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PAPER

Mg/Al-CO₃ layered double hydroxide nanorings†

Miaosen Yang,^{*a*} Junfeng Liu,^{*a*} Zheng Chang,^{*a*} Gareth R. Williams,^{*bc*} Dermot O'Hare,^{*b*} Xuehan Zheng,^{*a*} Xiaoming Sun^{*a*} and Xue Duan^{*a*}

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 $Mg/Al-CO_3$ Layered Double Hydroxide (LDH) nanorings with a 750 nm exterior diameter and 250 nm interior diameter were synthesized in an organic/water solvent system *via* a urea hydrolysis method, using $Mg_{10}(OH)_{18}Cl_2 \cdot 5H_2O$ nanowires as precursors. X-Ray diffraction and Fourier-transform infrared spectroscopy clearly revealed the nanorings to comprise $Mg/Al-CO_3$ LDH. The character of the precursor materials and the ratio of organic solvents to water used for reaction played crucial roles in determining the final ring-like morphology. A possible mechanism was proposed for the LDH nanoring formation. The unique LDH nanorings exposed a higher specific surface area and larger pore volume than plate-like and flower-like analogues, and thus were further explored for their catalytic activity using the Knoevenagel reaction between benzaldehyde and diethyl malonate as a probe reaction. The ring-like structure displayed a significantly enhanced catalytic performance above other analogues.

Introduction

Layered Double Hydroxides (LDHs) can be described using the general formula $M^{"}_{1-x}M^{"}_x$ (OH)₂(A^{n-})_{x/n}·mH₂O (where M["] and $M^{""}$ are metal cations, A^{n-} is an *n*-valent anion). They have a brucite-like structure and positive charged layers owing to partial substitution of M["] cations in the parent Mg(OH)₂ structure by M["] cations.¹ These materials have applications in a wide range of fields, including as catalysts or catalyst precursors,²⁻⁴ absorbents,⁵ anion exchangers,⁶ electro- and photo-active materials,⁷⁻¹¹ and bioactive nanocomposites.¹²⁻¹⁵

The morphological tailoring of LDHs is of significant scientific importance because it could influence their optical, electronic, magnetic, and catalytic properties.¹⁶⁻¹⁹ For example, three-dimensional ordered macroporous LDHs intercalated by decatungstate anions exhibit a higher photocatalytic activity than the standard plate-like counterparts.²⁰ However, the brucite-like two-dimensional (2D) crystal structure drives a strong 2D

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growth tendency in LDHs, and results in almost exclusively hexagonal plate-like morphologies.²¹ Synthesis of LDHs with other well defined morphologies is rare and challenging. Previously, hard or soft templating methods have been used for the morphology control of LDHs. For instance, hollow spheres have been obtained by growing the LDH on subsequently sacrificing hard templates such as carbon microspheres²² or polystyrene colloid crystal templates.^{20,23} One-dimensional LDH nanostructures (e.g. nanobelt or nanorod) have also been synthesized using surfactants or copolymer molecules as soft templates.^{24,25} However, the range of morphologies that can be induced is still limited. Furthermore, using templates or surfactants to tailor the LDH morphology often increases the risk of impurity introduction, and even causes structure collapse during template removal. Ring-like nanostructures have attracted particular attention,²⁶⁻³⁰ because they have relatively larger surface areas, higher chemical accessibility and more active sites than their plate-like counterparts.³¹⁻³³ Yet no ring-like structures of LDHs have been reported. Recently, LDHs and their oxides derived via thermal treatment have attracted remarkable interest as effective, environment-friendly solid base catalysts for many reactions such as aldol condensation, alkylation and isomerization.³⁴⁻³⁶ So the study of the catalytic performance of LDH materials with different morphologies is important.

Herein, we demonstrate the facile synthesis of Mg/Al-CO₃ LDH nanorings *via* a solvothermal treatment of Mg₁₀(OH)₁₈Cl₂·5H₂O nanowires in an organic/water mixed solvent system. Mg₁₀(OH)₁₈Cl₂·5H₂O was employed both as the magnesium source and also as a sacrificial hard template. This allowed us to exercise morphological control on the LDH products while ensuring phase purity. No surfactants were used in the synthesis of

^aState Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, P. R. China. E-mail: sunxm@mail.buct.edu.cn; changzheng@mail.buct.edu.cn

^bChemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford, UK OX1 3TA

^cSchool of Human Sciences, London Metropolitan University, Holloway Road, London, UK N7 8DB

[†] Electronic supplementary information (ESI) available: FT-IR pattern of MAC-R (Fig. S1), XRD pattern and TEM image of MAC-R calcined at 500 °C for 6 h (Fig. S2,S3), XRD pattern and FT-IR pattern of MAC-F (Fig. S4,S5), TEM image of MAC-R prepared after a reaction time of 40 min (Fig. S6), 3D stacked plot recorded for the transition of Mg10-NW into MAC-R (Fig. S7),TEM image of MAC-R prepared in pure water (Fig. S8), XRD pattern and TEM image of MAC-P (Fig. S9,S10). See DOI: 10.1039/c1jm12129d

Downloaded by Ryerson Polytechnic University on 23 February 2013 Published on 16 August 2011 on http://pubs.rsc.org | doi:10.1039/C1JM12129D either precursors or products, with the aim of reducing processing complexity. The Mg/Al-CO₃ LDH nanorings exposed high specific surface area, large pore volume, and thus displayed an enhanced catalytic performance compared to their plate-like and flower-like analogues in the Knoevenagel reaction. This unique structure might offer potential applications in catalysts, adsorbents, and drug delivery systems.

Experimental section

Materials

Dodecyl mercaptan (98%) was purchased from Alfa Aesar Chemical. Co. Ltd. Urea (AR), $MgCl_2 \cdot 6H_2O$ (AR), $AlCl_3 \cdot 6H_2O$ (AR), MgO (AR), 1-hexanol (99%), benzaldehyde (98.5%), diethyl malonate (99.5%), ethanol (99.7%), and acetone (HPLC grade) were purchased from Beijing Yili Fine Chemical. Co. Ltd., and used without further purification. Deionized water was used throughout the experimental processes.

Synthesis of Mg10(OH)18Cl2 · 5H2O nanowires

 $Mg_{10}(OH)_{18}Cl_2 \cdot 5H_2O$ nanowires were synthesized according to the method previously described.³⁷ In a typical procedure, $MgCl_2 \cdot 6H_2O$ (16.2640 g) was dissolved with 20 mL deionized water in a 50 mL beaker. The beaker was placed in a constanttemperature oil bath at 70 °C, and MgO powder (0.3224 g) was slowly added under vigorous stirring. The mixture was continually stirred for 1.5 h after the addition of MgO. Then the solution was left to stand at room temperature for 24 h. A white viscous colloidal precipitation was obtained. The resulting precipitation was poured into a 40 mL Teflon-lined stainless autoclave, sealed, and heated at 160 °C for 6 h, then allowed to cool to room temperature naturally. The product was washed with deionized water and pure ethanol, dried at 50 °C for 6 h, and denoted Mg10-NW.

Synthesis of Mg/Al-CO₃ LDH nanostructures

Mg/Al-CO₃ LDH ring-like nanostructures were synthesized using a simple urea hydrolysis method with Mg₁₀(OH)₁₈Cl₂·5H₂O nanowires as precursors. Urea (0.4054 g), AlCl₃·6H₂O (0.3018 g) and Mg₁₀(OH)₁₈Cl₂·5H₂O (0.2662 g) were dispersed in 25 mL of an organic/water mixed solvent. The volume of organic solvent (dodecyl mercaptan or 1-hexanol) was increased gradually from 0 to 20 mL, and water added to make the solvent volume up to 25 mL. The resulting suspension was stirred or agitated by ultrasonication for 10 min, then transferred into a 40 mL Teflon-lined stainless autoclave which was sealed and heated at 150 °C for times between 40 min and 6 h. The white precipitate formed after natural cooling in air was filtered, washed with deionized water and pure ethanol, and finally dried at room temperature. This product was denoted MAC-R.

Mg/Al-CO₃ LDH flower-like nanostructures were prepared using a similar method, but using MgCl₂·6H₂O (0.7624 g) instead of Mg₁₀(OH)₁₈Cl₂·5H₂O nanowire as the Mg²⁺ source; this product was denoted MAC-F.

For comparison, Mg/Al-CO₃ LDH plate-like nanostructures were also prepared using a traditional method. Urea (0.4054 g), AlCl₃· $6H_2O$ (0.3018 g) and MgCl₂· $6H_2O$ (0.7624 g) were dissolved into 25 mL aqueous solution, then transferred into a 40 mL Teflon-lined stainless autoclave and heated at 150 $^{\circ}$ C for 6 h. The product was filtered, rinsed and dried, and denoted MAC-P.

Characterization

Fourier transfer infrared (FT-IR) spectra were recorded on a Bruker Vector 22 using the KBr disk technique in the range 4000–400 cm⁻¹, with a resolution of 1 cm⁻¹. Scanning Electron Microscopy (SEM, Zeiss SUPRA 55) was operated at an acceleration voltage of 20 kV. Transmission Electron Microscopy (TEM) was performed on Hitachi 800 and JEM JEOL3010 microscopes equipped with energy dispersive X-ray spectroscopy (EDS) running at 200 kV. The low-temperature nitrogen adsorption-desorption experiments were carried out using a Quantachrome Autosorb-1C-VP system. Specific surface area was calculated from the adsorption branch according to the Brunnauer-Emmett-Teller (BET) method. The pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) model on the desorption branch. Prior to the measurements, samples were outgassed at 200 °C under vacuum for 4 h. In situ energy dispersive X-ray diffraction (EDXRD) data were obtained at the Diamond Light Source using Beamline I12.38 In order to access the low-q space $(q = 2\pi/d)$ necessary to follow LDH formation reactions, the 23-element detector was shifted horizontally with respect to the beam, and only one of the detector elements (number 23) employed for data collection. The relationship between q and the energy of diffracted X-rays was calculated from a standard sample ([LiAl₂(OH)₆]Cl·H₂O). X-Ray diffraction patterns were recorded at 65 s intervals for approximately 2.5 h.

Catalytic experiment

The Knoevenagel reaction between benzaldehyde and diethyl malonate was used as a probe reaction to examine the catalytic performance of MAC-R. Benzaldehyde (7.24 mL), Diethyl malonate (10.80 mL) and the catalyst (MAC-R, 0.19 g) were added together into a 25 mL three-necked flask. The reaction was carried out at 140 °C for 14 h with vigorous agitation. For comparison, parallel reactions with MAC-F (0.19 g) or MAC-P (0.19 g) as catalyst were carried out in the same conditions. Aliquots (0.3 mL) were aspirated using an micropipette at 2 h intervals, and then diluted to 30 mL in acetone (HPLC grade). The liquids were injected into a GC-Mass (Shimadzu OP2010) with FID detector on a RTX-5 column (30 m, 0.53 mm i.d.). The analysis programme held the samples for 3 min at 50 °C, then heated them at 10 °C min⁻¹ to 250 °C with a 10 min dwell. The conversion was calculated on the basis of the initial and final concentrations of diethyl malonate.

Results and discussion

Morphological and textural characterization of Mg₁₀(OH)₁₈Cl₂·5H₂O nanowires and Mg/Al-CO₃ LDH nanorings

The XRD pattern and TEM image of Mg10-NW are given in Fig. 1. As shown in curve A in Fig. 1a, the precursors exhibited a set of characteristic diffraction peaks which could be indexed as



Fig. 1 (a) XRD pattern of Mg10-NW (A) and MAC-R (B), (b) TEM image of Mg10-NW, (c) low-magnification TEM image of MAC-R (insert is the homologous high-magnification TEM image), (d) SEM image of MAC-R.

monoclinic $Mg_{10}(OH)_{18}Cl_2 \cdot 5H_2O$ (JCPDF No. 07-0409). The TEM image (Fig. 1b) of Mg10-NW depicted uniform wire-like nanostructures with a width typically in the range of 20–40 nm and length from tens to hundreds of micrometres.

The Mg10-NW were used as precursors and treated in dodecyl mercaptan/H₂O (20 mL/5 mL) at 150 °C for 6 h. The XRD pattern of the resulting samples (curve B in Fig. 1a) strongly indicated a crystal structure transformation from the precursor nanowires. All reflections could be indexed to a (001) diffraction line series and (110), (113) diffraction peaks of a rhombohedral symmetry $(R\bar{3}m)$ LDH (JCPDF 54-1030). The basal spacing of 0.75 nm, calculated from the characteristic (003) reflection, was in agreement with that reported for CO32- intercalated Mg_{1x}Al_x(OH)₂(CO₃)_{x/2}·mH₂O.³⁹ Complete absence of reflections corresponding to the Mg10-NW precursors suggested that the final product comprised a pure LDH phase, with complete conversion of the nanowires. The FT-IR absorption spectrum of MAC-R (Fig. S1 in ESI[†]) evidenced that a characteristic CO_{3²⁻} intercalated LDH was formed. The bands observed in the lowfrequency region 400–900 cm⁻¹ corresponded to lattice vibration modes of the LDH structure, and the most intense band at about 1364 cm⁻¹ could be assigned to the v_3 vibration of CO₃²⁻ anions, which can easily replace Cl⁻ between the LDH layers.³⁹

Fig. 1c and 1d respectively give typical TEM and SEM images of MAC-R at different magnifications. The LDH samples clearly displayed a unique hexagonal ring-like nanostructure, with a uniform size in the range of 700–800 nm but with obvious holes of average diameter about 250 nm in their centers, different from conventional plate-like and any other morphologies reported to date. The above results unambiguously revealed that the Mg/Al-CO₃ LDH nanoring structure was synthesized successfully without any surfactants involved. The XRD pattern of MAC-R calcined at 500 °C for 6 h (Fig. S2 in ESI[†]) indicated that the characteristic reflections of MgO (JCPDF 74-1225) were present while of LDH crystals completely disappeared. The TEM image of calcined MAC-R (Fig. S3 in ESI[†]) revealed that the ring-like morphology was mostly inherited, especially the obvious holes in the particle centers. It was clear that the ring-like morphology of MAC-R was stable because calcination at 500 °C completely destroyed the layered structure but retained the morphology of the LDH precursors.

Morphologic and textural characterization of Mg/Al-CO₃ LDH nanoflowers

To estimate the influence of the precursor on the LDH products, we used MgCl₂·6H₂O instead of Mg10-NW as the magnesium source. Synthesis in the same conditions (dodecyl mercaptan/H₂O mixed solvents, 150 °C, 6 h, etc.) yielded a Mg/Al-CO₃ LDH nanostructure with rose flower-like morphology (Fig. 2). The top view image showed polygon patterns with diameters in the range of 1.5-3 µm. Each polygon had a bright spot in the center and exhibited gradually increasing contrast from the center to edge, which implied a multivalve structure constructed with regularly stacked nanoplatelets around a center with discrete angles. The side view TEM image clearly exhibited a patchwork of several platelets, which looked exactly like rose flowers (as shown in the inset). The multivalve structures were also confirmed by SEM observation (Fig. 2c, 2d). The observation of a typical LDH XRD pattern with an interlayer spacing of 0.77 nm (Fig. S4 in ESI[†]) evidenced the phase purity of MAC-F.³⁶ The presence of CO₃²⁻ was further supported by the FT-IR spectrum (Fig. S5 in ESI[†]).³⁶

Discussion on the formation mechanism

It was clear that unique ring-like structures were closely related to the Mg10-NW precursor. A possible formation mechanism of



Fig. 2 (a) and (b) TEM images of the top and cross views of MAC-F, (c) SEM image of the top view of MAC-F, (d) high-magnification SEM image of a single flower-like structure, (e) photo of a rose flower.

the LDH nanorings is illustrated in Fig. 3. Experimental evidence for this mechanism was obtained by quenching the reaction at various time points, and investigating the materials recovered by TEM and XRD. At Stage I (the first ~40 min), the Mg10-NW were partially dissolved in an acidic environment due to the hydrolysis of Al³⁺ cations, which resulted in irregular fragments of the nanowires (see TEM image in Fig. S6 in ESI†) and significant weight loss (~60%) of the solid materials. The pH value of the solution gradually increased at the consequent stage (Stage II, 40~80 min) with urea hydrolysis and more Mg₁₀(OH)₁₈Cl₂·5H₂O dissolution. The induction time was relatively long because of slow dissolution of the nanowire precursors and hydrolysis of urea before the LDH formed.

At Stage II, Mg²⁺ and Al³⁺ began to co-precipitate as the LDH, which grew around the residual Mg10(OH)18Cl2 · 5H2O fragments and resulted in the regain of mass and formation of transitional core/shell structures. Formation of ring-like structures at the consequent stage (Stage III, 80~480 min) could be understood by the nanoscale Kirkendall effect, which leads to formation of kinds of hollow nanocrystals.40-42 That is, concomitant with Mg2+ and Al³⁺ co-precipitation and growth of LDH platelets on the surface of the heterogeneous structures, the Mg-rich cores gradually dissolved, were completely digested, and resulted in hollow ringlike structures, replicas of the templating fragments. A preliminary EDXRD study was conducted and supported the proposed mechanism. A three-dimensional plot of the data collected is given in Fig. S7 in the ESI.[†] No reflections were seen until ca. 40 min after the commencement of reaction, after which a strong reflection at $q \approx 0.8 \,\text{\AA}^{-1}$ corresponding to the (003) reflection of the Mg/ Al-CO₃ LDH was observed. The intensity increased gradually with reaction time. This confirmed the idea that M10-NW underwent significant dissolution before the LDH formed.

When using $MgCl_2 \cdot 6H_2O$ as precursor, however, the nanoring structure could not form, which might be related to a relatively quicker homogenous nucleation behavior, and absence of Mgrich cores. Another self-assembled growth process took place

and resulted in rose flower-like structures, which had been reported previously in the literature.⁴³ Moreover, the urea hydrolysis was indispensable for generation of the ring-like LDH, because the gradually increased pH was likely to benefit the Mg10-NW dissolution and LDH heterogeneous nucleation at the initial stages.

The mixed solvent was found to be critical for generation of the ring-like structures. A sample prepared in the same conditions (Mg10-NW, 150 °C, 6 h) with pure water as solvent only yielded regular hexagonal platelets (Fig. S8 in ESI†), which might be due to a very rapid dissolution of the Mg-rich precursors. However, surprisingly, when using organic molecules such as 1-hexanol to replace dodecyl mercaptan, nanorings still formed (Fig. 4a, 4b). Repeating the experiment in the revised solvent system but using Mg^{2+} salt as precursor resulted in flower-like structures (Fig. 4c, 4d), too. These two organic solvents might work in some similar ways, for instance tailoring the solubility or dissolution speed of the Mg-rich precursors, increasing the inner pressure and viscosity, and limiting the diffusion speed of the ions.

Catalytic application

To estimate the catalytic performance of Mg/Al-CO₃ LDH nanorings, the Knoevenagel reaction between benzaldehyde and diethyl malonate was used as a probe reaction. The plate-like sample (MAC-P) prepared *via* a traditional co-precipitation method and the flower-like counterpart (MAC-F) were used for comparison. The phase purity and size similarity of the plate-like sample were evidenced by XRD and TEM (Fig. S9, S10 in ESI†). The corresponding conversions of diethyl malonate over MAC-R, MAC-P and MAC-F are plotted in Fig. 5a. The catalytic



Fig. 3 Scheme of the formation mechanism of MAC-R.



Fig. 4 (a) TEM and (b) SEM images of MAC-R prepared in 1-hexanol/ H₂O mixed solvent using Mg10-NW as precursors (insert is the homologous high-magnification TEM image), (c) TEM and (d) SEM images of MAC-F prepared in 1-hexanol/H₂O mixed solvent using MgCl₂·6H₂O as precursors.

activity of MAC-R was significantly higher than that of the other morphologies: conversion reached 45.8% after achieving an approximate reaction balance (about 12 h), but conversion with MAC-P was only 34.3% and that with MAC-F was even lower. Moreover, the curve slope of conversion with MAC-R was largest, especially in the first 8 h, suggesting that its catalytic efficiency was the highest among the analogues. It was clear that the LDH morphology significantly affected the catalytic activity.

To understand the difference in catalytic performance, the specific surface areas and pore size distributions of MAC-R, MAC-F and MAC-P were studied via the N2 adsorption/ desorption method. The results are displayed in Fig. 5b. The isotherms were of type IV, which is characteristic of mesoporous materials.44 The insert in Fig. 5b suggested a significant difference in pore size distributions. The pore volumes of MAC-R, MAC-F and MAC-P were 0.2529, 0.1051 and 0.1012 cm³ g^{-1} , respectively. The pore volume of nanorings was significantly greater than that of the other morphologies. Generally, LDH materials possess poor porosity characteristics. The difference for MAC-R may be explained because the center holes in the LDH nanostructures helped to create more channels during the irregular stacking of different arrangements of parallel-assembled layers, resulting in an increase of porosity and pore volume. The specific surface area of MAC-R was 48.54 m² g⁻¹, almost three-times as large as its flower-like (18.04 $m^2 g^{-1}$) and plate-like (20.54 m² g⁻¹) analogues. The ring-like morphology introduced more irregular channels and subsequently increased the surface area of the LDH.

Moreover, according to a previous report, reactions using solid base catalysts usually occur on the entire outer crystal surface of the catalysts.⁴⁵ Therefore, the hollow-structured



Fig. 5 (a) Conversion curves of diethyl malonate over MAC-R, MAC-F and MAC-P, (b) N_2 adsorption–desorption isotherms and pore size distributions (insert) of MAC-R, MAC-F and MAC-P.

materials could expose more active sites located in the exterior and interior of the rings in accompany with the increase of specific surface areas, as supported by the work of de Jong *et al.*⁴⁶ It was proposed that, compared to the other morphologies, a ring-like morphology had the highest specific surface area, largest pore volume and its hollow interior structure allowed external reagents to approach, which all benefited the catalytic performance.

Conclusions

Unique Mg/Al-CO₃ LDH nanorings were synthesized by a urea hydrolysis method in organic/water mixed solvents. Using solid precursors (Mg²⁺-source), Mg₁₀(OH)₁₈Cl₂·5H₂O nanowires, rather than conventional Mg salts, was found critical for the nanoring formation, which is likely to be a result of their alternating the Mg²⁺-release and LDH nucleation/growth process. Comparison of the catalytic activities of ring-, plate- and flowerlike LDH nanostructures *via* solid base catalyzed Knoevenagel reaction indicated that the ring-like structure had better catalytic performance than its plate- or flower-like counterparts. The enhanced catalytic activity is thought to be related to the higher specific surface area and larger pore volume induced by the hollow structure. It is expected that LDH nanorings will provide advantageous materials for the future which not only in catalysis but also as adsorbents, drug delivery systems, *etc*.

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