

Supporting information for

Ultralight and Spongy La-Mn-based Perovskite Catalysts Modified by Alkali Metals and Ce: Facile Synthesis and Excellent Catalytic Performance for Soot Combustion

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Experimental details

The reaction rate (v and v^*), active redox sites (O^* amount), density of active redox sites (O^* density) and TOF values of catalysts were determined by isothermal reaction for soot combustion, and their values are calculated by the following equations^[1]:

$$TOF \text{ (s}^{-1}\text{)} = \frac{v}{O^* \text{ amount}}$$

$$v \text{ (mol s}^{-1} \text{ g}^{-1}\text{)} = -\frac{dn}{mdt} = \frac{x_{CO_2} \times n_{CO_2}}{m}$$

$$v^* \text{ (mol s}^{-1} \text{ m}^{-2}\text{)} = \frac{v}{S} = \frac{x_{CO_2} \times n_{CO_2}}{mS}$$

where x_{CO_2} is the mole fraction of CO_2 ; n_{CO_2} is the molar amount of CO_2 (mol); m is the mass of the catalyst (g); S is the BET specific surface area of catalyst (m^2/g)

$$O^* \text{ amount (mol g}^{-1}\text{)} = \frac{2P_0V \times A \times 10^{-6}}{RTm}$$

$$O^* \text{ density (nm}^{-2}\text{)} = \frac{O^* \text{ amount}}{S \times 10^{18}} \times 6.02 \times 10^{23}$$

where P_0 is the atmospheric pressure (Pa); A is the integrated area of CO_2 concentration as a function of time (s); V is the volumetric flow rate of gases (m^3/s); m is the mass of the catalyst (g); R is the gas constant (8.314 J/mol·K); T is room temperature (K); S is the BET specific surface area (m^2/g).

Table S1 Recipes for the synthesis of as-prepared La-Mn-based perovskite catalysts

Catalysts	La(NO ₃) ₃ · 6H ₂ O /g	Ce(NO ₃) ₃ · 6H ₂ O /g	Alkali metal nitrates	Mn(NO ₃) ₂ /g	Glucose /g	H ₂ O/ mL
LaMnO ₃	4.33	-	-	3.56	3.92	20
La _{0.98} Ce _{0.01} Cs _{0.01} MnO ₃	4.24	0.0434	0.0195 g CsNO ₃	3.56	3.92	20
La _{0.96} Ce _{0.02} Cs _{0.02} MnO ₃	4.16	0.0868	0.0390 g CsNO ₃	3.56	3.92	20
La _{0.94} Ce _{0.03} Cs _{0.03} MnO ₃	4.07	0.1302	0.0585 g CsNO ₃	3.56	3.92	20
La _{0.9} Ce _{0.05} Cs _{0.05} MnO ₃	3.90	0.217	0.0975 g CsNO ₃	3.56	3.92	20
La _{0.85} Ce _{0.075} Cs _{0.075} MnO ₃	3.68	0.325	0.146 g CsNO ₃	3.56	3.92	20
La _{0.8} Ce _{0.1} Cs _{0.1} MnO ₃	3.46	0.434	0.195 g CsNO ₃	3.56	3.92	20
La _{0.6} Ce _{0.2} Cs _{0.2} MnO ₃	2.59	0.868	0.390 g CsNO ₃	3.56	3.92	20
La _{0.8} Ce _{0.2} MnO ₃	3.46	0.868	-	3.56	3.92	20
La _{0.8} Cs _{0.2} MnO ₃	3.46	-	0.390 g CsNO ₃	3.56	3.92	20
La _{0.8} Ce _{0.1} Li _{0.1} MnO ₃	3.46	0.434	0.068 g LiNO ₃	3.56	3.92	20
La _{0.8} Ce _{0.1} Na _{0.1} MnO ₃	3.46	0.434	0.084 g NaNO ₃	3.56	3.92	20
La _{0.8} Ce _{0.1} K _{0.1} MnO ₃	3.46	0.434	0.101 g KNO ₃	3.56	3.92	20
La _{0.8} Ce _{0.1} Rb _{0.1} MnO ₃	3.46	0.434	0.147 g RbNO ₃	3.56	3.92	20

Table S2. Comparation for catalytic performance of as-prepared and reported catalysts for soot combustion

Catalyst	Soot/cat alyst weight ratio	Contact mode	Reaction conditions	Heating rate (°C/min)	T ₁₀ (°C)	T ₅₀ /T _m (°C)	T ₉₀ (°C)	Sm CO ₂ (%)	Ref
3DOM La ₂ NiCoO ₆	1/10	Loose	Flow 50 mL/min, 5%O ₂ +0.2%NO+ 5%H ₂ O+Ar balance	2	288	362	412	98.6	2
La _{(1-x)Ag_xCoO₃} (x=2.5%)	1/10	Loose	Flow 300 mL/min, 10%O ₂ +500 ppm NO+N ₂ balance	4	302	358	448	-	3
3DOM La _{0.95} K _{0.05} NiO ₃	1/10	Loose	Flow 50 mL/min, 5%O ₂ +2000 ppm NO+N ₂ balance	2	289	338	372	98.7	4
K–Mn/3DOM La _{0.8} Ce _{0.2} FeO ₃	1/9	Loose	Flow 50 mL/min, 5%O ₂ +500 ppm NO+N ₂ balance	2	316	377	430	96.5	5
LaCo _{0.94} Pt _{0.06} O ₃	1/10	Loose	Flow 100 mL/min, 2000 ppm NO/air	10	344	403	435	-	6
3DOM La _{0.5} Sr _{0.5} MnO ₃	1/9	Loose	Flow 100mL/min, 20% O ₂ +500ppm NO + N ₂ balance	5	320	385	428	-	7
La _{0.7} K _{0.3} FeO _{3-δ} nanotubes	1/9	Loose	Flow 100 mL/min, 20%O ₂ +500 ppm NO	2	355	393	429	94.0	8
Ce ₁ MnO _x	1/10	Loose	Flow 50 mL/min, 10%O ₂ +2000 ppm NO+Ar balance	2	268	332	369	99.4	9
K-OMS-2/3DOMMM Ti _{0.7} Si _{0.3} O ₂	1/10	Loose	Flow 50 mL/min, 10% O ₂ +0.2% NO+Ar balance	2	288	333	364	97.8	10
MnO _x –CeO ₂	1/9	Loose	Flow 100 mL/min, 10%O ₂ +N ₂ balance	3	314	346	383	-	11
3DOM Au ₂ Pt ₂ /Ce _{0.8} Zr _{0.2} O ₂	1/10	Loose	Flow 50mL/min, 10%O ₂ +0.2%NO+bal ance	2	236	345	397	99.5	12
3 wt.% Pt/Mn _{0.5} Ce _{0.5} O _{2-δ}	1/10	Loose	Flow 50 mL/min, 10% O ₂ +0.2% NO+Ar balance	2	290	342	373	96.7	13
Pt-CoO x/3DOM-Al ₂ O ₃	1/10	Loose	Flow 50 mL/min, 5%O ₂ +0.2%NO+Ar balance	2	281	368	416	99.1	14
PdAu@CeO ₂ /CZ	1/10	Loose	Flow 50mL/min, 5%O ₂ +0.2%H ₂ O+Ar balance	2	276	363	404	99.6	15
La _{0.8} Ce _{0.1} Cs _{0.1} MnO ₃	1/10	Loose	Flow 50 mL/min, 10%O ₂ +2000 ppm NO +Ar balance	2	268	315	350	98.5	This work
La _{0.8} Ce _{0.1} Cs _{0.1} MnO ₃	1/10	Loose	Flow 50 mL/min, 10%O ₂ +2000 ppm NO ++10%H ₂ O+Ar balance	2	265	304	329	96.7	This work

Table S3 The stability and sulfur water resistant of $\text{La}_{0.8}\text{Ce}_{0.1}\text{Cs}_{0.1}\text{MnO}_3$ catalysts for soot combustion

Catalysts	T ₁₀ /°C	T ₅₀ /°C	T ₉₀ /°C	S _{CO₂} m/%
La _{0.8} Ce _{0.1} Cs _{0.1} CoO ₃ -Cycle 1	268	314	350	98.5
La _{0.8} Ce _{0.1} Cs _{0.1} CoO ₃ -Cycle 2	272	319	350	98.3
La _{0.8} Ce _{0.1} Cs _{0.1} CoO ₃ -Cycle 3	269	318	351	98
La _{0.8} Ce _{0.1} Cs _{0.1} CoO ₃ -Cycle 4	280	329	361	97.5
La _{0.8} Ce _{0.1} Cs _{0.1} CoO ₃ -Cycle 5	279	329	361	97.8
10%H ₂ O+0 ppm SO ₂	265	304	329	96.7
10%H ₂ O+100 ppm SO ₂	296	332	442	93.8
10%H ₂ O+300 ppm SO ₂	387	459	500	82.8

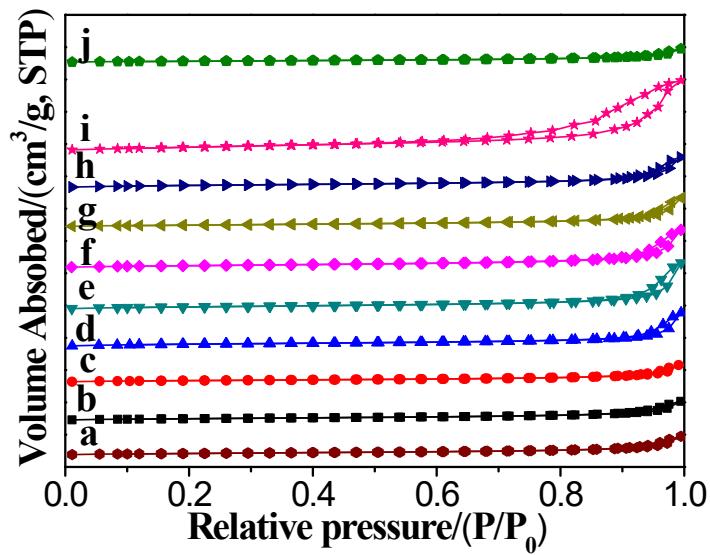


Figure S1. Nitrogen adsorption-desorption isotherms of La-Mn-based perovskite catalysts with different A sites
 (a: LaMnO_3 ; b: $\text{La}_{0.98}\text{Ce}_{0.01}\text{Cs}_{0.01}\text{MnO}_3$; c: $\text{La}_{0.96}\text{Ce}_{0.02}\text{Cs}_{0.02}\text{MnO}_3$; d: $\text{La}_{0.94}\text{Ce}_{0.03}\text{Cs}_{0.03}\text{MnO}_3$; e: $\text{La}_{0.9}\text{Ce}_{0.05}\text{Cs}_{0.05}\text{MnO}_3$; f: $\text{La}_{0.85}\text{Ce}_{0.075}\text{Cs}_{0.075}\text{MnO}_3$; g: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Cs}_{0.1}\text{MnO}_3$; h: $\text{La}_{0.6}\text{Ce}_{0.2}\text{Cs}_{0.2}\text{MnO}_3$; i: $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$; j: $\text{La}_{0.8}\text{Cs}_{0.2}\text{MnO}_3$)

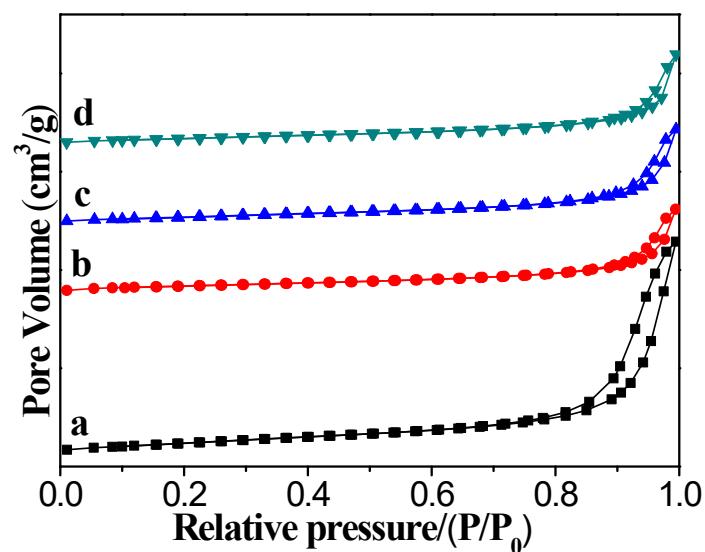


Figure S2. Nitrogen adsorption-desorption isotherms of $\text{La}_{0.8}\text{Ce}_{0.1}\text{A}_{0.1}\text{MnO}_3$ catalyst
(a: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Li}_{0.1}\text{MnO}_3$; b: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Na}_{0.1}\text{MnO}_3$; c: $\text{La}_{0.8}\text{Ce}_{0.1}\text{K}_{0.1}\text{MnO}_3$; d: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Rb}_{0.1}\text{MnO}_3$)

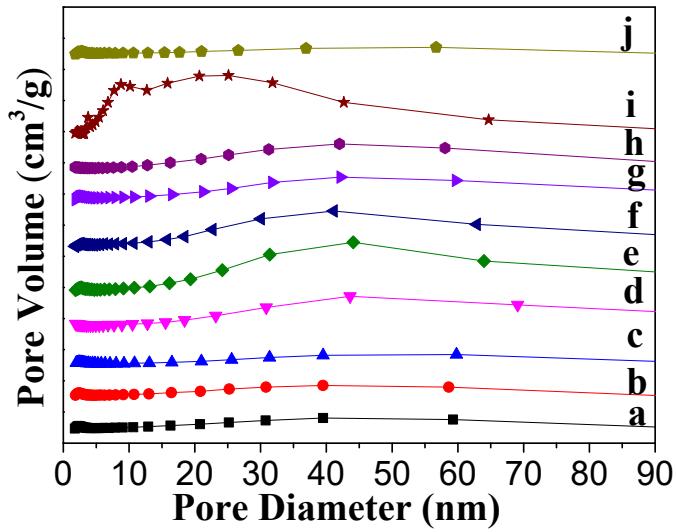


Figure S3. Pore distribution of La-Mn-based perovskite catalysts with different A sites
 (a: LaMnO_3 ; b: $\text{La}_{0.98}\text{Ce}_{0.01}\text{Cs}_{0.01}\text{MnO}_3$; c: $\text{La}_{0.96}\text{Ce}_{0.02}\text{Cs}_{0.02}\text{MnO}_3$; d: $\text{La}_{0.94}\text{Ce}_{0.03}\text{Cs}_{0.03}\text{MnO}_3$; e: $\text{La}_{0.9}\text{Ce}_{0.05}\text{Cs}_{0.05}\text{MnO}_3$; f: $\text{La}_{0.85}\text{Ce}_{0.075}\text{Cs}_{0.075}\text{MnO}_3$; g: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Cs}_{0.1}\text{MnO}_3$; h: $\text{La}_{0.6}\text{Ce}_{0.2}\text{Cs}_{0.2}\text{MnO}_3$; i: $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$; j: $\text{La}_{0.8}\text{Cs}_{0.2}\text{MnO}_3$)

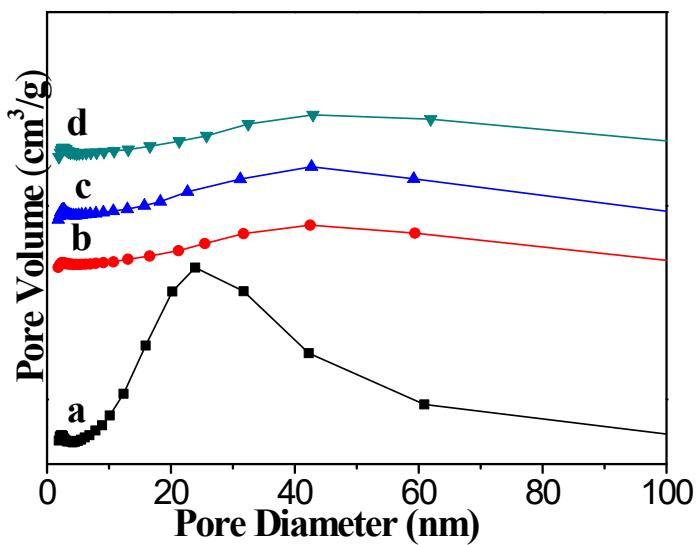


Figure S4. Pore distribution of $\text{La}_{0.8}\text{Ce}_{0.1}\text{A}_{0.1}\text{MnO}_3$ catalysts
(a: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Li}_{0.1}\text{MnO}_3$; b: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Na}_{0.1}\text{MnO}_3$; c: $\text{La}_{0.8}\text{Ce}_{0.1}\text{K}_{0.1}\text{MnO}_3$; d: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Rb}_{0.1}\text{MnO}_3$)

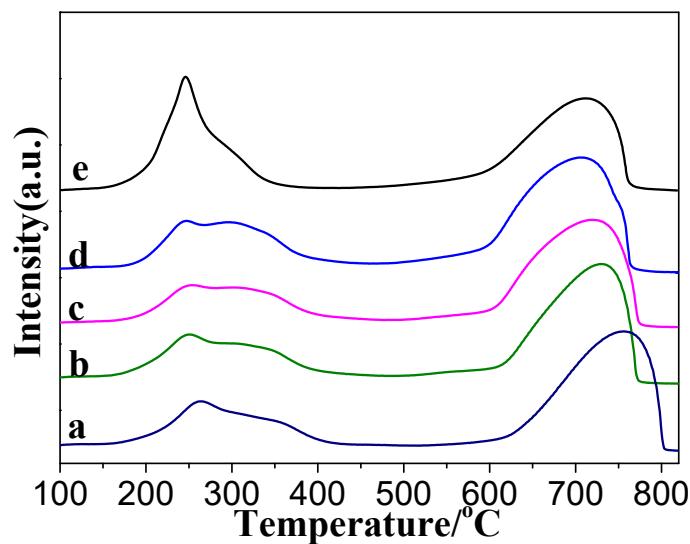


Figure S5. H₂-TPR curves of La-Mn-based perovskite catalysts with different A sites
a: LaMnO₃; b: La_{0.98}Ce_{0.01}Cs_{0.01}MnO₃; c: La_{0.96}Ce_{0.02}Cs_{0.02}MnO₃; d: La_{0.94}Ce_{0.03}Cs_{0.03}MnO₃; e: La_{0.85}Ce_{0.075}Cs_{0.075}MnO₃)

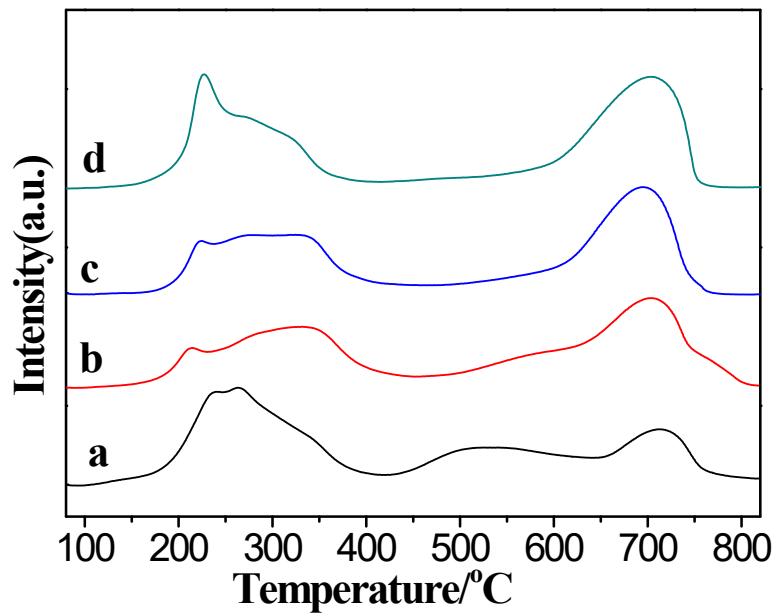


Figure S6. H₂-TPR curves of $\text{La}_{0.8}\text{Ce}_{0.1}\text{A}_{0.1}\text{MnO}_3$ catalysts
(a: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Li}_{0.1}\text{MnO}_3$; b: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Na}_{0.1}\text{MnO}_3$; c: $\text{La}_{0.8}\text{Ce}_{0.1}\text{K}_{0.1}\text{MnO}_3$; d: $\text{La}_{0.8}\text{Ce}_{0.1}\text{Rb}_{0.1}\text{MnO}_3$)

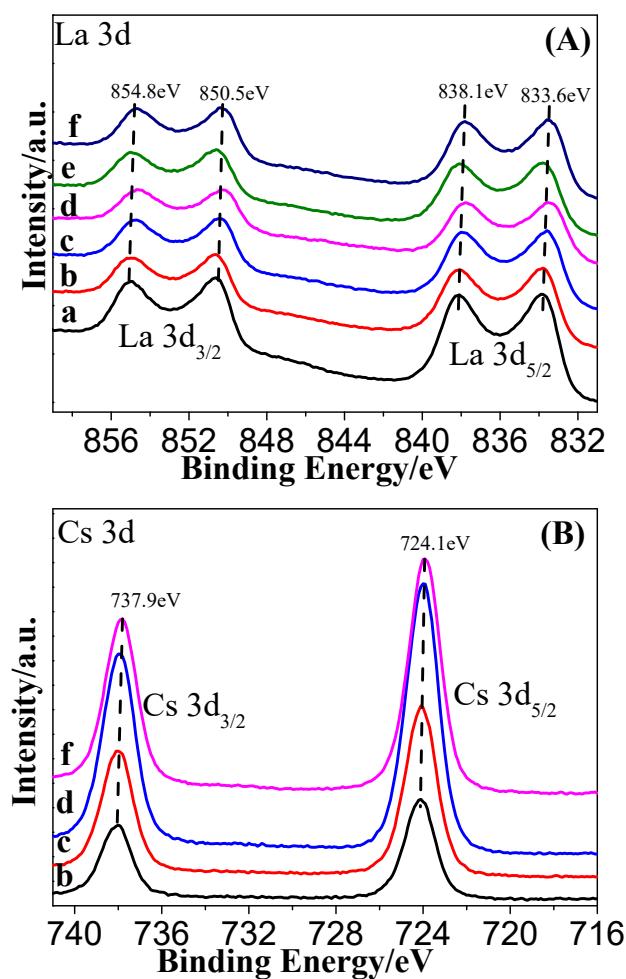


Figure S7. XPS spectra of La 3d (A) and Cs 3d (B) for as-prepared catalysts
 (a: LaMnO₃; b: La_{0.9}Ce_{0.05}Cs_{0.05}MnO₃; c: La_{0.8}Ce_{0.1}Cs_{0.1}MnO₃; d: La_{0.6}Ce_{0.2}Cs_{0.2}MnO₃; e: La_{0.8}Ce_{0.2}MnO₃; f: La_{0.8}Cs_{0.2}MnO₃)

References

- [1] Z. L. Zhang, D. Han, S. J. Wei and Y. X. Zhang, *J. Catal.*, 2010, **276**, 16-23.
- [2] X. L. Mei, J. Xiong, Y. C. Wei, Y. L. Zhang, P. Zhang, Q. Yu, Z. Zhao and J. Liu, *Appl. Catal. B: Environ.*, 2020, **275**, 119108.
- [3] L. J. He, Y. Zhang, Y. C. Zang, C. X. Liu, W. C. Wang, R. Han, N. Ji, S. T. Zhang and Q. L. Liu, *ACS Catal.*, 2021, **11**, 14224-14236.
- [4] X. Mei, J. Xiong, Y. Wei, C. Wang, Q. Wu, Z. Zhao and J. Liu, *Chin. J. Catal.*, 2019, **40**, 722-732.
- [5] N. J. Feng, C. Chen, J. Meng, G. Liu, F. Fang, L. Wang, H. Wan and G. F. Guan, *Appl. Surf. Sci.*, 2017, **399**, 114-122.
- [6] L. R. Zeng, L. Cui, C. Y. Wang, W. Guo and C. R. Gong, *J. Hazard. Mater.*, 2020, **383**, 121210.
- [7] P. Zhao, F. Fang, N. Feng, C. Chen, G. Liu, L. Chen, Z. Zhu, J. Meng, H. Wan and G. Guan, *Catal. Sci. Technol.*, 2019, **9**, 1835-1846.
- [8] F. Fang, N. Feng, L. Wang, J. Meng, G. Liu, P. Zhao, P. Gao, J. Ding, H. Wan and G. Guan, *Appl. Catal. B: Environ.*, 2018, **236**, 184-194.
- [9] D. Yu, C. Peng, X. H. Yu, L. Y. Wang, K. X. Li, Z. Zhao and Z. G. Li, *Fuel*, 2022, **307**, 121803.
- [10] X. Yu, Y. Ren, D. Yu, M. Chen, L. Wang, R. Wang, X. Fan, Z. Zhao, K. Cheng and Y. Chen, *ACS Catal.*, 2021, **11**, 5554-5571.
- [11] J. Gao, Y. Xiong, Q. Zhang, Y. Jiang, J. Wang, S. Zou, M. Fu, J. Wu, Y. Hu and D. Ye, *Chem. Eng. J.*, 2020, **398**, 125448.
- [12] Y. C. Wei, Z. Zhao, B. F. Jin, X. H. Yu, J. Q. Jiao, K. X. Li, and J. Liu, *Catal. Today*, 2015, **251**, 103-113.
- [13] X. Yu, J. Li, Y. Wei, Z. Zhao, J. Liu, B. Jin, A. Duan and G. Jiang, *Ind. Eng. Chem. Res.*, 2014, **53**, 9653-9664.
- [14] Y. C. Wei, P. Zhang, J. Xiong, Q. Yu, Q. Q. Wu, Z. Zhao and J. Liu, *Environ. Sci. Technol.*, 2020, **54**, 6947-6956.
- [15] J. Xiong, X. Mei, J. Liu, Y. Wei, Z. Zhao, Z. Xie, and J. Li, *Appl. Catal. B: Environ.*, 2019, **251**, 247-60.