Synthesis, Characterization, Ion Exchange, and Catalytic Properties of Nanobinary and Ternary Metal Oxy/Hydroxides

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Nanobinary (Mg−Al) and ternary (Ni−Mg−Al) metal oxy/hydroxides were synthesized by aerogel protocol. The key features of this method are homogenization of metal organic precursors in methanol−toluene mixture, controlled hydrolysis, gelation, hydrothermal treatment, and finally supercritical drying of solvent. The obtained materials, which on further drying at 120 °C, display high surface area, >500 $m^2\ g^{-1}$, and smaller particle size, <20 nm. The samples were further characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric and differential thermal analysis (TG-DTA), and solid state ^{27}Al nuclear magnetic resonance (NMR). The ion exchange and catalytic properties of the resulting nanomaterials were compared with hydrotalcite-like layered double hydroxides (LDHs) prepared by a conventional coprecipitation method. The nanoternary system exhibits 2−4-fold increase in activity of pre-reforming of naphtha.

Introduction

Nanomaterials have generated unprecedented interest due to their unusual physical and chemical properties with divergent applications. Nanocrystalline metal oxides such as MgO, Al_2O_3, CaO, BaO, SrO, ZnO, and TiO_2 exhibit unparalleled destructive adsorption properties of acid gases, polar organics, and even chemical/biological warfare agents.[1] Due to the high surface area, these nanostructured solid materials display good catalytic activity in isomerization and alkylation,[2a] benzylation,[2b] reforming,[2c] and dehydrohalogenation reactions.[2d] Nanomaterials allow fabrication of various microstructures, for example, the zeolite nanoparticles assembly into thin films, membranes, or fibers,[3] with the quasi-spherical ZnO nanoparticles into nanorods.[4] Nanocrystalline binary mixed oxides such as TiO_2/SnO_2, ZnO/Al_2O_3, and Al_2O_3/MgO synthesized recently showed higher photocatalytic activity, variation in band gap, and enhanced reactivity with chemical warfare surrogate and acid gas, respectively.[5−7b] Nanoparticles of $BaO.6Al_2O_3$ realized with superior chemical homogeneity by using reverse-microemulsion exhibited excellent catalytic methane combustion activity over conventionally prepared samples.[8]

Layered double hydroxides (LDHs) which consist of alternate cationic $M^{II}_{1-x}M^{III}_x(OH)_2^{x+}$ and anionic $A^{n-}\cdot zH_2O$ layers have received much attention in recent times in view of their potential applications in catalysis,[9] biomaterials for controlled drug delivery, and gene reservoirs.[10] Many synthetic methods such as coprecipitation,[9a,b] urea hydrolysis,[11a] and sol−gel[11b,c] have been used to synthesize LDH particles. In situ colloidal milling[7c] during coprecipitation protocol yielded Mg−Al hydrotalcites in the range of 60−80 nm. A further innovated and modified aerogel method produced intimately intermingled mixed nanometal oxides of the Mg−Al binary system (with Mg/Al ratios 1:1, 2:1, and 1:2) with enhanced chemical activities.[7b] We herein report the synthesis of homogeneous nanobinary oxy/hydroxides comprising Mg−Al and nanoternary oxy/hydroxides comprising Ni−Mg−Al by aerogel protocol for the first time. The anion

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(1) (a) Richards, R.; Li, W.; Decker, S.; Davidson, C.; Koper, O.; Zaikovski, V.; Volodin, A.; Rieker, T.; Klabunde, K. J. *J. Am. Chem. Soc.* **2000**, *122*, 4921. (b) Lucas, E.; Decker, S.; Khaleel, A.; Seitz, A.; Fultz, S.; Ponce, A.; Li, W.; Carnes, C.; Klabunde, K. J. *Chem Eur. J.* **2001**, *7*, 2505.

(2) (a) Sun, N.; Klabunde, K. J. *J. Catal.* **1999**, *185*, 506. (b) Choudary, B. M.; Mulukutla, R. S.; Klabunde, K. J. *J. Am. Chem. Soc.* **2003**, *125*, 2020. (d) Xu, B.-Q.; Wei, J. M.; Wang, H.-Y.; Sun, K.-Q.; Zhu, Q.-M. *Catal. Today* **2001**, *68*, 217. (e) Wagner, G. W.; Koper, O. B.; Lucas, E.; Decker, S.; Klabunde, K. J. *J. Phys. Chem. B* **2000**, *104*, 5118.

(3) Huang, L.; Wang, Z.; Sun, J.; Miao, L.; Li, Q.; Yan, Y.; Zhao, D. *J. Am. Chem. Soc.* **2000**, *122*, 3530.

(4) Pacholski, C.; Kornowski, A.; Weller, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1188.

(5) Yang, J.; Li, D.; Wang, X.; Yang, X.; Lu, L. D. *J. Solid State Chem.* **2002**, *165*, 193.

(6) Jose, J.; Khadar, M. A. *Nanostruct. Mater.* **1999**, *11*, 1091.

(7) (a) Utamapanya, S.; Klabunde, K. J.; Schlup, J. R. *Chem. Mater.* **1991**, *3*, 175. (b) Carnes, C. L.; Kapoor, P. N.; Klabunde, K. J. *Chem. Mater.* **2002**, *14*, 2922. (c) Zhao, Y.; Li, F.; Zhanf, R.; Evans, D. G.; Duan, X. *Chem. Mater*. **2002**, *14*, 4286.

(8) Zarur, J.; Ying, J. Y. *Nature* **2000**, 403.

(9) (a) Miyata, S.; Kumura, T. *Chem. Lett.* **1973**, *8*, 843. (b) Miyata, S. *Clays Clay Miner*. **1975**, *23*, 369 (c) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173. (d) Reichle, W. T. *J. Catal*. **1985**, *94*, 547. (e) Vaccari, A. *Appl. Clay. Sci.* **1999**, *14*, 161. (f) Corma, A.; Martin-Aranda, R. M. *J. Catal.* **1991**, *130*, 130. (g) Choudary, B. M.; Kantam, M. L.; Rahman, A.; Reddy, C. V.; Rao, K. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 763. (h) Sels, B.; DeVos, D.; Buntinx, M.; Pierard, F.; Mesmaeker, A. K.-D.; Jacobs, P. A. *Nature* **1999**, *400*, 855. (i) Choudary, B. M.; Chowdari, N. S.; Jyothi, K.; Kantam, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 5341.

(10) (a) Khan, A. I.; O'Hare, D. *J. Mater. Chem.* **2002**, *12*, 3191. (b) Choy, J. H.; Kwak, S. Y.; Park, J. S.; Jeong, Y. J.; Portier, J. *J. Am. Chem. Soc.* **1999**, *121*, 1399. (c) Choy, J. H.; Kwak, S. Y.; Jeong, Y. J.; Park, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4042.

(11) (a) Costantino, U.; Marmottini, F.; Nocchetti, M.; Vivani, R. *Eur. J. Inorg. Chem.* **1998**, *10*, 1439. (b) Lopez, T.; Bosch, P.; Ramos, E.; Gomez, R.; Navaro, O.; Acosta, D.; Figueras, F. *Langmuir* **1996**, *12*, 189. (c) Aramendia, M. A.; Borau, V.; Jimenez, C.; Marinas, M.; Ruiz, J. R.; Urbano, F. J. *J. Solid State Chem.* **2002**, *168*, 156.

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exchange capacity of nanobinary oxy/hydroxides with respect to chlorides and biphosphates was studied in detail. The nanoternary system exhibits a 2−4-fold increase in activity of pre-reforming of naphtha, compared to conventionally prepared catalyst. For comparative evaluation, binary and ternary hydroxides composed of Mg−Al and (Ni + Mg)−Al of identical composition (2:1 and 3:1) as above was prepared by the conventional coprecipitation method.

Experimental Section

Synthesis of Binary (Mg−Al−CO_3) and Ternary (Ni−Mg−Al−CO_3) by Coprecipitation Method. In a typical experiment, 24.037 g of $Mg(NO_3)_2 \cdot 6H_2O$ (0.094 M) and 17.584 g of $Al(NO_3)_3 \cdot 9H_2O$ (0.047 M) with Mg^{2+}/Al^{3+} ratio of 2:1 (denoted as CPB2 system) were dissolved in deionized water (140 mL) to give solution A. NaOH (0.8 g, 0.22 M) and Na_2CO_3 (5.959 g, 0.056 M) were dissolved in deionized water (140 mL) to give solution B. To solution B taken in a round-bottomed flask, solution A was added dropwise under continuous stirring at room temperature. The resultant slurry was aged at 60 °C for 18 h. The precipitate was filtered, washed with deionized water, and dried at 120 °C in a hot air oven. Binary system Mg/Al in the ratio of 3:1 denoted as CPB3, ternary systems (Ni + Mg)/Al with ratios of 2:1 [(0.7 + 1.3):1] denoted as CPT2 and 3:1 [(1.1 + 1.9):1] denoted as CPT3 using nickel nitrate as nickel precursor were synthesized by following the same procedure.

Synthesis of Binary (Mg−Al−Cl) by Coprecipitation Method. $MgCl_2 \cdot 6H_2O$ (10.174 g, 0.1 M) and $AlCl_3 \cdot 6H_2O$ (6.035 g, 0.45 M) with Mg^{2+}/Al^{3+} ratios of 2:1 were dissolved in decarbonated water (200 mL) to give solution A; 14 g of NaOH (0.35 M) is dissolved in decarbonated water (200 mL) to give solution B. Solution A and Solution B were simultaneously added dropwise to a 100 mL round-bottomed flask in a glovebox in order to prevent the interaction of atmospheric carbonate during the reaction. The mixing was done at room temperature. The resultant slurry was aged at 60 °C for 18 h. The precipitate was then filtered, washed with decarbonated water, and dried at 120 °C in a hot air oven.[9a]

Synthesis of Nanobinary (Mg−Al) and Nanoternary (Ni−Mg−Al) Metal Oxy/Hydroxides by Aerogel Method. In this method, 2.4 g of magnesium turnings (0.1 M) were allowed to react with freshly dried 100 mL of methanol under argon flow. Under vigorous stirring, 300 mL of dry toluene was added to the resultant magnesium methoxide solution and stirred for 2 h. To this 10.235 g of aluminum isopropoxide (0.05 M) (for 2:1 system (NB2)) was added and stirred for 2 h. To the resultant solution 4.85 mL of deionized water was added using a capillary addition pump over a period of 0.5 h. The solution was kept under stirring for 18 h at room temperature. The pH of the solution was basic and found to be >9. The above solution was placed in an autoclave, heated to 265 °C, kept for 10 min, vented to obtain an aerogel material, and further dried at 120 °C to remove the traces of solvent to obtain a fine powder. The same procedure was followed to prepare the binary system Mg/Al in the ratio of 3:1 denoted as NB3, ternary systems (Ni + Mg)/Al with ratios of 2:1 [(0.7 + 1.3):1] denoted as NT2 and 3:1 [(1.1 + 1.9):1] denoted as NT3 using nickel(II) acetylacetonate as the precursor for nickel.

Ion Exchange. Experiments were carried to study the ion exchange properties of the aerogel-prepared material with that of the conventionally prepared material. In all these experiments, 0.1 g of aerogel material and 20 mL of 0.025 M anionic solutions (Cl^-, CO_3^{2-}, HPO_4^{2-}) were stirred in a closed reactor for 24 h at room temperature and the samples were withdrawn at different time intervals. The slurry was filtered, washed with deionized water, and dried at 120 °C. Finally, the solids were analyzed for the anion content.

Table 1. Particle Size and BET Surface Area of As-Prepared Samples

sample	particle size (TEM/SEM)	S_{BET}, m^2/g	sample	particle size (TEM/SEM)	S_{BET}, m^2/g
NB2	2−20 nm	765	CPB2	>1 μm	85
NB3	2−10 nm	674	CPB3	>1 μm	79
NT2	2−10 nm	600	CPT2	>1 μm	70
NT3	2−10 nm	533	CPT3	>1 μm	80

Preparation of Pellets. Five grams of poly(vinyl alcohol) (PVA) dissolved in 245 mL of distilled water and to this 2 g of graphite blended with 100 g of calcined ternary metal oxide were added. The excess water is removed on a water bath. The dried powder was compressed under pressure to 4 × 6 mm pellets, which were further crushed and sieved through 18/25 BSS mesh to avoid mass-transfer limitations and were used in the reaction. The NT2 powder sample was compressed at different pressures during the pelletization process.

Pre-reforming of Naphtha. Twenty milliliters of the sieved catalyst was loaded into a microreactor system and reduced at 550 °C under atmospheric pressure of hydrogen at the flow rate of 10 L/h for 16 h. Then steam was charged at the rate of 190 mL/h simultaneously with the increased flow of hydrogen to maintain 5 bar pressure in the reactor to prevent reoxidation of the catalyst. After 15 min, naphtha was introduced at 5 liquid hour space velocity (LHSV) and pre-reforming was conducted at 5 bar pressure in a continuous flow of hydrogen at the rate of 2 L/h. The evolved gases were analyzed by gas chromatography.

Characterization. X-ray powder diffraction data were collected on a Siemens/(D5000) diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) with a scan speed of $2\theta = 0.045/0.5$ s in the range of 2−65°. The crystallite size was estimated by using the Scherrer equation in angstroms. Specific surface areas are calculated from BET nitrogen isotherms determined at 77 K on a Micromeritics pulse ASAP 2010 instrument. The samples were degassed in a vacuum at 200 °C for 3 h before measurement. TEM was performed on a TECNAI 12 FEI TEM instrument. The samples were suspended in dry toluene, treated with ultrasound, and applied to a carbon carrier foil (LaB6, KO-AP3, $D = 50$ μm, single tilt holder). Thermogravimetric analysis and TGA-MS thermograms were recorded on a Mettler-Toledo TGA/SDTA 821 instrument coupled to a Blazers Thermostar GSD300T in the temperature range of 25−600 °C with a heating rate of 10 °C/min in a nitrogen atmosphere. Solid state ^{27}Al Nuclear magnetic resonance (NMR) was measured using a Gemini Varian at 400 MHz spectrometer.

Chemical Analysis. About 100 mg of calcined aerogel material was dissolved in 2 mL of concentrated HCl and the cationic contents were analyzed by AAS (Perkin-Elmer AAanalyst 300) after suitable dilution. Phosphorus content was analyzed by a UV−visible spectrophotometer (GBC Cintra 10e UV−Vis−DRS Spectrometer) at 830 nm wavelength. The evolved gases in the pre-reforming of naphtha were examined using a Chemito gas chromatograph with a thermal conductivity detector (TCD). High-purity argon was used as a carrier gas with a flow rate of 30 mL/min. A 12 ft stainless steel column packed with 5 Å molecular sieves was activated with flowing argon (30 mL/min, 250 °C, and 24 h). During analysis, the column is held at 50 °C, the injection port at 100 °C, and the detector compartment at 100 °C. A calibration gas mixture containing CO, CO_2, CH_4, and H_2 was used for qualitative and quantitative analysis.

Results and Discussion

In general, the LDHs obtained by the coprecipitation method produce metal hydroxy layers intercalated by car-

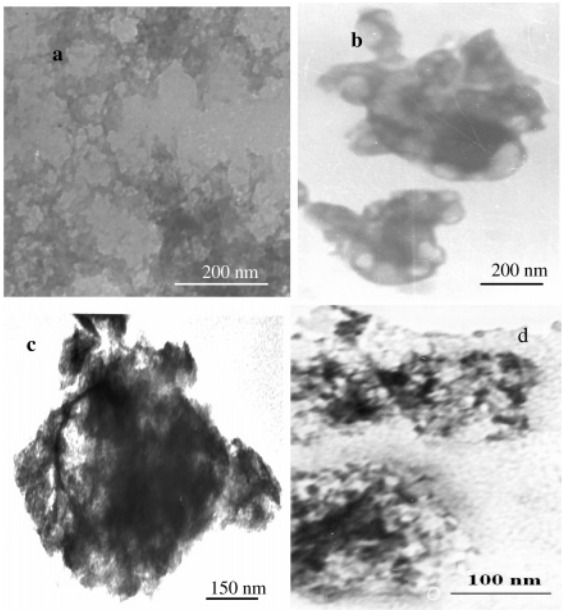

Figure 1. TEM images showing assembly of Mg−Al nano mixed hydroxides in the presence of CO_3^{2-} (NB2) with time: (a) as-prepared; (b) after 15 min; (c) after 30 min; (d) after 1 h.

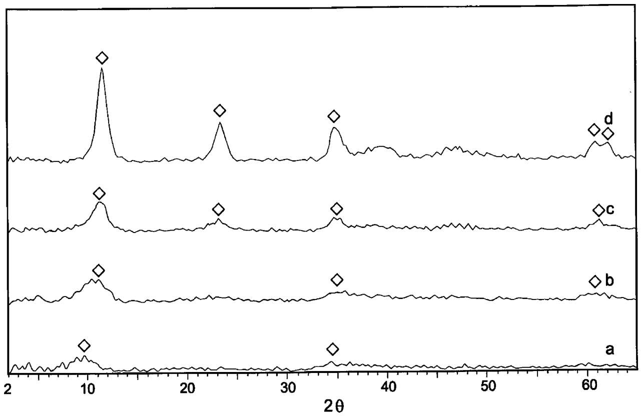

Figure 2. XRD patterns of nano Mg−Al hydroxide (NB2) (a) and its intercalation of CO_3^{2-} with time: 1 h (b), 3 h (c), and 24 h (d). ◇ Hydrotalcite phase.

bonates or other anions such as chloride and nitrate. The aerogel method employing alcohol−toluene mixtures, rapid hydrolysis and gelation, and supercritical drying of solvent in the present study produces metal oxy/hydroxides with high surface area and smaller particle size (Table 1). These nanobinary and ternary oxy/hydroxides on treatment with carbonate anion forms layered double hydroxides. Figure 1a shows the TEM photograph of an as-prepared NB2 sample exhibiting a particle size in the range of 10−20 nm and arranged in a layer of single-particle thickness. However, there is an overlapping of these layers at different places as shown in Figure 1a.

The XRD patterns of as-prepared nanobinary and ternary systems show amorphous phase as shown in Figure 2a and 3a. The TG-DTA of the nanobinary (NB2) shows only one endotherm at 385−400 °C, indicating the dehydroxylation of metal hydroxides. The ^{27}Al MAS NMR of NB2 as shown in Figure 4a indicates the presence of both octahedral and tetrahedral aluminum. The presence of tetrahedral aluminum in the aerogel-prepared material is due to supercritical drying of the material at 265 °C since at this temperature some of the aluminum becomes dehydrated.[12a] On further calcination at 450 °C, there was an increase in the tetrahedral aluminum as shown in Figure 4b.[12b] All these studies demonstrate that materials obtained by the aerogel protocol were indeed nanoparticles of mixed metal oxy/hydroxides.

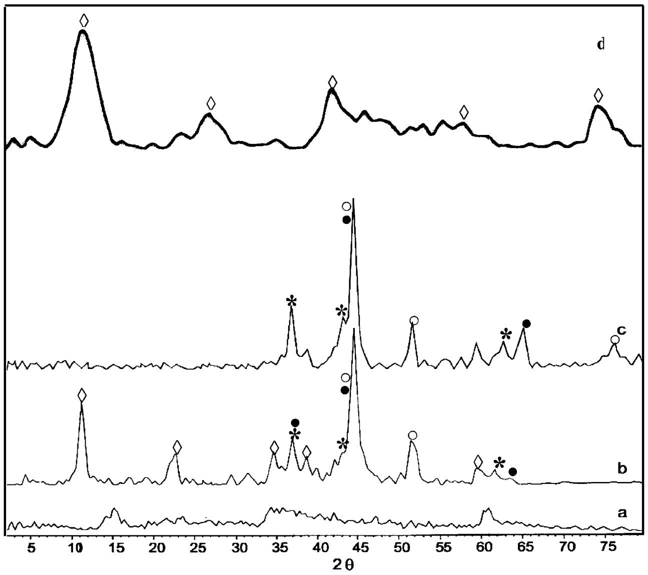

Figure 3. XRD spectra of nano Ni−Mg−Al hydroxide NT2 (a), used CPT2 (b), and used NT2 (c). ◇, Hydrotalcite phase; ●, $NiAl_2O_4$ phase; ∗, NiO phase; ○, Ni phase.

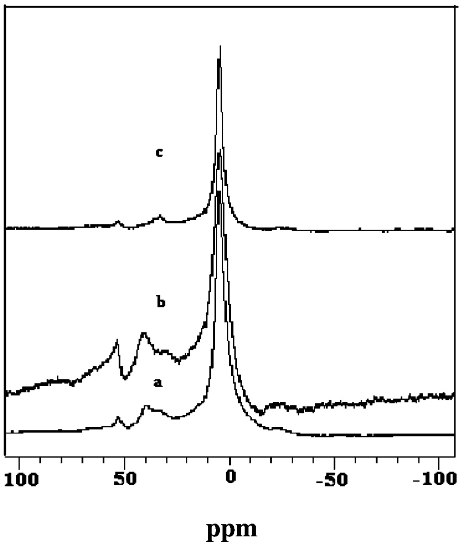

Figure 4. ^{27}Al MAS NMR of nano Mg−Al NB2 (a), after calcinations of NB2 (b), and on intercalation of CO_3^{2-} (c).

Ion Exchange. The treatment of carbonate anion with NB2 sample is studied by TEM and XRD. Figure 1b−d shows the TEM photographs of carbonate anion for 0.25−1 h, respectively. The overlapping of layers with time, triggered by carbonate anions, leading to a three-dimensional network, is observed. The XRD of carbonate ion intercalated material shows characteristic hydrotalcite phase (Figures 2d and 3d). The intensities of basal reflection increases markedly with increase in time, and the reflections follow a symmetrical

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(12) (a) Roelofs, J. C. A. A.; Bokhoven, J. A. V.; Dillen, A. J. V.; Geus, J. W.; Jong, K. P. D. *Chem. Eur. J.* **2002**, *8*, 5571. (b) Weir, M. R.; Kydd, R. A. *Inorg. Chem.* **1998**, *37*, 5619. (c) Bellotto, M.; Rebours, B.; Clause, O.; Lynch, J.; Bazin, D.; Elkaim, E. *J. Phys. Chem.* **1996**, *100*, 8535.

Table 2. Lattice Parameters, Crystallite Size, and Ion-Exchange Capacity of Nanobinary Hydroxides Prepared by Aerogel and Coprecipitation Methods

		carbonate exchanged			
		lattice parameters (Å)			
sample	MII/MIII ratio	*a*	*c*	crystallite size[a] (Å)	%P[b]
NB2	2:1	3.044	22.983	52.93	7.05
NB3	3:1	3.046	22.83	52.92	6.6
CPB2	2:1	3.038	22.584	160.21	6.1
CPB3	3:1	3.068	23.733	179.49	7.25

[a] Determined by XRD. [b] UV−Vis spectrophotometer at 830 nm wavelength.

Table 3. Results of Pre-reforming of Naphtha

sample	% nickel	T^a (°C)	T^b (°C)	% naphtha conv.	quantity of naphtha processed/g of nickel/h
CPT3	33.1	550	450	24.4	3.6
NT3	28.7	550	450	98.5	17.5
CPT2	28.3	550	450	74.0	12.7
NT2	28.7	550	450	99.0	22.9 (23.4)[d]
Com.[c]	45−47	550	450	98.0	21.5

[a] Reduction temperature. [b] Reaction temperature. [c] Commercial catalyst (Süd-Chemie India Limited). [d] The value in parentheses corresponds to pellets compressed at 15000 lb and tested at 7 LHSV.

pattern of normal LDH. These results indicate that the stacking of layers progress with time. The *a* and *c* lattice constants of ion-exchanged materials have constant values of 3.0 and 22.9 Å similar to that of normal LDHs (Table 2).[9b] The TG-DTA of the these materials exhibit two endotherms at 200−225 °C and 385−400 °C as a typical normal LDH pattern corresponding to loss of water of crystallization and decarboxylation, respectively. The ^{27}Al MAS NMR spectra exhibit only octahedral aluminum (Figure 4c), similar to LDH prepared by coprecipitation.[12c] The same phenomena was observed using the above techniques for the intercalation of anions such as Cl^- and NO_3^-.

The XPS study of the chloride intercalated aerogel material shows that binding energies of Mg 2p, Al 2p, and Cl 2p levels vary between 50.2 and 50.7 eV, between 74.1 and 74.5 eV, and between 198.0 and 200.0 eV, respectively. These values are in close agreement with the LDHs prepared by the conventional method, which indicate perfect intercalation of Cl^- ion. The chloride intercalated materials on treatment with bivalent anions such as hydrogen phosphate show an equal uptake of the phosphate anion as determined by spectrophotometer analysis of phosphate ion (Table 2). Further, the TG-MS analysis of phosphate intercalated material heated to 600 °C shows no detectable chloride ions, confirming the proposed statement.

Pre-reforming. A few reports have shown that mixed metal oxides derived from LDHs are active catalysts in steam reforming.[13] The ternary systems were evaluated for pre-reforming of naphtha at 5 bar; the reaction conditions and results are given in Table 3. The GC analysis showed 80% of methane with the remaining 20% accounted to CO, CO_2, and hydrogen, and the untreated naphtha was collected by condensation.

The powder samples of NT2 with the bulk density of 0.6 cm^3/g, when compressed at different pressures at 3000 and 15000 lb during the pelletization process, displayed increased bulk density, 0.7 and 0.85 cm^3/g, respectively. This is in agreement with the earlier results.[1a] In view of this, the loading of the NT2 in a defined volume of 20 mL is also correspondingly increased. However, the quantity of the naphtha processed/g of nickel/h remains more or less constant (Table 3) for the NT2 samples compressed as indicated above. This result rules out any diffusion problems. Therefore, the nanoternary hydroxides on calcination display 2−4-fold superior catalytic activity over the LDHs prepared by the coprecipitation method and the NT2 (Ni + Mg/Al 2:1) is proved to be the best one in terms of activity.

The TPR profile for NT2 showed the reduction at 480 °C and CPT2 at 680 °C and chemisorption studies at 550 °C reveals the Ni metal dispersion in NT2 sample is 6 times more than CPT2. Thus, the higher activity is ascribed to the higher nickel dispersion possible in nanomaterials. The NT2 and CPT2 samples were tested for 30 h, which showed no change in the selectivity and activity. The XRD of the used CPT2 indicates metallic Ni and metal oxide phases,[14] and partially regained LDH structure due to memory effect as shown in Figure 3b,[9a] whereas the used nanoternary hydroxides (NT2) display metallic Ni and metal oxide phases only without regaining its LDH structure (Figure 3c) due to highly dispersed Ni stabilized on the support. With lower nickel content and without promoters, the NT2 catalyst is as active as the commercial catalyst, which possesses higher nickel content with promoters. The CHNS analysis of used catalysts showed the presence of 1% coke and no sulfur.

Conclusions

In conclusion, nanobinary and ternary oxy/hydroxides with different M^{II}/M^{III} ratios prepared by the aerogel method, which are indeed nanoparicles of LDH, exhibit superior catalytic properties. The compositions and thermal behavior of the aerogel materials are comparable with the LDHs prepared by the conventional method. The aerogel material initially intercalated with monovalent Cl^- undergoes ion exchange with divalent HPO_4^{-2} anion. The ion-exchanged materials resemble the typical hydrotalcite pattern with less crystallite sizes. XRD studies confirm the layer formation of LDH nanoparticles in the presence of added anions, which was shown to be time-dependent. The nanoternary hydroxides display 2−4-fold superior catalytic activity for pre-reforming of naphtha over the LDHs prepared by the coprecipitation method and the NT2 (Ni + Mg/Al = 2:1) was proved to be the best one in terms of activity. With lower nickel content and without promoters, the NT2 catalyst was as active as the commercial catalyst, which possesses higher nickel content with promoters.

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(13) (a) Segal, S. R.; Anderson, K. B.; Carrado, K. A.; Marshall, C. L. *Appl. Catal., A* **2002**, *231*, 215. (b) Neilsen, J. R. R. In *Catalysis, Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1984; Vol. 5, Chapter 1.

(14) (a) Basile, F.; Basini, L.; Amore, M. D'.; Fornasari, G.; Guarinoni, A.; Matteuzzi, D.; Piero, G. D.; Trifiro, F.; Vaccari, A. *J. Catal.* **1998**, *173*, 247. (b) Cesteros, Y.; Salagre, P.; Medina, F.; Sueiras, J. E. *Appl. Catal., B* **2000**, *25*, 213.