

## Supporting information

### High-Entropy Oxides derived Cu catalyst for enhanced dehydrogenation of cyclohexanol coupling with hydrogenation of acetone

#### Authors:

Rui Li,<sup>a</sup> Yingdan Ye,<sup>a</sup> Yibin Zhang,<sup>a</sup> Huaiyuan Zhao,<sup>ab</sup> Weichen Du,<sup>b</sup> Zhaoyin Hou<sup>\*ab</sup>

<sup>a</sup> Key Laboratory of Biomass Chemical Engineering of Ministry of Education,  
Department of Chemistry, Zhejiang University, Hangzhou 310028, China.

<sup>b</sup> Zhejiang Hengyi Petrochemical Research Institute Co., Ltd., Hangzhou 311200,  
China.

\* Corresponding author

Zhaoyin Hou

Tel/Fax: 86-571-88273283

Email: zyhou@zju.edu.cn

**Preparation of Cu/MgO, Cu/Al<sub>2</sub>O<sub>3</sub>, Cu/ZnO:** 1.902 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.5 g Cu) was dissolved in the corresponding amount of deionized water, and 4.5 g pretreated MgO (Al<sub>2</sub>O<sub>3</sub>, ZnO) was added to the solution under stirring. After that, the mixture was pretreated in an ultrasonic bath for 30 min and left to stand for 24 h. Then it was dried in an oven at 120 °C for 12 h and calcinated in a muffle furnace at 400 °C for 4 h. The CuO/MgO (Al<sub>2</sub>O<sub>3</sub>, ZnO) precursor was pressed, crushed, and sieved to obtain 40~60 mesh particles. Before the catalytic reaction, CuO/MgO (Al<sub>2</sub>O<sub>3</sub>, ZnO) was reduced at 300 °C for 1 h in 10% H<sub>2</sub>/N<sub>2</sub> and the final 10 wt% Cu/MgO (Al<sub>2</sub>O<sub>3</sub>, ZnO) catalyst was obtained.

**Preparation of Cu<sub>0.7</sub>/Mg<sub>7.3</sub>Al<sub>2</sub>O<sub>10.3</sub>:** 1.721 g Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 18.686 g Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 7.503 g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were mixed and dissolved in 200 mL deionized water, which was labeled as solution A. 16 g NaOH and 13.25 g Na<sub>2</sub>CO<sub>3</sub> were dissolved in 400 mL deionized water and recorded as solution B. Solution A and solution B were mixed by peristaltic pump and added dropwise with a controlled pH of 9.5. After that, the suspension was transferred into a 500 mL Teflon-lined stainless-steel autoclave and kept at 100 °C for 14 h. The formed solid was filtered and washed with deionized water until the pH of the filtrate was close to 7, and then it was dried in an oven at 80 °C overnight and denoted as Cu<sub>0.7</sub>Mg<sub>7.3</sub>Al<sub>2</sub>(OH)<sub>20</sub>CO<sub>3</sub>. The above precursor was calcinated in a muffle furnace at 400 °C for 4 h with a heating rate of 5 °C/min. The obtained solid was pressed into 40~60 mesh particles and designated as

$\text{Cu}_{0.7}\text{Mg}_{7.3}\text{Al}_2\text{O}_{11}$ . Before the catalytic reaction, the above  $\text{Cu}_{0.7}\text{Mg}_{7.3}\text{Al}_2\text{O}_{11}$  was reduced at 300 °C for 1 h in 5%  $\text{H}_2/\text{N}_2$  and the final  $\text{Cu}_{0.7}/\text{Mg}_{7.3}\text{Al}_2\text{O}_{10.3}$  catalyst was obtained.

**Preparation of  $\text{Cu}_{0.8}/\text{Mg}_{7.2}\text{Sc}_2\text{O}_{10.2}$ :** 1.867 g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 18.531 g  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 5.188 g  $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$  were mixed and dissolved in 200 mL deionized water, which was labeled as solution A. 16 g NaOH and 13.25 g  $\text{Na}_2\text{CO}_3$  were dissolved in 400 mL deionized water and recorded as solution B. Solution A and solution B were mixed using peristaltic pump and added dropwise with a controlled pH of 9.5. Subsequently, the above mixture was transferred into a 500 mL Teflon-lined stainless steel autoclave and kept at 100 °C for 14 hours. The formed solid was filtered and washed with distilled water until the pH of the filtrate was close to 7, and then it was dried in an oven at 80 °C overnight and denoted as  $\text{Cu}_{0.8}\text{Mg}_{7.2}\text{Sc}_2(\text{OH})_{20}\text{CO}_3$ . The above precursor was calcinated in a muffle furnace at 400 °C for 4 h with a heating rate of 5 °C/min. The obtained solid was pressed into 40~60 mesh particles and designated as  $\text{Cu}_{0.8}\text{Mg}_{7.2}\text{Sc}_2\text{O}_{11}$ . Before the catalytic reaction, the above  $\text{Cu}_{0.8}\text{Mg}_{7.2}\text{Sc}_2\text{O}_{11}$  was reduced at 300 °C for 1 h in 5%  $\text{H}_2/\text{N}_2$  and the final  $\text{Cu}_{0.8}/\text{Mg}_{7.2}\text{Sc}_2\text{O}_{10.2}$  catalyst was obtained.

**Table S1.**

Performance of reported Cu-based catalysts for cyclohexanol dehydrogenation.

Catalyst	Temp (°C)	Pressure (atm)	N <sub>2</sub> (cm <sup>3</sup> ·min <sup>-1</sup> )	Velocity (mL·h <sup>-1</sup> )	Conv (%)	Sel. (%)	Ref.
Cu/Al <sub>2</sub> O <sub>3</sub>	250	1	50	5 <sup>b</sup>	81	79	[1]
CuO-ZnO-Cr <sub>2</sub> O <sub>3</sub>	240	1	10	1	80	60	[2]
Cu-ZnO/SiO <sub>2</sub>	300	1	-	3000 <sup>c</sup>	91	85	[3]
Cu/N-rGO	250	1	N <sub>2</sub>	57 <sup>b</sup>	85.8	86.3	[4]
Cu/ZrO <sub>2</sub>	250	-	20	1	62	93	[5]
Cu/SiO <sub>2</sub>	250	-	-	1.5	60	90	[6]
Cu/SBA-15	250	-	-	7.7 <sup>b</sup>	55	95	[7]
Cu-SBA-15	250	-	20	1	70	99	[8]
CuO-ZnO-MgO	260	-	-	2.34 <sup>b</sup>	55	99.2	[9]
Cu/MgO-SBA15	250	1	10 <sup>a</sup>	1860 <sup>c</sup>	78	96	[10]
Cu-MgO	250	-	-	1.2	64.3	100	[11]
WS <sub>90</sub> <sup>300</sup>	250	1	-	1	56.5	99.8	[12]

<sup>a</sup> N<sub>2</sub>/CHOL = 10.<sup>b</sup> WHSV, weight hourly space velocity.<sup>c</sup> GHSV, gaseous hourly space velocity.**Table S2.**

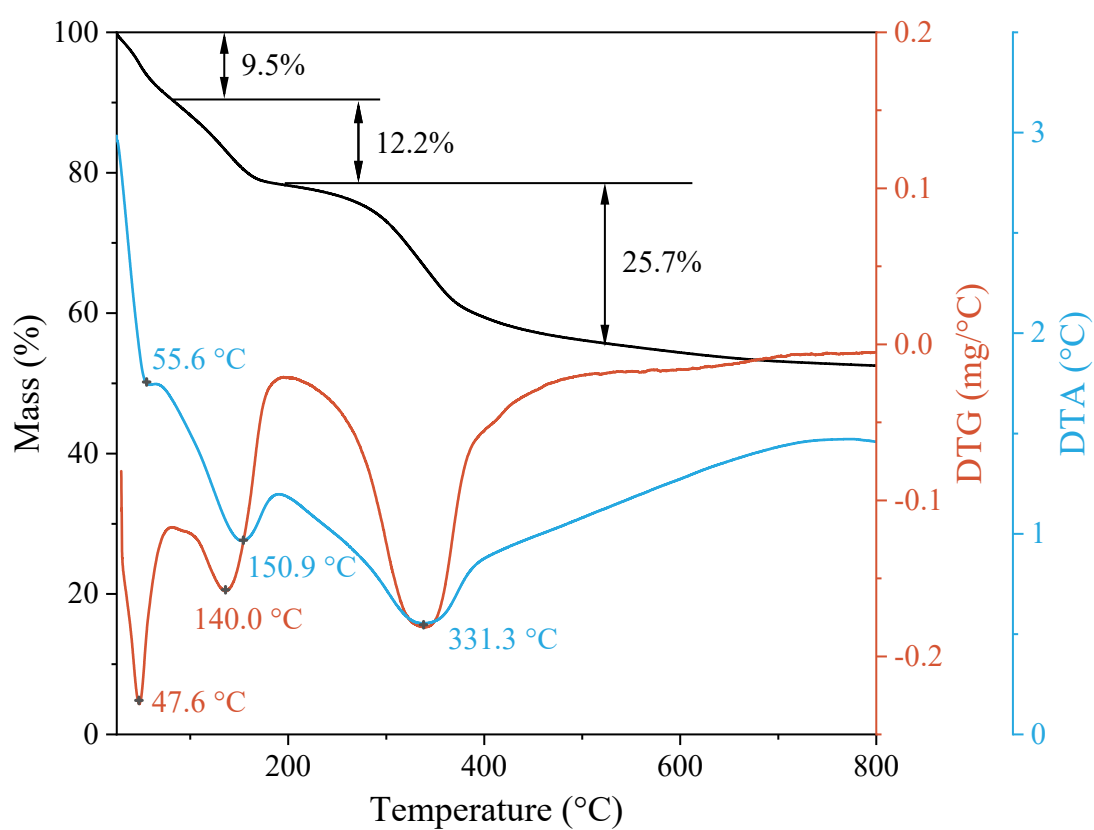
Catalyst composition and raw material feeding.

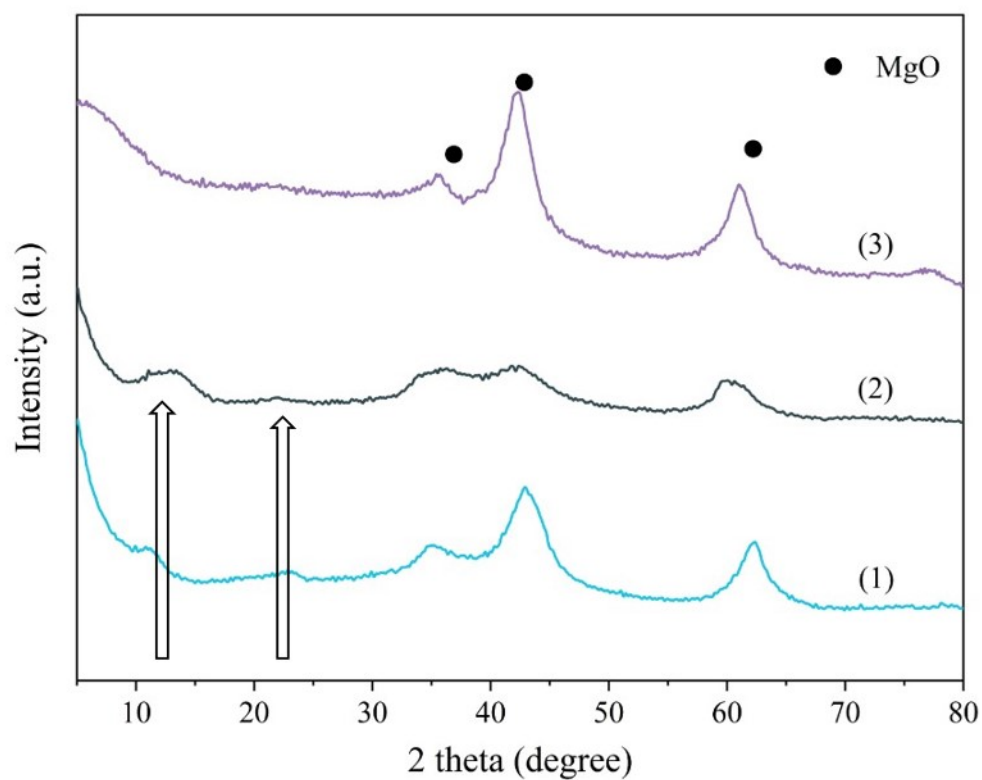
Catalyst	Cu <sup>a</sup> (g)	Zn <sup>b</sup> (g)	Mg <sup>c</sup> (g)	Al <sup>d</sup> (g)	Sc <sup>e</sup> (g)
Redeucd Cu <sub>0.72</sub> Zn <sub>0.14</sub> Mg <sub>7.14</sub> Al <sub>2</sub> O <sub>11</sub> -HEO	1.745	0.430	18.290	7.503	/
Redeucd Cu <sub>0.78</sub> Zn <sub>0.16</sub> Mg <sub>7.06</sub> Sc <sub>2</sub> O <sub>11</sub> -HEO	1.893	0.466	18.102	/	5.188

<sup>a</sup> Cu: Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O.<sup>b</sup> Zn: Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.<sup>c</sup> Mg: Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.<sup>d</sup> Al: Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O.<sup>e</sup> Sc: ScCl<sub>3</sub>·6H<sub>2</sub>O.

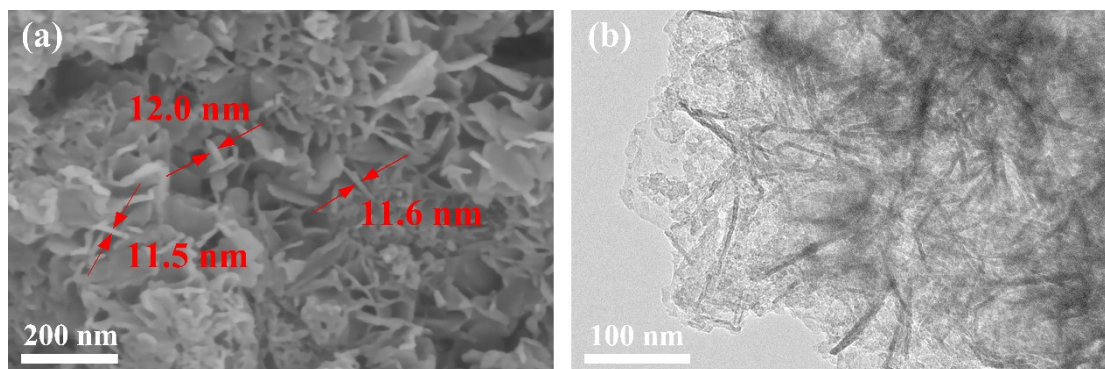
**Table S3.**Cell parameters of  $\text{Cu}_x\text{Zn}_{0.2x}\text{Mg}_{8-1.2x}\text{Al}_y\text{Sc}_{2-y}(\text{OH})_{20}\text{CO}_3$  precursors.

LDH precursor	$d_{003}$ (Å)	$d_{110}$ (Å)	$a$ (Å) <sup>a</sup>	$c$ (Å) <sup>b</sup>
$\text{Cu}_{0.72}\text{Zn}_{0.14}\text{Mg}_{7.14}\text{Al}_2(\text{OH})_{20}\text{CO}_3$	7.809	1.535	3.07	23.43
$\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1(\text{OH})_{20}\text{CO}_3$	7.908	1.558	3.12	23.72
$\text{Cu}_{0.78}\text{Zn}_{0.16}\text{Mg}_{7.06}\text{Sc}_2(\text{OH})_{20}\text{CO}_3$	7.841	1.578	3.16	23.52

<sup>a</sup> parameter  $a = 2d_{110}$ .<sup>b</sup> parameter  $c = 3d_{003}$ .**Figure S1.** TG-DSC curves of  $\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1(\text{OH})_{20}\text{CO}_3$ .



**Figure S2.** XRD patterns of  $\text{Cu}_x\text{Zn}_{0.2x}\text{Mg}_{8-1.2x}\text{Al}_y\text{Sc}_{2-y}\text{O}_{11}$ -HEOs.  
 (1)  $\text{Cu}_{0.72}\text{Zn}_{0.14}\text{Mg}_{7.14}\text{Al}_2\text{O}_{11}$ -HEO; (2)  $\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1\text{O}_{11}$ -HEO;  
 (3)  $\text{Cu}_{0.78}\text{Zn}_{0.16}\text{Mg}_{7.06}\text{Sc}_2\text{O}_{11}$ -HEO.

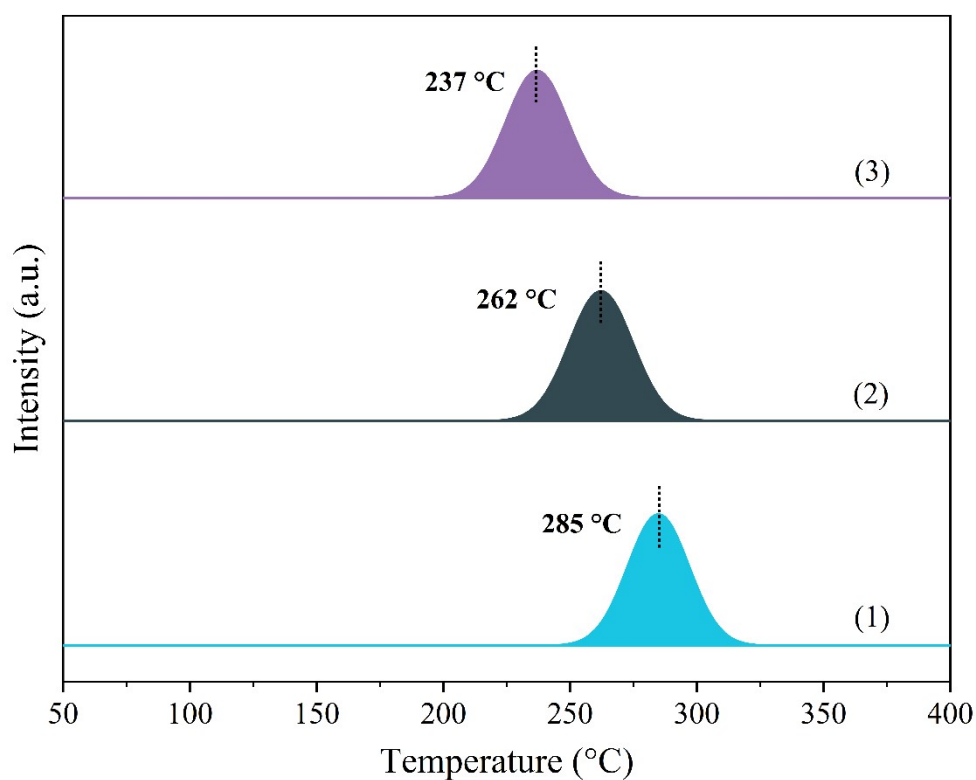


**Figure S3.** SEM (a) and HRTEM images (b) of  $\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1\text{O}_{11}$ -HEO.

**Table S4.**

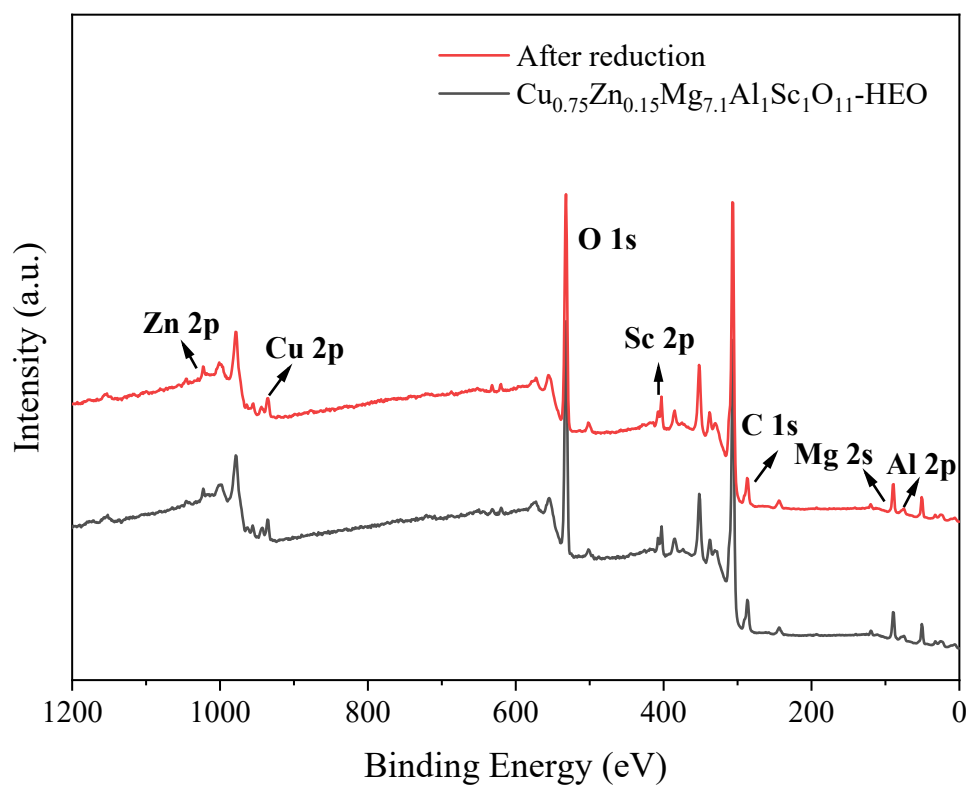
Textural properties of other Cu-based catalysts.

Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)	Cu dispersion (%) <sup>a</sup>
Cu <sub>0.7</sub> /Mg <sub>7.3</sub> Al <sub>2</sub> O <sub>10.3</sub>	106	3.9	0.65	58.9
Cu <sub>0.8</sub> /Mg <sub>7.2</sub> Sc <sub>2</sub> O <sub>10.2</sub>	129	6.5	0.70	50.5
Cu/Al <sub>2</sub> O <sub>3</sub>	123	5.6	0.54	38.8
Cu/MgO	21	3.2	0.26	24.5
Cu/ZnO	2	3.5	0.02	3.2

<sup>a</sup> Calculated from N<sub>2</sub>O titration after the catalysts were reduced in H<sub>2</sub> at 300 °C.**Figure S4.** H<sub>2</sub>-TPR profiles of Cu<sub>x</sub>Zn<sub>0.2x</sub>Mg<sub>8-1.2x</sub>Al<sub>y</sub>Sc<sub>2-y</sub>O<sub>11</sub>-HEOs.(1) Cu<sub>0.72</sub>Zn<sub>0.14</sub>Mg<sub>7.14</sub>Al<sub>2</sub>O<sub>11</sub>-HEO; (2) Cu<sub>0.75</sub>Zn<sub>0.15</sub>Mg<sub>7.1</sub>Al<sub>1</sub>Sc<sub>1</sub>O<sub>11</sub>-HEO;(3) Cu<sub>0.78</sub>Zn<sub>0.16</sub>Mg<sub>7.06</sub>Sc<sub>2</sub>O<sub>11</sub>-HEO.

**Table S5.**Density of desorbed  $\text{NH}_3$  and  $\text{CO}_2$  in  $\text{Cu}_x\text{Zn}_{0.2x}\text{Mg}_{8-1.2x}\text{Al}_y\text{Sc}_{2-y}\text{O}_{11}$ -HEOs.

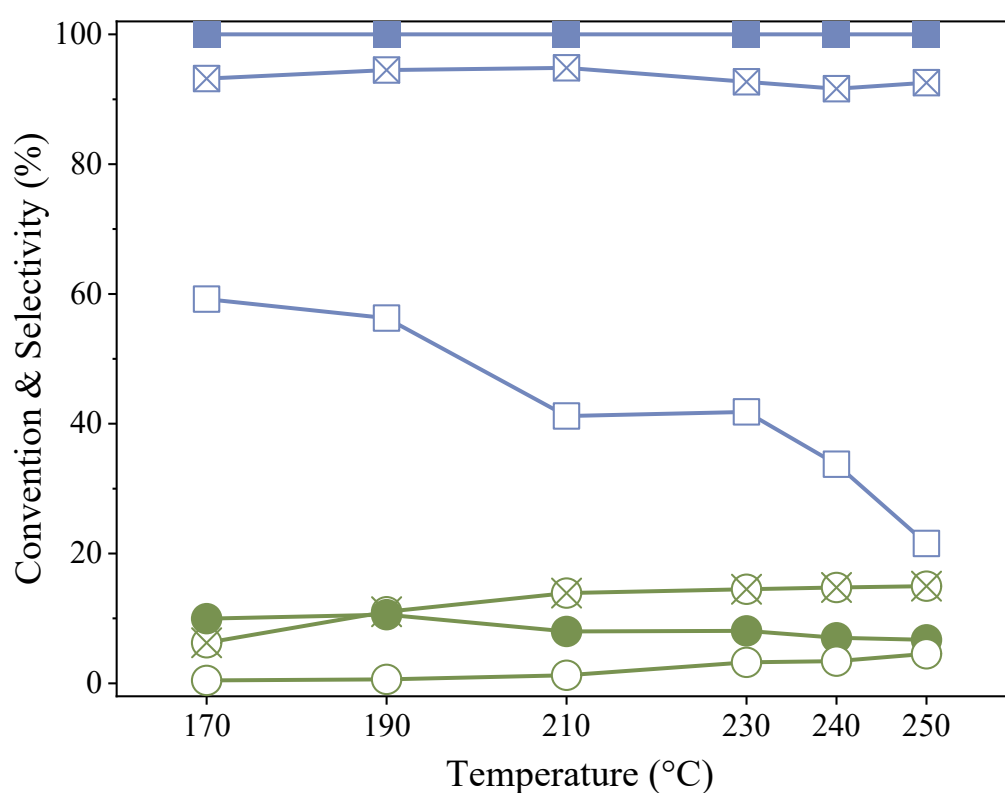
Catalyst	Acidity ( $\mu\text{mol}/\text{m}^2$ ) <sup>a</sup>			Tota	Basicity ( $\mu\text{mol}/\text{m}^2$ ) <sup>b</sup>			Tota
	Weak	Medium	Strong	1	Weak	Medium	Strong	1
$\text{Cu}_{0.72}\text{Zn}_{0.14}\text{Mg}_{7.14}\text{Al}_2\text{O}_{11}$ -HEO	0.25	0.45	0.30	1.0	0.87	0.99	0.62	2.5
$\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1\text{O}_{11}$ - HEO	0.27	0.32	0.19	0.8	1.19	1.34	0.75	3.3
$\text{Cu}_{0.78}\text{Zn}_{0.16}\text{Mg}_{7.06}\text{Sc}_2\text{O}_{11}$ -HEO	0.24	0.26	0.13	0.6	1.96	1.73	1.06	4.7

<sup>a</sup> Calculated from  $\text{NH}_3$ -TPD and  $S_{\text{BET}}$ ;<sup>b</sup> Calculated from  $\text{CO}_2$ -TPD and  $S_{\text{BET}}$ .**Figure S5.** *In-situ* XPS survey of  $\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1\text{O}_{11}$ -HEO before and after reduction.



**Table S6.**Composition of  $\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1\text{O}_{11}$ -HEO before and after reduction.

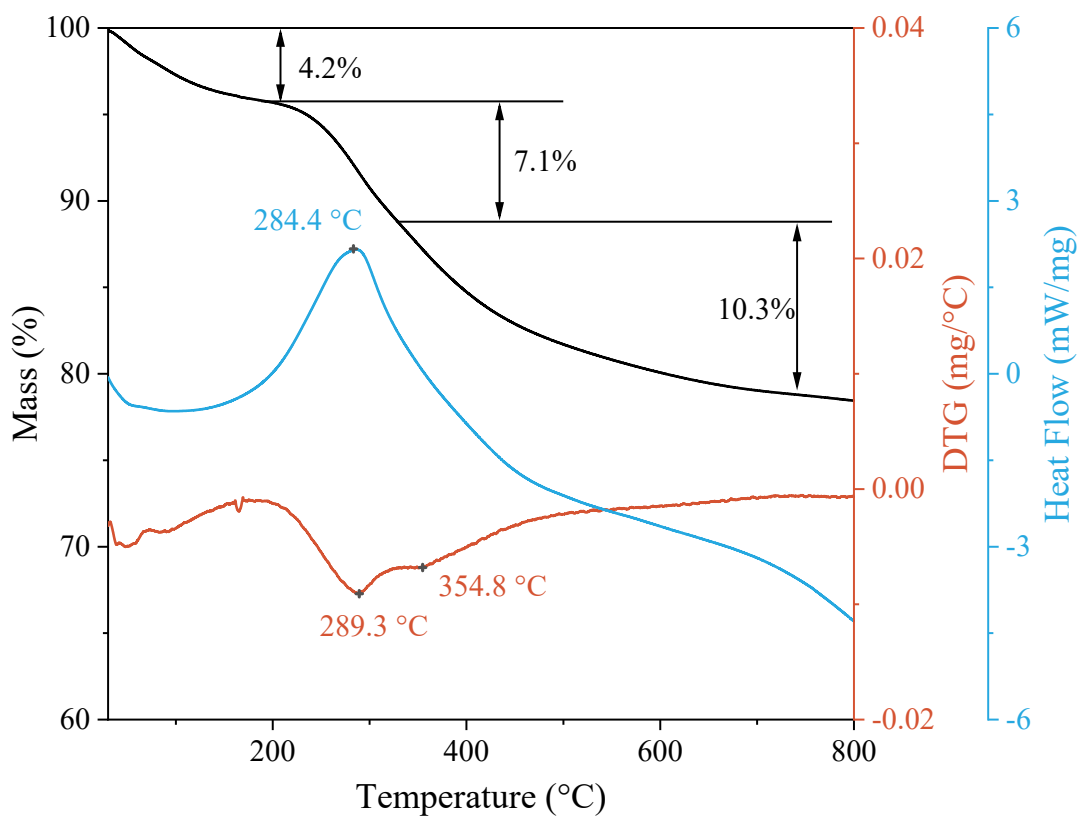
Catalyst	Surface content (Atomic%)				
	Cu	Zn	Mg	Al	Sc
$\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1\text{O}_{11}$ -HEO <sup>a</sup>	7.3	1.6	70.2	10.5	10.4
After reduction <sup>a</sup>	7.4	1.6	70.1	10.6	10.3
Theoretical <sup>b</sup>	7.5	1.5	71.0	10.0	10.0

<sup>a</sup> Surface content calculated from XPS analysis.<sup>b</sup> Theoretical content calculated from the actual amount of feed.**Figure S6.** Separated hydrogenation of acetone with H<sub>2</sub> and coupling hydrogenation of acetone with dehydrogenation of cyclohexanol.

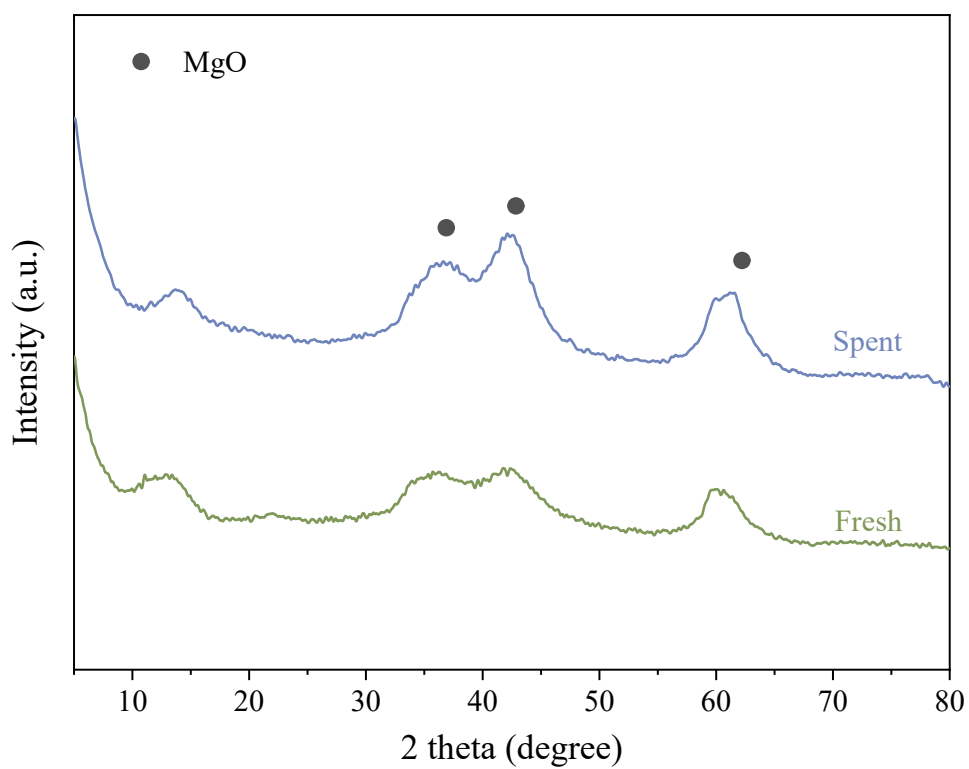
- Conversion of ACE and □ Selectivity of iPrOH in ACE:H<sub>2</sub>=6:1.
- Conversion of ACE and ■ Selectivity of iPrOH in ACE:CHOL=1:1.
- ⊗ Conversion of ACE and ⊗ Selectivity of iPrOH in ACE:H<sub>2</sub>=1:3.

Reaction conditions:  $\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1\text{O}_{11}$ -HEO 0.3 g, WHSV of acetone 11.3 h<sup>-1</sup>.

At the same time, hydrogenation of acetone with molecular H<sub>2</sub> and cyclohexanol (as the H donor) at different temperatures were performed and compared in Figure S6. It was found that the conversion of acetone increased with the increasing ratio of H<sub>2</sub>/acetone in feed, indicating that Cu<sub>0.75</sub>Zn<sub>0.15</sub>Mg<sub>7.1</sub>Al<sub>1</sub>Sc<sub>1</sub>O<sub>11</sub>-HEO was also active for the separated hydrogenation of acetone. And the detected conversion of acetone in molecular H<sub>2</sub> was similar or even higher than that in cyclohexanol (as the H donor). More interestingly, the selectivity of isopropanol in cyclohexanol was higher than that in molecular H<sub>2</sub>.



**Figure S7.** TG-DSC curves of reduced Cu<sub>0.75</sub>Zn<sub>0.15</sub>Mg<sub>7.1</sub>Al<sub>1</sub>Sc<sub>1</sub>O<sub>11</sub>-HEO in spent.



**Figure S8.** XRD patterns of reduced  $\text{Cu}_{0.75}\text{Zn}_{0.15}\text{Mg}_{7.1}\text{Al}_1\text{Sc}_1\text{O}_{11}$ -HEO in fresh and spent.

## References

- 1 N. P. Tangale, P. S. Niphadkar, S. S. Deshpande and P. N. Joshi, *Appl. Catal., A*, 2013, **467**, 421–429.
- 2 V. Siva Kumar, S. Sreevardhan Reddy, A. H. Padmasri, B. David Raju, I. Ajitkumar Reddy and K. S. Rama Rao, *Catal. Commun.*, 2007, **8**, 899–905.
- 3 D. Ji, W. Zhu, Z. Wang and G. Wang, *Catal. Commun.*, 2007, **8**, 1891–1895.
- 4 A. Mageed, D. Radiah, S. Ali, S. Izhar, M. Abdul Razak and B. Ayodele, *Bull. Chem. React. Eng. Catal.*, 2020, **15**, 568–578.
- 5 P. Nagaiah, C. V. Pramod, M. Venkata Rao, B. David Raju and K. S. Rama Rao, *Catal. Lett.*, 2018, **148**, 3042–3050.
- 6 M. Gliński, U. Ulkowska and E. Iwanek, *J. Chem. Educ.*, 2016, **93**, 1623–1625.
- 7 C. Soumini, S. Sugunan and S. Haridas, *J. Porous Mat.*, 2019, **26**, 631–640.
- 8 B. Sridevi, P. Nagaiah, A. H. Padmasri, B. David Raju and K. S. Rama Rao, *J. Chem. Sci.*, 2017, **129**, 601–608.
- 9 S. V. Sancheti and G. D. Yadav, *Mol. Catal.*, 2021, **506**, 111534.
- 10 R. K. Marella, V. R. Madduluri, S. K. Lakkaboyana, M. M. Hanafiah and S. Yaaratha, *RSC Adv.*, 2020, **10**, 38755–38766.
- 11 K. N. Patil, P. Manikanta, R. R. Nikam, P. M. Srinivasappa, A. H. Jadhav, H. P. Aytam, K. S. Rama Rao and B. M. Nagaraja, *Results Eng.*, 2023, **17**, 100851.
- 12 I. Ali, T. Kon’kova, V. Vanchurin, D. Solntseva, T. A. Kurniawan, A. A. Alothman, M. S. S. Mushab and G. Imanova, *Catal Lett*, 2024, 1–11.