

1 **Engineering surface Mn-enriched and regulating active oxygen**
2 **species over LaMnO₃ catalysts by synergistic modification of acid**
3 **etching and potassium supported for soot removal**

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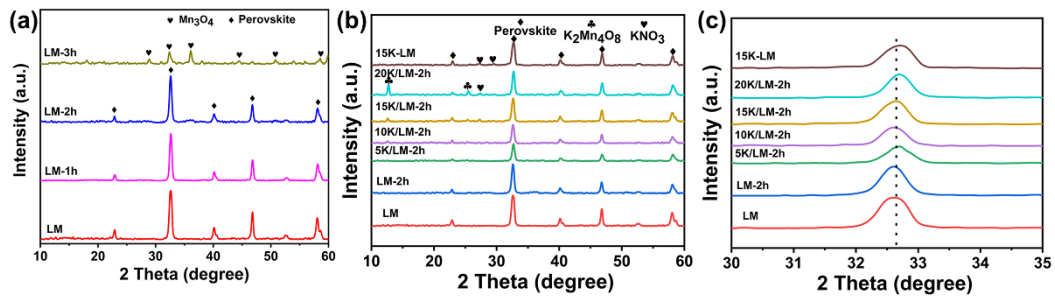
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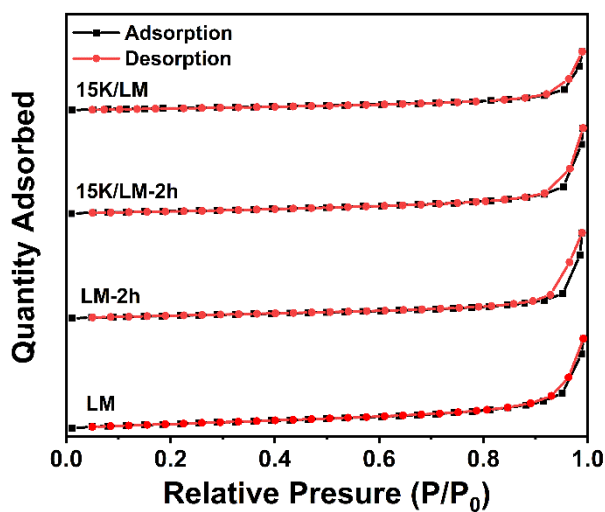
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29 **Fig. S1** (a) XRD patterns of LM, LM-1h, LM-2h, and LM-3h; (b) XRD patterns of LM, LM-2h,

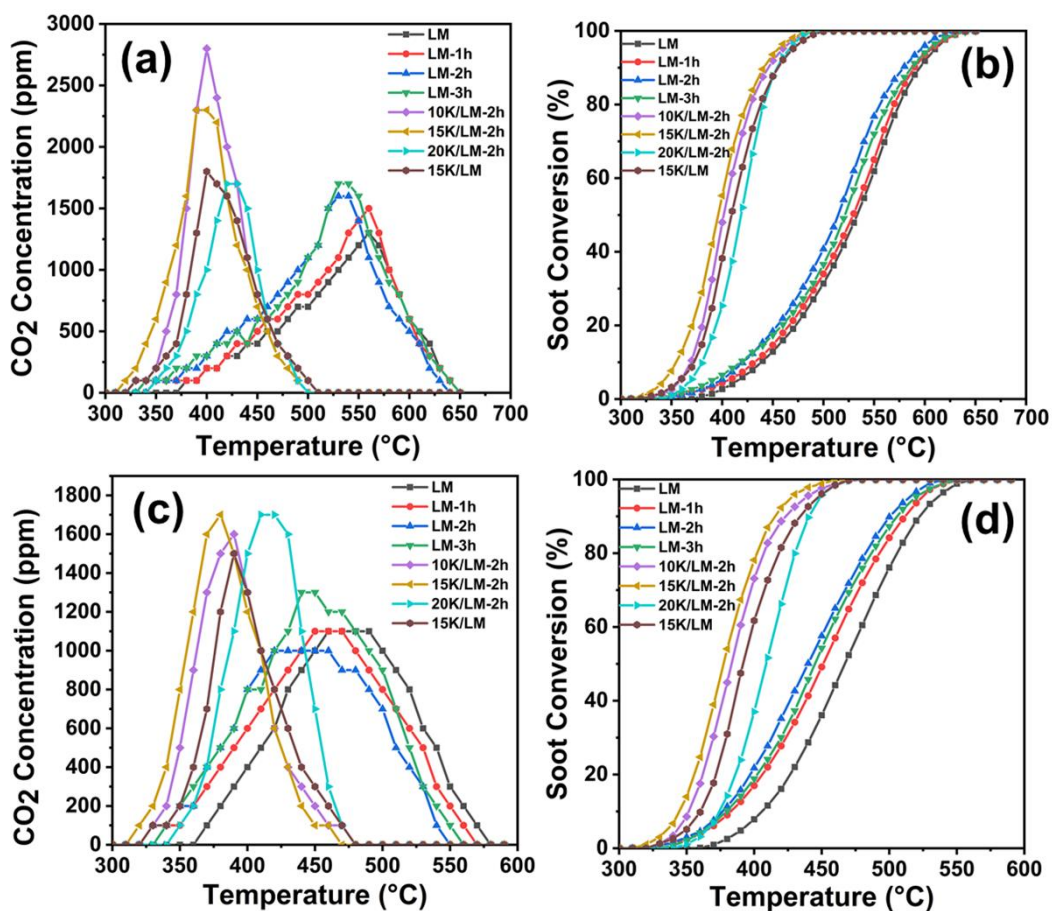
30 xK/LM-2h, and 15K/LM; (c) XRD patterns of characteristic peak amplification



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32 **Fig. S2** Nitrogen adsorption and desorption curves of LM, LM-2h, 15K/LM-2h, and 15K/LM

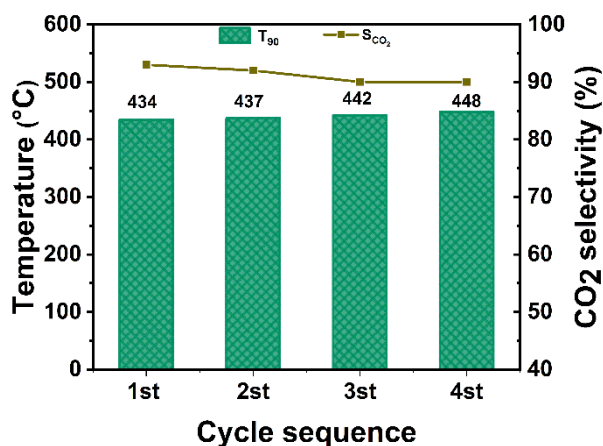
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35 **Fig. S3** CO₂ concentration and total soot conversion of the as-prepared catalysts during TPO

36 under (a, b) loose contact condition without NO and (c, d) loose contact condition with NO



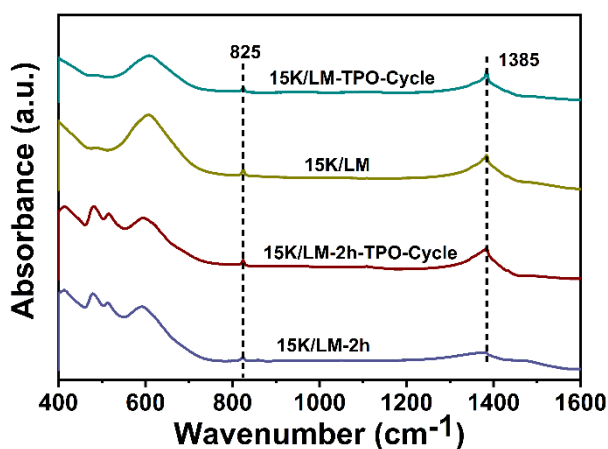
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38 **Fig. S4** Stability tests of 15K/LM

39 In order to investigate the stability of catalysts, the 15K/LM was further examined by
 40 reusing the catalyst in soot combustion 4 times under the presence of NO conditions.

41 As shown in Fig. S4, after cycles of 15K/LM, there is a fluctuation range with an

42 acceptable increase in the T_{90} in the catalyst's four cycles and the CO_2 selectivity
43 remained over 90%, which indicated the 15K/LM catalyst has good stability.



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45 **Fig. S5** FT-IR spectra of 15K/LM-2h and 15K/LM catalysts and the reused catalyst.

46 In order to investigate whether NO^{3-} remains in 15K/LM and 15K/LM-2h samples
47 after the cyclic TPO test, FT-IR tests were carried out on the catalysts, and the
48 obtained curves were shown in Fig S5. For the 15K/LM-2h and 15K/LM samples, the
49 two strong peaks at around 1384 cm^{-1} and 825 cm^{-1} could be observed, which are
50 associated with the typical antisymmetric stretching mode of free NO^{3-} ions and the
51 angular antisymmetric deformation of O–N–O respectively. Meanwhile, the peak of
52 NO^{3-} could still be observed after the TPO cycles. It is reported that in the presence of
53 gas-phase O_2 , the consumption and the regeneration of the active surface NO^{3-} groups
54 can reach an equilibrium state quickly^{1,2}.

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63 **Table S1.** Catalytic performance of catalysts for soot combustion under loose contact with or
 64 without NO

| Catalysts | T ₁₀ (°C) | T ₅₀ (°C) | T ₉₀ (°C) | S _{CO₂} (%) |
|------------------------|----------------------|----------------------|----------------------|---------------------------------|
| blank | 523 | 581 | 621 | 51 |
| LM ^a | 440 | 533 | 595 | 97 |
| LM-1h ^a | 430 | 530 | 590 | 97 |
| LM-2h ^a | 420 | 514 | 580 | 98 |
| LM-3h ^a | 421 | 521 | 588 | 97 |
| 10K/LM-2h ^a | 370 | 401 | 445 | 96 |
| 15K/LM-2h ^a | 354 | 397 | 440 | 96 |
| 20K/LM-2h ^a | 380 | 418 | 454 | 96 |
| 15K/LM ^a | 372 | 408 | 455 | 95 |
| LM ^b | 406 | 467 | 524 | 96 |
| LM-1h ^b | 383 | 452 | 516 | 97 |
| LM-2h ^b | 377 | 440 | 500 | 98 |
| LM-3h ^b | 380 | 445 | 506 | 97 |
| 10K/LM-2h ^b | 351 | 383 | 423 | 93 |
| 15K/LM-2h ^b | 344 | 377 | 416 | 93 |
| 20K/LM-2h ^b | 374 | 406 | 440 | 93 |
| 15K/LM ^b | 360 | 392 | 434 | 94 |

65 ^a Reaction atmosphere: 5% O₂, 10% H₂O, 50 mL/min

66 ^b Reaction atmosphere: 5% O₂, 500 ppm NO, 10% H₂O, 50 mL/min

67 **Table S2.** The temperature for soot combustion with catalysts under tight contact conditions.

| Catalysts | T ₁₀ (°C) | T ₅₀ (°C) | T ₉₀ (°C) | S _{CO₂} (%) |
|-----------|----------------------|----------------------|----------------------|---------------------------------|
| LM | 330 | 381 | 420 | 97 |
| LM-2h | 296 | 353 | 394 | 98 |
| 15K/LM-2h | 276 | 308 | 327 | 95 |
| 15K/LM | 290 | 329 | 360 | 95 |

68 Reaction atmosphere: 5% O₂, 10% H₂O, 50 mL/min

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78 **Reference**

- 79 1. X. Feng, S. Zhang, R. Liu, J. Ma, X. Xu, J. Xu, X. Fang and X. Wang, *Phys*
80 *Chem Chem Phys*, 2022, **24**, 3250-3258.
- 81 2. N. Feng, J. Meng, Y. Wu, C. Chen, L. Wang, L. Gao, H. Wan and G. Guan,
82 *Catalysis Science & Technology*, 2016, **6**, 2930-2941.

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