

Mechanochemically synthesized MgAl layered double hydroxide nanosheets for efficient catalytic removal of carbonyl sulfide and H₂S

Jinxing Mi, Xiaoping Chen, Qiuyun Zhang, Yong Zheng, Yihong Xiao, Fujian Liu*, Chak-tong Au and Lilong Jiang*

National Engineering Research Center of Chemical Fertilizer Catalyst, College of Chemical Engineering, Fuzhou University, Fuzhou 350002, Fujian, P. R. China

*Corresponding author: fjliu@fzu.edu.cn; jll@fzu.edu.cn

Experimental section

Chemicals and reagents

Magnesium ethylate, aluminium isopropoxide, and sodium carbonate of analytical grade were from Sinopharm group Co. Ltd., China. They were used as received.

MgAl-LDHs preparation

The MA-LDHs-x samples were prepared by a one-step solid-state mechanochemical method. First, 3.36 g of magnesium ethylate and 2 g of aluminium isopropoxide (in molar ratio of 3:1) were mechanically ground for 30 min, then x mL ($x=1, 3, 5,$ and 7) of sodium carbonate solution (1 M) was added, and the mixture was further ground for 30 min. The resulted paste was transferred into a teflon liner autoclave (100 mL), and then heated to 150 °C at a heating rate of 10 °C/min and held at 150 °C for 1 h. The process is simple, time saving, and does not consume much solvent. Furthermore, it is easy to scale up the production. It was demonstrated that under the defined conditions, MA-LDHs-5 generation could be increased by a factor of 2 or 5 following the same procedure without causing any degradation of product crystallinity and morphology (Figs. S15–S17). The product was collected by suction filtration using deionized water, and dried at 100 °C overnight, and is denoted herein as MA-LDHs-x. It is worth pointing out that grinding the raw materials separately before mixing would result in poor formation of MA-LDHs-x. It is hence deduced that the frictional heat generated in the grinding of pre-mixed materials is essential for successful formation of MA-LDHs-x.

MA-LDHs-water-free: It was prepared using a one-step solid-state mechanochemical and solvent-free method. First, 3.36 g of magnesium ethylate, 2 g of aluminium isopropoxide and 0.53 g of sodium carbonate were mixed and mechanically ground in an agate mortar for 30 min. Then the mixture was transferred into a teflon liner autoclave (100 mL), and then heated to 150 °C at a heating rate of 10 °C/min and held at 150 °C for 1 h. The obtained product was collected by suction filtration and dried at 100 °C overnight, and is herein denoted as “MA-LDHs-water-free”.

MA-LDHs-HT: First, 3.36 g of magnesium ethylate, 2 g of aluminium isopropoxide and 0.53 g of sodium carbonate were mixed in a beaker (50 mL water solvent) with stirring for 60 min. Then the mixture was transferred into a teflon liner autoclave (100 mL), and then heated to 150 °C at a heating rate of 10 °C/min and held at 150 °C for 24 h. The obtained product was collected by suction filtration and dried at 100 °C overnight, and is denoted herein as MA-LDHs-HT.

MA-LDHs-cp: The MA-LDHs-cp sample was prepared by co-precipitation method. An aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Mg/Al molar ratio=3/1) was added under stirring into a beaker containing an aqueous solution of sodium carbonate at room temperature. The pH of the solution was adjusted and kept at 10 ± 0.5 using an aqueous solution of sodium hydroxide. The suspension was then aged at 90 °C for 24 h. The precipitate was filtered out, washed several times with de-ionized water, and dried at 100 °C for 12 h.

Scale-up preparation of MA-LDHs-5: The production of MA-LDHs-5 sample could

be scaled up following to the one-step solid-state mechanochemical method. To increase production by a factor of 2, 6.72 g of magnesium ethylate and 4 g of aluminium isopropoxide were mechanically ground for 30 min, then 10 mL of sodium carbonate solution (1 M) was added, and the mixture was further ground for 30 min in a mortar (10 cm in diameter). The resulted paste was transferred into a teflon liner autoclave (100 mL), and then heated to 150 °C at a heating rate of 10 °C/min and held at 150 °C for 1 h. The obtained product was collected by suction filtration using deionized water, and dried at 100 °C overnight, and is denoted herein as MA-LDHs-5(2). Similarly, the production of MA-LDHs-5 could be increased by a factor of 5. First, 16.8 g of magnesium ethylate and 10 g of aluminium isopropoxide were mechanically ground for 30 min using a big mortar (18 cm in diameter), then 25 mL of sodium carbonate solution (1 M) was added, and the mixture was further ground for 30 min. The resulted paste was transferred into a teflon liner autoclave (200 mL), and then heated to 150 °C at a heating rate of 10 °C/min and held at 150 °C for 1 h. The obtained product was collected by suction filtration, and dried at 100 °C overnight, and is denoted herein as MA-LDHs-5(5).

MA-LDHs can also be synthesized using a ball-milling machine (designated as BM-MA-LDHs-x). First, 3.36 g of magnesium ethylate and 2 g of aluminium isopropoxide (in molar ratio of 3:1) were ground for 30 min using a ball-milling machine, then x mL (x = 3 and 5) of sodium carbonate solution (1 M) was added, and the mixture was further ground for 30 min. The resulted paste was transferred into a teflon liner autoclave (100 mL), and then heated to 150 °C at a heating rate of 10

°C/min and held at 150 °C for 1 h. Finally, the resulted BM-MA-LDHs-3 and BM-MA-LDHs-5 were collected by suction filtration, and dried at 100 °C overnight. Notably, the MA-LDHs-x samples (41.3%~45.1%) show crystallinity similar to those of BM-MA-LDHs-x (41.3%~42.6%, Fig. S18).

For comparison, commercial MA-LDHs (denoted as C-MA-LDHs), supplied by Aladdin reagent co. Ltd., was characterized and tested for COS hydrolysis and H₂S oxidation.

Characterizations

The X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on a PANalytical diffractometer (X'PertPro, Panalytical Corp.) with an X'Celerator detector, using Cu K α radiation ($\lambda=0.154\ 06\ \text{nm}$) at 45 kV and 40 mA. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a NETZHCS STA2500 Regulus TG/DSC system under flowing N₂ with a ramping rate of 10 °C/min. Fourier transformed infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrometer, and the MA-LDHs-x were prepared in the form of KBr pellets. The solid state ²⁷Al NMR spectra were collected on a Varian Infinity Plus-300 spectrometer. The morphologies and microstructures of MA-LDHs-x were studied by scanning electron microscopy (SEM) (S-4800, Hitachi, Japan). HRTEM images were collected on a Zeiss Libra200 TEM at 200 kV (acceleration voltage). Atomic force microscope (AFM) studies were conducted on a Nanoscope IVA electron microscope.

COS hydrolysis

The hydrolysis of carbonyl sulfide (COS) over MA-LDHs-x was performed in a fixed-bed reactor at atmospheric pressure using 200 mg of catalyst (20–40 mesh). At the steady state of reaction, a flow of N₂ containing COS (110 mg/m³) was introduced into the reactor at a total flow rate of 20 mL/min. H₂O was injected into the reactor from a thermostatic water bath through a controlled saturator. By adjusting the temperature of the water bath (25, 40 and 60 °C), the relative humidity of the reaction gas (water vapor contents were 2.91%, 6.54% and 13.79%, respectively) was controlled. The concentration of COS in the reactor effluent was monitored on-line by a gas chromatograph (FL 9720 II) equipped with a flame photometric detector (FPD). The conversion of COS was determined on the basis of the initial and the current temperature-peak areas of COS. In this study, the COS conversion was calculated as follows:

$$\text{COS conversion (\%)} = (C_0 - C_T)/C_0 \times 100\% \quad \text{Equation 1}$$

Where, C₀ and C_T is the peak area of COS at the initial temperature and a particular reaction temperature, respectively.

The Arrhenius plots of COS hydrolysis over MA-LDHs-x were obtained in specific experiments which were performed at the conditions of low temperatures (30–90 °C) and high WHSV (48 000 mL/(g·h)).

Meanwhile, the effect of WHSV on COS hydrolysis over MA-LDHs-3 was obtained through changing the mass weight (25–200 mg) of catalyst at a total flow rate of 20 mL/min and 40 °C water temperature.

In addition, the effect of water contents on COS hydrolysis over MA-LDHs-3 was

obtained through changing the water temperature to 25, 40 and 60 °C at a WHSV of 12 000 mL/(g·h).

H₂S selective catalytic oxidation

Selective catalytic oxidation of H₂S over MA-LDHs-x was performed in a continuous flow fixed-bed reactor at atmospheric pressure. First 100 mg of catalyst (20–40 mesh) was placed in the central section of the reactor. A mixture gas containing 5000 ppm of H₂S, 2500 ppm of O₂ and balance gas (N₂) was introduced into the reactor at a total flow rate of 20 mL/min (WHSV=12 000 mL/(g·h)) for reaction in the temperature range of 90–210 °C. At the outlet, the effluent stream was analyzed by a gas chromatograph (FL 9720 II) equipped with a FPD and thermal conductivity detector (TCD). A condenser was located at the bottom of the reactor to trap sulfur in the effluent stream. Instantaneous fractional conversion of H₂S, sulfur selectivity, and sulfur yield are defined as follows:

$$\text{H}_2\text{S conversion (\%)} = \frac{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}}}{(\text{H}_2\text{S})_{\text{in}}} * 100\% \quad \text{Equation 2}$$

$$\text{H}_2\text{S selectivity (\%)} = \frac{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}} - (\text{SO}_2)_{\text{out}}}{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}}} * 100\% \quad \text{Equation 3}$$

$$\text{Sulfur yield (\%)} = (\text{H}_2\text{S conversion}) * (\text{H}_2\text{S selectivity}) * 100\% \quad \text{Equation 4}$$

Table S1 Preparation parameters of the MA-LDHs obtained by different methods.

Samples	Reaction time (h)	Yields (%) ^a	Solvent (mL)
MA-LDHs-1	1	97.6	1
MA-LDHs-3	1	98.9	3
MA-LDHs-5	1	95.3	5
MA-LDHs-7	1	95.1	7
MA-LDHs-HT	24	85.8	50
Mg-Al-CO ₃ -LDHs ^b	1	80.7	5
MA-LDHs-cp	24	77.5	200

^a The yield percentage is defined as “actual production mass/theoretical production mass x 100%”.

^b Mg-Al-CO₃-LDHs was prepared according to Ref. [S1](#).

Table S2 Structural parameters of MA-LDHs obtained by different methods after Rietveld refinement.

Sample	Crystallinity (%)	a (nm)	b (nm)	c (nm)	d(003) (nm)	d(110) (nm)
MA-LDHs-1	41.31	0.308	0.308	2.319	7.768	1.526
MA-LDHs-3	43.69	0.306	0.306	2.391	7.940	1.536
MA-LDHs-5	45.10	0.307	0.307	2.340	7.842	1.530
MA-LDHs-7	43.46	0.308	0.308	2.357	7.850	1.530
C-MA-LDHs	39.29	0.309	0.309	2.315	7.626	1.525
MA-LDHs-HT	40.15	0.305	0.305	2.309	7.843	1.531
Mg-Al-CO ₃ -LDHs	39.97	0.306	0.306	2.378	7.834	1.524
MA-LDHs-cp	38.85	0.308	0.308	2.311	7.740	1.528

Table S3 Data of thermogravimetric analysis over MA-LDHs-x, C-MA-LDHs and MA-LDHs-cp.

Sample	1st mass loss (%)	2nd mass loss (%)	3rd mass loss (%)
MA-LDHs-1	14.2	7.02	36.3
MA-LDHs-3	13.8	8.53	34.6
MA-LDHs-5	12.7	9.93	33.9
MA-LDHs-7	12.3	8.21	37.1
C-MA-LDHs	11.6	11.0	32.5
MA-LDHs-cp	16.2	12.8	26.9

The calculation method (Taking 1 g of MA-LDHs-x as reference) is as follows:

$$\text{OH}^- \text{ content (mmol/g)} = \{[1 \text{ g} \times (\text{2nd mass loss}/100)] / (17 \text{ g/mol})\} \times (1000 \text{ mmol/mol}) / (1 \text{ g})$$

Table S4 Comparison of catalysts used for H₂S selective oxidation.

Feed gases	Catalyst	WHSV (mL/(g·h))	Temperature (°C)	Sulfur capacity	Sulfur yield (%)	Ref.
H ₂ S, 5000 ppm O ₂ , 2500 ppm	MA-LDHs-3	12 000	90		97.2	This work
H ₂ S, 5000 ppm O ₂ , 2500 ppm	MA-LDHs-5	12 000	90		99.3	This work
H ₂ S, 3000 ppm O ₂ , 3000 ppm	Mn/Active carbon	3000	180	0.14		[S2]
H ₂ S, 1000 ppm O ₂ , 2.5%	Macroscopic N- CNTs		190		68.1	[S3]
H ₂ S, 5000 ppm O ₂ , 2500 ppm	7Fe ₂ O ₃ -Al ₂ O ₃	12 000	100		78.4	[S4]
H ₂ S, 5000 ppm O ₂ , 2500 ppm	Al ₂ O ₃	10 500	180	63.2	94.6	[S5]
H ₂ S, 5000 ppm O ₂ , 2500 ppm	CNU-P600	3000	90		45.3	[S6]
H ₂ S/O ₂ =1/2.5	6%V ₂ O ₅ /Zr-PILC	10 000	300		93.4	[S7]
H ₂ S/O ₂ =2	5%V ₂ O ₅ /TiO ₂ -PILC	10 000	220		97.5	[S8]
H ₂ S, 5000 ppm O ₂ , 2500 ppm	NH ₂ -MIL-53(Fe)	3000	90		92.6	[S9]
H ₂ S/O ₂ =2	7%Fe/Al-Lap	7000	180		95.3	[S10]
H ₂ S/O ₂ =2	5%V ₂ O ₅ /CeO ₂ -Lap	7000	180		98.7	[S11]

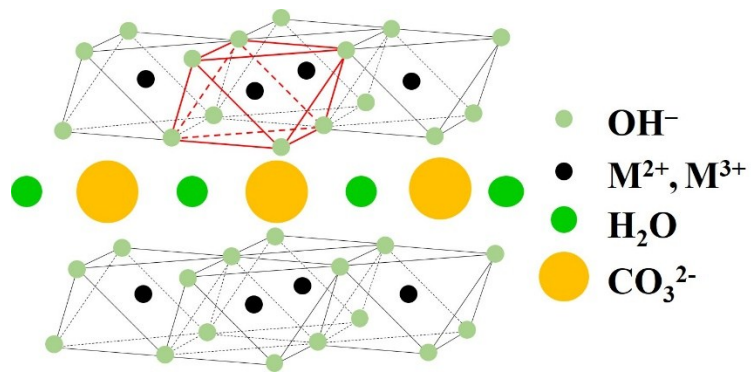


Fig. S1 Structure diagram of MgAl hydrotalcite-like materials.

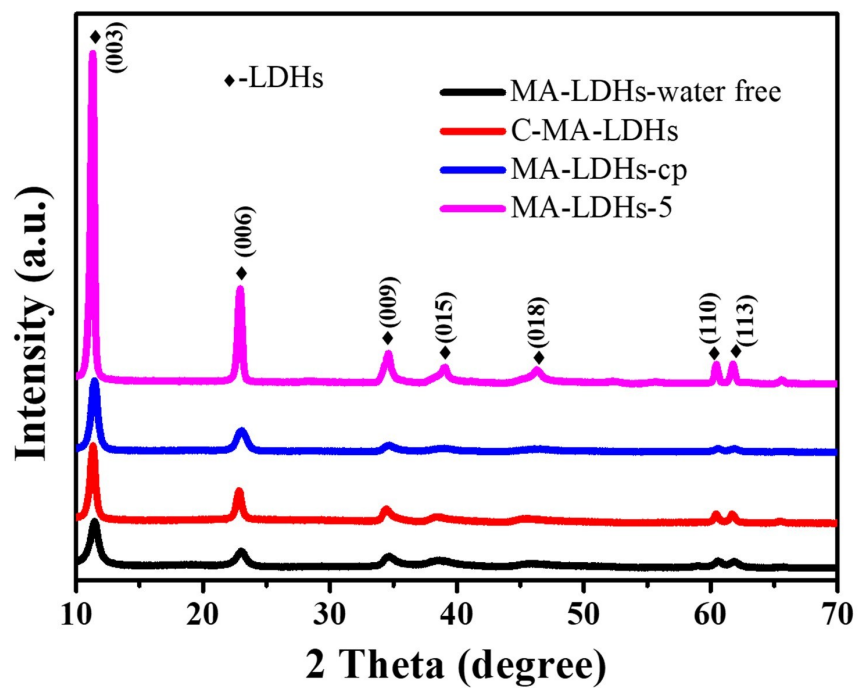


Fig. S2 XRD patterns of (bottom to top) MA-LDHs-water free, C-MA-LDHs, MA-LDHs-cp and MA-LDHs-5 samples.

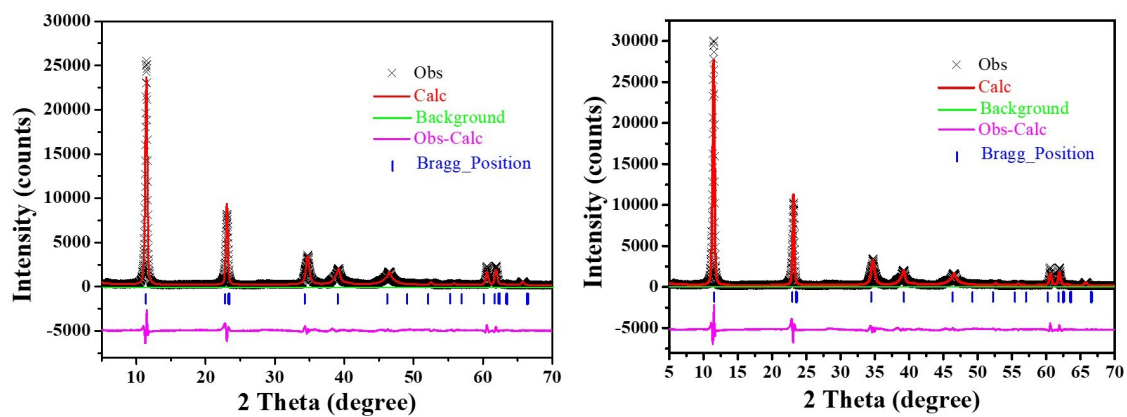


Fig. S3 Powder XRD patterns of MA-LDHs-3 (left) and MA-LDHs-5 (right) with Rietveld refinements using different structural models.

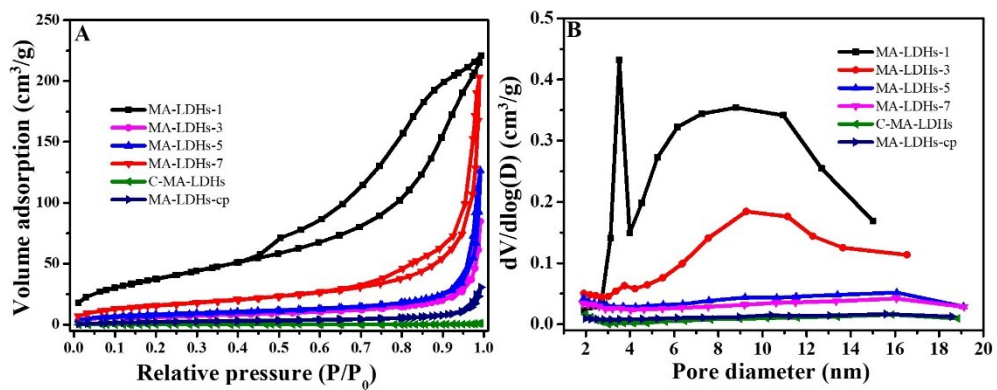


Fig. S4 (A) Low-temperature N₂ adsorption-desorption curves and (B) pore size distribution curves of MA-LDHs-xs, C-A-LDHs and MA-LDHs-cp.

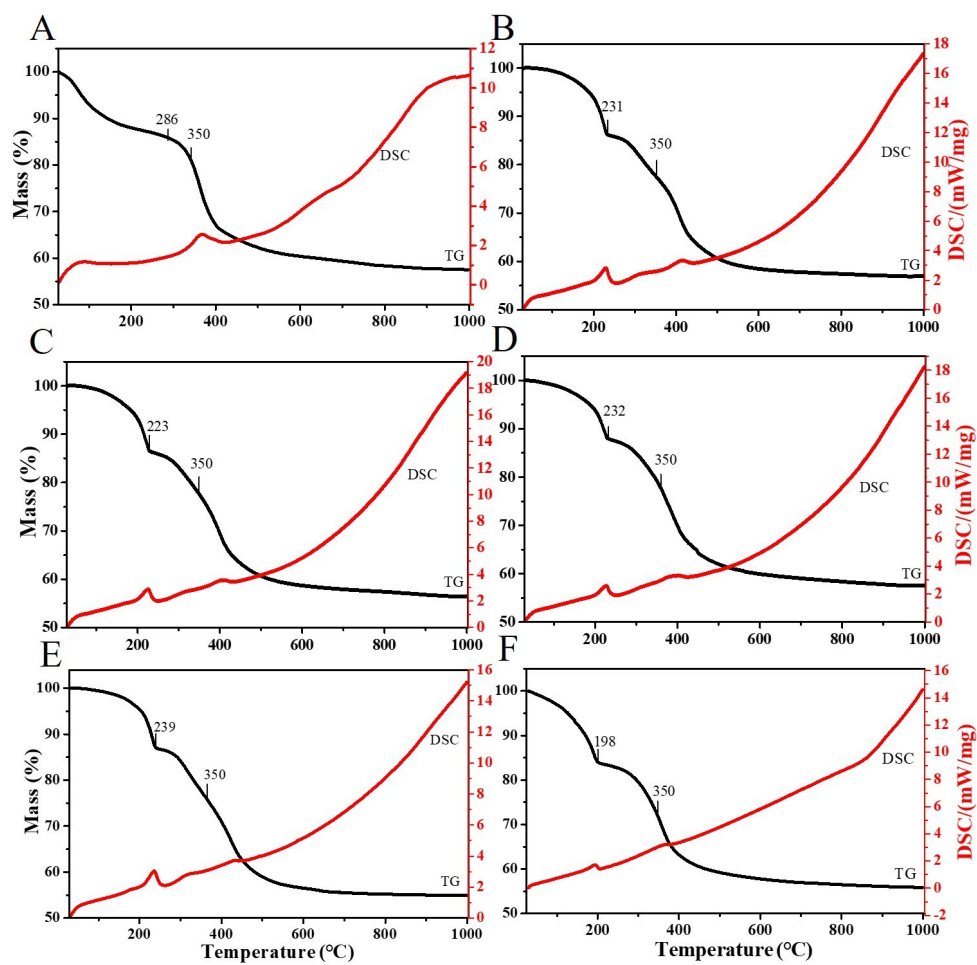


Fig. S5 TG (black) and DSC (red) curves of MA-LDHs-x: (A) MA-LDHs-1, (B) MA-LDHs-3, (C) MA-LDHs-5, (D) MA-LDHs-7, (E) C-MA-LDHs, and (F) MA-LDHs-cp.

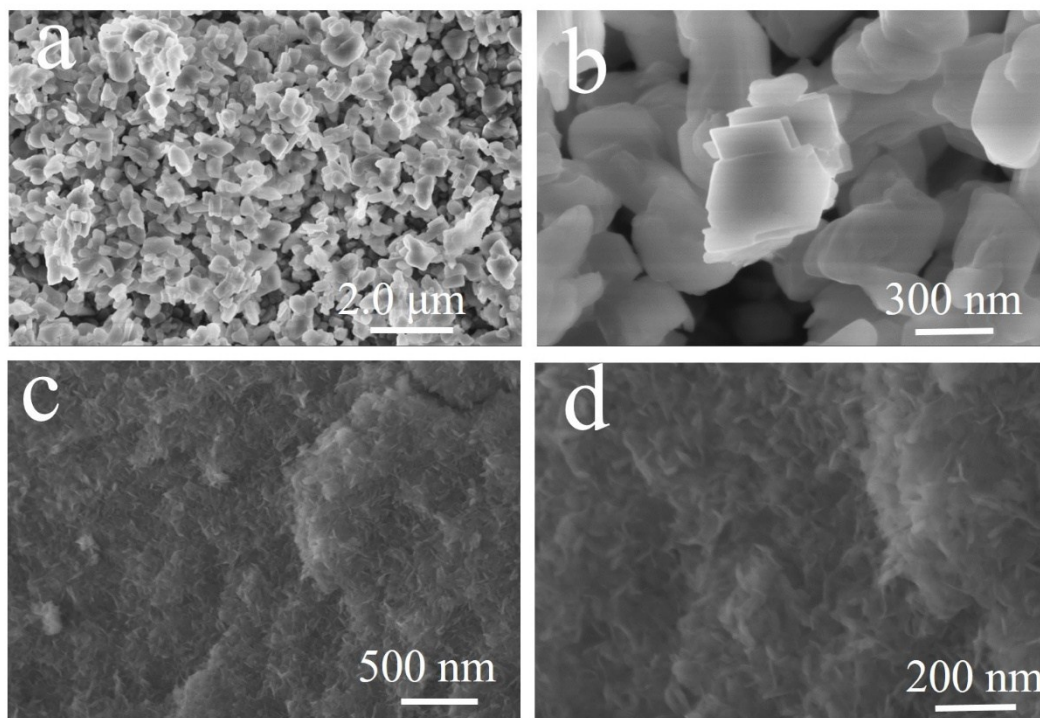


Fig. S6 SEM images of (a, b) C-MA-LDHs and (c, d) MA-LDHs-cp.

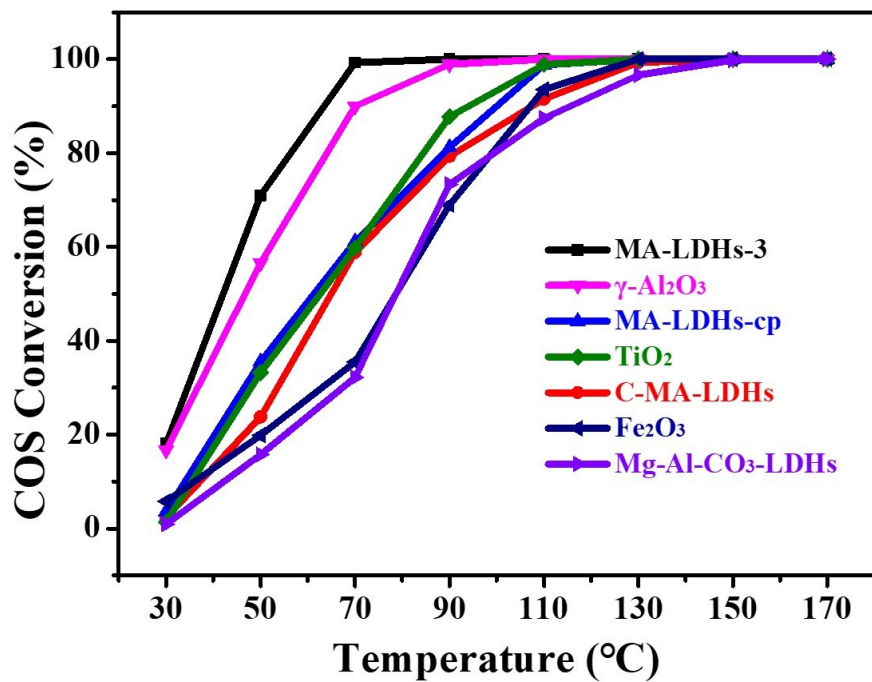


Fig. S7 Effect of temperature on COS hydrolysis over various kinds of catalysts. Reaction condition: 200 mg of catalyst, feed gas 110 mg/m³ COS/N₂, WHSV (6000 mL/(g·h)), water temperature 40 °C. (Mg-Al-CO₃-LDHs was prepared using manual grinding method according to Ref. [S1](#))

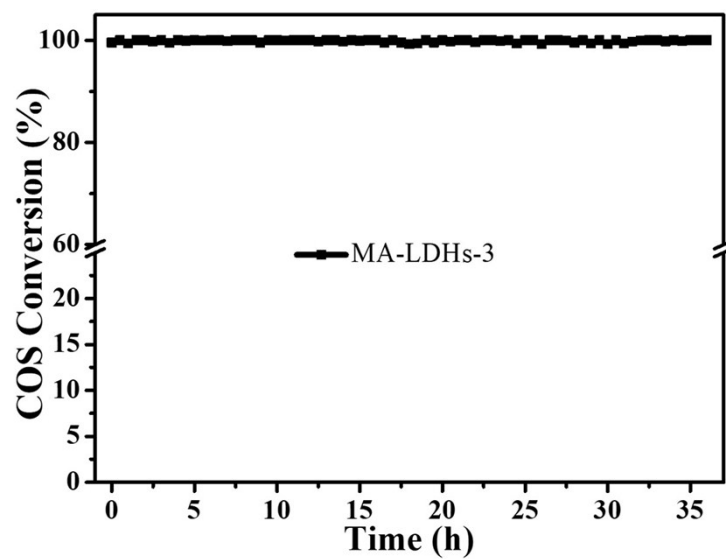


Fig. S8 Time-on-stream behavior of COS hydrolysis over MA-LDHs-3 at 110 °C. Reaction condition: 50 mg of catalyst, feed gas 110 mg/m³ COS/N₂, WHSV (24 000 mL/(g·h)), water temperature 40 °C.

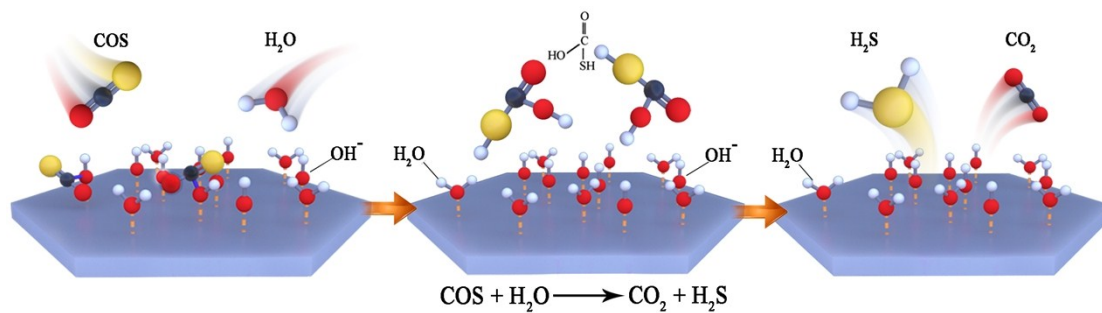


Fig. S9 Possible reaction pathway of COS hydrolysis over MA-LDHs-x.

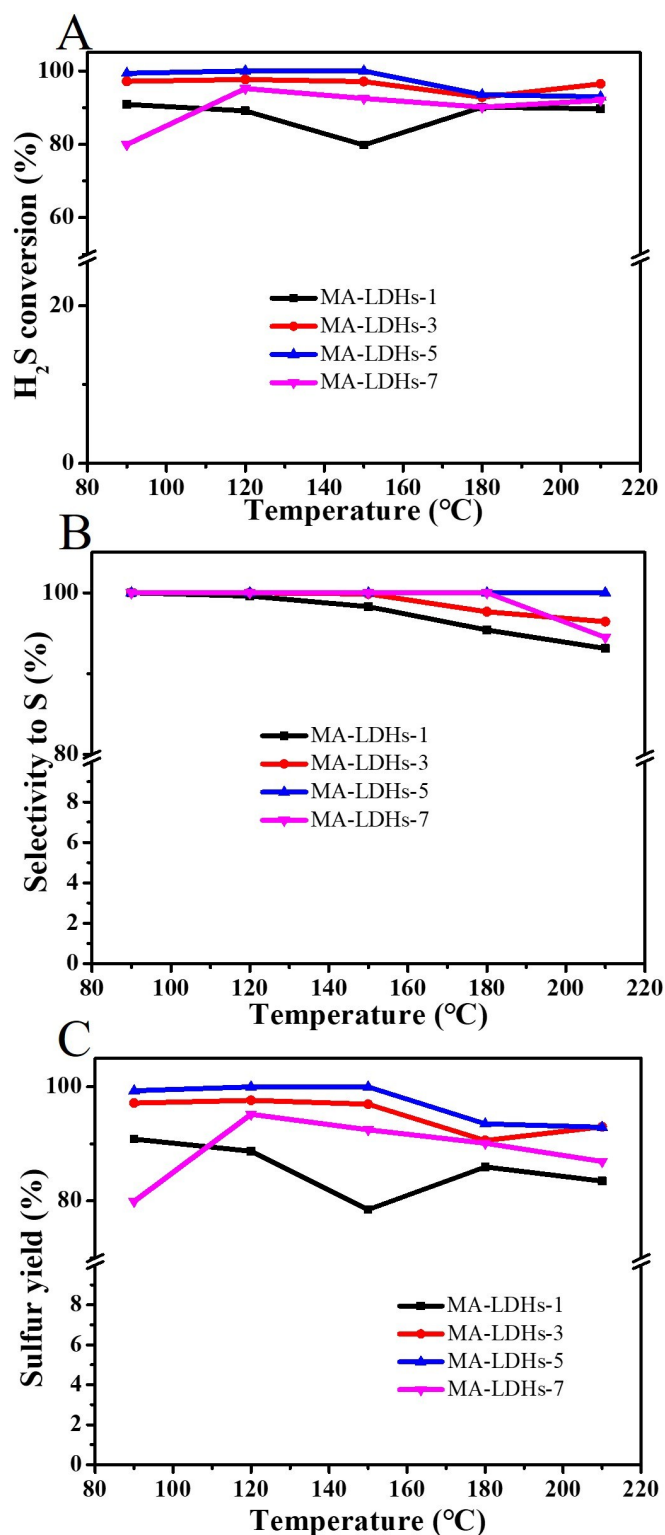


Fig. S10 Effect of reaction temperature on (A) H₂S conversion, (B) H₂S selectivity and (C) Sulfur yield of MA-LDHs-x in H₂S selective oxidation. Reaction condition: catalyst (100 mg), H₂S/O₂/N₂=0.5/0.25/99.25 (wt%), WHSV (12 000 mL/(g·h)).

H₂S conversions over MA-LDHs-xs versus reaction temperatures are displayed in Fig. S9(A). It is noted that the catalytic activities of MA-LDHs-3 and MA-LDHs-5 are higher than those of MA-LDHs-1 and MA-LDHs-7 in the temperature ranges of

90~210 °C. It is apparent that the OH⁻ contents have an effect on H₂S conversion. For instance, H₂S conversion over MA-LDHs-5 was nearly 100% at 120 °C, whereas the conversions of H₂S over MA-LDHs-1, MA-LDHs-3 and MA-LDHs-7 are 89.1, 97.6% and 95.2%, respectively. All the MA-LDHs samples exhibit a decrease of H₂S conversion with increased reaction temperature to 150 °C (MA-LDHs-1) or 180 °C (MA-LDHs-3, 5 & 7), which could be caused by the partial loss of OH⁻ content. It is understandable because H₂S adsorption ability is strongly dependent on the availability of basic OH⁻ sites.^{S12,S13} Furthermore, the basic sites can promote the adsorption of O₂ due to its strong electron donating ability.^{S14,S15} A high concentration of adsorbed oxygen and enrichment of H₂S are beneficial factors for H₂S selective oxidation. Therefore, MA-LDHs-5 shows the best performance in H₂S selective oxidation as well as S selectivity among the MA-LDHs samples.

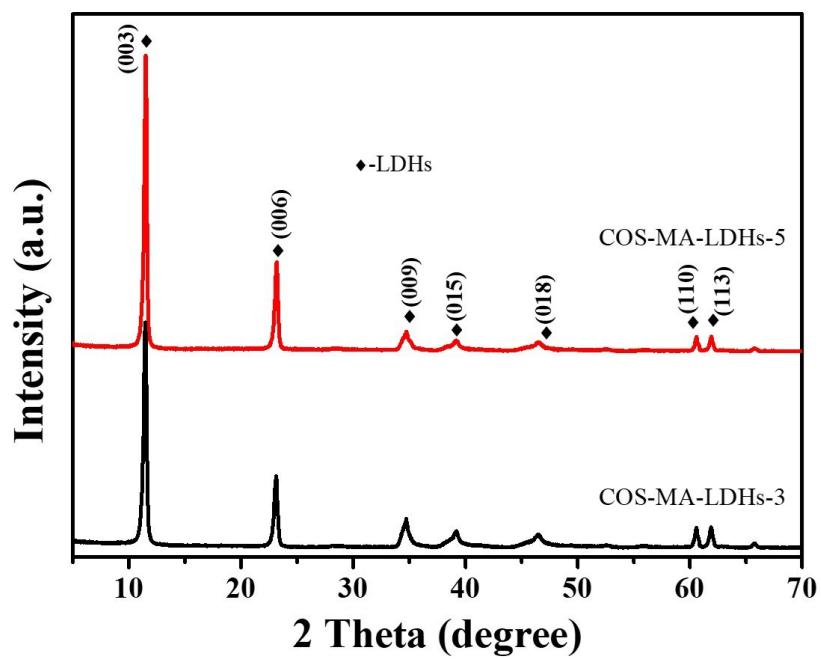


Fig. S11 XRD patterns of MA-LDHs-3 and MA-LDHs-5 after COS hydrolysis at 150 °C for 3 h.

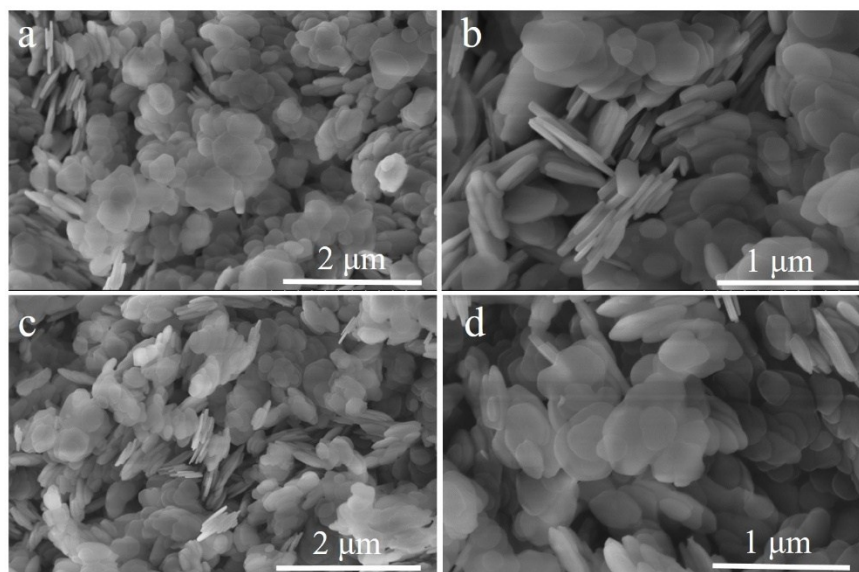


Fig. S12 SEM images of (a, b) MA-LDHs-3 and (c,d) MA-LDHs-5 after COS hydrolysis at 150 °C for 3 h.

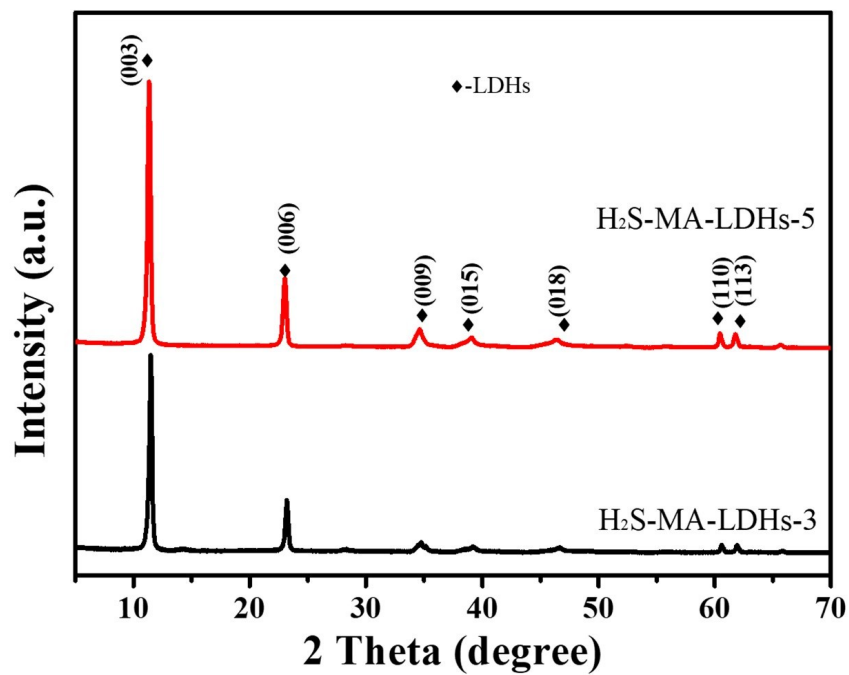


Fig. S13 XRD patterns of MA-LDHs-3 and MA-LDHs-5 after H₂S selective oxidation at 150 °C for 3 h.

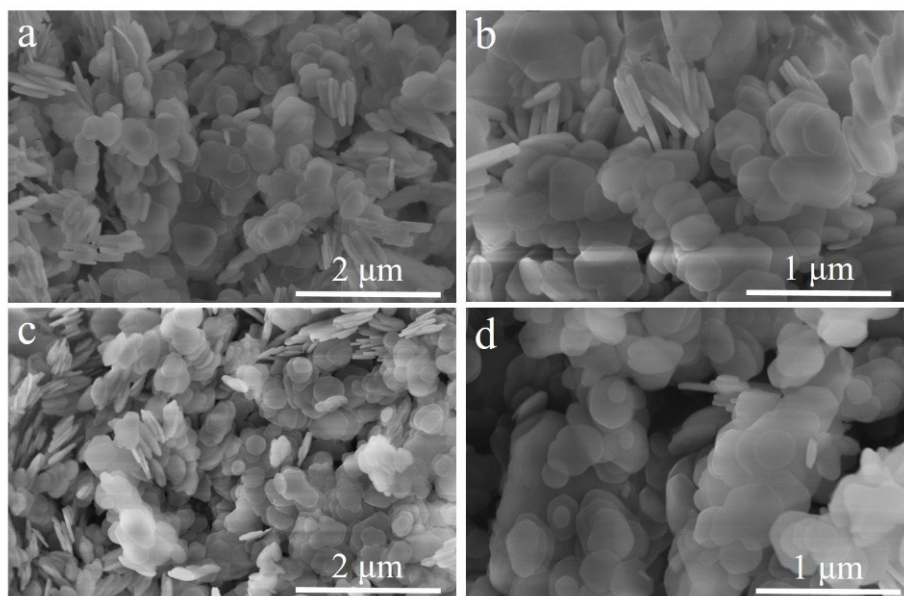


Fig. S14 SEM images of (a,b) MA-LDHs-3 and (c,d) MA-LDHs-5 after H₂S selective oxidation at 150 °C for 3 h.

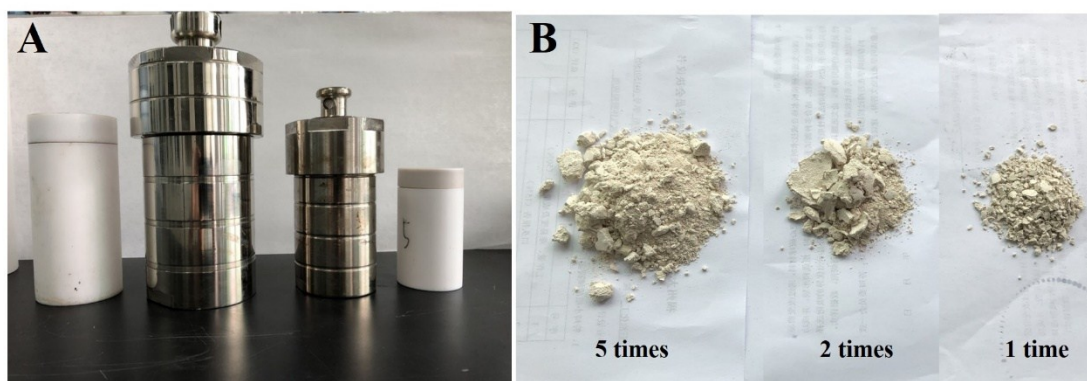


Fig. S15 (A) Experimental facilities and (B) pictures of products in scale-up synthesis.

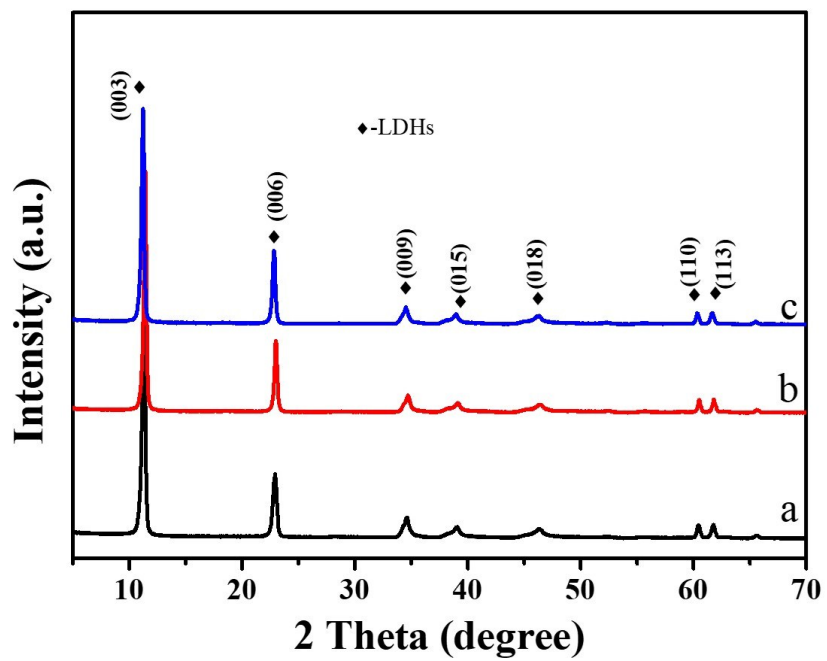


Fig. S16 XRD patterns of MA-LDHs-5 in scale-up synthesis: (a) MA-LDHs-5, (b) MA-LDHs-5(2), (c) MA-LDHs-5(5).

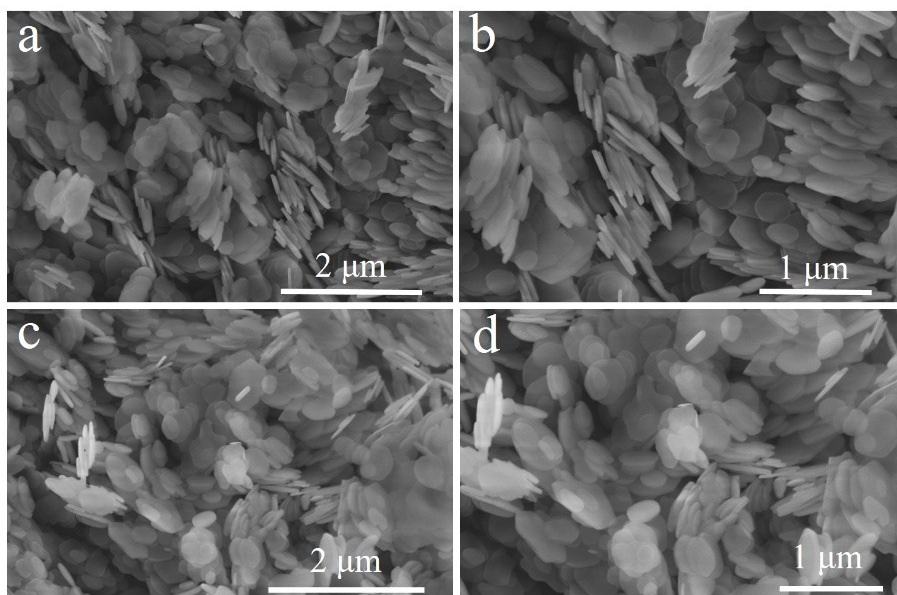


Fig. S17 SEM images of MA-LDHs-5 in scale-up synthesis: (a, b) MA-LDHs-5(2) and (c, d) MA-LDHs-5(5).

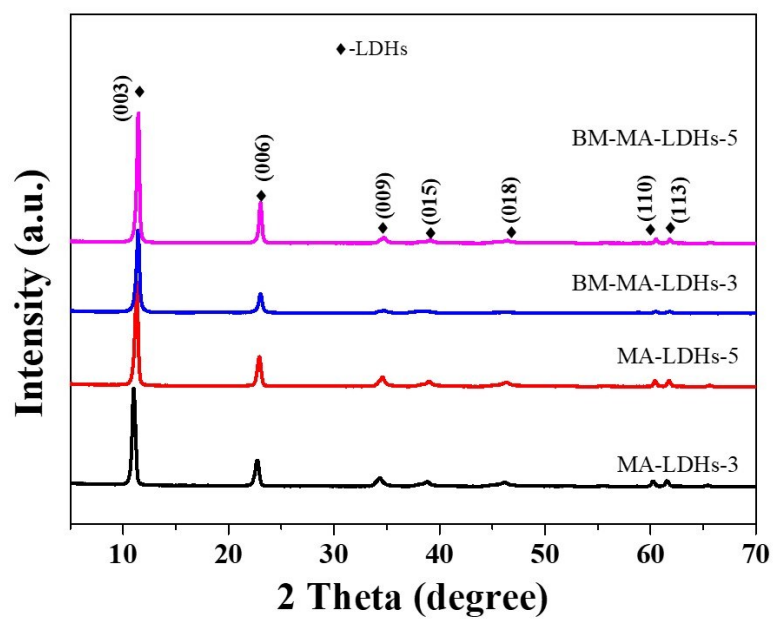


Fig. S18 XRD patterns of samples obtained by manual grinding (i.e., MA-LDHs-3 and MA-LDHs-5) and ball milling (i.e., BM-MA-LDHs-3 and BM-MA-LDHs-5).

Supplementary References

- S1. X. Q. Zhang, F. L. Qi, S. P. Li, S.H. Wei and J. H. Zhou, *Appl. Surf. Sci.*, 2012, **259**, 245.
- S2. H. B. Fang, J. T. Zhao, Y. T. Fang, J. J. Huang and Y. Wang, *Fuel*, 2013, **108**, 143.
- S3. K. Chizari, A. Deneuve, O. Ersen, I. Florea, Y. Liu, D. Edouard, I. Janowska, D. Begin and C. Pham-Huu, *ChemSusChem*, 2012, **5**, 102.
- S4. W. T. Zhao, X. H. Zheng, S. J. Liang, X. X. Zheng, L. J. Shen, F. J. Liu, Y. N. Cao, Z. Wei and L. L. Jiang, *Green Chem.*, 2018, **20**, 4645.
- S5. L. J. Shen, X. H. Zheng, G. C. Lei, X. Li, Y. N. Cao and L. L. Jiang, *Chem. Eng. J.* 2018, **346**, 238.
- S6. G. C. Lei, Y. N. Cao, W. T. Zhao, Z. J. Dai, L. J. Shen, Y. H. Xiao and L. L. Jiang, *ACS Sustainable Chem. Eng.*, 2019, **7**, 4941.
- S7. K. V. Bineesh, D. K. Kim, D. W. Kim, H. J. Cho and D. W. Park, *Energy Environ. Sci.*, 2010, **3**, 302.
- S8. P. Nguyen, D. Edouard, J. M. Nhut, M. J. Ledoux, C. Pham and C. Pham-Huu, *Appl. Catal. B-Environ.*, 2007, **76**, 300.
- S9. X. X. Zheng, L. J. Shen, X. P. Chen, X. H. Zheng, C. T. Au and L. L. Jiang, *Inorg. Chem.*, 2018, **57**, 10081.
- S10. X. Zhang, G. Y. Dou, Z. Wang, L. Li, Y. F. Wang, H. L. Wang and Z. P. Hao, *J. Hazard. Mater.*, 2013, **260**, 104.
- S11. X. Zhang, G. Y. Dou, Z. Wang, J. Cheng, H. L. Wang, C. Y. Ma and Z. P. Hao, *Catal. Sci. Technol.*, 2013, **3**, 2778.
- S12. X. Zhang, Z. Wang, N. L. Qiao, S. Q. Qu and Z. P. Hao, *ACS Catal.*, 2014, **4**, 1500.
- S13. S. Li, K. Li, J. M. Hao, P. Ning, L. H. Tang and X. Sun, *Chem. Eng. J.*, 2016, **302**, 69.
- S14. M. J. T. C. van der Niet, A. den Dunnen, L. B. F. Juurlink and M. T. M. Koper, *Angew. Chem. Int. Ed.*, 2010, **49**, 6572.
- S15. H. S. Song, M. G. Park, S. J. Kwon, K. B. Yi, E. Croiset, Z. W. Chen and S. C. Nam, *Appl. Surf. Sci.*, 2013, **276**, 646.