3) by using a mesh wire filter at 80 mesh (aperture: 180 μm, which was much larger than the size of unsupported precipitates). This separation process can be ensured by the color of the materials, as the unsupported precipitates have an earth-brown color while the supported $Co^{II}Al$-HTlcs show a light yellow-brown color. The supported samples were washed thoroughly with deionized water. The above processes were all carried out at room temperature. The samples were then dried in a vacuum desiccator at room temperature overnight. To further validate the above separation method, the as-received γ-Al_2O_3 pellet support (uncrushed; large size at $\phi = 3.2$ mm, $h = 3.4$ mm) was also used in the preparation of supported $Co^{II}Al$-HTlcs using the same processes as those in the particulate support (sized at 345−1000 μm).

Table 1. Synthesis Conditions and Resulted Cobalt Weight Percentage in the Supported HTlcs

sample	concentration (M)[a]	method[b]	aging time (h)	Co wt %[c]
A1	0.2	A	18	2.21
A2	0.5	A	18	3.06
A3	0.8	A	18	3.37
B1	0.5	B	48	3.64
B2	0.5	B	72	4.18
B3	0.8	B	18	4.52
B4	0.8	B	48	5.87
B5	0.8	B	72	6.07

[a] Concentrations of both Co^{2+} and $NH_3 \cdot H_2O$ solutions are the same. [b] 20.0 mL Co^{2+} solution reacts with 50.0 mL $NH_3 \cdot H_2O$ solution in different addition orders (see the text and Figure 1). [c] Weight percentage of cobalt element with respect to the total weight of sample (supported HTlc + γ-Al_2O_3 support) determined by ICP analysis.

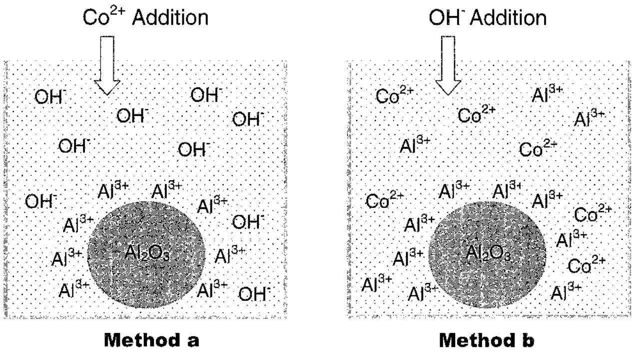

Figure 1. Two methods used in the present coprecipitation experiment, noting that the counterions of the starting reagents are not shown.

The homogeneous coprecipitation method was also used to prepare pure-phase samples for reference purposes. In particular, the HTlc of $CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47} \cdot 2.2H_2O$ was prepared in the following way. Briefly, 20.0 mL of 1.0 M aqueous cobalt and aluminum nitrate solution at a Co^{2+}:Al^{3+} ratio equal to 2:1 was added to 100.0 mL of 0.5 M ammoniacal solution rapidly in the same reaction flask with additional aging at 25 or 65 °C for 18 h. Before the samples were used for catalytic decomposition of N_2O, they (including as-received γ-Al_2O_3 support) were calcined at 500 °C in static air for 4 h. Two other reference compounds, brucite-like β-$Co(OH)_2$ and hydrotalcite-like $CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23} \cdot 2.0H_2O$, were prepared respectively according to literature reports.[4,8]

Materials Characterization. *XRD Measurement.* The crystallographic information of the samples was investigated by powder X-ray diffraction (XRD). The XRD patterns with diffraction intensity versus 2θ were recorded in a Shimadzu X-ray diffractometer (model 6000) with Cu Kα radiation ($\lambda = 1.5418$ Å) from 5° to 70° at a scanning speed of 1° min^{-1}. X-ray

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tube voltage and current were set at 40 kV and 30 mA, respectively. The average crystallite sizes of the samples were estimated using the Debye−Scherrer formula from the full-width at half maximum (fwhm) of some intense peaks.[19]

FTIR Measurement. The as-prepared samples were characterized by Fourier transform infrared (FTIR) spectroscopy in a Shimadzu spectrometer (model 8108), using the potassium bromide (KBr) pellet technique. The weight ratio of sample to KBr was fixed at 1:100. One hundred scans were performed for each spectrum to ensure a good signal-to-noise ratio.

ICP Measurement. The weight percentage of cobalt in the samples was measured with inductive coupled plasma (ICP) elemental analysis in a Perkin−Elmer ICP instrument (model OPTIMA-300).

CHN Measurement. The weight percentages of carbon, hydrogen, and nitrogen in the samples were provided by CHN analysis in a Perkin−Elmer 2400 CHN elemental analyzer.

TGA/DrTGA Measurement. Around 15 mg of each sample was analyzed by thermogravimetric analysis (TGA, Shimadzu TGA-50). The furnace temperature was heated from room temperature to 600 °C at a rate of 10 °C min^{-1} and then cooled naturally. The whole TGA measurement was made under an air atmosphere at a gas flow rate of 60 mL min^{-1}.

XPS Measurement. X-ray photoelectron spectroscopy (XPS) investigation was conducted in an AXIS-Hsi spectrometer (Kratos Analytical) using a monochromated Al Kα X-ray source (1486.6 eV). The XPS spectra of the studied elements were measured with the constant analyzer pass energy of 20.0 eV. All binding energies (BE) were referenced to the C 1s peak (BE = 284.7 eV) arising from adventitious carbon. Prior to the peak deconvolution, X-ray satellites and inelastic background (Shirley-type) were subtracted for all spectra.

BET Measurement. Adsorption isotherms of nitrogen at −195.8 °C on the 500 °C-calcined samples (including a 500 °C-heated γ-Al_2O_3 support) were measured at various partial pressures in a Quantachrome NOVA-1000 apparatus. Specific surface areas were determined with the Brunauer−Emmett−Teller (BET) method. Before the measurements, the samples were degassed for 3 h at 350 °C in an outgassing station of the adsorption apparatus.

Catalytic Activity Measurement. For N_2O decomposition experiments, 1.0 g of the 500 °C-heated samples was loaded into a quartz tube reactor (i.d. = 1.0 cm), which was fed with a gas stream of 30 mol % N_2O (balanced with helium) at atmospheric pressure. The inlet gas flow rate was kept at 25 mL min^{-1} (or GHSV at 1245 h^{-1}). The particle size of the catalysts was between 45 and 16 mesh (aperture: 345−1000 μm). All catalysts were kept at 400 °C overnight in the reactor with the same feed gas flowing before the acquisition of conversion data.[7,9] Gas composition of the outlet was analyzed by gas chromatography (GC) in a Perkin−Elmer Autosystem XL using a thermal conductivity detector (TCD) and a Porapak Q column (4 feet in length and 80−100 mesh).

Results and Discussion

Synthesis and Structural Determination. Two methods used in sample preparation (Co^{2+} and Al^{3+} coprecipitation) are depicted in Figure 1. In method A, γ-Al_2O_3 particles were soaked in ammoniacal solution for 1 day and the Al^{3+} could be partially dissolved in solution before Co^{2+} was introduced. As expected when using this method, the coprecipitation reaction is proportional to both the amount of Co^{2+} cations added and the initial concentration of ammoniacal solution, which is reflected in the increasing cobalt weight gain in the samples shown in Table 1 (A1−A3). Nonetheless, with method B, the above coprecipitation reaction can be significantly enhanced (sample series B1−B5). With the same amounts of initial Co^{2+} and OH^- (such as A3 versus B3, 18 h of aging, Table 1), more cobalt metal could be deposited on the γ-Al_2O_3 support (Co = 3.37 wt % versus 4.52 wt %). In addition to the variations in the initial concentrations of Co^{2+} and $NH_3\cdot H_2O$ solutions, the aging effect was also examined in the samples B1−B5, which indicates that the cobalt content on the γ-Al_2O_3 support is also proportional to the aging time adopted.

The above cobalt weight gain using method B can be attributed to a higher concentration of dissolved Al^{3+} in the solution. With a dialysis membrane, dissolution of Al^{3+} from solid alumina had been examined.[14] This dissolution investigation indicates a significant weight loss of alumina when Ni^{2+} or Co^{2+} is added, even with the neutral solution at pH = 7.2, and the promotion effect of these cations on the alumina dissolution has been since proposed.[14] It is thus understandable that the higher content of cobalt found in the B1−B5 samples is a result of the coprecipitation of Co^{2+} and Al^{3+} on the alumina support, noting that the solubility product K_{sp} of the Co^{II}Al-HTlcs is much smaller than those of individual metal precipitates of either Co^{2+} or Al^{3+} in a basic medium.[20]

Figure 2 shows the XRD patterns for the above-prepared samples along with that of the γ-Al_2O_3 support.[21,22] It is clear that the diffraction patterns of the hydrotalcite-like phase are superimposed on top of the γ-Al_2O_3 diffractions, indicating the formation of HTlcs on the surface of the alumina support. These diffraction patterns also show that the major composition in all samples is γ-Al_2O_3 and it is quite amorphous. To have a better XRD assignment for the supported HTlcs in Figure 2, XRD patterns of pure reference compounds β-$Co(OH)_2$ (R1), $CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47}\cdot 2.2H_2O$ (R2), and $CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23}\cdot 2.0H_2O$ (R3) are also plotted in Figure 3. In comparison, the formation of simple cobalt hydroxide (R1) on γ-Al_2O_3 can be ruled out immediately because there is no similarity among the diffraction patterns. The layered structures of $CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47}\cdot 2.2H_2O$ and $CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23}\cdot 2.0H_2O$ exhibit sharp symmetric peaks for (003), (006), (110), and (113) planes and broad asymmetric peaks for (009), (012), and (015) planes.[1] The inter-brucite-like sheet distances (d_{003}) for the above two compounds are 8.71 and 7.53 Å, respectively. In the presently prepared A1−A3 and B1−B5 samples, most of the above diffraction peaks can be identified, which indicates that the desired compounds, Co^{II}Al-HTlcs, are indeed present in these samples. More specifically, the peak positions of XRD patterns for the supported Co^{II}-Al-HTlcs are closer to those of $CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23}\cdot 2.0H_2O$ (R3), noting that carbonate anions are intercalated in this reference compound.

The effects of concentrations and aging time on the HTlc formation are quite obvious. As reported in Table 2, it is found that the increase of the concentrations of starting chemicals results in higher crystallinity for the samples by comparison of the shape and intensity of the peaks in Figure 2. The intensity of the diffraction

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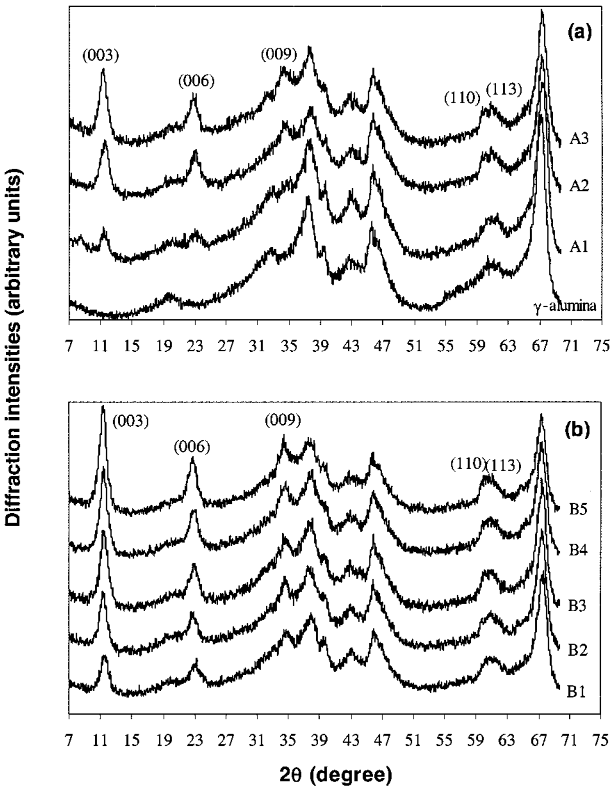

Figure 2. XRD patterns of the supported HTlcs (peaks are labeled with indices of reflection plane): (a) sample series A1–A3 (together with the diffraction pattern of γ-Al_2O_3 support) and (b) sample series B1–B5.

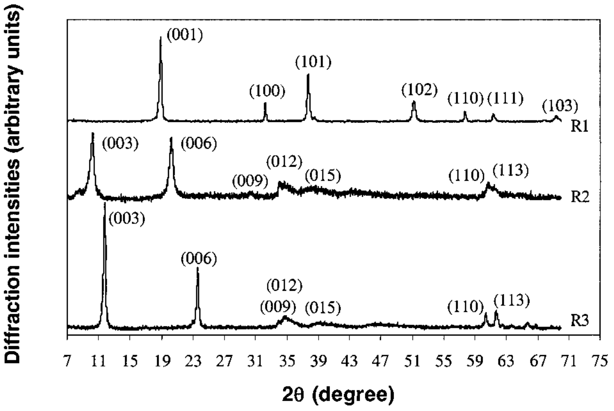

Figure 3. XRD patterns of three reference compounds: β-$Co(OH)_2$ (R1), $CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47}{\cdot}2.2H_2O$ (R2), and $CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23}{\cdot}2.0H_2O$ (R3).

pattern that resembles the HTlcs is proportional to the cobalt content in each sample series. Further XRD analysis for B-series samples indicates that the crystallite size is increased with the increase of aging time when the concentration of the starting reactants is high. For instance, the average crystallite size of sample B5 (0.8 M, aging time 72 h, Table 1) is higher than that of B4 (0.8 M, aging time 48 h, Table 1), as aging allows the formed HTlcs to grow in size and/or to be better crystallized on the support. On the other hand, for the sample pair of B1 and B2, which were prepared in lower concentration solutions (0.5 M, Table 1), their average crystallite sizes are about the same (Table 2). The ICP analysis also shows a consistent increase of the weight percentage of cobalt as the aging time is increased.

Table 2. Structural Data for Some Reference and Supported HTlcs

sample	d_{003} (Å)	crystallite size (nm)		
R2	8.71	12.6[a]	13.0[b]	12.8[c]
R3	7.53	27.4	26.4	26.9
B1	7.65	6.4	5.1	5.7
B2	7.77	6.3	5.0	5.7
B4	7.73	6.1	5.3	5.7
B5	7.79	7.1	5.8	6.5

[a] fwhm of peak (003) is used in calculation. [b] fwhm of peak (006) is used in calculation. [c] Average value of crystallite size from the notes *a* and *b*.

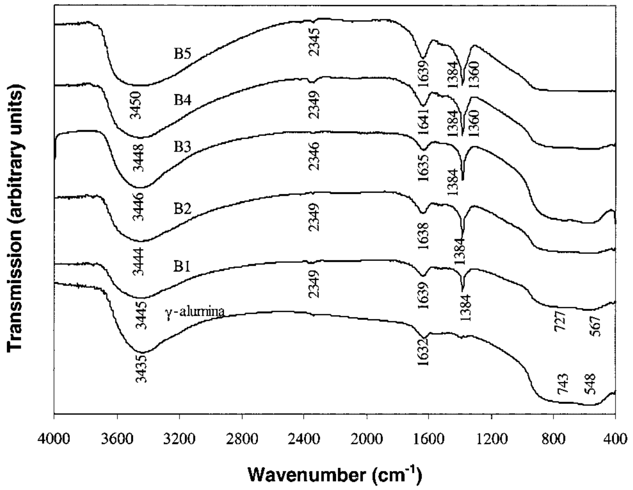

Figure 4. FTIR spectra of five supported hydrotalcite-like compounds B1, B2, B3, B4, and B5.

Compared to the work reported in the literature,[14,15] the crystallinity of our supported HTlcs in the present study has been sufficiently high for us to perform some preliminary crystallographic investigation for the supported samples, such as the d_{003} and crystallite size reported in Table 2, although the (110) peaks are still not well resolved for calculation of *a* constants. Interestingly, d_{003} spacings (7.65–7.79 Å) of the supported samples range between those of R2 and R3, which suggests that the supported samples may contain both NO_3^- and CO_3^{2-} anions in the interlayer space, which will be addressed further shortly.

It should be mentioned that the supported $Co^{II}Al$-HTlcs on the large γ-Al_2O_3 pellet support (uncrushed) give essentially the same XRD patterns as those reported in Figure 2. Because the small, unsupported precipitates (XRD pattern indicates they are a mixture of β-$Co(OH)_2$ and $Co^{II}Al$–HTlcs) can be easily separated and washed away from these large $Co^{II}Al$-HTlcs/γ-Al_2O_3 pellets, we confirm the presence of $Co^{II}Al$-HTlcs on the surfaces of all the supports.

Determination of Chemical Composition. Figure 4 displays FTIR spectra of samples B1–B5 along with that of the support γ-Al_2O_3. A broad absorption band centered at $\approx$3444–3450 cm^{-1} present in all samples is attributed to O–H stretching vibration of hydrogen-bonded hydroxyl groups in the brucite-like sheets and of water in the interlayer space.[6,23,24] Such a band is also present in the spectrum for the γ-Al_2O_3, but

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centered in a lower wavenumber region, 3435 cm^{-1}. The blue shift in O−H vibration in the B1−B5 spectra indicates the formation of supported HTlcs on the γ-Al_2O_3, as the unsupported Co^{II}Al-HTlcs had shown a O−H stretching at ≈3500 cm^{-1}.[4b] Water-bending vibrations of the interlayer water are observed for all samples at 1641−1632 cm^{-1}. The intensity of this band is proportional to the cobalt content in the supported HTlcs. The sharp peaks at 1384 cm^{-1} can be assigned to NO_3^- anions (D_{3h} symmetry; ν_3 mode) intercalated in the interlayer space of the HTlcs.[6,23,25] It is noted that the base of the 1384-cm^{-1} peak is rather broad. In fact, there are also absorption bands at around 1425 and 1360 cm^{-1} shouldering both sides of the peak. These absorption bands can be assigned to the CO_3^{2-} anion (C_{2v} symmetry and D_{3h} symmetry, respectively) in the interlayer space.[1,6,25] Therefore, two types of intercalated anions ($NO_3^- + CO_3^{2-}$) are present in the interlayer. The weak absorptions of CO_3^{2-} can also be found in the γ-Al_2O_3 support, owing to original impurities or the ability of CO_2 adsorption on the support surface. The absorptions at 2349−2345 cm^{-1} are due to the equipment detection of atmospheric CO_2. Finally, broad bands at wavenumbers 500−800 cm^{-1} are attributed to metal−oxygen vibrations, especially for Al−O vibration from the support material.[1,6,26]

In agreement with the above FTIR analysis, our investigation with the TGA/DrTGA method also indicates the formation of HTlcs on the alumina support. As shown in Figure 5, the broad bands in DrTGA curves before 150 °C are attributed to the release of interlayer water molecules. Unlike the pure-phase HTlcs (R2 and R3), the supported Co^{II}Al-HTlcs show a weak long-lasting water-release process. The weak band is simply due to only a small amount of HTlcs on the support while the long-lasting feature can be attributed to diffusion processes inside the pores of γ-Al_2O_3. The underneath hydrated alumina substrate is unlikely to contribute to this band, as its signal is negligible (refer to DrTGA curve of the γ-Al_2O_3). After all these considerations, the weight loss data over the 60−150 °C range have been utilized for determination of the interlayer water. In Figure 5, the bands of DrTGA curves that indicate the decomposition transition of the hydrotalcite-like phase to metal oxides (spinels) are centered at a similar temperature of 211−217 °C. Likewise, the pure-phase HTlcs (R2 and R3) would give sharper DrTGA peaks at higher temperature because of the well-crystallized samples. For example, the sample $CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47}\cdot 2.2H_2O$ (R2) aged at 65 °C gives an endothermic peak (decomposition of hydrotalcite-like structure) at 276 °C. However, when the same precipitate (R2) is aged at room temperature, the decomposition temperature is shifted down to 255 °C. This temperature shift can be attributed to the reduction in crystallite size because smaller crystallites are observed in the 25 °C-aged sample. As revealed in the data in Table 2, the average crystallite sizes for the supported HTlcs are only half of that for the R2 sample. It is therefore not surprising to observe the low decomposition temperatures of the supported samples.

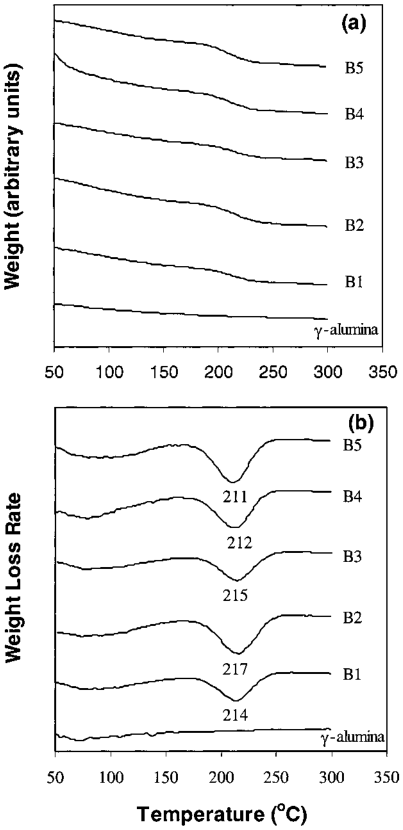

Figure 5. TGA curves (a) and DrTGA curves (b) of five supported hydrotalcite-like compounds B1, B2, B3, B4, and B5, together with those of the γ-Al_2O_3 support; air flow rate at 60 mL min^{-1}.

Table 3 summarizes the measured weight percentages of Co, C, and N for some selected samples. The result of CHN analysis confirms that both carbonate and nitrate anions could be present in the interlayer, as detailed in the chemical formulas listed. It is clear now that the relative content of CO_3^{2-} (related to NO_3^-) in the interlayer space is much higher than that of R2, which results in a significant reduction in d_{003} because one CO_3^{2-} is equivalent to two NO_3^- anions for the charge neutrality and the replacement of NO_3^- with CO_3^{2-} will reduce the number of total anions in the interlayer space. The d_{003} values of B1−B5 are thus closer to that of R3 (Table 2). The carbonate anions intercalated in our supported HTlcs can be traced back to the γ-Al_2O_3 that was used as both an aluminum source and a support in the present study. As mentioned earlier, the CO_2 can be easily adsorbed on the γ-Al_2O_3, and indeed our carbon elemental analysis indicates there is 0.10 wt % of C in the as-received γ-Al_2O_3 support. Of course, atmospheric CO_2 could also dissolve into our ammoniacal solutions during the base preparation, although it is less likely, because only a negligible amount of carbonate anions was found in the pure-phase HTlcs (R2) that were prepared with aluminum nitrate instead of the γ-Al_2O_3 (see Experimental Section). The deduced molar ratios of Co^{2+}:Al^{3+} are based on the total charge balance between the brucite-like sheets and the intercalated anions.[1] The range of Co^{2+}:Al^{3+} = 2.5 to 4.0 agrees well with the common expected values of M^{II}:M^{III} (2.0 to 4.0) for the formation of pure HTlcs.[1]

Further compositional confirmation of the above-supported HTlcs has been made by the XPS study, and

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Table 3. Chemical Composition Analysis for Some Reference and Supported HTlcs

sample	C[a]	N[a]	Co[b]	Co^{2+}:Al^{3+} [c]	chemical formula of HTlcs[d]	HTlcs wt %[e]
R2	0.12	3.40	30.42	2.00	$CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47}\cdot 2.2H_2O$	100
R3	1.62	0.01	34.65	2.21	$CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23}\cdot 2.0H_2O$	100
B1	0.05	0.23	3.64	2.49	$CoAl_{0.40}(OH)_{2.80}(CO_3)_{0.07}(NO_3)_{0.27}\cdot 1.7H_2O/\gamma\text{-}Al_2O_3$	10.45
B2	0.02	0.24	4.18	3.46	$CoAl_{0.29}(OH)_{2.58}(CO_3)_{0.02}(NO_3)_{0.24}\cdot 1.6H_2O/\gamma\text{-}Al_2O_3$	11.05
B4	0.04	0.25	5.87	4.06	$CoAl_{0.25}(OH)_{2.50}(CO_3)_{0.03}(NO_3)_{0.18}\cdot 1.5H_2O/\gamma\text{-}Al_2O_3$	14.71
B5	0.08	0.29	6.07	3.03	$CoAl_{0.33}(OH)_{2.66}(CO_3)_{0.06}(NO_3)_{0.20}\cdot 1.3H_2O/\gamma\text{-}Al_2O_3$	15.66

[a] Weight percentages of carbon and nitrogen elements with respect to the total weight of sample (supported HTlc + γ-Al_2O_3 support) determined by CHN analysis. These data have been calibrated with the background contents contributed from γ-Al_2O_3 support. [b] Weight percentage of cobalt element with respect to the total weight of sample (supported HTlc + γ-Al_2O_3 support) determined by ICP analysis. [c] Molar ratios of divalent cobalt to the trivalent aluminum in the supported HTlcs. [d] Based on the data in the notes *a*, *b*, and *c*. Water content in the formulas is determined from weight loss data of TGA (60−150 °C). [e] Weight percentage of the supported HTlcs with respect to the total sample weight (supported HTlc + γ-Al_2O_3 support).

Table 4. XPS Analysis Results on Binding Energies (Core Levels of Co 2p and Al 2p) of the Reference Samples and Supported HTlcs and Chemical Formulas of Spinel Oxides Derived from Their Respective Precursor HTlcs after Heating at 500 °C for 4 h

chemical formula	Co 2p (eV)	Al 2p (eV)	spinels formed
β-$Co(OH)_2$ (R1)	780.7		
$CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47}\cdot 2.2H_2O$ (R2)	781.6	74.7	$Co^{II}Co_{1.00}{}^{III}Al_{1.00}O_4$
$CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23}\cdot 2.0H_2O$ (R3)	780.8	74.1	$Co^{II}Co_{1.07}{}^{III}Al_{0.93}O_4$
$CoAl_{0.40}(OH)_{2.80}(CO_3)_{0.07}(NO_3)_{0.27}\cdot 1.7H_2O/\gamma\text{-}Al_2O_3$ (B1)	780.8	74.1	$Co^{II}Co_{1.14}{}^{III}Al_{0.86}O_4/\gamma\text{-}Al_2O_3$
$CoAl_{0.29}(OH)_{2.58}(CO_3)_{0.02}(NO_3)_{0.24}\cdot 1.6H_2O/\gamma\text{-}Al_2O_3$ (B2)	781.0	74.3	$Co^{II}Co_{1.33}{}^{III}Al_{0.67}O_4/\gamma\text{-}Al_2O_3$
$CoAl_{0.25}(OH)_{2.50}(CO_3)_{0.03}(NO_3)_{0.18}\cdot 1.5H_2O/\gamma\text{-}Al_2O_3$ (B4)	780.8	74.1	$Co^{II}Co_{1.41}{}^{III}Al_{0.59}O_4/\gamma\text{-}Al_2O_3$
$CoAl_{0.33}(OH)_{2.66}(CO_3)_{0.06}(NO_3)_{0.20}\cdot 1.3H_2O/\gamma\text{-}Al_2O_3$ (B5)	781.0	74.2	$Co^{II}Co_{1.26}{}^{III}Al_{0.74}O_4/\gamma\text{-}Al_2O_3$

the binding energies (eV) for metal elements are listed in Table 4. The binding energies of Co 2p for β-$Co(OH)_2$ (R1) and $CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23}\cdot 2.0H_2O$ (R3) are about the same (780.7 and 780.8 eV respectively), whereas that of $CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47}\cdot 2.2H_2O$ (R2) shows a pronounced shift of +0.8 eV to 781.6 eV when the anions CO_3^{2-} are replaced by NO_3^-. The binding energies of Co 2p for the supported HTlcs strongly indicate the CO_3^{2-} anions are also intercalated, in addition to NO_3^-, because the observed binding energies (in the region of 780.8−781.0 eV) are very similar to that of the pure sample R3 (with a only positive derivation of 0 to +0.2 eV). The similarity can be attributed to similar chemical states of cobalt in these samples (or similar chemical environment), which in turn gives similar inter-brucite-like sheet distances observed for the R3 and B1−B5 (d_{003}, Table 2). Further comparison of Al 2p binding energies, which indicates a +0.6-eV shift (74.1 eV for R3 versus 74.7 eV for R2, Table 4), gives also a conclusion that the chemical state of aluminum cations in HTlcs is strongly influenced by the type of the intercalated anions, in a manner similar to that of cobalt. The XPS results are therefore in good agreement with those from the CHN elemental analysis.

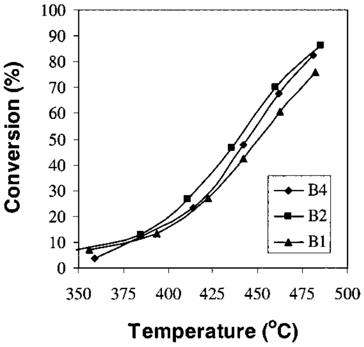

Figure 6. Conversion-versus-temperature curves for some representative 500 °C-calcined samples. Input stream of N_2O (30 mol %, balanced with He) was fed at a flow rate of 25 mL min^{-1}.

Evaluation of Catalytic Activity. After the supported HTlcs are heated at 500 °C in air, a cubic spinel phase is formed on the surface of the γ-Al_2O_3. The XRD patterns of the spinel phase can be clearly observed (not shown here), which are superimposed on that of the γ-Al_2O_3 support. The peak locations are similar to the oxide spinels prepared from pure HTlcs of $CoAl_{0.50}(OH)_{3.00}(CO_3)_{0.02}(NO_3)_{0.47}\cdot 2.2H_2O$ and $CoAl_{0.45}(OH)_{2.90}(CO_3)_{0.23}\cdot 2.0H_2O$, although the peaks are not as sharp due to a smaller weight percentage of the precursor phase (HTlcs) and nanosize crystallites in the samples (Table 2). The formation of these oxide spinels ($Co^{II}Co_{2-x}{}^{III}Al_xO_4/\gamma\text{-}Al_2O_3$, Table 4) requires some of the divalent cobalt to be oxidized.[27] It should be reported that the specific surface areas of γ-Al_2O_3 and $Co^{II}Co_{2-x}{}^{III}Al_xO_4/\gamma\text{-}Al_2O_3$ have similar values, 73−78 $m^2\ g^{-1}$, after the samples were heated at 500 °C for 4 h, compared to 90 $m^2\ g^{-1}$ for the as-received γ-Al_2O_3 support.

Chemical reactivity of the 500 °C-calcined samples ($Co^{II}Co_{2-x}{}^{III}Al_xO_4/\gamma\text{-}Al_2O_3$, Table 2) has been tested in the catalytic decomposition of nitrous oxide, which converts the greenhouse gas N_2O into harmless N_2 and O_2.[7,9,28] Three samples, B1, B2, and B4, were selected for the test in view of their gradual increase in the Co:Al ratio in the supported HTlcs (Table 3) while having similar crystallite sizes for the HTlc phase before calcination (Table 2). The resultant conversion-versus-temperature curves are displayed in Figure 6 for comparison. As expected, all conversion curves increase as the reaction temperature is increased. Among the three samples, B2 gives the highest catalytic activity compared to B1 and B4. Although the weight percentage of cobalt is increased in the order of B1, B2, and B4

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(3.64, 4.18, and 5.87 wt %), higher loading of the active metal would not necessarily lead to higher conversion. In heterogeneous catalysis, the fundamental factors that influence the catalyst activity are the specific surface area, number of active sites per specific surface area, and the activity of the active site.[9] When the amount of cobalt exceeds a certain level, final dispersion of the active sites (which are cobalt related in the current case[7,9]) on the support surface will be poor and the catalytic activity will no longer increase linearly, which explains our observation that sample B4 has lower activity than sample B2. Other factors contributing to the activity should also be considered. For example, a "right" molar ratio of Co^{2+}:Al^{3+} in the precursor HTlcs may help to generate more active sites in the final spinel catalysts, in addition to the absolute cobalt content. The activity of sample B2 at 485 °C is ≈16 mmol (N_2O) g^{-1} h^{-1}, which is higher than that of a reported Ru/γ-Al_2O_3 catalyst tested under similar conditions with activity of 12.6 mmol (N_2O) g^{-1} h^{-1}.[28]

Conclusions

In summary, nanocrystalline supported Co^{II}Al-hydrotalcite-like compounds $CoAl_x(OH)_{2+2x}(CO_3)_y(NO_3)_{x-2y}\cdot nH_2O/\gamma\text{-}Al_2O_3$ ($x = 0.25-0.40$; $y = 0.02-0.07$; $n = 1.3-1.7$) can be prepared at various cobalt contents (in the total sample) using the alumina dissolution and reprecipitation method. The initial concentrations of metal and base, aging time, and addition sequence of the metal or base solution are important synthesis parameters in determining final structure and composition of the supported Co^{II}Al-HTlcs. The distance of inter-brucite-like sheets (d_{003}), which is in the range of 7.65−7.79 Å, depends largely on the type of anions intercalated. Similar binding energies of metal species (Co 2p and Al 2p) observed among the supported Co^{II}Al-HTlcs can be attributed to similar inter-brucite-like distances. The decomposition temperature of the supported Co^{II}Al-HTlcs at 211−217 °C, which is markedly lower than that of unsupported pure HTlcs, can be explained by the formation of nanosize crystallites (5−7 nm). Air calcination converts the supported Co^{II}Al-HTlcs into cubic spinel oxides $Co^{II}Co_{2-x}{}^{III}Al_xO_4/\gamma\text{-}Al_2O_3$, and the highest activity for a high-concentration N_2O (30 mol %) decomposition test is ≈16 mmol (N_2O) g^{-1} h^{-1} using an optimal supported spinel under the studied conditions.

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