

Supporting information

Synthesis of $\text{Cu}_1\text{Mg}_3\text{Sc}_2(\text{OH})_{12}\text{CO}_3$ layered double hydroxide and its derived catalyst for hydrogenation of DMCD to CHDM

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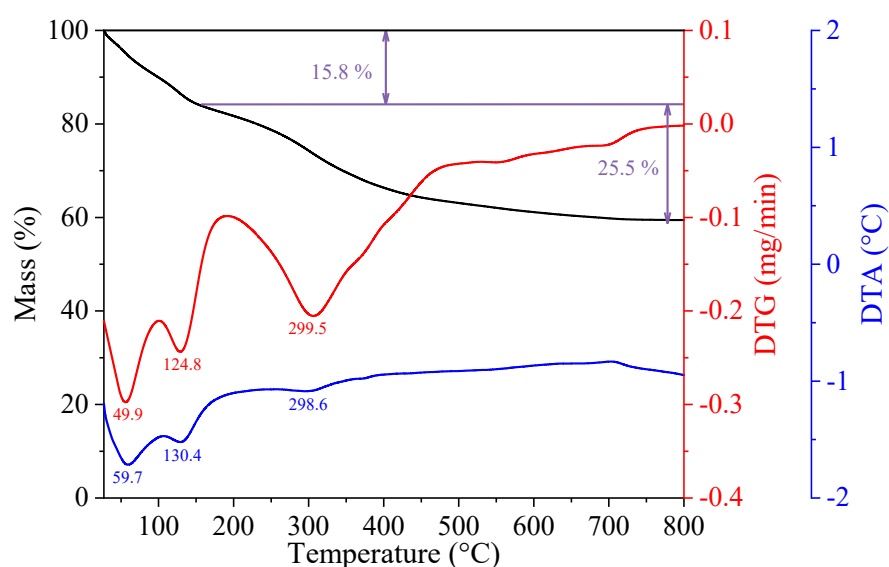
Synthesis of $\text{Cu}_1/\text{Mg}_3\text{Al}_2\text{O}_6$: 6.03 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 19.23 g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 18.73 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 400 mL water, which was designated as solution A; 12.80 g NaOH and 10.60 g Na_2CO_3 were dissolved in 400 mL water and labelled as solution B. Solution A and solution B were added dropwise into a beaker under stirring, and the pH of the combined solution was maintained at 9.5 with an online pH meter. Subsequently, the above mixture was vigorously stirred at room temperature for 3 h. And then, the formed solid was filtered, washed with water until the pH of filtrate was close to 7, and the resulting solid was dried at 80 °C for 12 hours and denoted as $\text{Cu}_1\text{Mg}_3\text{Al}_2(\text{OH})_{12}\text{CO}_3$. After calcination (at 400°C for 4 h), above LDH structured precursor was designated as $\text{Cu}_1\text{Mg}_3\text{Al}_2\text{O}_7$. Before catalytic reaction, $\text{Cu}_1\text{Mg}_3\text{Al}_2\text{O}_7$ was further reduced in H_2 (at 300 °C for 1 h) and the final catalyst was labelled as $\text{Cu}_1/\text{Mg}_3\text{Al}_2\text{O}_6$.

Synthesis of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ -IM: Firstly, supporter $\text{Mg}_3\text{Sc}_2\text{O}_6$ was prepared by the same steps as preparation of $\text{Cu}_1\text{Mg}_3\text{Sc}_2\text{O}_7$. Subsequently, 3.04 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 4 ml water and stirred well, and then 4.00 g $\text{Mg}_3\text{Sc}_2\text{O}_6$ was added to above solution. After ultrasonic treatment for 30 min, the mixture was dried in an oven at 80 °C for 12 h. After calcination (at 400°C for 4 h), above sample was designated as $\text{CuO}/\text{Mg}_3\text{Sc}_2\text{O}_6$ -IM. Before catalytic reaction, $\text{CuO}/\text{Mg}_3\text{Sc}_2\text{O}_6$ -IM was further reduced in H_2 (at 300 °C for 1 h) and the final catalyst was labelled as $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ -IM.

Table S1

The lattice parameters of LDH precursors.

Sample	d_{003} (nm)	d_{110} (nm)	a (nm) ^a	c (nm) ^b
$\text{Cu}_1\text{Mg}_3\text{Al}_2(\text{OH})_{12}\text{CO}_3$	0.7584	0.1528	0.3056	2.2752
$\text{Cu}_1\text{Mg}_3\text{Sc}_2(\text{OH})_{12}\text{CO}_3$	0.7691	0.1585	0.3170	2.3073
$\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$	-	-	0.3060	2.3400

^a parameter $a = 2d_{110}$.^b parameter $c = 3d_{003}$.**Fig. S1.** TG-DSC curve of $\text{Cu}_1\text{Mg}_3\text{Sc}_2(\text{OH})_{12}\text{CO}_3$.Theoretical mass loss from $\text{Cu}_1\text{Mg}_3\text{Sc}_2(\text{OH})_{12}\text{CO}_3$ to $\text{Cu}_1\text{Mg}_3\text{Sc}_2\text{O}_7$:

$$m_{\text{theoretical}} = (M_{\text{LDH}} - M_{\text{LDO}} / M_{\text{LDH}} \times 100\% = (490.53 - 338.40) / 490.53 \times 100\% = 31.0\%$$

Actual mass loss of hydroxyl and carbonate in DG-DSC curves of

 $\text{Cu}_1\text{Mg}_3\text{Sc}_2(\text{OH})_{12}\text{CO}_3$:

$$m_{\text{actual}} = (m_{3\text{rd}} / (100\% - m_{1\text{st}} - m_{2\text{nd}})) \times 100\% = 25.5\% / (100\% - 15.8\%) \times 100\% = 30.3\%$$

The above calculations showed that $m_{\text{theoretical}}$ is in good agreement with m_{actual} .

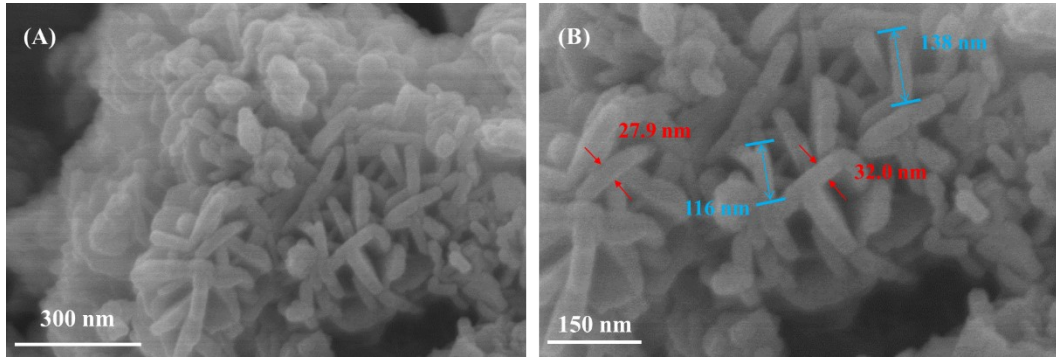


Fig. S2. SEM images of $\text{Cu}_1\text{Mg}_3\text{Al}_2(\text{OH})_{12}\text{CO}_3$.

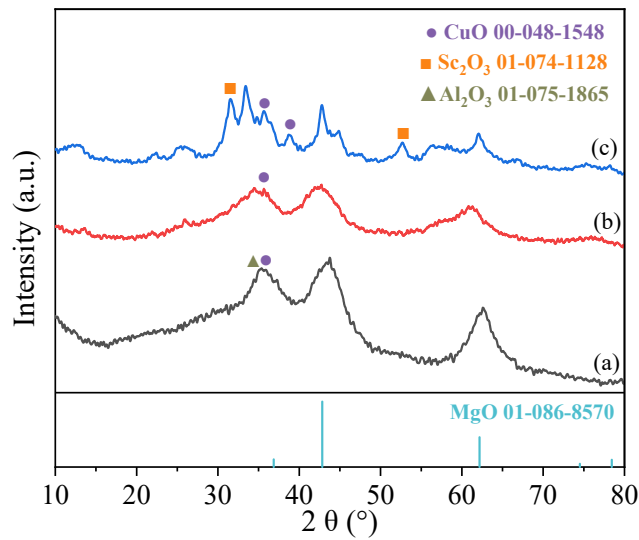


Fig. S3. XRD patterns of calcined samples.

(a) $\text{Cu}_1\text{Mg}_3\text{Al}_2\text{O}_7$; (b) $\text{Cu}_1\text{Mg}_3\text{Sc}_2\text{O}_7$; (c) $\text{CuO}/\text{Mg}_3\text{Sc}_2\text{O}_7\text{-IM}$.

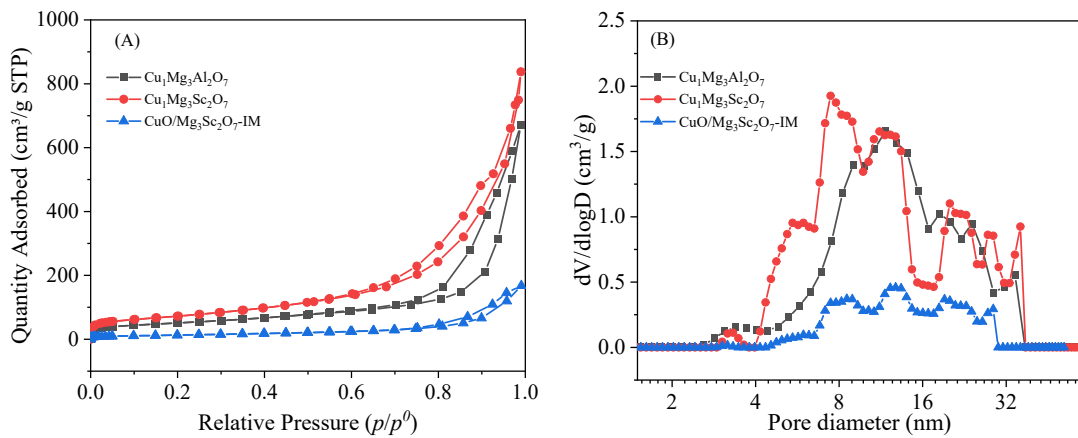


Fig. S4. N_2 adsorption-desorption isotherms (A) and pore size distribution patterns (B) of calcined samples.

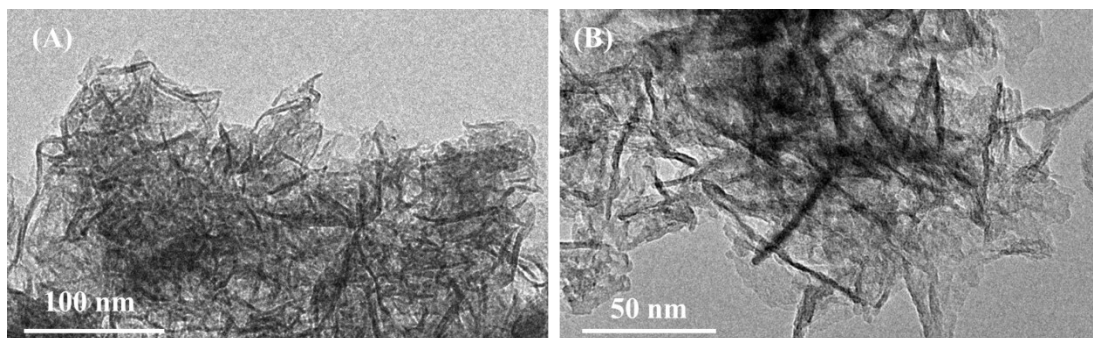


Fig. S5. HRTEM images of $\text{Cu}_1\text{Mg}_3\text{Sc}_2\text{O}_7$.

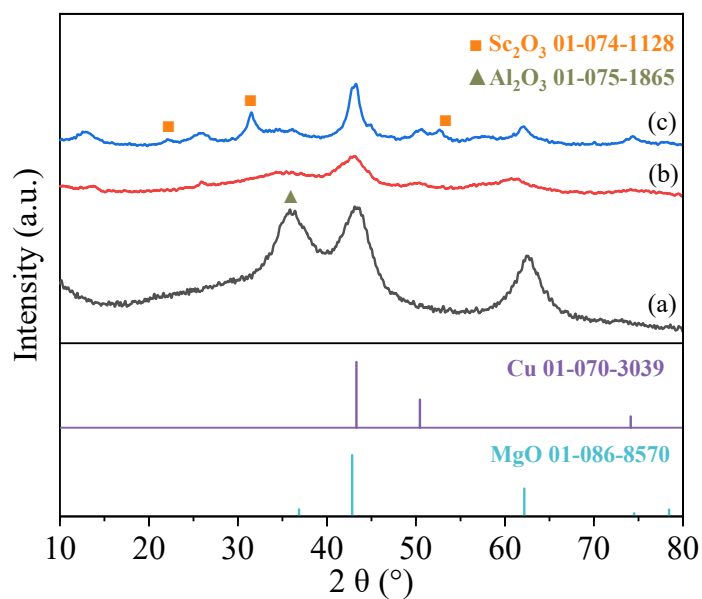


Fig. S6. XRD patterns of various catalysts.

(a) $\text{Cu}_1/\text{Mg}_3\text{Al}_2\text{O}_6$; (b) $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$; (c) $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6\text{-IM}$.

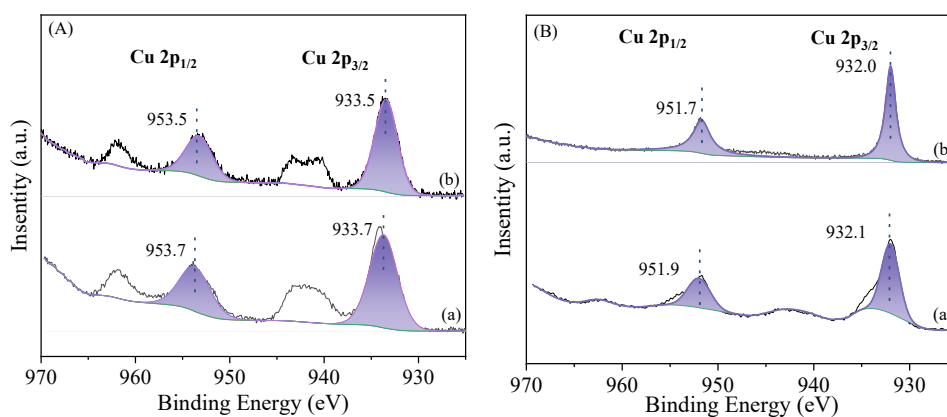


Fig. S7. XPS spectra of calcined samples (A) and reduced samples (B). (a)

$\text{Cu}_1/\text{Mg}_3\text{Al}_2\text{O}_6$; (b) $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$.

Table S2

Comparison of various catalysts for the hydrogenation of DMCD

Number	Catalyst	Temp. (°C)	P _{H₂} (MPa)	H ₂ /DMCD (mol/mol)	WHSV _{DMCD} (g·g _{cat} ⁻¹ ·h ⁻¹)	Con. _{DMCD} (%)	Sel. _{CHDM} (%)	STY _{CHDM} (g·g _{cat} ⁻¹ ·h ⁻¹)	Reference
1	Cu ₁ /Mg ₃ Sc ₂ O ₆	250	2.0	120	0.49	99.3	97.0	0.34	This work
2	Cu-ZZ-35	220	8.0	-	0.44	99.4	97.4	0.31	[1]
3	Cu-3	220	6.0	203	0.09	100	99.8	0.06	[2]
4	R-CAZ-10	220	8.0	-	-	98.8	95.8	-	[3]
5	Cu-600	220	8.0	406	0.44	99.8	95.8	0.30	[4]
6	Cu-55	220	6.0	220	3.3	97.3	96.1	2.2	[5]
7	CSNTs-623	220	5.0	260	0.08	100	96.3	0.05	[6]
8	Re ₅ /AC	220	10.0	-	-	99	67	-	[7]

Table S3

Hydrogenation activity of DMCD reaction solution with various concentration.

DMCD concentrations (wt%)	Con. (%)	Selectivity (%)				C.B. (%) ^e
		MHMCC ^a	CHDM ^b	MCHM ^c	MOMCM ^d	
13	99.3	1.0	97.0	1.4	0.3	99.7
20	99.4	4.6	94.1	0.9	0.2	99.8
30	99.5	6.3	92.0	1.0	0.4	99.7
40	99.1	7.6	90.7	0.8	0.5	99.6

Reaction conditions: 1.0 g catalyst, 2.0 MPa, 250 °C, WHSV_{DMCD}=0.49 h⁻¹, H₂/DMCD=120 (mol/mol).^a MHMCC, methyl 4-hydroxymethyl-cyclohexane carboxylate.^b CHDM, 1, 4-cyclohexane dimethanol.^c MCHM, 4-methyl-cyclohexane methanol.^d MOMCM, 4-((Methoxymethyl)cyclohexyl) methanol.^e Carbon balance, defined as (All carbon atoms detected in liquid products) / (All carbon atoms in feed) × 100%

Table S3 indicated that the conversion of DMCD was higher than 99% even with a 40wt% concentration of DMCD in feed. But the selectivity of CHDM decreased slightly from 97% to 90.7%, as the selectivity of intermediate (MHMCC) increased.

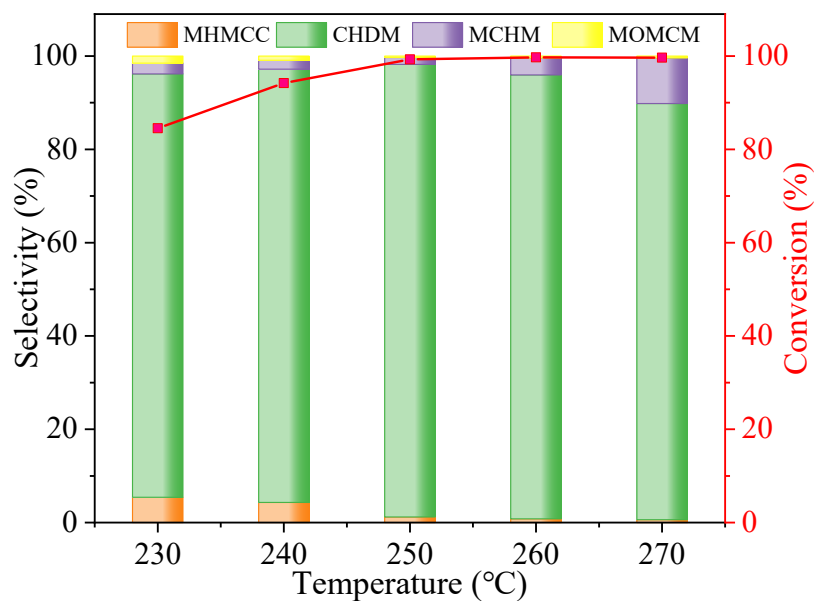


Fig. S8. Performance of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ under varied reaction temperature.

Reaction conditions: 1.0 g catalyst, 2.0 MPa, $\text{WHSV}_{\text{DMCD}}=0.49 \text{ h}^{-1}$,
 $\text{H}_2/\text{DMCD}=120$ (mol/mol).

The performance of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ catalyst under various reaction temperatures (Fig. S8) indicated that the conversion of DMCD increased quickly from 84.5% (230 °C) to above 99.3% (250 °C) and nearly fully conversion after that. While the selectivity of CHDM increased from 90.4% (230 °C) to 97% (250 °C), and then decreased slightly with the increasing temperature because the deep hydrogenation of CHDM to MCHM.

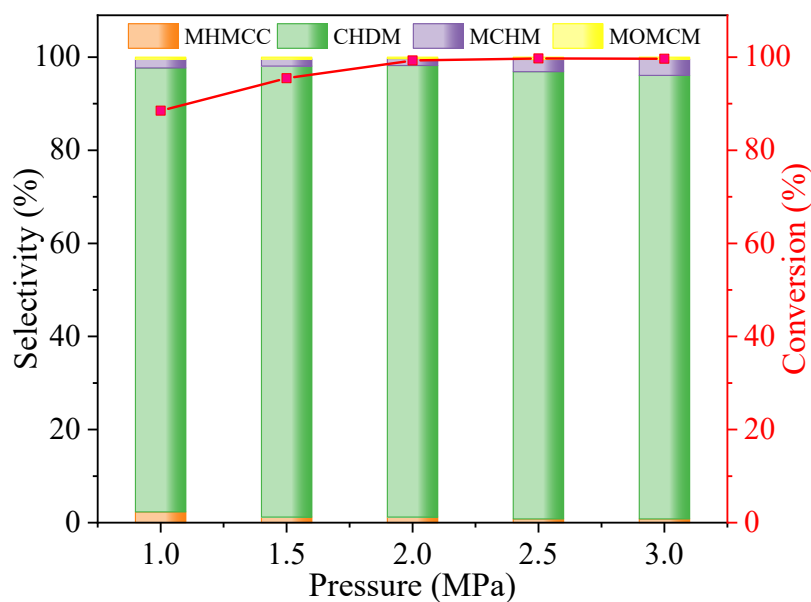


Fig. S9. Performance of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ under varied H_2 Pressure. Reaction conditions: 1.0 g catalyst, 250 °C, $\text{WHSV}_{\text{DMCD}}=0.49 \text{ h}^{-1}$, $\text{H}_2/\text{DMCD}=120$ (mol/mol).

The performance of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ catalyst under various reaction pressure (Fig. S9) confirmed that it is active even at a very low H_2 pressure (1.0 MPa) and the conversion of DMCD reached 88.5%. The conversion of DMCD increased continuously with the raising pressure, while the selectivity of CHDM changed slightly during the varied reaction pressure.

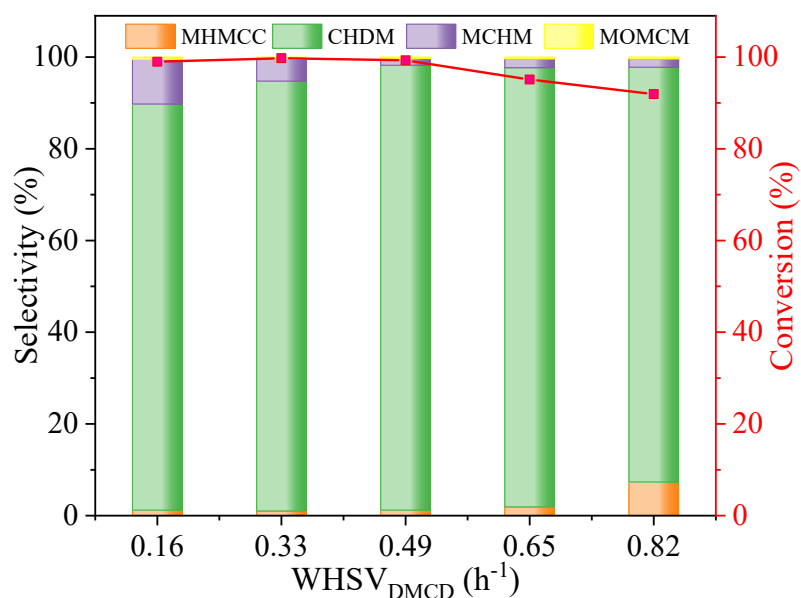


Fig. S10. The activity of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ under different $\text{WHSV}_{\text{DMCD}}$.
 Reaction conditions: 1.0 g catalyst, 250 °C, 2.0 MPa, $\text{H}_2/\text{DMCD}=120$ (mol/mol).

Fig. S10 exhibited the performance of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ catalyst for the hydrogenation of DMCD at various $\text{WHSV}_{\text{DMCD}}$ at (250 °C, 2 MPa). It was found that DMCD has been converted completely when $\text{WHSV}_{\text{DMCD}}$ was less than 0.49 h^{-1} , but the selectivity of over-hydrogenation product (MCHM) was higher at 0.16 and 0.33 h^{-1} , which depressed the selectivity of CHDM. On the other hand, the conversion of DMCD decreased with the increasing WHSV to 0.82 h^{-1} , and the selectivity of intermediate (MHMCC) increased.

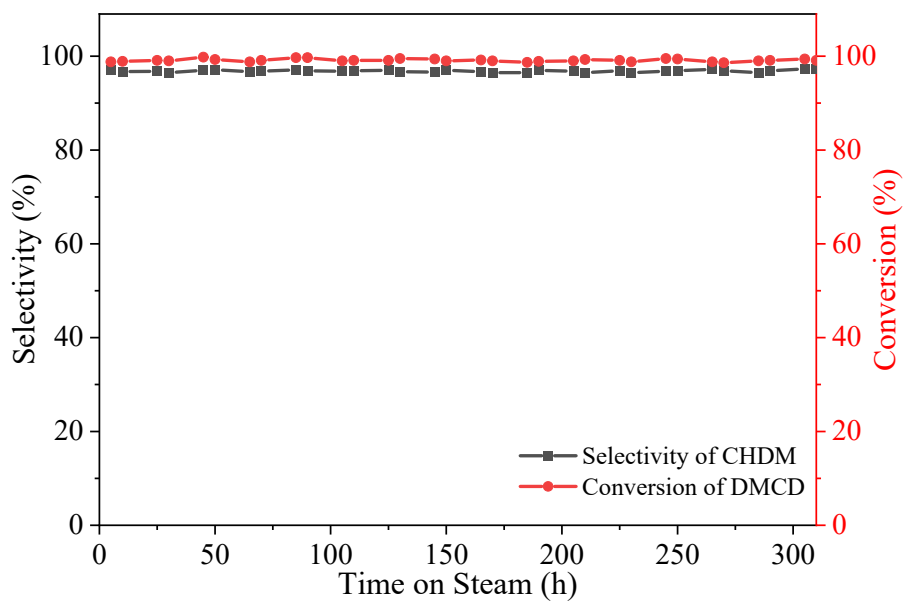


Fig. S11. Stability of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ for the hydrogenation of DMCD.

Reaction conditions: 1.0 g catalyst, 250 °C, 2.0 MPa, $\text{WHSV}_{\text{DMCD}}=0.49 \text{ h}^{-1}$, $\text{H}_2/\text{DMCD}=120$ (mol/mol).

Fig. S11 exhibited the stability of $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ for hydrogenation of DMCD under optimized reaction conditions (2.0 MPa, 250 °C, $\text{WHSV}_{\text{DMCD}}=0.49 \text{ h}^{-1}$, $\text{H}_2/\text{DMCD}=120$ (mol/mol)), it was confirmed that $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$ can remain its performance for more than 300 h on stream.

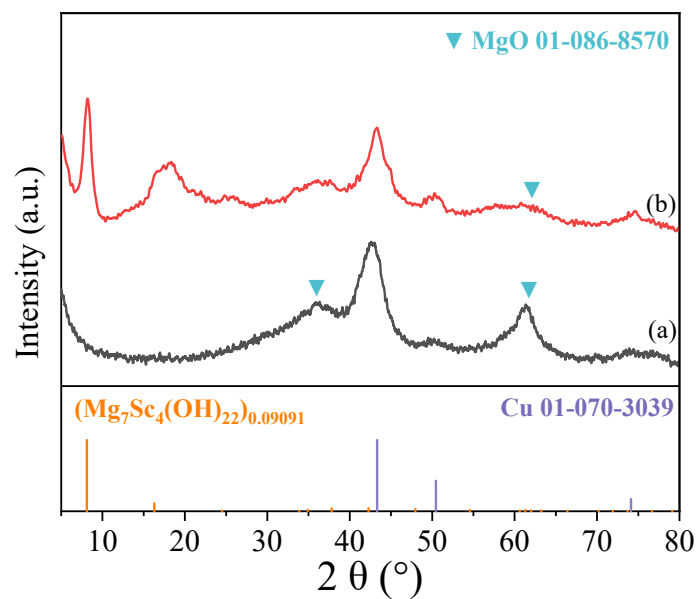


Fig. S12. XRD patterns of (a) fresh $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$; (b) spent $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$.

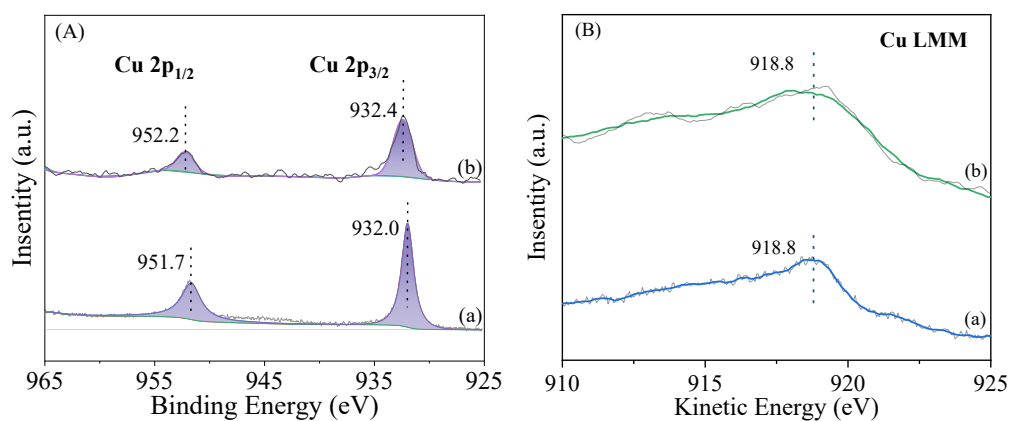


Fig. S13. XPS spectra (A) and corresponding AES spectra (B).

(a) fresh $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$; (b) spent $\text{Cu}_1/\text{Mg}_3\text{Sc}_2\text{O}_6$.

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