In situ assembly of layered double hydroxide nano-crystallites within silica mesopores and its high solid base catalytic activity†

Liang Li[a] and Jianlin Shi*[ab]

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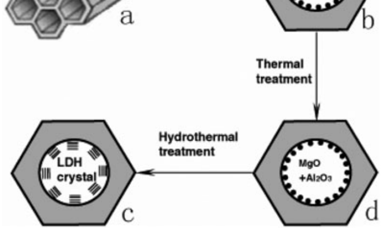
Mg-Al layered double hydroxide (LDH) nanocrystallites with a lateral size less than 9 nm were *in situ* synthesized within the pore channels of mesoporous silica materials, creating one of the most active heterogeneous base catalysts owing to the high number of active edge sites.

Layered double hydroxides (LDHs) are a class of promising solid base catalysts which have the general formula of $\mathrm{Me}_{1-x}{}^{\mathrm{II}}\mathrm{Me}_x{}^{\mathrm{III}}(\mathrm{OH})_2\mathrm{A}_x\cdot n\mathrm{H}_2\mathrm{O}$, where Me(II) and Me(III) are metal cations and A denotes anions. The structure of LDHs consists of brucite-like layers, with Me(II) cations partially substituted by Me(III) cations resulting in a net positive charge which is neutralized by the incorporation of exchangeable anions in the hydrated interlayer region.[1,2] The basic properties of LDHs and the materials derived from them can be tailored by altering the identity of cations in the layers, the Me(II)/Me(III) ratio, the nature of compensating anions, and activation conditions. The resulting materials are environmentally friendly solid base catalysts effective for reactions such as aldol condensations, alkylation and isomerization.[3] Recent studies showed that the actual active sites participating in catalysis are situated at the edges of the platelets.[4–9] Generally, the number of exposed edge active sizes is limited by the lateral size of the LDH crystallites and increases with decreasing particle size. So that solid base catalysts composed of nanometer sized particles should have more active sites on the surface than those of larger particles, and thus will have enhanced catalytic activity. Efforts have been made to minimize the lateral size of the LDH in recent years.[4–6] However, for nanometer sized catalyst particles, there are considerable difficulties in separating and reclaiming the catalyst at the end of the reaction in liquid systems. An effective solution to this problem is to select appropriate materials as catalyst support. Recently, Winter *et al.* reported carbon nanotube-supported LDH platelets with a lateral size of 20 nm, and the resulting activated catalyst showed relatively high activity in the self-condensation of acetone and in the condensation of citral with acetone. The significant increase in efficiency was found to be related to the small crystallite size of the LDH platelets.[10] It can be expected that synthesizing even smaller LDH crystallites will be beneficial to obtain more efficient catalysts.

Mesoporous silica material as a kind of common support for catalysts has attracted considerable attention in the past decade due to its nanosized pore structure and relatively good thermal and chemical stability.[11] Its large surface area and well-defined tunable nano-pore size provides a good opportunity for confining the growth of guest materials. Various kinds of guests such as metals, oxides, sulfides and organic molecules have been successfully loaded in the pore channels.[11] However, no reports can be found on loading layered materials within the mesopore channels, probably due to the difficulties in preventing the formation of large guest particles outside of the pore structure. In this paper, a typical layered double hydroxide, nano-crystalline Mg–Al LDH was *in situ* and exclusively synthesized within the nanosized pore channels of mesoporous silica SBA-15 by using the pore channels as the micro-reactors and the resulting material was used as a highly active catalyst for base catalysis applications.

A schematic illustration of the synthetic pathway to mesopore confined LDH nano-catalyst is shown in Scheme 1. The mesoporous silica SBA-15 with high hydrothermal stability was synthesized according to the literature procedure using triblock poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide), $(\mathrm{EO}_{20}\mathrm{PO}_{70}\mathrm{EO}_{20})$, as a template under acidic conditions.[12–13] Before being used as a template to confine the growth of LDH, the outer surface of SBA-15 was modified with hydrophobic Si–CH_3 groups and then the surfactant was removed from the pore channels by solvent extraction, as in our previous studies.[14] This pre-treatment was necessary to prevent the formation of large LDH crystals outside the pore channels of SBA-15, as will be described later.



Scheme 1 Schematic illustration of synthetic pathways for mesopore confined LDH base catalyst. (a) SBA-15 pre-modified with Si–CH_3 on out ersurface; (b) nitrate loaded in mesopore; (c) oxide incorporated composites; (d) formation of LDH within the pore channels.

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[a] *Laboratory of Advanced Functional Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China*
[b] *State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. E-mail: jlshi@sunm.shcnc.ac.cn*

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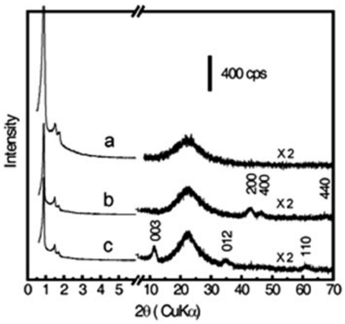

Fig. 1 XRD patterns of (a) SBA–CH_3, (b) SBA–oxide and (c) SBA–LDH.

Mg–Al LDH nano-crystallites were *in situ* fabricated by using the pore channels as the micro-reactors under a hydrothermal condition similar to the recent report.[15] First, $Mg(NO_3)_2$ and $Al(NO_3)_3$ were introduced into SBA-15, which had been pre-modified with Si–CH_3 groups on the outer surface, by immersing in the mixed nitrate solution. The strong hydrophobic property of the outer surface with Si–CH_3 groups and the strong hydrophilic property of the inner surface made it possible for the nitrate to be loaded only in the pore channels of the mesoporous material. After calcination at 600 °C for 6 h, the nitrates were converted to oxides. And then, through hydrothermal treatment, MgAl LDH in hydroxide form formed and was finally confined only in the pore channels of SBA-15.

The formation of mesopore confined MgAl LDH nano-crystallites was confirmed by XRD analysis measured immediately after each step. The small angle X-ray diffraction patterns of the samples are shown at the left side of Fig. 1. One major peak at about 0.9°, together with two additional peaks, can be observed, which are the characteristic reflections of the hexagonally mesoporous-structured SBA-15. Although their intensity decreases following each step due to the immobilization of the guest materials, the still well-resolved peaks indicate that the samples possess long-range-ordered structure. The hexagonal structure of SBA-15 has been very well retained after surface modification, calcination and even the hydrothermal treatment. The right-hand section of Fig. 1 shows the wide-angle XRD patterns of the samples in different steps. The original –CH_3 modified SBA-15 only has a halo in the 2θ range of 20–25° due to the scattering of silica (line a). When loaded with nitrates and calcined, three peaks appeared in the higher 2θ range. A peak at $2\theta = 42.9°$ can be assigned as 200 reflection of MgO, another two peaks at $2\theta = 45.8°$ and 67° are 400 and 440 reflections from Al_2O_3. The nitrates have been converted into oxides through calcination. The relative lower and wider peaks indicate that the particle sizes of MgO and Al_2O_3 in the pore channel are in the range of a few nanometers. All these peaks totally disappeared and a layered structure with a gallery height of 0.76 nm ($2\theta = 11.3°$) was obtained after subsequent hydrothermal treatment, indicating the formation of LDH in hydroxide form.[2] Besides, there also exist two additional peaks at 34.8° and 60.5° which can be attributed to reflections of 012 and intra-sheet 110 bands from a two-dimensional hexagonal cell ($a = 0.31$ nm), respectively, further confirming that the LDH architecture formed in the process.[1–2,16]

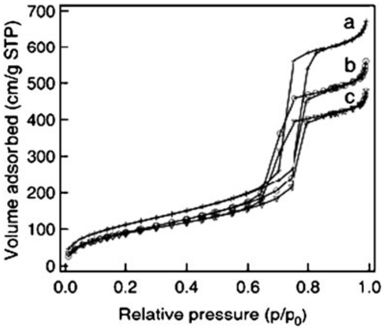

Fig. 2 TEM images of SBA–LDH with electron beam parallel and perpendicular to the pore channels.

The nitrogen adsorption–desorption isotherms for samples are attached in ESI.† The pore structure parameters of samples are summarized in Table 1. Typical type-IV isotherm curves with a well-defined step clearly indicate that these materials possess mesoporous structure. The decreases of the BET surface area, BJH pore volume and average pore size together with the increased thickness of the pore walls, can be attributed to the incorporation of guest nanoparticles in the channel. However, it can also be seen from the Table that the BET surface area and the BJH pore volume still maintain large values after metal oxide loading and the formation of LDH nano-crystallites in pore channels. This suggests that the incorporated LDH crystallites have occupied limited pore space and that most of the nano-pore channels of the host silica remain open. This result is very important for the application of catalysis.

Fig. 2 shows HRTEM images of sample SBA–LDH with the electron beam parallel and perpendicular to the pore channels, respectively. In agreement with the above SAXRD results, the mesoporous channels are well ordered with a characteristic hexagonal structure. No large LDH crystallites on the outer surface could be found, which indicates that almost all the LDH crystallites have been confined in the pores of the matrix. Thus, the lateral size of synthesised LDH is less than 9 nm. Different from some metal or metal oxide immobilized mesoporous materials, the morphology and

Table 1 Pore structure parameters of (a) SBA–CH_3, (b) SBA–oxide and (c) SBA–LDH

Sample	A_{BET}/m^2 g^{-1a}	V_{BJH}/m^3 g^{-1}	D_{BJH}/nm	d_{100}/nm	Thickness of pore wall/nm
SBA-CH_3	423	1.03	8.06	9.93	3.41
SBA-oxide	377	0.91	6.65	9.93	4.82
SBA-LDH	331	0.79	6.16	9.93	5.31

[a] A_{BET}: BET surface area; V_{BJH}: BJH pore volume; D_{BJH}: BJH pore diameter; d_{100}: plane separation.

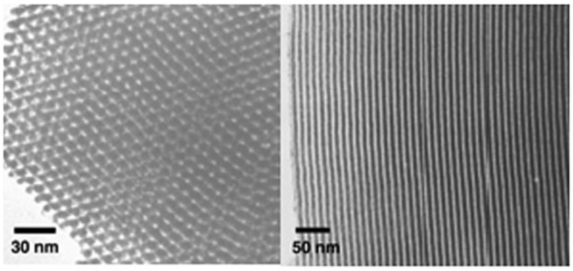

Fig. 3 Conversions as a function of time for the reaction of acetone self-condensation at 273 K.

distribution of LDH nanoparticles in the channel cannot be identified from the TEM image. This may be due to the relative lower scattering contrast of LDH crystallites compared with the silica matrix. The existence of LDH can be further proved by energy dispersive spectroscopy analysis of X-rays (EDAX),† which reveals a composition of about 5 wt% of LDH on average (calculated on the basis of the content of Mg element).

The catalytic properties of the mesopore-confined LDH nanocrystal was investigated with aldol condensation reactions. Different from other synthesized supported or unsupported LDH platelets,[4–9] this kind of material has a high catalytic activity without any activation due to its original hydroxide form LDH structure (containing large amount of Brønsted base sites). Fig. 3 shows the results of the self-condensation of acetone using SBA–LDH as catalyst†. The initial activity of the catalyst is given in Table 2. The catalytic activity of SBA–LDH based on LDH-weight is extremely high, about eight times of that of unsupported LDH platelets. The thermodynamic equilibrium (23%) was achieved in 1.5 h of reaction. In order to understand the real reason for such high catalytic activity, CO_2 absorption measurement was adopted to ascertain the total number of accessible active sites of the catalysts. A remarkably larger number of active sites of as-synthesized catalyst was found compared to unsupported LDH platelets and even the carbon nanotube supported nanosized LDH, as shown in Table 2. This high reactivity must be ascribed to the mesopore-confined LDH crystallites with extremely small sizes in the lateral dimension (<9 nm), which implies a large number of active edge sites. On the other hand, this result further proved the assumption that the actual active sites are situated at the edge of the platelets.

SBA–LDH catalyst recycling studies were also performed using the same reaction under the same conditions. Before reuse, the solid was separated from the reaction medium by filtration, reactivated by heat treatment and rehydration. The results are shown in Fig. 3; the reaction conversion indicates that the immobilized catalyst can be repeatedly used without apparent decrease in its catalytic activity.

Table 2 Catalytic properties and the number of active sites as determined with CO_2 adsorption

Sample	CO_2 adsorption/ μmol g_{LDH}^{-1}	Initial rate[a]/ $mmol_{DAA}\ g_{LDH}^{-1}h^{-1}$	TOF[b]/s^{-1}
LDH act	153	121	0.43
HT/CNT-act [10]	750	542	0.40
SBA-LDH	1210	1003	0.51

[a] Condensation of acetone at 273 K. [b] Turn over frequency based on CO_2 adsorption.

In conclusion, a new heterogeneous catalyst system SBA–LDH has been successfully developed by an *in situ* assembly method. Mesoporous SBA-15 was used as the support to confine the growth of LDH crystallites within its well defined and large open pore system. The combination of nanosized LDH crystallites and open pore structure of the mesoporous support provide excellent catalytic activities for aldol condensation reactions.

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Notes and references

1 (*a*) P. S. Braterman, Z. P. Xu and F. Yarberry, in *Handbook of Layered Materials: Layered Double Hydroxides (LDH)*, ed. S. M. Auerbach, K. A. Carrado and P. K. Dutta, Marchl Dekker, New York, 2004.

2 A. Roy, C. Forano, K. E. Malki and J.-P. Besse, Anionic Clays Trends in Pillaring Chemistry, in *Synthesis of Microporous Materials*, ed. M. L. Occelli and H. E. Robson, Van Nostrand Reinhold, New York, 1992.

3 M. J. Climent, A. Corma, S. Iborra and A. Velty, *J. Catal.*, 2004, **221**, 474.

4 J. C. A. A. Roelofs, D. J. Lensveld, A. J. van Dillen and K. P. de Jong, *J. Catal.*, 2001, **203**, 184.

5 S. Abelló, F. Medina, D. Tichi, J. Pérez-Ramirez, J. C. Groen, J. E. Sueiras, P. Salagre and Y. Cesteros, *Chem.–Eur. J.*, 2005, **11**, 728.

6 S. Abelló, F. Medina, D. Tichi, J. Pérez-Ramirez, Y. Cesteros, P. Salagre and J. E. Sueiras, *Chem. Commun.*, 2005, 1453.

7 F. Winter, V. Koot, A. J. Van Dillen, W. G. John and K. P. de Jong, *J. Catal.*, 2005, **236**, 91.

8 H. C. Greenwell, P. J. Holliman, W. Jones and B. V. Velasco, *Catal. Today*, 2006, **114**, 397.

9 R. Prihod'ko, M. Sychev, I. Kolomitsyn, P. J. Stobbelaar, E. J. M. Hensen and R. A. van Santen, *Microporous Mesoporous Mater.*, 2002, **56**, 241.

10 F. Winter, A. J. Van Dillen and K. P. de Jong, *Chem. Commun.*, 2005, 3977.

11 J. L. Shi, Z. L. Hua and L. X. Zhang, *J. Mater. Chem.*, 2004, 795.

12 Y. Liu and T. J. Pinnavaia, *Chem. Mater.*, 2002, **14**, 3.

13 Zeolite precursor seeds were prepared by reacting $Al_2(SO_4)_3$, TEOS aqueous solution mixture with NaOH and TPAOH under vigorous stirring at room temperature followed by aging at 60 °C overnight. $Al_2(SO_4)_3 : TEOS : NaOH : TPAOH : H_2O = 1 : 100 : 20 : 10 : 10\,000$.

14 (*a*) L. Li, J. L. Shi, J. N. Yan, H. G. Chen and X. G. Zhao, *J. Mol. Catal. A: Chem.*, 2004, 227; (*b*) L. Li and J. L. Shi, *Adv. Synth. Catal.*, 2005, **347**, 1745.

15 Z. P. Xu and G. Q. (Max) Lu, *Chem. Mater.*, 2005, **17**, 1055.

16 (*a*) L. Li, R. Ma, Y. Ebina, K. Fukuda, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2007, **129**, 8000; (*b*) L. Li, R. Ma, Y. Ebina, N. Iyi and T. Sasaki, *Chem. Mater.*, 2005, **17**, 4386.