

# Synthesis and coating of silica supported Nickel Oxide particles over ceramic pre-forms through sol–gel derived layered double hydroxides

Mridusmita Mishra · Manash Ranjan Das ·  
Rajib Lochan Goswamee

Received: 28 October 2009 / Accepted: 7 January 2010  
© Springer Science+Business Media, LLC 2010

**Abstract** Silica supported Nickel Oxide fine particles have been synthesized through sol–gel derived Ni–Al Layered Double Hydroxide (LDH) and coated over honeycomb ceramic pre-forms through dip-coating technique. The powder products of supported materials have low crystallinity, negative zeta potential, exhibit high dispersibility and suitable for further processing by coating techniques. The powder X-ray diffraction (XRD) patterns have shown that there is an increase of basal spacing by 3.02 Å in acetylacetonate intercalated LDH. The particles of <2 µm size increase with the rise of LDH component in the composite. The particles of NiO structure formed on decomposition of composites have crystallite size <20 nm. Due to the interlayer reduction of NiO crystallites, the unsupported LDH on calcination gives Ni<sup>0</sup> particles of size around 4.18 nm. The Scanning Electron Microscopy (SEM) patterns of coated supported suspensions over ceramic substrates show formation of thin, crack free coats with uniform distribution of particles.

**Keywords** Ni–Al LDH · Ni<sup>0</sup> crystallites · Dip-coating · Supported NiO

## 1 Introduction

Layered materials are considered as an important group of solids bearing enormous application prospects in various fields. Layered Double Hydroxides (LDH) are a group of such important materials where elementary layers possess

some positive charge due to the substitution of bivalent metal ions in the parent brucite like structure by trivalent metal ions [1]; the positive charge thus generated is neutralized by the interlayer anions like Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup> etc. LDH on thermal degradation forms various phases like non-stoichiometric oxides, segregated spinels, layered bivalent oxides, metal nano-particles etc. at different temperatures and conditions. The non-stoichiometric oxides formed at around 400 °C basically maintain the structure of the concerned bivalent metal oxide where trivalent metal ions are distributed in the form of solid solutions [2, 3]. Due to their layered structure and size these metal oxides are very reactive species e.g. the layered ZnO derived from Zn–Cr LDH and supported on thermally decomposed montmorillonite shows higher reversible adsorption of H<sub>2</sub>S gas [4] than normal ZnO powders. The oxides derived from LDH precursors have innumerable such applications in various fields like catalysis, adsorbents, sensors etc. Apart from this, due to their layered structure LDH also has the prospects of being shaped as thin films [5] but their high charge density do not allow them to easily swell and disperse like montmorillonite in an appropriate liquid medium. This non-dispersibility property makes it difficult to coat them over solid surfaces by using standard coating techniques like spin or dip-coating.

Generally, LDH is prepared in aqueous medium by co-precipitation in aqueous medium under controlled reaction conditions; however, non-aqueous sol–gel route is also used to obtain finer LDH particles [6–8]. Such finer LDH particles when supported over suitable carrier and thermally degraded may give highly reactive metal oxide or metal nano particles for catalytic reactions with gaseous reactants. It has been previously observed that ZnO supported on silica particles through sol–gel route gives attractive characteristics of pore size, surface area and porosity [9]. Reports are

M. Mishra · M. R. Das · R. L. Goswamee (✉)  
North-East Institute of Science & Technology (NEIST),  
Jorhat 785006, Assam, India  
e-mail: rajibgoswamee@yahoo.com

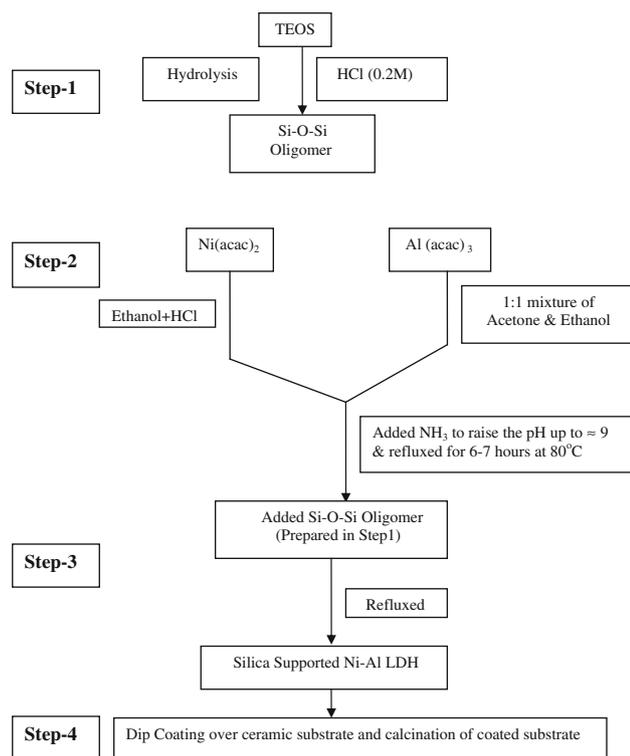
also there for the synthesis of NiO nano-particles supported on silica through hydrolysis of Ni salts upon Tetraethylorthosilicate (TEOS) [10] by sol-gel route.

The aim of this present work is to advantageously utilize the sol-gel route to prepare silica supported LDH which firstly would be in a stable dispersible form so that it can be coated on a solid surface in the form of a thin film and secondly on calcination would provide smoothly distributed supported metal oxide nano particles.

## 2 Experimental details

Ni(acac)<sub>2</sub> (98%, M/S E. Merck) and Al(acac)<sub>3</sub> (98%, M/S Aldrich) were used as such. The ethanol used were first refluxed with Mg turnings (5 g/L) in presence of iodine (0.5 g/L) and then distilled. Acetone was refluxed with a small portion of KMnO<sub>4</sub> and also distilled [11]. The waters used in the experiments were distilled twice.

To synthesize 1:1 SiO<sub>2</sub>:LDH composite and its coated product steps given below from 1 to 4 were carried out. Similarly, to synthesize composites with varied SiO<sub>2</sub>:LDH ratios, the corresponding required changes in the amount of the key reactants were made. However, the Ni:Al ratios of Ni–Al LDH component in the series were maintained at 3:1. The synthesis scheme followed is depicted in Fig. 1.



**Fig. 1** Scheme for synthesis and coating of silica supported NiO over solid surface

*Step-1:* A total of 4.5 cm<sup>3</sup> TEOS, 0.72 cm<sup>3</sup> conc. HCl and 3.5 cm<sup>3</sup> purified ethanol were mixed and agitated for 45 min at room temperature.

*Step-2:* About 0.02 M Ni(acac)<sub>2</sub> dissolved in 80 cm<sup>3</sup> purified ethanol and 0.007 M Al(acac)<sub>3</sub> in 80 cm<sup>3</sup> 1:1 ethanol and acetone mixture were mixed at pH 6 and temperature 80 °C. To it added hydrolyzed TEOS obtained in Step-1.

*Step-3:* Slowly raised the pH of the suspension to around 9 by adding 4 cm<sup>3</sup> NH<sub>4</sub>OH solution and refluxed for 6–7 h at 80 °C. A free flowing gel was obtained, a part of it filtered off and dried at room temperature under a flow of air maintained at a rate of 20 cm<sup>3</sup>/min by circulating it through an aqueous solution of CaCl<sub>2</sub>·6H<sub>2</sub>O [12]. The other portion of the gel, kept separately in a corked bottle, remained suspended even after 3 months.

*Step-4:* The supported LDH was coated over cordierite honeycomb surface (from Ceramic Technology Institute, M/S Bharat Heavy Electricals Limited, Bangalore, India) by dipping it in a 4% (w/v) suspension obtained in Step-3, using a Dip-coater (M/S KSV Instruments) at 20 mm/min dipping rate, residence time 60 s and 20 mm/min withdrawal rate. The coated products were initially dried at 50 °C for 30 min, followed by drying at 110 °C for 90 min. Finally, the dried products were calcined at 400 °C for 30 min in air atmosphere.

A portion of the dried products from Step-3 was calcined at around 400 °C in an electric furnace for 30 min. The air flow inside the furnace was controlled by closing the lid at the centre of the furnace.

XRD characterizations of different products were carried out using Cu *k*<sub>α</sub> radiation at a scan rate of 0.2° 2θ/min (Rigaku-Ultima IV). The crystallite size of the products formed on calcination was calculated by using the Scherrer Equation [13].

In case of the Ni<sup>0</sup> particles (111) prominent peak at 44.37° is partly overlapped with (012) peak of the NiO phase, therefore, the crystallite size was determined from (200) peaks at 52°. In case of NiO phase the crystallite size was determined from the diffraction peak of (012) at 43.28°. The unit cell calculation of unsupported acetyl-acetate intercalated LDH was carried out with the help of data interpretational software, POWD.

The thermo-gravimetric measurements of dried products collected at Step-3 were carried out in a simultaneous TG-DTA analyzer (SDT2960, M/S TA Instruments) using Al<sub>2</sub>O<sub>3</sub> as reference at 10 °C/min heating rate in air atmosphere. The evaluation of kinetic parameters of some selected conversions were carried out using model free iso-conversional approach [14] which is a convenient method for determination of activation energy of conversions having multiple overlapping decompositions.

Fourier Transform Infrared (FTIR) spectra were recorded in spectrophotometer (Perkin-Elmer 2000 System) in

4,000–400  $\text{cm}^{-1}$  range at a spectral resolution of 4  $\text{cm}^{-1}$  using KBr pellets.

The particle size distribution was measured with particle size analyzer CILAS 1180, in the range 0.04–500.00  $\mu\text{m}/100$  classes.

The BET surface area measurements of some selected samples were made using a Quantachrome Instrument with nitrogen as analysis gas.

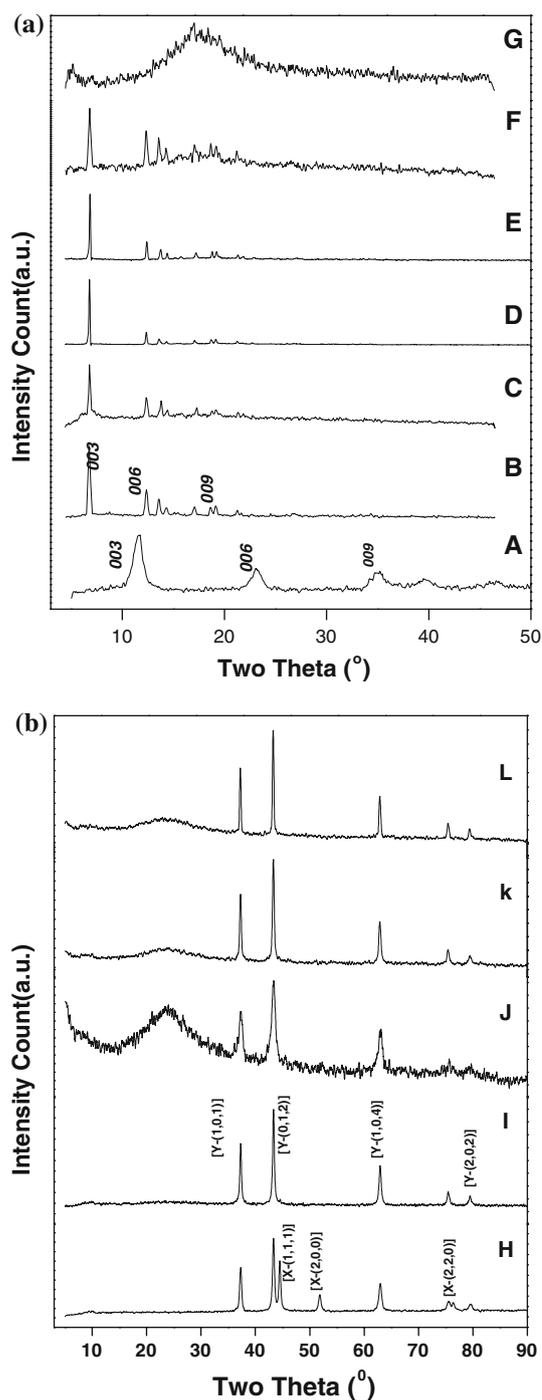
For the zeta potential measurement a homogeneous aqueous suspension of 2% (w/v) of dried product was prepared, using a Ti horn of diameter 13 mm at 23% amplitude and 3 min time by ultrasonication (Vibracell, VCX500). The zeta potential was measured by the technique of electrophoresis in Zetasizer 3000HS (Malvern Instruments).

### 3 Results and discussion

The XRD patterns (Fig. 2) have shown that the basal (001) peak in the co-precipitated sample (pattern i-A) appears at  $11.69^\circ$  ( $\sim d = 7.56 \text{ \AA}$ ) whereas in sol-gel derived product the same appears at (pattern i-B) at  $8.24^\circ$  ( $\sim d = 10.58 \text{ \AA}$ ) corresponding to an increase of  $d$  value by  $3.02 \text{ \AA}$ . This is due to intercalation of larger acetylacetonate molecules in the inter-layers of sol-gel derived LDH. Indexing of observed peaks of pattern i-B was tried with a Takovite type structure [15]. Due to various factors like poorer crystallinity of sol-gel products, turbostratic distortion of layers and hetero-chemical nature of the inter-layers, an accurate set of cell parameters was difficult to achieve. However, with a  $\sim 3.1 \text{ \AA}$  and a three layered hexagonal cell system a set of indexed planes were calculated which are shown in pattern i-B of Fig. 2. The FTIR patterns show peaks around  $1,630 \text{ cm}^{-1}$  due to C=O stretching bands of enolic form of acetylacetonate. FTIR patterns also show broad absorptions due to -OH stretching modes in  $3,700\text{--}3,000 \text{ cm}^{-1}$  region [16].

The thermo-gravimetric analysis profile for the composites with different ratio of LDH:silica show three different weight loss regions viz., room temperature to around  $100$ ,  $100\text{--}200$  and  $200\text{--}400^\circ\text{C}$ . The first weight loss corresponds to evaporation of surface adsorbed water or organic solvent molecules. The second weight loss is attributed to the loss of interlayer water and organic solvent molecules. The third weight loss corresponds to removal of hydroxide ions from the brucite like layers, formation of metal oxides as well as conversion of remaining interlayer species to oxides of carbon [2].

The size of the  $\text{Ni}^0$  particles formed on calcination from sol-gel derived unsupported Ni-Al LDH as determined by Scherrer equation is around  $4.18 \text{ nm}$ . The reason for the presence of  $\text{Ni}^0$  metal (JCPDS-PDF 4-850) can be



**Fig. 2** XRD patterns of unsupported and supported LDH at different silica to LDH ratios- **a** Uncalcined products viz., A-unsupported Ni-Al LDH (non sol-gel), B-G-silica supported sol-gel LDH at  $\text{SiO}_2$ :LDH ratios 0:1, 1:1, 2:1, 3:1, 4:1 and 1:0, respectively **b** H-L after calcination at  $400^\circ\text{C}$  products with  $\text{SiO}_2$ :LDH ratios 0:1, 1:1, 2:1, 3:1 and 4:1, respectively (here, X-Ni<sup>0</sup> phase and Y-NiO phase)

explained as due to the reduction of NiO by CO produced during the thermal decomposition of intercalated acetylacetonate molecules around  $400^\circ\text{C}$ . The formation of  $\text{Ni}^0$

particles over thermally exfoliated graphite surface due to reduction of NiO by CO at around 400 °C is already reported [17]. Similar formation of Cu<sup>0</sup> particles on thermal decomposition of Cu(acac)<sub>2</sub> complexes is also reported [18].

The formation of Ni<sup>0</sup> particles have not been observed in supported LDH. The release of interlayer CO type decomposition products is expected to be faster in supported systems than in non-supported one. In the former, the LDH particles are well dispersed over support surfaces while in the later the layers are more stacked and aggregated. As a result the exfoliation of the layers by the outward internal pressure of decomposition products in the supported system is easier than in the unsupported systems. This causes longer stay of CO type decomposition products in the unsupported system, leading to formation of Ni<sup>0</sup> particles due to reduction of NiO species. The kinetic parameter for the weight loss from 200 to 400 °C calculated through iso-conversional method show that activation energy of conversion in sol-gel derived Ni-Al LDH is 16.43 kJ mol<sup>-1</sup> which is higher than 14.61 KJ mol<sup>-1</sup> found in coprecipitacional product. This is partly due to the additional conversion of NiO particles to Ni<sup>0</sup> in this temperature range by reaction of CO molecules formed on decomposition of acetylacetonate in the sol-gel product.

It has been observed that use of silica support increases the surface area by eight times from 9.46 m<sup>2</sup>/g in unsupported Ni-Al LDH to 77.09 m<sup>2</sup>/g in uncalcined silica supported Ni-Al LDH where SiO<sub>2</sub> to LDH ratio is 2:1.

The particle size distribution of the products shows that the sol-gel approach gives higher amount of particles in the sub-micron colloidal range. In case of composites, the higher the amount of LDH component in the system, higher is the amount of particles below 2 μm range. In pure silica due to the process of oligomerisation most of the particles are above 20 μm.

Similarly, the negative zeta potential of the composite particles rises with the amount of silica in the system (Table 1). The corresponding pH values are also given in

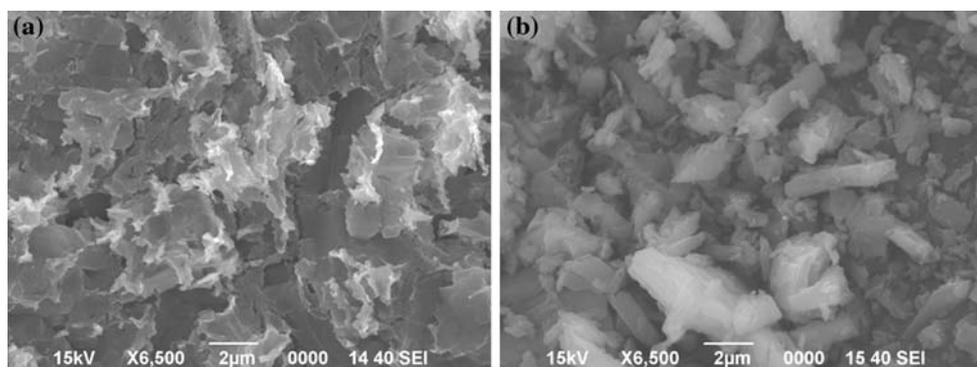
**Table 1** Zeta-potential and pH values of synthesized composite powder samples

Composite type	Zeta-potential (mV)	pH
Hydrolyzed TEOS	13.3	2.7
Sol-gel Ni-Al LDH	36.1	8.8
Silica supported Ni-Al LDH with Silica:LDH = 1:1	-26.8	8.7
Silica supported Ni-Al LDH with Silica:LDH = 2:1	-30.1	9.0
Silica supported Ni-Al LDH with Silica:LDH = 3:1	-35.2	8.8
Silica supported Ni-Al LDH with Silica:LDH = 4:1	-35.3	7.7

the Table 1. As such iso-electric point of silica varies in the pH range 2 to <4 whereas for LDH the same is around 12 [19]. Therefore, with the rise of LDH component in the composite the magnitude of zeta potential decreases yet it overall remains negative, which helps in dispersibility of the system paving way for the formation of thin films by dip-coating over solid surfaces [20]. SEM image of dried powders and a thin coat of the composite over ceramic honeycomb pre-forms after calcination is shown in Fig. 3a and b, respectively. It shows formation of thin coat with uniform distribution of finer layered particles over the pre-form surface after calcination.

#### 4 Conclusion

The present work illustrates that high surface area LDH particles can be supported over silica surface by sol-gel route to provide flowing dispersions which can be coated over a solid body, paving way to fabricate novel devices having a thin film of fine particles of calcined metal oxides. Further works to use them as gas purifying device is under progress.



**Fig. 3** a 1:1 Silica supported Ni-Al LDH b its SEM pattern after coating upon honeycomb pre-form and calcination at 450 °C

**Acknowledgments** We thank Dr P. G. Rao, Director, North East Institute of Science & Technology, Jorhat and Council of Scientific & Industrial Research, New Delhi for the financial support and permission to carry out the work.

## References

1. Vaccari A, Clause O, Coelho MG et al (1993) *Appl Clay Sci* 8:169
2. Kovanda F, Balek V, Dornicak V et al (2003) *J Therm Anal Calorim* 71:727
3. Reichle WT, Kang SY, Everhardt DS (1986) *J Catal* 101:352
4. Goswamee RL, Ayril A, Bhattacharyya KG et al (2000) *Mater Lett* 46:105
5. Gardner E, Humtoon KM, Pinnavaia TJ (2001) *Adv Mat* 13:1263
6. Prinetto F, Ghiotti G, Griffin P et al (2000) *Micropor Mesopor Mat* 39:229
7. Lopez T, Bosch P, Ramos E et al (1996) *Langmuir* 12:189
8. Jitianu M, Zaharescu M, Balasoiu M et al (2003) *J Sol-Gel Sci Techn* 26:217
9. Goswamee RL, Bosc F, Cot D et al (2004) *J Sol-Gel Sci Techn* 29:97
10. Ryoji T, Satoshi S, Toshiaki S et al (1999) *Chem Lett* 28:305
11. Perrin DD, Armarego WLF (1980) *Purification of laboratory chemicals*. Pergamon, Oxford
12. Motzet H, Pöllmann H (1999) *Cem Concre Res* 29:1005
13. Deraz NM, Selim MM, Ramadan M (2009) *Mater Chem Phys* 113:269
14. Vyazkovin S (2000) *Thermo Acta* 355:155
15. von Allmann R (1970) *Chimia* 24(3):99
16. Nakamoto K (1978) *Infrared and raman spectra of inorganic and coordination compounds*. Wiley, London
17. Buldarin VL, Diyuk V, Matzui L et al (2000) *J Therm Anal Calorim* 62:345
18. Nasibulia AG, Altman IS, Kauppinen EI (2003) *Chem Phys Lett* 367:771
19. Kosmulski M (2002) *J Colloid Interf Sci* 253:77
20. Bielewicz D (1988) *Arch Mining Sci* 33:499