Supplementary Information

Modulation of Acid-Basic and Metal-Carrier Interactions in CO_2-assisted Propane Dehydrogenation over Ga_2La_x/ZSM-5 Catalysts

Xiude Peng [a,c,d], Xiaohua Cao[a,c,d *], Huaiyu Xu [a,b,c,d], Ruibin Xiong[a,c,d], Dedong He[a,c,d], Dingkai Chen[a,c,d], Yongming Luo[a,b,c,d *]

a Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, China.

b Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China.

c Key Laboratory of Yunnan Province for Synthesizing Sulfur-containing Fine Chemicals, Kunming 650500, P. R. China.

d The Innovation Team for Volatile Organic Compounds Pollutants Control and Resource Utilization of Yunnan Province, Kunming 650500, China.

* Corresponding author.

xiaohuacao@kust.edu.cn (X. Cao)

environcatalysis@kust.edu.cn (Y. Luo)

Text S1. Catalyst characterization

X-ray diffraction (XRD) patterns of as-prepared samples were recorded on an X-ray diffractometer (D/Max-2200, Rigaku, Japan) using Cu Kα irradiation (k = 0.154 nm), operating at 30 mA and 40 kV. The structural properties (specific surface area and pore size distribution) of the catalyst were determined by N_2 adsorption-desorption experiments, which were performed on a NOVA 4200e instrument at -196 °C. The scanning electron microscopy (SEM, ZEISS Sigma 360, Germany) was used to detect morphologies.NH_3/CO_2 temperature programmed desorption (NH_3/CO_2-TPD) profiles were conducted to monitor the intensity of the desorbed using a highly sensitive thermal conductivity detector (TCD). Before performing NH_3/CO_2-TPD measurements, 0.05g catalyst was pretreated at 450 °C for 30 min and cooled down to 100 °C under a He purge. Then 10vol % NH_3/CO_2 (He as the carrier gas, 30ml/min) was introduced into the reactor for 2 h. The aim was to saturate the acidic sites of the measured samples. Finally, the NH_3/CO_2-TPD analysis was performed at 30 ml/min He flows with the temperature rising from 100 to 800 °C. X-ray photoelectron spectroscopy (XPS) of samples was recorded on an ESCALAB 250XI spectrometer (XPS, Thermo Scientific K-Alpha, USA) using an Al Kα X-ray source. Thermogravimetric Analysis (TGA, NETZSCHSTA2500, Germany) for measurement of carbon deposition in reaction materials. The spent samples were heated in the air at a ramp rate of 10 °C/min from room temperature up to 800 °C. Diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) was recorded on a Nicolet iS50 FT-IR (Thermo Fisher, America) using an in-situ cell. To further verify the intermediate, the reaction pathway, and the reaction mechanism for CO_2-PDH. Each sample was loaded and pretreated for 30 minutes at 550 °C under a stream of nitrogen (30 mL/min) and a DRIFTS spectrum was collected as background. C_3H_8: CO_2: N_2 (1:1:4) was then ramped up from 30 °C to 550 °C at a flow rate of 30 mL/min. And the DRIFTS spectra were recorded automatically every 30 s by OMNIC™ Series Software.

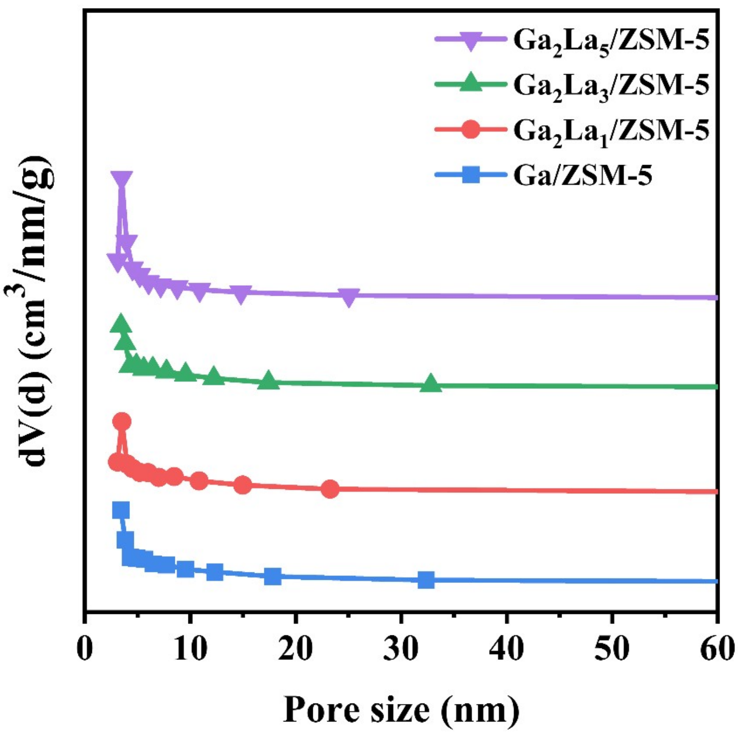

Fig. S1. Pore size distribution curves of Ga/ZSM-5 and Ga_2La_x/ZSM-5 (x = 1, 3, 5) catalysts.

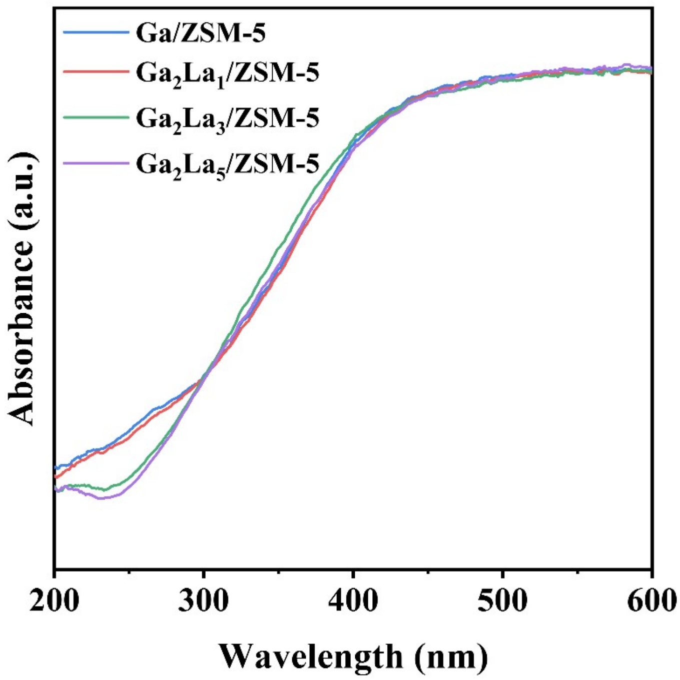

Fig. S2. The UV-vis DRS of Ga/ZSM-5 and Ga_2La_x/ZSM-5 (x = 1, 3, 5) catalysts.

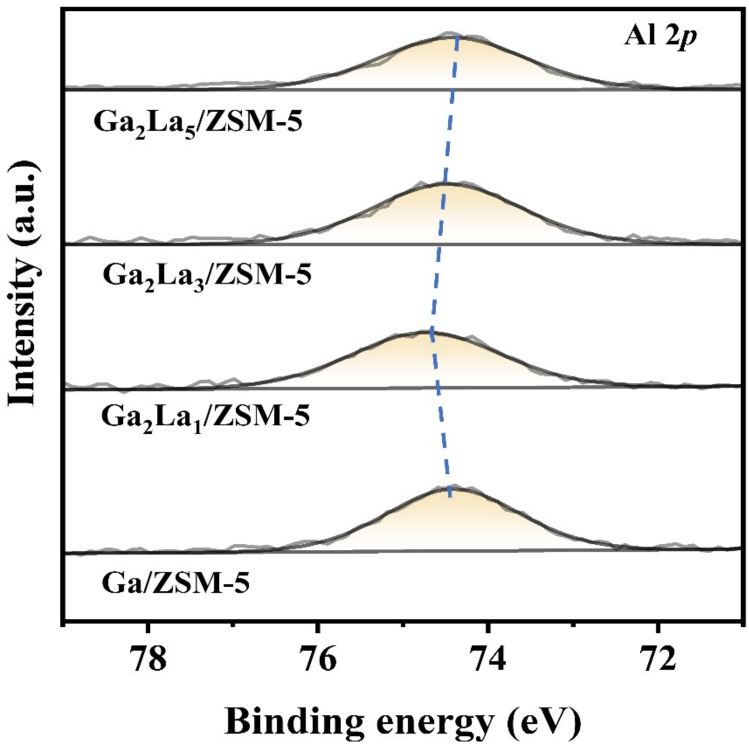

Fig. S3. XPS spectra of Al 2p for Ga/ZSM-5 and Ga_2La_x/ZSM-5 (x = 1, 3, 5) catalysts.

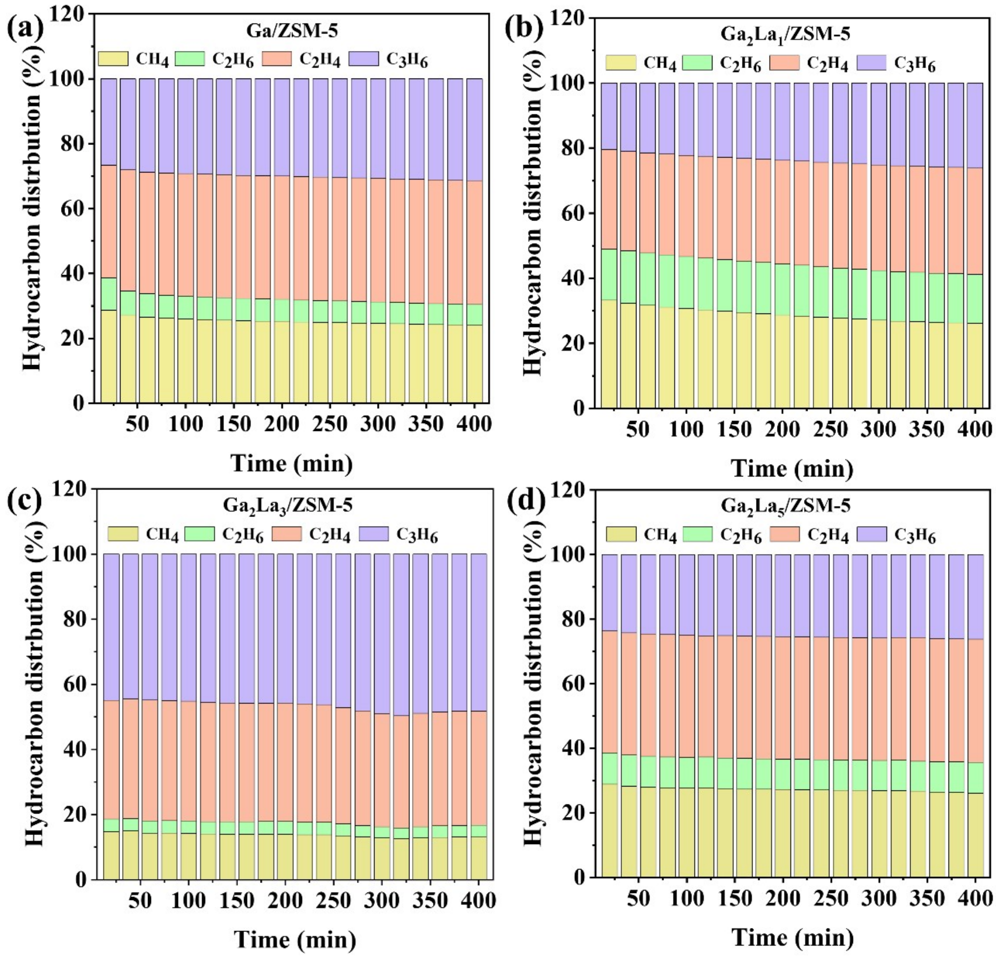

Fig. S4. Hydrocarbon distribution of Ga/ZSM-5 and Ga_2La_x/ZSM-5 (x = 1, 3, 5) catalysts

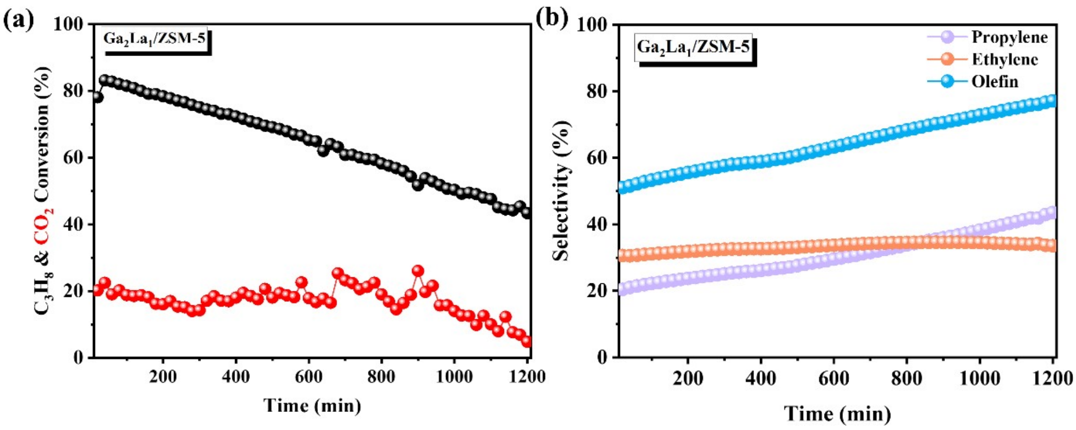

Fig. S5. Long-term stability test for CO_2-ODHP conversion (a) and selectivity (b) over Ga_2La_1/ZSM-5 catalyst.

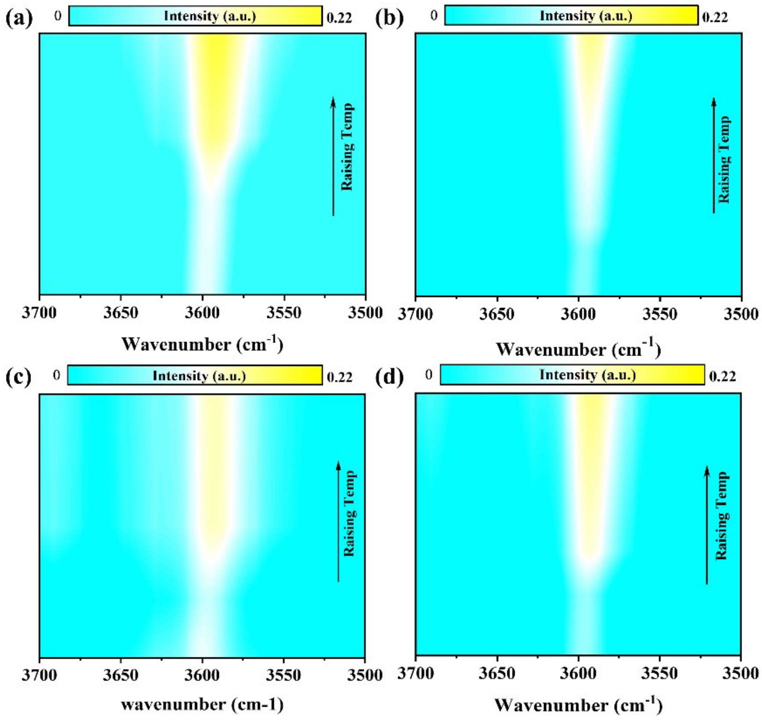

Fig. S6. Color-mapping spectra in the 3700–3500 cm $^{-1}$ range of Si-OH-Ga on the Ga/ZSM-5 (a), Ga_2La_1/ZSM-5 (b), Ga_2La_3/ZSM-5 (c) and Ga_2La_5/ZSM-5 catalysts (d).

Note: The data in the plots are from in situ infrared. The Si-OH-Ga groups in the region of 3700-3500 cm^{-1} in the *in situ* DRIFTS were selected for the contour mapping. The color gradation is from cyan to yellow, and the darker the color, the stronger the signal strength of Si-OH-Ga. The intensity of Si-OH-Ga groups of the four catalysts was visualized as a reflection of the change in the intensity of the Si-OH-Ga groups with temperature.

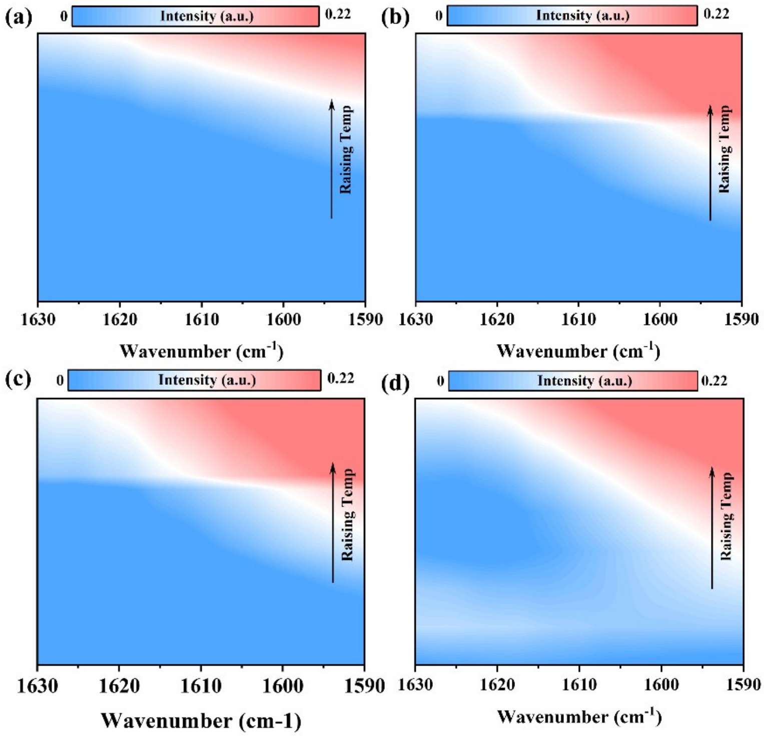

Fig. S7. Color-mapping spectra in the 1630-1590 cm^{-1} range of $HCOO^*$ on the Ga/ZSM-5 (a), Ga_2La_1/ZSM-5 (b), Ga_2La_3/ZSM-5 (c) and Ga_2La_5/ZSM-5 catalysts (d).

Note: The data in the plots are from in situ infrared. The $HCOO^*$ groups in the region of 1630-1590 cm^{-1} in the *in situ* DRIFTS were selected for the contour mapping. The color gradation is from blue to red, and the darker the color, the stronger the signal strength of $HCOO^*$. The intensity of $HCOO^*$ groups of the four catalysts was visualized as a reflection of the change in the intensity of the $HCOO^*$ groups with temperature.

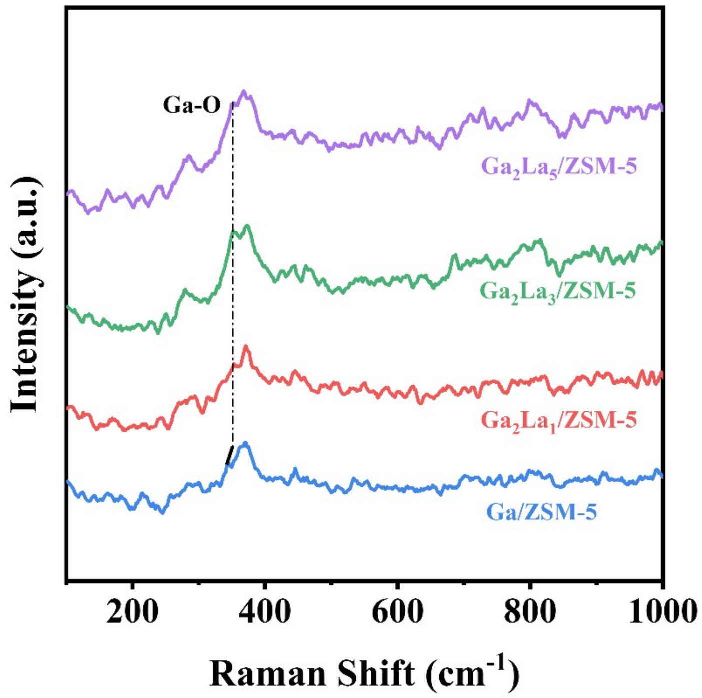

Fig. S8. Raman spectra of Ga/ZSM-5 and Ga_2La_x/ZSM-5 (x = 1, 3, 5) catalysts

Table S1. Comparison of Ga_2La_1/ZSM-5 catalyst performance with previously reported catalysts.

Catalyst	m/g	T/°C	$C_3H_8/CO_2/N_2$	WHSV[a]	X /C_3H_8	S /C_3H_6	Stability	Ref
5GaN/NaZSM-5(470)	0.2	600	1：2：7	9000	45%	87.8%	48h, 17%	1
5GaN/2000-Fe-Silicalite-1	0.2	600	1.5：3：25.5	9000	55%	70%	20h, 28%	2
5GaN/HS-1	0.2	600	1：2：7	9000	67%	58%	40h, 20%	3
5.2V-MSNS	0.2	600	1：4：4	4500	58%	89%	24h, 18%	4
6.8V-MCM-41	0.2	600	1：4：4	4500	58%	90%	2h, 30%	5
$Fe_3Ni-CeO_2$	0.1	550	1：1：2	24000	4%	58.2%	14h, %	6
$PtSn_{1.5}/SiO_2$	0.2	550	1：1：20	3000	50%	96%	20h,38%	7
$2CrO_x$/Silicalite-1	0.5	550	4：20：1	3000	43%	85%	2h, 35%	8
5%Cr/$Ce_{0.2}Zr_{0.8}O_2$	0.2	600	1：2：37	6000	56%	79.4%	6h, 28%	9
3.4V/In	0.1	500	1：1：27	18000	2.5%	90%	/	10
PtCoIn/CeO_2	0.1	550	1：1：2	12000	50%	95%	20h, 47%	11
HEI/CeO_2	0.1	600	1：1：2	12000	25%	90%	50h,19%	12
ZnFe2O_x/S-1	0.2	580	1：1：4	7200	38%	95%	110h，25%	13
5Fe-5V-Al_2O_3	0.2	600	15：15：70	15000	43%	80%	1h, 80%	14
Ga/Na-SSZ-39(9)	0.5	600	1：1：18	7200	39%	63%	2h, 39%	15
Cr-CNFp	0.5	600	1：2	3600	20%	56.2%	/	16
Pt1Co1-SiBeta	0.1	550	1：1：3	12000	51.8%	91.8%	6h, 35%	17
MoC_x/Si-1	0.1	550	1：1：2	12000	13%	94%	20h, 5%	18
PtZn/Co@S-1	0.1	550	1：1：4	2000	59.7%	94.9%	60h, 40%	19
Ga_2La_1/ZSM-5	0.2	580	1：1：4	7200	80.31%	30%	20h, 43%	This work

[a]WHSV: $mL/g^{-1}\cdot h^{-1}$

References:

1 Z.-Y. Wang, Z.-H. He, Y. Xia, L. Zhang, K. Wang, W. Wang, Y. Yang, J.-G. Chen and Z.-T. Liu, *Ind. Eng. Chem. Res.*, 2021, **60**, 2807–2817.

2 L.-Y. Li, Z.-Y. Wang, S.-Y. Yang, J.-G. Chen, Z.-H. He, K. Wang, Q.-X. Luo, Z.-W. Liu and Z.-T. Liu, *ACS Catal.*, 2022, **12**, 8527–8543.

3 Z.-J. Zhu, Z.-H. He, Y. Tian, S.-W. Wang, Y.-C. Sun, K. Wang, W. Wang, Z.-F. Zhang, J. Liu and Z.-T. Liu, *ACS Catal.*, 2024, **14**, 10376–10391.

4 X.-L. Xue, W.-Z. Lang, X. Yan and Y.-J. Guo, *ACS Appl. Mater. Interfaces*, 2017, **9**, 15408–15423.

5 Z.-F. Han, X.-L. Xue, J.-M. Wu, W.-Z. Lang and Y.-J. Guo, *Chin. J. Catal.*, 2018, **39**, 1099–1109.

6 E. Gomez, S. Kattel, B. Yan, S. Yao, P. Liu and J. G. Chen, *Nat Commun*, 2018, **9**, 1398.

7 P. Zhai, Z. Xie, E. Huang, D. R. Aireddy, H. Yu, D. A. Cullen, P. Liu, J. G. Chen and K. Ding, *Chem*, 2023, **9**, 3268–3285.

8 J. Wang, Y.-H. Song, Z.-T. Liu and Z.-W. Liu, *Appl. Catal. B: Environ*, 2021, **297**, 120400.

9 J. Dou, J. Funderburg, K. Yang, J. Liu, D. Chacko, K. Zhang, A. P. Harvey, V. P. Haribal, S. James. Zhou and F. Li, *ACS Catal.*, 2023, **13**, 213–223.

10 X. Jiang, B. M. Lis, S. C. Purdy, S. Paladugu, V. Fung, W. Quan, Z. Bao, W. Yang, Y. He, B. G. Sumpter, K. Page, I. E. Wachs and Z. Wu, *ACS Catal.*, 2022, **12**, 11239–11252.

11 F. Xing, Y. Nakaya, S. Yasumura, K. Shimizu and S. Furukawa, *Nat Catal*, 2022, **5**, 55–65.

12 F. Xing, J. Ma, K. Shimizu and S. Furukawa, *Nat Commun*, 2022, **13**, 5065.

13 X. Zhang, J. Li, W. Liu, Y. Zheng, J. An, W. Xin, Z. Liu, L. Xu, X. Li and X. Zhu, *ACS Catal.*, 2023, **13**, 14864–14873.

14 S. Zhang, C. Zhou, S. Wang, Z. Qin, G. Shu, C. Wang, L. Song, L. Zheng, X. Wei, K. Ma and H. Yue, *Chem. Eng. J.*, 2024, **481**, 148231.

15 W. Zhou, Y. Jiang, Z. Sun, S. Zhou, E. Xing, Y. Hai, G. Chen and Y. Zhao, *Catalysts*, 2023, **13**, 896.

16 S. A. Chernyak, A. L. Kustov, D. N. Stolbov, M. A. Tedeeva, O. Ya. Isaikina, K. I. Maslakov, N. V. Usol'tseva and S. V. Savilov, *Appl. Surf. Sci.*, 2022, **578**, 152099.

17 H. Wang, X. Zhang, Z. Su and T. Chen, *Fuel*, 2024, **358**, 130248.

[18] B. Xu, J. Ma, S. Cao, Y. Ma, G. Giambastiani and Y. Liu, *ACS Catal.*, 2025, **15**, 4089–4100.

[19] W. Li, T. Wang, X. Cao, Y. Li, G. Miao, N. Sun, J. Li, W. Han, W. Wei and X. Chen, *Adv. Funct. Mater.*, 2025, **35**, 2414231.