reactions of molecular precursors offer the advantage of a cluster size distribution that is controlled by the reactant structure rather than the kinetics of the cluster formation reaction. Of course, in the case we have investigated, the homogeneous cluster size of the starting material appears to be lost during the transition from the intermediate to the extended solid. Nevertheless, the controlled chemistry that occurs during the first step suggests a number of possible ways to use ligand reactivity to influence the course of the solid-state reactions.

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Main Effects in the Syntheses of Cu/Cr Layered Double Hydroxides

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Introduction

Layered double hydroxides (LDHs) are layered materials with anion-exchange properties. These materials are based on the layered mineral brucite, which consists of hydroxyl layers surrounding Mg^{2+} ions in an octahedral coordination.

The formula of LDHs can be written as follows:

$$M_x^{2+}M_y^{3+}(OH)_{2x+2y}A_{y/n}\cdot zH_2O$$

Divalent and trivalent cations are bound in edge-shared octahedra of hydroxyl ions. Anions (A^{n-}) can be intercalated, and water molecules are loosely bound between hydroxyl layers.

Considerable recent interest in LDHs is most likely due to their numerous uses. LDHs have been used as selective heterogeneous catalysts and, surprisingly, are quite thermally stable. Some of the pillared phases used for catalysis are stable over 500 °C.[1] LDHs containing halide ions have shown promise in converting alkyl bromides to the respective alkyl halides.[2] Alkyl halide products were normally obtained with 80% yields at temperatures of 150 °C. Larger (100%) yields could be attained if excess LDH was used. A variety of different cations and anions have been used to prepare transition-metal LDHs.[3] Anions recently used to pillar LDHs include the ruthenium tris(4,7-diphenyl-1,10-phenanthrolinedisulfonate) anion ($Ru(BPS)_3^{4-}$), the first transition-metal luminescent complex to be incorporated into an LDH host,[4] and the anionic dyes indigo carmine and new coccine.[5]

Anions incorporated between the octahedral layers in LDHs are mobile. This anionic mobility has led to research on these materials as ionic conductors. Ionic conductivities of 10^{-3} and 10^{-4} Ω^{-1} cm^{-1} have been reported.[6] Anion mobility is unusually high due to swelling of the layers by a considerable H_2O sorption. Halides, nitrates, and carbonates have been studied. Proton-hopping mechanisms have also been reported. Proton hopping in LDHs occurs via H_2O molecules in the anionic layers.[7,8]

LDHs are good anion exchangers due to the mobility of anions. The anion exchange capacity of LDHs allows preparation of new LDH materials containing anions that do not incorporate by direct crystallization from aqueous solution. The anions Cl^-, ClO_4^-, and SO_4^{2-} have been incorporated in LDHs via anion exchange of hydrotalcite.[9] Miyata has used naphthol yellow S, an anionic dye, to study anion-exchange capacities of LDH or hydrotalcite-like compounds.[10] Other anions that have been exchanged into LDHs include silicate anions[11] and short- and long-chain organic anions.[12] Drezdzon has exchanged isopolymetalate ions, $Mo_7O_{24}^{6-}$ and $V_{10}O_{28}^{6-}$, into hydrotalcite.[13] In this technique, a hydrotalcite containing terephthalate (TA) is used as a precursor and is synthesized prior to the anion-exchange step. Once the Mg_4Al_2-

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$(OH)_{12}(TA)\cdot xH_2O$ has been made, the $Mo_7O_{24}^{6-}$ and $V_{10}O_{28}^{6-}$ ions can readily exchange into the hydrotalcite. Using terephthalate, isopolymetalate ions can be exchanged into the LDH much more readily than they can into naturally occurring hydrotalcite-type materials.

LDHs can be prepared by a variety of methods. Most LDHs are synthesized by coprecipitation of a divalent/trivalent salt with an alkaline solution. However, a number of LDHs have been prepared by reacting a divalent oxide with a trivalent salt solution.[14-16] Many synthetic parameters for LDHs have been studied by Reichle.[17] The M^{2+}/M^{3+} ratio, pH, and crystallization temperature have been found to be important parameters. Various literature reports suggest that each different LDH has its own synthetic peculiarities, in turn implying that a wide range of possible products can be prepared. The preparation, properties and applications of LDH materials has recently been reviewed by Lagaly et al.[18] and Cavani et al.[19]

This paper concerns the use of screening design techniques for the preparations of Cu^{2+}/Cr^{3+} LDHs. These cations were chosen because they are both paramagnetic and are of the correct size to fit in divalent and trivalent octahedral sites. Electron transfer between divalent Cu^{2+} and trivalent Cr^{3+} ions was also of interest and was monitored by electron paramagnetic resonance.

Cu/Cr LDH literature reports[16,17] suggest that the system might not be able to be synthesized using a coprecipitation of Cu/Cr salt with alkaline solution. Our results suggest that under certain synthetic conditions Cu/Cr LDHs can be synthesized by coprecipitation methods.

Experimental Section

Materials. The following chemicals were obtained in ACS reagent grade from Baker: $CrCl_3\cdot 6H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, $Cr(NO_3)_3\cdot 9H_2O$, and all NaOH pellets. $CuCl_2\cdot 3H_2O$ from Fisher was also used in some syntheses. All water used was both distilled and deionized (DDW).

Synthesis. The synthesis of LDHs is usually achieved by addition of the divalent and trivalent salts with alkaline solution, resulting in precipitation of the desired product. All procedures reported in this paper used this method.

A typical synthesis of a Cu/Cr/Cl LDH involved mixing a solution of $CuCl_2\cdot 3H_2O$ and $CrCl_3\cdot 6H_2O$ until the desired ratio of Cu^{2+} to Cr^{3+} was obtained. This solution was placed in one separatory funnel, and sodium hydroxide solution was placed in another separatory funnel. The two funnels were then fitted onto a 250-mL, three-neck, round-bottom flask. Approximately 50 mL of DDW was placed in the flask, and the two solutions were added, dropwise or in stream, with or without stirring, at 100 °C or at room temperature, depending on the desired conditions. After addition of the solutions was complete, the contents of the flask were allowed to age for the desired time. Finally, the contents of the flask were suction filtered, washed, and dried to yield the solid product. These solids were typically hard, glassy materials that were ground into powders prior to spectroscopic experiments.

A Cr^{3+}-doped $Cu/Al/NO_3$ LDH sample was prepared by adding 1 mL of 0.5 M $Cr(NO_3)_3$ solution to 30 mL of 1.5 M $Cu(NO_3)_2$ solution and 29 mL of 0.5 M $Al(NO_3)_3$ solution in order to make the M^{2+}/M^{3+} salt. This was added, dropwise, at the same time as the NaOH solution in a three-neck, round-bottom flask containing approximately 50 mL of DDW. The solution was stirred throughout the entire synthesis. The resulting precipitate of this LDH synthesis was the Cr^{3+}-doped $Cu/Al/NO_3$ LDH product. The undoped $Cu/Al/NO_3$ LDH was prepared the same way except no $Cr(NO_3)_3\cdot 9H_2O$ solution was added to the $Cu/Al/NO_3$ salt solution.

Table I. High and Low Limits of Variables of Screening Design[a]

parameter	level[b] low (−1)	high (+1)
Cu^{2+}/Cr^{3+} ratio	3	9
anion	Cl^-	NO_3^-
dripping rate	drop	stream
temperature	RT	100 °C
concentration of Cu^{2+}/Cr^{3+}	0.2 M	1 M
cation of OH^-	Na^+	K^+
stirring	Off	On
aging time after mixing	5 min	24 h
solution addition	same time	OH^- first
atmosphere	air	N_2
drying	oven	air at RT

[a] Various screening design parameters are discussed in section 2.3. [b] In analysis of the data, the low values are coded −1 and the high values are coded as +1 so that regression analysis can be done on the results. By coding all of the parameters as −1 or +1 the relative effects of one parameter to another can be obtained by direct comparison of the coefficient from the regression.

Screening Design. Syntheses reported here primarily concern Cu^{2+}/Cr^{3+} LDH materials. This particular system was studied using a screening design in which several synthetic parameters were varied in order to optimize synthetic conditions yielding the purest product. The synthetic parameters that were used and low and high limits of the screening design are given in Table I.

Eleven synthetic parameters were vaired in this screening design. *Cu^{2+}/Cr^{3+} ratio* is the ratio between the Cu^{2+} and Cr^{3+} ions, *anion* denotes the type of anion incorporated between the layers of hydroxide octahedra, *dripping rate* is the rate the reactant solutions drip from the separatory funnels to the reaction flask, *temperature* is the temperature of reaction, *concentration of Cu^{2+}/Cr^{3+}* is the sum of concentrations of Cu^{2+} and Cr^{3+} in the mixed Cu^{2+}/Cr^{3+} solution (in this way a Cu^{2+}/Cr^{3+} concentration of 1 M would be 0.75 M Cu^{2+} and 0.25 M Cr^{3+} if the Cu^{2+}/Cr^{3+} ratio were 3), *cation of OH^-* refers to the cation associated with the hydroxide used, *stirring* denotes whether the mixture was stirred or not during reaction, *aging time after mixing* is the amount of time the reaction is allowed to proceed after all reactant solutions are added, *solution addition* refers to the order in which the solutions are added, *atmosphere* is the gaseous atmosphere under which the reaction takes place, and *drying* is the method of drying the product.

These parameters were varied in such a way as to design 12 different syntheses, each synthesis being composed of different low and high limits for the parameters. The low and high limits were chosen as reasonable end members for the preparation of Cu^{2+}/Cr^{3+} LDHs. These 12 syntheses compose the screening design and are presented in Table II.

Each synthesis was performed following conditions described in Table II to obtain 12 different products. These products were evaluated by XRD, EPR, and TGA to determine which parameters of the screening design were important. Analyses of the data were done with an experimental design program, SYSTAT.

X-ray Powder Diffraction. Crystallinity of materials was determined by X-ray powder diffraction using a General Electric DIANO-XRD 800 X-ray powder diffractometer equipped with a Philips electronic source. Copper Kα radiation was used, and the scanning rate was used was 2° 2θ/min. All powder samples were mounted on glass slides, lightly coated with petroleum jelly. Patterns were calibrated against a NaCl standard.

Thermogravimetric Analysis. Thermogravimetric analyses were performed using a Du Pont 9900 thermogravimetric analyzer. A Du Pont 9900 computer/thermal analyzer was used both to run the thermogravimetric analyzer and analyze data. For these experiments the sample powder was placed in a platinum boat at the end of a quartz holder, and a stream of dried N_2 gas flowed through the system during analysis. Temperatures were ramped at approximately 20 °C/min up to around 700 °C. Run times typically lasted 35–40 min. Sample masses typically ranged from 27 to 52 mg.

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Table II. Screening Design Parameters[a]

screening design no.	Cu^{2+}/Cr^{3+} ratio	anion	dripping rate	temp, °C	concn of Cu^{2+}/Cr^{3+} M	cation of OH^-	stirring	aging time after mixing	solution addition	atmos-phere	drying
1	3	chloride	stream	RT[b]	1	K^+	off	24 h	same time	air	oven
2	9	chloride	drop	RT	1	Na^+	on	24 h	OH^- first	nitrogen	oven
3	3	nitrate	stream	RT	1	K^+	on	5 min	OH^- first	nitrogen	air at RT
4	9	nitrate	stream	RT	0.2	Na^+	on	5 min	same time	air	oven
5	9	chloride	stream	100	0.2	K^+	on	24 h	OH^- first	air	air at RT
6	3	nitrate	stream	100	0.2	Na^+	off	24 h	OH^- first	nitrogen	oven
7	9	nitrate	drop	100	1	K^+	off	5 min	OH^- first	air	oven
8	9	nitrate	drop	RT	0.2	K^+	off	24 h	same time	nitrogen	air at RT
9	3	chloride	drop	RT	0.2	Na^+	off	5 min	OH^- first	air	air at RT
10	3	nitrate	drop	100	1	Na^+	on	24 h	same time	air	air at RT
11	9	chloride	stream	100	1	Na^+	off	5 min	same time	nitrogen	air at RT
12	3	chloride	drop	100	0.2	K^+	on	5 min	same time	nitrogen	oven

[a] Definition is in text. [b] RT = room temperature

Table III. Phases Present and Rankings of Screening Designs

screening design no.	color	CuO	Cr_2O_3	$Cu(OH)_2$	$Cr(OH)_3$	Cu/Cr LDH[a]	rank
1	olive green	no	no	no	no	yes	7
2	brown black	yes	no	no	no	no	1
3	green blue	no	yes	no	trace	yes	5
4	brown	yes	yes	no	no	no	1
5	brown black	yes	no	no	no	no	0
6	brown	yes	no	no	no	no	1
7	dark brown	yes	no	no	trace	yes	3
8	light brown	yes	trace	yes	no	no	1
9	blue green	no	no	trace	no	yes	5
10	brown	yes	no	no	trace	no	1
11	brown black	yes	no	no	no	no	1
12	green brown	yes	no	no	no	yes	5

[a] LDH = layered double hydroxide. yes = phase is present. no = phase is not present. trace = a trace of the phase may be present.

Electron Paramagnetic Resonance. Electron paramagnetic resonance (EPR) spectra of the solid samples were measured using a Varian E-3 X-band EPR spectrometer. A Hewlett-Packard transfer oscillator Model 540B was used in conjunction with a Heath Schlumberger frequency counter in order to obtain nodal frequencies. Samples were sealed off in quartz tubes and evacuated to pressures of 1×10^{-3} Torr or lower. EPR spectra were obtained at an attenuation of 10 mW, a frequency of approximately 9.1 GHz, and a modulation amplitude of 4.0 G. All spectra were taken at liquid nitrogen temperatures.

Transmission Electron Microscopy. Transmission electron microscopy (TEM) experiments were done by grinding Cu/Cr LDH in a mortar with a pestle and loading sample onto a Cu grid. A Phillips EM 420 TEM instrument was used for all studies.

Results

Synthesis. Colors of the products were observed after each of the compounds synthesized was dried and ground into a powder. Colors ranged from a green blue to a brown black, with assorted intermediates. Since all compounds contained Cu^{2+}/Cr^{3+} as their divalent and trivalent cations, respectively, a large variety of colors was not observed for these screening design compounds. Various compounds with corresponding colors and screening design numbers are listed in Table III. Again, Table II should be referred to regarding specific synthetic details for each compound.

X-ray Powder Diffraction. Evaluations of the screening design were provided mainly by X-ray diffraction (XRD) analysis. XRD patterns were taken for each of the compounds synthesized and compared with the pattern for pure Cu/Cr/Cl LDH prepared by El Malki and coworkers from oxide precursors.[16] The peaks for the Cu/Cr LDH that were desirable and easily identified were the 003 peak at d = 7.27, the 006 peak at d = 3.74, the 012 peak at d = 2.57, the 015 peak at d = 2.30, the 018 peak at d = 1.96, and the doublet 110 and 113 peaks at d = 1.56 and 1.53. If a synthetic product exhibited these peaks it was evaluated as a desirable product. Samples were evaluated via XRD and weighted from 0 (undesirable) to 10 (desirable) on the basis of phases present and their observed

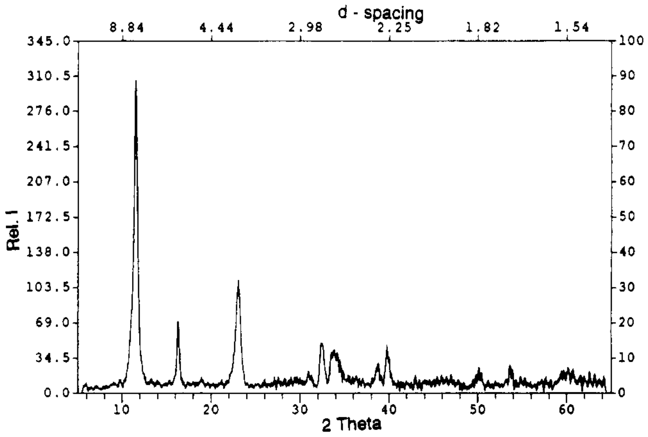

Figure 1. XRD pattern for pure Cu/Cr LDH phase.

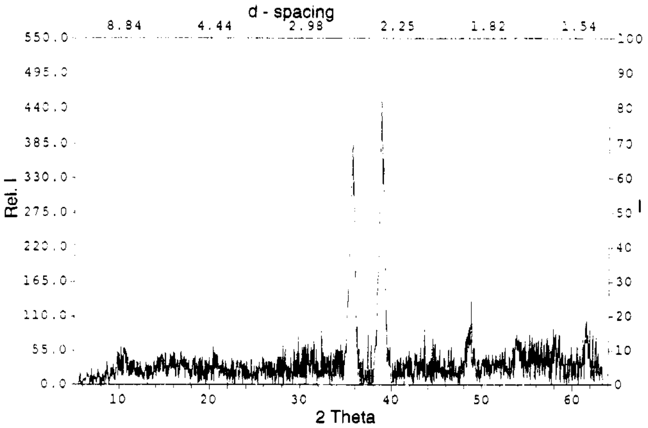

Figure 2. XRD pattern for oxide impurity phase.

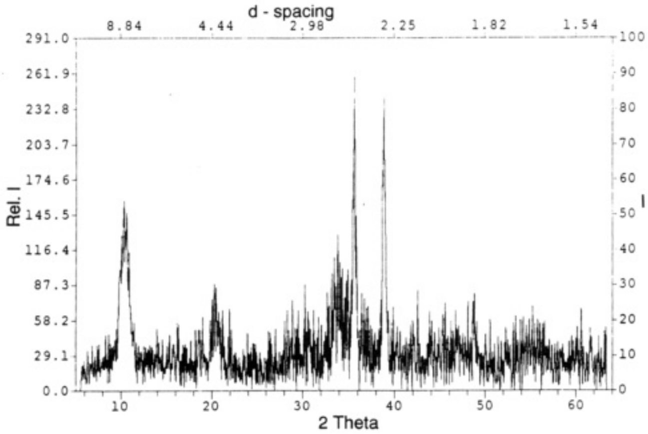

Figure 3. XRD pattern for mixed LDH/oxide phases.

Table IV. Regression Coefficient and Normalized Effect of Variables

variable	regression coefficient	normalized
constant ($b0$)	2.583	
Cu/Cr ratio	−1.417	−1.00
anion	−0.583	−0.41
drip rate	−0.083	−0.06
temperature	−0.75	−0.53
Cu/Cr concentration	0.417	0.29
cation of OH^-	0.917	0.65
stirring	−0.417	−0.29
aging after mixing	−0.75	−0.53
solution addition	0.083	0.06
atmosphere	0.25	0.18
drying	0.417	0.29

intensities. Examples of XRD patterns that are favorable, unfavorable, and in between can be found in Figures 1–3, respectively.

Peaks at $d = 2.523$ (intensity = 100), $d = 2.323$ (96), and $d = 2.530$ (49) are indicative of copper oxide, and peaks at $d = 2.666$ (100), $d = 2.480$ (95), $d = 1.672$ (90), and $d = 3.633$ (75) are indicative of chromium oxide. XRD patterns exhibiting these peaks with these intensity ratios indicated the presence of less of the desired LDH product. Peaks at $d = 3.73$ (100), $d = 5.30$ (90), and $d = 2.63$ (70) are indicative of copper hydroxide, and peaks at $d = 4.58$ (100), $d = 4.87$ (55), and $d = 3.34$ (55) are indicative of chromium hydroxide. As with the oxide peaks, these hydroxide phases were undesirable in the patterns of the analyzed products. The pattern in Figure 1 shows a compound containing mostly the LDH phase and no oxide impurities. Figure 2 shows a pattern corresponding to a compound that has no LDH phase present and is mostly oxide impurities. Figure 3 shows a compound that contains both the LDH phase and oxide impurity phases. Table III specifies which of these phases were either present or absent for each screening design.

Screening Design. The screening design was evaluated using the XRD pattern rankings for each of the compounds synthesized. A rank was assigned to the product of each synthesis on a scale of 0–10, 0 indicating only impurity product, and 10 indicating pure LDH product. The individual experiments in the screening design and their corresponding ranks are contained in Table III. These ranks were then analyzed by standard multiple linear regression techniques which calculated regression coefficients. These were normalized to facilitate evaluation of the relative effectiveness. This information is summarized in Table IV, and the relative effect of these variables on the purity of the products synthesized is shown in Figure 4. Table IV indicates whether the high or low parameters were more desirable for purer products, and Figure 4 shows which of the parameters themselves were most important.

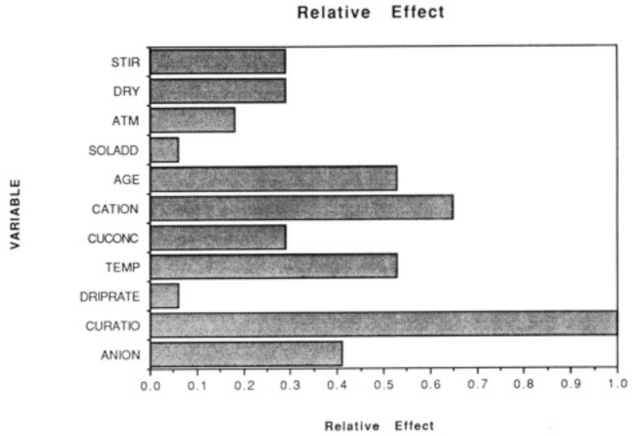

Figure 4. Relative effects of variables on screening design products.

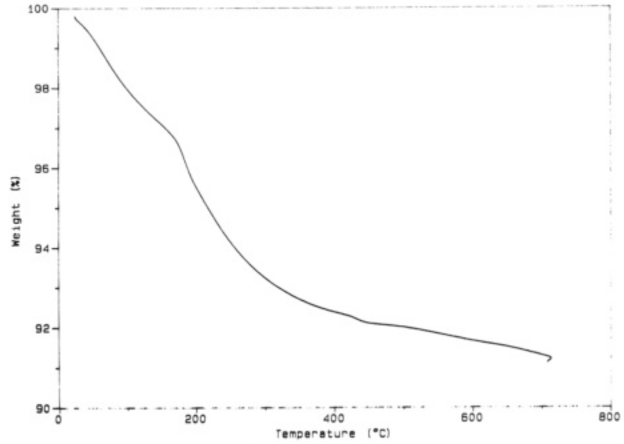

Figure 5. TGA curve for impure Cu/Cr screening design sample.

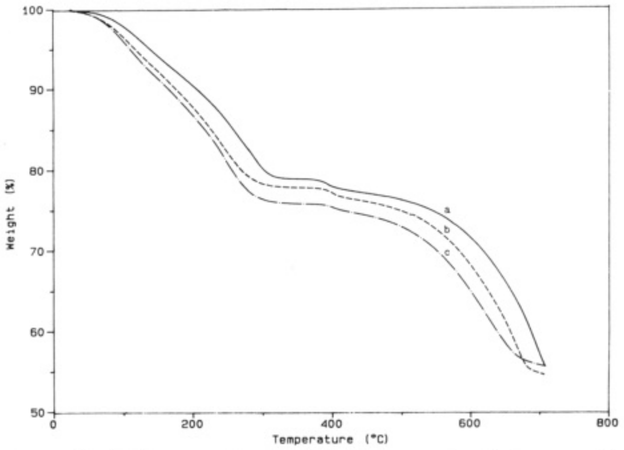

Figure 6. TGA curves for pure Cu/Cr screening design samples: (a) product of screening design 1; (b) product of screening design 12; (c) product of screening design 9.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was used to further analyze the products of the screening design. A TGA was taken for each product, and all TGA curves were compared to each other. Figure 5 shows a typical TGA curve. There is very little weight loss, less than 10%, throughout the entire heating range. There is no plateau on the curve; the weight decreases steadily until it slowly levels off. Figure 6 shows three different TGA curves superimposed on the same scale. In this case all the curves show almost 50% weight loss when ramped to 700 °C. Also, the weight loss is not one steady progression, as in Figure 5; there is a leveling

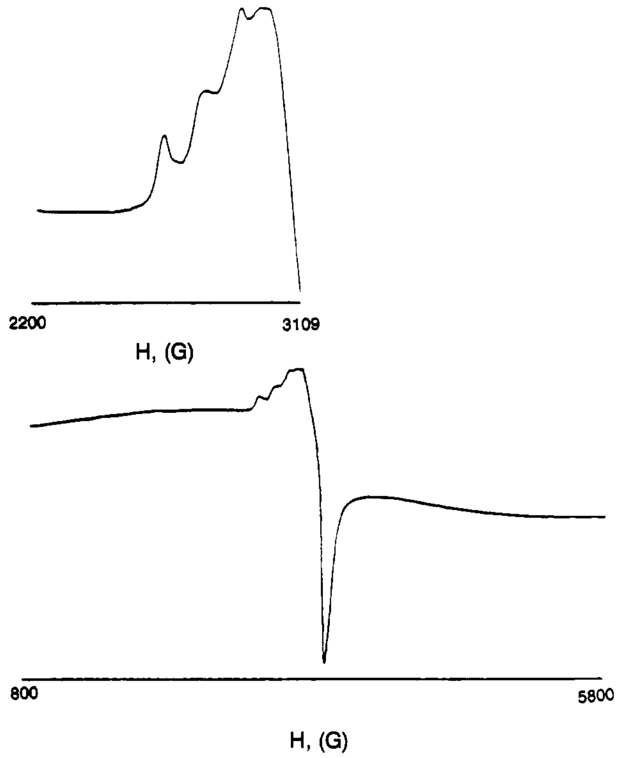

Figure 7. EPR spectrum for undoped Cu/Al/NO_3 LDH sample.

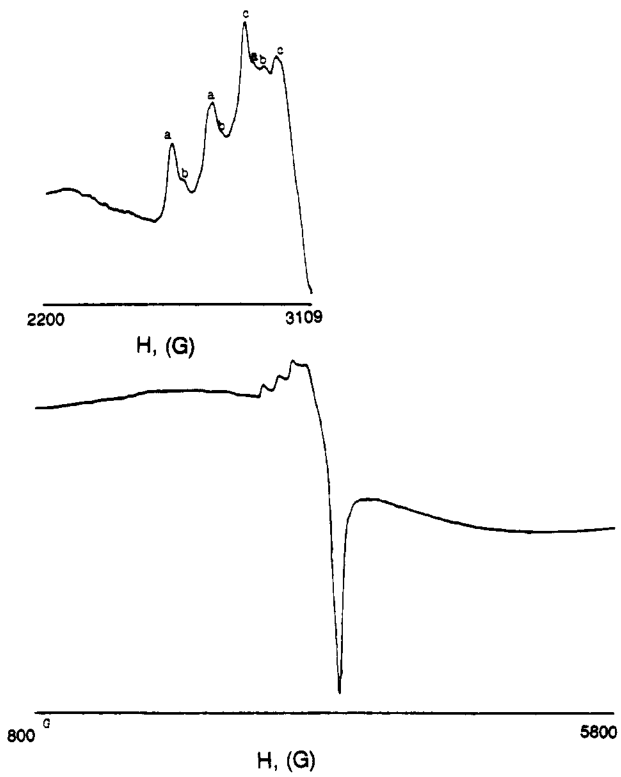

Figure 8. EPR spectrum for Cu/Al/NO_3 LDH sample doped with Cr^{3+}.

off in the middle of the curves. The shape of the curves suggests an initial weight loss up to 300 °C, followed by a leveling off between 300 and about 400 °C, followed by a second weight loss above 400 °C. The only three curves that had this shape correspond to screening design experiments numbers 1, 9, and 12. This two stage weight loss is similar to that reported for hydrotalcite.[20-23]

Electron Paramagnetic Resonance. EPR experiments were carried out in order to determine the number of Cu and Cr species in the LDH and to observe whether exchange reactions occur between the Cu^{2+} and Cr^{3+} ions in these materials. Two LDHs were analyzed using electron paramagnetic resonance (EPR) spectroscopy. The first compound was a Cu/Al/NO_3 LDH. The second was a Cu/Al/NO_3 LDH doped with Cr^{3+}. These two compounds were analyzed to see if the presence of Cr^{3+} affects the Cu^{2+} in the LDH. All of the screening design products were analyzed using EPR; however, in Cu^{2+}/Cr^{3+} LDHs the Cr^{3+} signal overwhelms the Cu^{2+} signal so that the broad Cr^{3+} signal is the only one observed in the spectrum. The Cu/Al/NO_3 LDH was chosen to look at the isolated Cu^{2+} signal, and the chromium-doped Cu/Al/NO_3 LDH was chosen to observe the Cu^{2+} signal in the presence of Cr^{3+} without Cr^{3+} overwhelming the Cu^{2+} signal.

Figure 7 shows the EPR spectrum of the undoped LDH, and Figure 8 shows the spectrum of the doped LDH. Both of these are Cu^{2+} signals. The number, intensity, and shape of the EPR signals of Figures 7 and 8 are different. In particular, the two peaks at highest magnetic field are sharper and spaced further apart in the doped sample (Figure 8) than in the undoped sample (Figure 7).

TEM Studies. TEM micrographs of the Cu/Cr LDH material suggest that at least 90% of the particles are crystalline on the basis of electron diffraction experiments. A magnification of 294 000 was used for all experiments.

Discussion

Characterization. Thermogravimetric analysis methods are valuable in assessing the proper preparation of LDHs. The data contained in Figure 6 show that screening design experiment numbers 1, 9, and 12 show weight loss patterns indicative of LDH materials. Similar results have previously been reported in the literature.[3,20-23] These experiments correspond to the only three *chloride* products that were rated favorably as shown in Table III. These data suggest that TGA may be used to determine whether LDHs are pure or impure. Figure 5 shows a TGA curve that corresponds to the more impure compounds, whereas Figure 6 corresponds to the purer compounds. The initial weight loss in Figure 6 is likely due to loss of H_2O from the compound. The second weight loss may correspond to decomposition of OH^- to oxide. This type of curve in Figure 6 is expected for purer LDH compounds where the hydroxyl ions and water molecules are abundant. However, impure compounds would tend to contain mostly oxide impurities and so the weight loss would mostly be due to H_2O and would not be very substantial if a smaller percentage of LDH was present. Impure compounds would contain very little OH^-, so that the second weight loss present in the purer compounds (Figure 6) would not be observed at higher temperatures (near 400 °C) where these oxides continue to be stable. This scenario is supported by the TGA data of Figure 5, which is a TGA curve for an impure product, and typical of all but three screening design products. The other three purer products contain two versions of weight loss as is shown in Figure 6. In certain runs, there are anomalies between XRD and TGA data. In these cases it is necessary to identify the species evolved during thermal treatment in order to determine whether loss of LDH constituents besides water is occurring.

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X-ray diffraction results for the purer compounds (design numbers 1, 9, and 12) made in this coprecipitation screening design show peaks indicative of a pure Cu/Cr LDH as compared to similar transition metal LDHs (Cu/Cr) produced by a divalent oxide precursor.[16] The XRD patterns of impure Cu/Cr LDHs typically contain either the single metal oxide or hydroxide species. The peak at 16° 2θ has also been observed as an impurity phase in other studies.[16]

Electron paramagnetic resonance data of Figures 7 and 8 show hyperfine interaction indicative of Cu^{2+} and mixed Cu^{2+}/Cr^{3+} systems, respectivley. For monomeric isolated Cu^{2+} ions or Cr^{3+} ions the total number of lines predicted is four. If dimers exist where electrons are delocalized over two metal ions (two Cu^{2+}, two Cr^{3+}) then seven peaks are expected. For two separate ions that are both EPR active, eight peaks are predicted. For coupling between one Cu^{2+} and one Cr^{3+} ion, 16 peaks are expected. Other possibilities include several Cu^{2+} and Cr^{3+} species leading to a myriad of splittings.

Electron paramagnetic resonance data of Figure 7 for the undoped $Cu/Al/NO_3$ sample consist of a four-line pattern with an average a value of 113.6 G. This a value and the overall EPR spectrum are consistent with Cu^{2+} in an axial environment in the LDH. This may be due to a Jahn–Teller distortion of Cu^{2+} ions.

The observed EPR data of Figure 8 show that at least four species exist in this Cr^{3+} doped $Cu/Al/NO_3$ LDH sample. The large broad signal is due to saturation broadening of Cr^{3+}. The sharper transitions are hyperfine splittings that are consistent with three Cu^{2+} species in axial environments.

Three different splittings are coupled as evidenced by similar spacings in the EPR data of Figure 8. Three sets of quartets, labeled a–c are shown. The specific a values are $a = 143.0$ G, $b = 140.8$ G, and $c = 107.1$ G. Two of the four splittings of the c quartet are under the intense peak near $g = 1.97$ and not clearly resolved. The a, b, and c values are consistent with Cu^{2+} ions that are in an axial field, perhaps due to a Jahn–Teller distortion of six-coordinate species. It is likely that the ligands are a mixture of O^{2-} ions and perhaps OH^- or H_2O molecules in the layered structure. The Cr^{3+} ions are expected to be in octahedral symmetry with no distortion or lowering of symmetry due to a stable d^3 configuration and a favorable crystal field stabilization energy.

Screening Design. In the screening design 11 independent variables are studied in a series of 12 different syntheses. High and low values are set for each of the variables to provide large differences in the levels tested. These high and low values are coded +1 and −1 for the purpose of data analysis (Table I). The particular synthesis conditions for the design are selected based on a Plackett–Burman or main effects design.[24] The 12 experiments were conducted and the extent of LDH formation was ranked for each of these experiments on a scale of 0–10 (Table III). These rankings are combined with the coded variables that determined the settings to give a set of 12 simultaneous equations. These equations are analyzed using a multiple linear regression routine from a commercial statistical software package.[25] This analysis gives coefficients for each of the independent variable terms. Since all of the independent variables were coded on a +1 to −1 scale, the absolute magnitude of the resulting coefficient can be used to rate the relative importance of the independent variables. These compounds were analyzed by TGA and XRD and evaluated. The importance of the individual parameters were evaluated by a computer program. The relative effect of each of the parameters on product formation is shown in Figure 4. To show whether a particular effect was positive or negative, Table IV lists the regression coefficients along with the normalized effect of each variable. Figure 4 indicates that the most important variable was the Cu/Cr ratio, while Table V shows that a low Cu/Cr ratio gave better results than the high value.

All of the parameters and their relative importance in the screening design are plotted in Figure 4. How each parameter should be optimized to produce the best synthetic result can be inferred from Tables II–IV. All of the results of the screening design are summarized in Figure 4 and Table IV.

The relatively large effect of the cation of the hydroxide on product formation is surprising. This is the second most important variable following the Cu/Cr ratio. The Cu/Cr ratio is expected to be the most important variable for charge balance and stiochiometric reasons. However, one might assume that Na^+ or K^+ ions would simply be spectator ions and that the hydroxide source would only supply the hydroxide. We found the choice of NaOH or KOH has a significant effect on the synthesis. The specific role of the cation in synthesis of LDHs is unknown and its importance previously unrecognized. However, the purity of starting reagent, the ionic strength of the different activity coefficients of K^+ versus Na^+ may influence nucleation. The role of the cation of the base hydroxide reagent may be as an aid in the formation of the layered structure. It is possible that a hydrated cation may serve as a template in such systems.

Temperature is the fourth most important variable, with the lower temperature (room) yielding purer LDH product than higher temperature (100 °C). The five most important variables (Cu^{2+}/Cr^{3+} ratio, cation of the hydroxide, aging, temperature, and anion) are under investigation in an experimental design[22] in order to understand the relationships among these variables.

The six least important variables in the screening design (Figure 4) are also interesting to examine. The effect of drip rate, whether done slowly by dripping or rapidly in a stream is least important. This is surprising since it might be expected that kinetics of mixing of such solutions would be important. This observation is further supported by the relative unimportance of how solutions are added together (OH^- first versus simultaneous addition).

The atmosphere for preparation is also relatively unimportant. This is an interesting observation since the amount of water, oxygen and other impurities does not seem to matter. This is surprising since carbonate anions are known to precipitate in LDHs.[2,3,10,16–17,20] The drying and stirring procedures also do not appear to be critical for the preparation of pure Cu/Cr LDH.

For future preparations of Cu/Cr LDH it is suggested that the conditions used for the six least important variables be chosen so as to simplify the preparation. For example, the drip rate could be slow, the solutions could be added together at the same time, and the concentrations of the solutions could be a total of 1 M. The reaction could be carried out under air and without stirring. Finally, the product could be dried in an oven. Keeping these parameters constant, the others could be studied with less confusion and in more detail.[26]

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A comparison of the rank of different products to the color of the sample (Table III) is interesting. The four products that were found to be the purest, including the nitrates, were products corresponding to screening design numbers 1, 3, 9, and 12. These are the only four compounds to exhibit a green color (Table III). This may suggest that the desired color of the Cu/Cr LDHs tends to be a green rather than brown or black. The color of the CuCr LDH powder may be another indicator of the purity of the Cu/Cr LDH. The separate Cu/Al LDH and Zn/Cr LDH materials are blue and lavender, respectively, suggesting there is an electronic interaction between Cu^{2+} and Cr^{3+} ions in Cu/Cr LDH. Since a range of colors exist for the Cu/Cr LDHs prepared here, it is likely that different degrees of interaction between Cu^{2+} and Cr^{3+} ions exist in these materials. Our results are specific for the preparation of Cu/Cr LDH and are not expected to be applied universally for all LDH compounds. Similar conclusions regarding the nonstandardized conditions for preparations of specific combinations of cations in LDHs have also been reached by others.[14-17]

Conclusions

These results of this study clearly show that screening design experiments can be used to determine the factors of major importance in preparing Cu/Cr LDH materials. Thermogravimetric, EPR, and XRD techniques were used to evaluate the 12 synthesized products for purity, Cu^{2+} and Cr^{3+} interactions, and crystallinity. The apparent importance of the cation of the hydroxide (NaOH or KOH) was unexpected and will be interesting to examine in future work. Also, the lack of importance of some variables such as drip rate and atmosphere was unexpected. This suggests that kinetics of mixing and carbonate impurities are not as important in the Cu/Cr LDH system as one would expect. Results of the screening design suggest that the Cu/Cr LDH system is far from being completely understood and that small changes in synthetic parameters may result in large changes in the prepared product. Also, LDH systems other than Cu/Cr may have their own synthetic preferences which need to be explored and discovered to optimize the purity and desired properties of these LDHs. Further studies are underway to establish relationships among the most important synthetic variables determined in this study. The electronic properties of these Cu/Cr systems are under investigation in our laboratories.

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$LiMoN_2$: The First Metallic Layered Nitride

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We report the first example of a layered ternary lithium nitride in which the lithium can be deintercalated and reintercalated. The synthesis of $LiMoN_2$ is also the first example of a ternary nitride formed from either the ammonolysis of a molecular organometallic molecule, $Li_2Mo(N^tBu)_4$ or the ammonolysis of a ternary oxide, Li_2MoO_4. Elucidation of the unique structure, in a classic illustration, required both synchrotron X-ray and neutron diffraction data. The space group is $R3$ with lattice parameters (Å; from the neutron data) of $a = 2.8674$ (2) and $c = 15.801$ (2). The ideal structure consists of MoN_2 layers with Mo in trigonal prismatic holes and Li in octahedral holes between the MoN_2 layers. The presence of cation anti-site defects was clearly indicated by the joint X-ray/neutron data refinement; the structure is best described as $(Li_{0.85}Mo_{0.15})_{oct}(Mo_{0.85}Li_{0.15})_{tp}N_2$. $LiMoN_2$ is Pauli paramagnetic with $\chi_0 = 0.59 \times 10^{-6}$ emu g^{-1}. We have employed a variety of different oxidizing agents for the deintercalation of the lithium from $LiMoN_2$ and have been able to deintercalate up to 64% of the lithium. This deintercalated species can be reintercalated with *n*-butyllithium at room temperature. In contrast, electrochemical studies show a large hysteresis in the charge/discharge cycles with no reversibility.

Introduction

Since the discovery of high-T_c superconducting oxides, literally thousands of research groups worldwide have been investigating them in order to quantify their structural and physical properties, as well as attempting to improve their superconducting behavior. We are searching for families of compounds other than oxides that will exhibit this phenomenon. We have chosen to focus on ternary (or higher) nitrides since "N^{3-}" is most similar to O^{2-} with respect to size, polarizability, and electronegativity. Also, and perhaps more importantly, little work has been done

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