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Reduction of $Ni^{2+}-Al^{3+}$ and $Cu^{2+}-Al^{3+}$ Layered Double Hydroxides to Metallic Ni^0 and Cu^0 via Polyol Treatment

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The reduction of nickel (Ni^{2+}) and copper (Cu^{2+}) to their metallic forms is reported for Ni−Al and Cu−Al layered double hydroxides (LDHs). Ethylene glycol is used as the reducing agent (the so-called polyol process). The degree of reduction of both cations was found to be dependent on the time and temperature of treatment and the nature of the anions located between the hydroxide layers. The process was found to be more efficient in reducing Cu^{2+} than Ni^{2+}; substantial reduction of Cu^{2+} was obtained after 3 h at 200 °C, whereas the Ni^{2+} is not completely reduced after 192 h of treatment at this temperature.

Introduction

There is considerable interest in the chemistry and potential uses of layered double hydroxides (also referred to as anionic clays).[1] Their structure consists of positively charged metal hydroxide sheets with anions and water molecules located between the layers. They have the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]A_{x/n}\cdot mH_2O$, where M^{II} is a divalent cation, M^{III} is a trivalent cation, and A^{n-} an anion of charge n.

The preparation of small monodispersed transition metal particles by reducing metal salts in ethylene glycol (the so-called polyol process) has been reported.[2] This reduction occurs at a much lower temperature than can be achieved in a hydrogen atmosphere.[2] The method has also been used to prepare metallic copper and nickel supported on montmorillonite[3] and zeolites.[4] When supported on porous materials, such as zeolites[5,6] and pillared clays,[7,8] the metals possess interesting catalytic properties.[5,6]

In contrast to the reduction of nickel or copper in zeolite or clay frameworks, few studies have been reported concerning the reduction of nickel contained within a layered double hydroxide matrix—using either the polyol process[9] or hydrogen.[10,11]

Here, we describe the reduction of nickel and copper in a LDH with aluminum as the trivalent cation in the hydroxide layers. The influence which the nature of the interlayer anion has on the reduction process is also investigated. The resulting materials were examined by powder X-ray diffraction (PXRD), chemical analysis, Fourier transform infrared spectroscopy (FTIR), and temperature-programmed reduction (TPR) techniques.

Experimental Section

Preparation of Samples. The carbonate Ni−Al and Cu−Al LDHs ($Ni-Al-CO_3$ and $Cu-Al-CO_3$) were prepared by standard coprecipitation methods.[12] A nitrate solution (100 cm^3) containing 0.4 mol of nickel (or copper, 0.1 mol) and aluminum nitrate (with M^{2+}/M^{3+} ratio equal to 2) was added dropwise to a solution of 100 mL of 0.5 M of sodium carbonate. The pH was kept close to 10 by continuous addition of sodium hydroxide solution (2 M). The resulting slurry was aged at 55 °C for 18 h, filtered, washed, and dried at 60 °C overnight.

The terephthalate (TA) LDH precursors were prepared by the direct synthesis method.[13] Nickel or copper nitrate (0.056 mol) and 0.028 mol of aluminum nitrate were dissolved in 50 cm^3 of deionized water (Ni/Al or Cu/Al close to 2). The mixture was added dropwise (in air) to a solution of 0.056 mol of TA acid dissolved in a sodium hydroxide solution at 55 °C. The pH was held constant at 10 by the addition of 2 M sodium hydroxide solution. The resulting slurry was aged at 55 °C for 18 h, filtered, washed with 2 L of boiled deionized water and dried at 60 °C overnight. The samples are designed Ni−Al−TA and Cu−Al−TA.

The decavanadate LDHs ($Ni-Al-V_{10}O_{28}$ and $Cu-Al-V_{10}O_{28}$) were prepared by anion exchange of the carbonate LDHs.[14] The air-dried $Ni-Al-CO_3$ or $Cu-Al-CO_3$ (1.5 g) was suspended in 100 mL of water for 2 h. Sodium metavanadate (3 g, $NaVO_3$) was dissolved in 75 mL of deionized water and the pH of the solution adjusted to a value of 4.5 by the addition of 0.5 M HCl. The metavanadate solution was then added dropwise to the LDH suspension, and the pH of the mixture maintained at 4.5 by the further addition of 0.5 M HCl solution. The resulting suspension was aged for 3 h, filtered,

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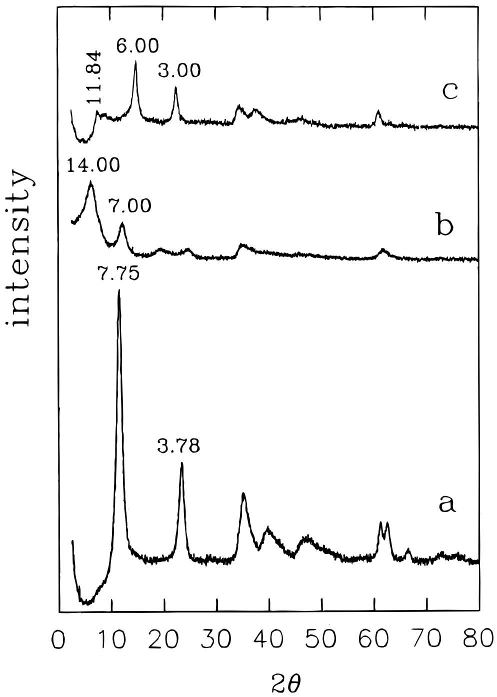

Figure 1. PXRD patterns of the Ni−Al LDHs intercalated with different anions: (a) CO_3 (carbonate), (b) TA (terephthalate), and (c) $V_{10}O_{28}$ (decavanadate).

and washed with hot deionized water. Samples were dried at 60 °C overnight. The samples are designed Ni−Al−$V_{10}O_{28}$ and Cu−Al−$V_{10}O_{28}$.

For the polyol reduction process, approximately 500 mg of LDH sample was suspended in 100 mL of ethylene glycol and kept under reflux (200 °C) for periods from 3 to 192 h. A similar procedure was also followed for temperatures in the 25−150 °C range. After cooling, the solid was separated by centrifuge and excess ethylene glycol removed by washing several times with methanol. The product was dried in air at 60 °C.

Characterization. Powder X-ray diffraction (PXRD) patterns were obtained using a Philips APD 1700 instrument with Ni-filtered Cu Kα radiation using a 0.02° (2θ) step size. The scan time was around 1 h. Elemental analysis for nickel, copper, aluminum, and vanadium was obtained using a Camscan S4 scanning electron microscope at 20 kV. The samples were mounted on carbon tape stuck to a conducting Bakelite mount and scanned with a small raster scan at low magnification (between ×25 and ×40) in order to cover a representative area (ca. 8 mm^2). The data were processed through a ZAF4 program running on a Link 860 series 2 processor. The amount of carbon in the terephthalate LDH was determined using a Carlo Erba Strumentazione Model 1106 elemental analyzer. FTIR spectra were recorded on a Nicolet 205 spectrometer using the KBr pellet technique. TPR analysis was carried out in Micrometrics TPR-TPD 2900 instrument, at a heating rate of 10 °C/min, and using ca. 15 mg of sample and a H_2/Ar (5% vol) mixture as reducing agent (60 mL/min). The experimental conditions for TPR runs were chosen according to data reported elsewhere[15] in order to reach good resolution of the component peaks.

Results and Discussion

I. Starting LDHs. The PXRD patterns of the Ni−Al LDHs with carbonate, terephthalate, and decavanadate anions are presented in Figure 1. The recorded patterns are typical of a LDH and are indexed on the basis of an hexagonal unit cell. The *c* parameter (which corresponds to 3 times the distance between adjacent hydroxide layers) depends upon the nature and the size of the anions intercalated between the layers. Figure 1a shows for the Ni−Al−CO_3 LDH, a 003 reflection at 7.75 Å. In the case of the Ni−Al−TA LDH compound, the PXRD pattern (Figure 1b) corresponds to a LDH structure intercalated with terephthalate anions in a vertical orientation with respect to the hydroxides layers,[16,17] with a corresponding gallery height of 9.2 Å (assuming the thickness of the brucite layer is 4.8 Å[18]). After anion exchange of carbonate anions by decavanadate, the relative intensities of the first two reflections are reversed, and their positions are shifted to a spacing of approximately 11.8 and 6.0 Å (Figure 1c), respectively. The gallery height determined for the exchanged sample is approximately 7 Å, which corresponds to the size of a $[V_{10}O_{28}]^{6-}$ anion located between the layers with its main C_2 axis parallel to the layers and is in agreement with previous reports.[16] The broad reflection close to 10 Å has been attributed to either the formation of Ni and/or Al vanadate salts generated during anion exchange[14] or to defective hydroxide layers. Similar PXRD data are obtained for the Cu−Al LDH compounds.

The FTIR spectrum obtained for the Ni−Al−CO_3 LDH shows a characteristic band at 1370 cm^{-1} assigned to the ν_3 mode of the carbonate anion.[19] In the case of Ni−Al−TA, two strong bands at 1567 and 1390 cm^{-1} are recorded and are attributed to the antisymmetric (ν_{as}) and symmetric (ν_s) stretching modes of the carboxylate group, respectively.[20] These bands are similar to those observed for a Mg−Al LDH intercalated with terephthalate.[21] After anion-exchange with decavanadate, the ν_3 band of carbonate is absent, and new bands at 960, 820, 737, 670, and 595 cm^{-1} are observed. These bands coincide with those reported in the literature for decavanadate anions between the layers.[14,22] The band at 960 cm^{-1} can be assigned to the symmetric stretching mode of the VO_2 species, the 737 cm^{-1} band is attributed to a V−O stretching vibration, and the bands near 800 and 600 cm^{-1} are attributed to antisymmetric and symmetric modes of the V−O−V chain, respectively.[14] Similar observations are again made for the corresponding Cu−Al LDHs.

II. Reduced LDHs. PXRD: Carbonate Materials. The PXRD patterns obtained for Ni−Al−CO_3 LDH after treatment for 18 h with ethylene glycol at different temperatures are presented in Figure 2. The PXRD pattern of the starting Ni−Al−CO_3 LDH is shown for comparison.

Little change in the PXRD pattern occurs with treatment temperatures up to 80 °C. At higher temperatures new phases are obtained. The 003 reflections at 8.94 Å (at 115 °C) and 9.8 Å (at 150 °C) may correspond to the presence of ethylene glycol or the corresponding alkoxy radical between the layers.[23] When the suspension is treated at 200 °C, the color of the LDH changes

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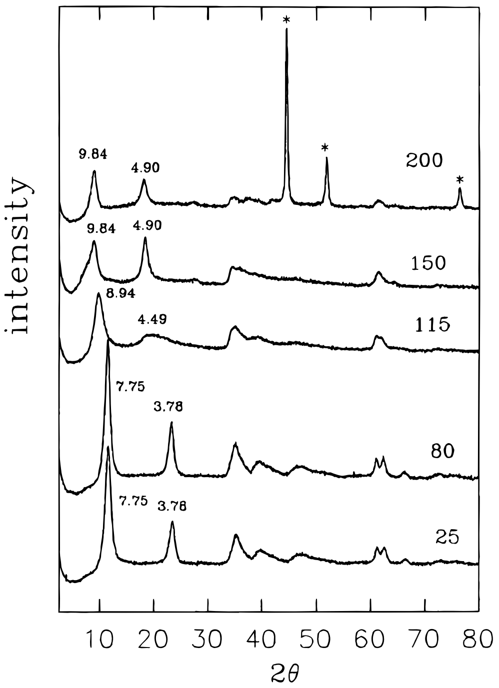

Figure 2. PXRD patterns of Ni—Al—CO_3 treated with ethylene glycol at the temperatures (°C) given for 18 h. The asterisks correspond to the reflections of Ni^0.

from light green to black, most likely as a result of the reduction of nickel cations to metallic nickel (Ni^0). Three peaks are observed at 2.035, 1.764, and 1.246 Å (characteristic of metallic nickel, JCPDS Card 4-850), along with 003 and 006 reflections at 9.84 and 4.90 Å, corresponding to a LDH phase (Figure 2). Only partial reduction of the nickel has therefore been achieved.

For the Cu—Al—CO_3 LDH (Figure 3), the layered structure is destroyed and various new phases are detected at 115 and 150 °C. At a treatment temperature of 200 °C, the color of the suspension becomes red, indicating the presence of a metallic copper (Cu^0) phase with three reflections detected at 2.09, 1.81, and 1.28 Å (JCPDS Card 4-836). At this temperature only traces of the LDH structure are detected. These observations clearly indicate that the copper cation is more readily reduced in the LDH than nickel.

Figure 4 presents the PXRD patterns of the Ni—Al—CO_3 materials obtained for different times of polyol treatment at 200 °C. The intensities of the peaks for the Ni—Al LDH phase decrease after treatment for 192 h, and intense reflections of metallic nickel (Ni^0) are observed; however a residual amount of LDH remains. For the Cu—Al—CO_3 LDH phase, after 3 h of polyol treatment at 200 °C (see Figure 3), only traces of LDH structure remained and by 72 h treatment total reduction was achieved.

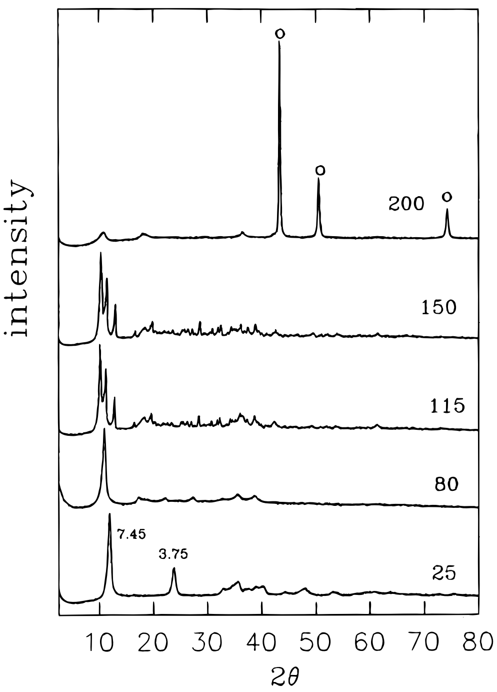

Figure 3. PXRD patterns of Cu—Al—CO_3 treated with ethylene glycol at the temperatures (°C) given for 18 h. (○) Reflections of Cu^0.

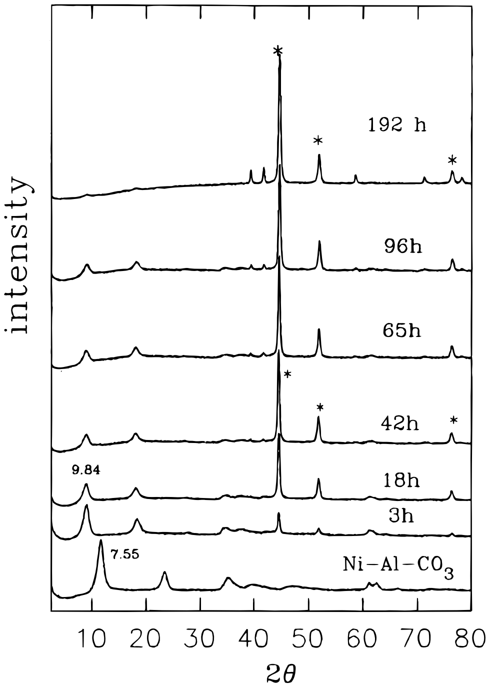

Figure 4. PXRD patterns of Ni—Al—CO_3 treated in ethylene glycol at 200 °C for the periods of time (hours) given. The asterisks correspond to the reflections of Ni^0.

Terephthalate Anions. After polyol treatment of Ni—Al-TA LDH for a period of 18 h at 200 °C, a partial reduction of Ni is obtained, with the residual LDH phase remaining intercalated by terephthalate anions (reflection at 14.0 Å). Prolonged treatment (up to 72 h) increases the diffraction intensity of metallic nickel and, simultaneously, decreases the Ni—Al—TA LDH phase. At 120 h a small amount of terephthalate LDH is detected. Unlike the case of Ni—Al—CO_3, it appears that the terephthalate anion is not exchanged with glycerol. For the Cu—Al—TA LDH, however, treatment for 18 h results in complete reduction, confirming again that the reduction of copper is easier compared to the nickel cations.

Decavanadate Anion. The PXRD patterns for Ni—Al—$V_{10}O_{28}$ LDH refluxed with ethylene glycol for different periods of time are presented in Figure 5. After 18 h treatment, the pattern indicates the presence metallic nickel (Ni^0) and residual Ni—Al—$V_{10}O_{28}$ LDH.

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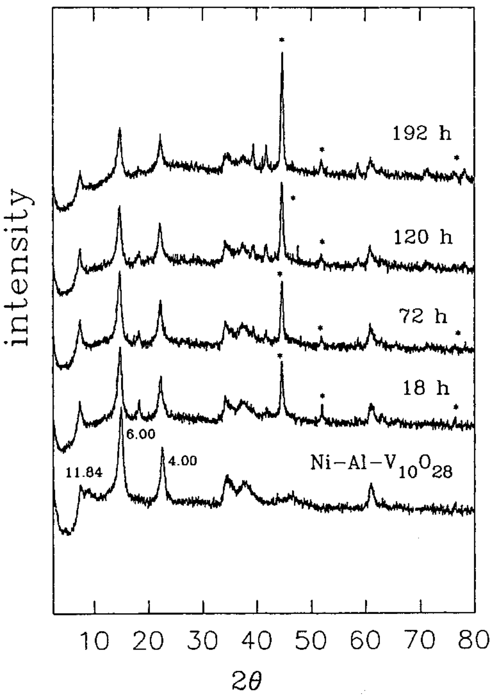

Figure 5. PXRD patterns of Ni−Al−$V_{10}O_{28}$ LDH refluxed in ethylene glycol at 200 °C for the periods of time (hours) given. The asterisks correspond to the reflections of Ni^0.

Table 1. Hydrogen Consumption for Samples Treated with Ethylene Glycol at 200 °C, for Different Periods of Time (mol of Hydrogen/mol of Divalent Cation)[a]

sample	H_2/M^{2+}	sample	H_2/M^{2+}
Ni−Al−CO_3−NTR	1.20	Cu−Al−CO_3−NTR	1.12
TR 3 h	1.20	TR 3 h	0.07
TR 18 h	0.92	TR 18 h	0.09
TR 42 h	0.86	TR 144 h	0.04
TR 65 h	0.69		
TR 96 h	0.45		
TR 192 h	0.36		

[a] NTR, nontreated; TR, treated.

Lengthening the period of treatment does not decrease the amount of Ni−Al−$V_{10}O_{28}$ phase detected. The decavanadate $(V_{10}O_{28})^{6-}$ anion is very stable against thermal decomposition, compared to carbonate or terephthalate, and the LDH structure is maintained even after treatment of 192 h. The reduction of the nickel cation is more difficult to achieve than in the case of carbonate and terephthalate LDHs. In the case of the Cu−Al−$V_{10}O_{28}$ LDH, after treatment for 18 h, all the copper is reduced, and Cu−Al−$V_{10}O_{28}$ LDH phase is not detected by PXRD.

TPR Measurements. Table 1 includes the H_2/Ni and H_2/Cu molar ratio values determined from TPR experiments for samples refluxed for different periods of times in ethylene glycol solution at 200 °C. It is clear that hydrogen consumption during TPR analysis decreases as the time of polyol treatment is extended. As TPR measures the amount of hydrogen needed for reduction of Ni^{2+} (or Cu^{2+}), this means that the average oxidation state of the cation decreases as the time of polyol treatment is extended. The initial value of 1.20 for the Ni−Al LDH reflects the generally accepted accuracy of such measurements. After 3 h of ethylene glycol treatment of Cu−Al−CO_3 a significant reduction in hydrogen consumption occurs, in agreement with the PXRD data which showed the predominance of metallic copper (Cu^0) peaks (see Figure 3) and only a residual amount of LDH. In comparison, the H_2/Ni molar ratio for the Ni−Al−CO_3 sample treated for 192 h indicates that a significant amount of H_2 is still consumed.

For samples containing two reducible species, i.e., Ni or Cu along with decavanadate or TA, it is unlikely that the reducibility characteristics will be a simple combination since reduction of one of the species may provide reaction sites that favor (kinetically) the reduction of the other species. As a result, when analyzing the reduction of samples containing two reducible species, it is not possible to subtract hydrogen consumption associated with TA reduction for Mg−Al−TA, for example, from the value determined for a Ni−Al−TA sample. Consequently it is not possible to determine the hydrogen consumption required to reduce Ni and hence, the initial oxidation state of Ni species in the Ni−Al−TA material.

Discussion

During the polyol treatment, the reduction of Ni^{2+} from Ni−Al−CO_3 LDH is likely to take place via an intermediate step of exchange of carbonate by ethylene glycol. It has been reported that the reaction between the Mg−Al−CO_3 LDH and glycerol involves dissolution and recrystallization of the LDH with the incorporation of polyol at elevated temperature.[24] The presence of aluminum in the nickel hydroxide layer decreases the reduction rate of nickel in comparison to the pure $Ni(OH)_2$ compound, in which total reduction of nickel has been achieved after a few hours of polyol treatment.[25] It appears that the copper cation is more readily reduced in ethylene glycol, compared to nickel, and similar results have been reported on the reduction of nickel and copper supported for zeolites[4] using both the polyol process and molecular hydrogen.[26] Although the experimental conditions are markedly different, this can be related to the fact that standard reduction potential for Cu^{2+}/Cu has a value of 0.339 V, while that for Ni^{2+}/Ni is −0.236 V.[27]

In the case of Ni−Al−TA and Ni−Al−$V_{10}O_{28}$ LDH, the reduction of nickel is not as complete compared to Ni−Al−CO_3 LDH. Neither the TA nor the decavanadate anions are completely exchanged. The decavanadate anions appear stable in the organic solution, although previous studies have reported a depolymerization of decavanadate after heating at 150 °C in air.[14,28] It is proposed that the nickel situated in the edge of the hydroxide layers are attacked and dissolved in the ethylene glycol and then reduced. The leaching of the nickel from the hydroxide layers could be explained in the same manner as the acid-activation process of clay minerals where removal of cations from the octahedral sheets has been reported to occur by proton attack at layer edge sites[29] in the early stages of acid attack.

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However, in the case of copper, a complete reduction is achieved, regardless of the nature of the intercalated anions, and the reduction seems to be related particularly to the treatment temperature (as we described above).

The TPR data confirm that not all the nickel is reduced starting from the Ni−Al−CO_3 LDH, and traces of no reduced nickel are present, which is not in the case of Cu−Al−CO_3 LDH, where the consumption of hydrogen is very low for a sample treated for 3 h.

Conclusions

The rate of reduction by ethylene glycol of Ni^{2+} cations in an LDH framework has been shown to be strongly dependent on the temperature and time of treatment; a complete reduction was not achieved after treatment at 192 h for the Ni−Al−CO_3. Copper was more easily reduced compared to nickel, and complete reduction was achieved after 3 h of polyol treatment. The Ni−Al−CO_3 precursor was also more stable than Cu−Al−CO_3. The effect of the anions in the starting materials is also reported, the reduction of copper seems to be independent of the nature of the anions intercalated between the layers. In the case of the Ni−Al LDHs, an improvement in the ease of reduction of the nickel is observed when terephthalate is the charge-balancing anion rather than $V_{10}O_{28}$.

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