Supporting information

Catalytic hydrodeoxygenation of biomass-derived oxygenates to bio-fuels over Co-based bimetallic catalysts

Zhen-Hong He,*[a] Chong-Shan Jiang,[a] Zhong-Yu Wang,[a] Kuan Wang,[a] Yong-Chang Sun,[a] Man-Qing Yao,[a] Zhu-Hui Li,[a] Zhao-Tie Liu*[ab]

[a]Shaanxi Key Laboratory of Chemical Additives for Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an, China

[b]School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China

*Corresponding author: hezhenhong@sust.edu.cn (Zhen-Hong He), ztliu@snnu.edu.cn (Zhao-Tie Liu)

Experimental section

Materials

HMF (>97%), furfural (99%), $Zn(NO_3)_2·6H_2O$ (99%), $Co(NO_3)_2·6H_2O$ (99%) and $Al(NO_3)_3·9H_2O$ (99%) were purchased from Aladdin. Furfuryl alcohol (Adamas-beta, >99%), 5-methylfurfural (>99%), 2,5-furandimethanol (>98%), 4-hydroxy-3-methoxybenzaldehyde (>99%), levulinic acid (>99%), 2-hydroxyanisole (>99%) and $Cu(NO_3)_2·3H_2O$ (99.0%) were provided by Adamas-beta. H_2 (99.99%) and N_2 (99.999%) were purchased from Xi'an Teda Cryogenic Equipment Co., Ltd. China. All other chemicals were obtained from commercial companies and used without purification.

Catalysts preparation

The bimetallic $Co_5Zn_1O_x$ catalyst was synthesized by a simple co-precipitation method. Initially, $Co(NO_3)_2·6H_2O$ (5.0 mmol) and $Zn(NO_3)_2·6H_2O$ (1.0 mmol) were dissolved into 20 mL deionized water to form a homogeneous solution, which was then dropped slowly (approximate 1 drop in 1 second) to 100 mL solution of a mixture of NaOH and Na_2CO_3 (0.4 M NaOH and 0.1 M Na_2CO_3) under vigorous stirring at room temperature. A solid was precipitated and the mixture was stirred for 12 h. After that, the obtained solid was filtered and washed with 500 mL of deionized water until pH = 7 and dried at 110 °C for 12 h. The nubbly solid was grinded into powder in an agate mortar and then transferred to a porcelain cup and calcined in a muffle furnace at 500 °C for 3 h with a heating rate of 5 °C/min in air. Afterwards, the obtained precursor powder was transferred into a porcelain boat which was placed in a tube furnace and reduced with pure H_2 (50 mL/min) at 500 °C for 3 h with 5 °C/min. After reduction, the catalyst was passivated in 1% O_2/N_2 flow with 30 mL/min for 30 min at room temperature, and the obtained catalyst denoted as $Co_5Zn_1O_x$. Other catalysts such as $Co_5Al_1O_x$, $Co_5Ce_1O_x$, $Co_5La_1O_x$, $Co_5Zr_1O_x$, $Co_5Mg_1O_x$, $Co_5Ca_1O_x$, $Co_5Fe_1O_x$, and $Co_5Cu_1O_x$ *etc.* were prepared by the same method as preparation of $Co_5Zn_1O_x$.

Characterization of catalysts

The TEM images were measured on a JEM-2100 electron microscope operated at 200 kV. Prior to test, approximately 2 mg of catalyst were dispersed in 20 mL of ethanol under ultrasonic treatment for 30 min and then collected on a Cu grid which was covered with carbon film. Approximately 100 particles were counted to determine the particle size distribution.

The N_2 adsorption/desorption tests were carried out on an ASAP 2460 (Micromeritics, USA). Prior to measurement, the catalyst was degassed at 200 °C for 10 h under vacuum (lower than 0.1 mbar). All the tests contained 57 points, which included 29 points for adsorption and 28 points for desorption in the P/P_0 range of 0 ~ 1. During the test, the equilibration time was set to be 30 seconds. After the test, 8 points in the P/P_0 range of 0.10 ~ 0.35 were chose to calculate the BET surface area, and all the C_{BET} constants were given in Table S3. The pore size distribution was obtained by applying the BJH method.

The FT-IR spectra of the catalysts were recorded on a Bruker Fourier infrared spectrometer. About 10 mg of catalyst were dispersed in 2.0 g of KBr, which was grinded evenly and then placed in a tableting machine to tablet for test.

The XRD tests were carried out on a Rigaku D/max 2500 with nickel filtered Cu Kα ($\lambda = 0.154$ nm) at 40 kV and 20 mA with a scanning rate of 10°/min. XRD patterns were recorded on a Rigaku D/max 2500 X-ray diffractometer using nickel filtered Cu Kα radiation ($\lambda = 0.154$ nm) over a 2θ range of 5−90° at 40 kV and 20 mA with a scanning rate of 10 ° /min. The samples were ground into powder and then placed on a glass slide located in the path of an X-ray beam.

The XPS spectra were performed using a Kratos AXIS Supra equipped with 300 W Al Kα (hν = 1486.6 eV) radiation with a hemispherical energy analyser. Prior to the tests, the catalyst fines (5 mg) were pasted on double-sided conductive tape, which was then tested under vacuum (lower than 6.7×10^{-9} Torr). The sample holder model was plain dual height, the emission current was 10 mA, and the detector type was an array detector. The spectra were decomposed by using the ratio of 20% Gaussian/Lorentzian and a

Shirley-type background method with an XPSPEAK 4.1 software package. Prior to the treatments, the binding energies of the spectra were referenced by C1s peak with 284.8 eV.

The Raman spectra were tested on a Laser microscopic Raman imaging spectrometer (Thermo Fisher, USA) equipped with a 532 nm Ne laser and a high-grade Leica microscope (long working distance objective 50). The single crystal silicon was used for the position correction.

The metal loadings of the prepared catalysts were tested by ICP-OES. Prior to the tests, the catalysts were dissolved in a mixture of HNO_3 and HCl solvent. The H_2-TPR curves were recorded on an Autochem II 2920 (Micromeritics, USA). The catalyst was heated to 200 ^oC and maintained for 60 min in He with a flow rate of 50 mL/min, and then cooled down to 50 ^oC. Then the gas was changed to 10% H_2/Ar (50 mL/min) and held for 60 min, and the catalyst was heated to 600 ^oC with a heating rate of 10 ^oC /min. The consumption of H_2 was detected by a thermal conductivity detector (TCD).

The CO_2-TPD and NH_3-TPD analysis were recorded on the above Autochem II 2920 instrument. A typical procedure was carried out as follows: the catalyst was heated to 200 ^oC (10 ^oC/min) in He and held for 60 min, and then it was cooled to 50 ^oC. After that, 10%CO_2/He (or 5%NH_3/He) was passed through the catalyst with a flow rate of 50 mL/min and held for 60 min until the adsorption was fully saturated. Then the mixture gas was changed to He at the same flow rate to remove the residual CO_2 (or NH_3) from the surface of catalyst. After 60 min, the catalyst was heated from 50 ^oC (100 ^oC for NH_3-TPD) to 700 ^oC with a heating rate of 10 °C /min, and the desorbed CO_2 or NH_3 was recorded on TCD.

HDO of biomass-derived oxygenates

Taking the HDO of 5-HMF as an example, the reaction was performed in a 16 mL stainless steel autoclave with a Teflon inner container. In a typical procedure, catalyst 30 mg, 5-HMF (1.0 mmol), and THF 2 mL were added into the reactor, which was then sealed and charged with 1 MPa of H_2 for 3 times to remove the air in the reactor. After the reactor was charged with 3.0 MPa of H_2, it was heated to 180 ^oC and reacted for 12 h with a stirring speed of 200 rpm. Upon reaction completion, the reactor was cooled in ice-water and the gas was released slowly. The liquid products were analysed by a gas chromatograph (GC9720, Zhejiang Fuli Analytical Instruments Co., Ltd. China) equipped with a flame ionization detector and an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) by using toluene as an internal standard and GC-MS (Agilent 6890N-5975) with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The carbon balance for each test was calculated to be 100 ± 2%. The catalyst was washed with THF for four times and dried at 60 ^oC under vacuum, and then it was used directly in the next run. The other reactions such as HDO of vanillin, furan-2-carbaldehyde and furfuryl alcohol and hydrogenation of levulinic acid were carried out with the same procedures as above.

Table S1. Hydrodeoxygenation of 5-HMF to DMF over various heterogeneous catalysts.

Entry	Catalyst	T (°C)	T (h)	Solv.	P_{H2} (MPa)	Conv. (%)	Sele. (%)	Ref.
1	Ni (II)/WO_3	180	6	H_2O	1	>99.0	>95.0	[1]
2	Pd/C/Zn	150	8	THF	0.8	>99.0	85.0	[2]
3	Pd/C	150	15	THF	in situ	-	70.0	[3]
4	Ni/Co_3O_4	130	24	THF	1	>99.0	66.0	[4]
5	Rh/C	120	1	[EMIM]Cl	6.2	16.0	6.0	[5]
6	Raney Ni	180	15	1,4-dioxane	1.5	100.0	88.5	[6]
7	Ru/C+FA	150	1	THF+H_2SO_4	in situ	-	32.0	[7]
8	Ni_2-Fe_1 /CNTs	200	3	*n*-butanol	3	100.0	91.3	[8]
9	CuZn	200	6	CPME	2	100.0	90	[9]
10	Cu-Co@C	180	8	ethanol	5	100.0	99.4	[10]
11	Cu−Ni-TiO_2	200	8	1,4-dioxane	2.5	100.0	84.3	[11]
12	5%Ru/C	150	3	dioxane	2	86.8	80.3	[12]
13	NC-Cu/ MgAlO	220	0.5	cyclohexanol	N_2	100.0	96.1	[13]
14	Cu_2O-Ru-PMO	220	12	EtOH	5	97.5	81	[14]
15	Cu_3Al-A	240	1.5	methanol	N_2	> 99	94.9	[15]
16	1%Ir/SiO_2 + H_2SO_4	60	30min	-	1	70.0	23	[16]
17	5 wt.% Ru/Co_3O_4	130	24	THF	0.7	>99	93.4	[17]
18	PtCo@HCS-500	160	2	butanol	1	100.0	98	[18]
19	Cu/Al_2O_3	240	6	methanol	in situ	100.0	73.9	[19]
20	CuCo@C-TsOH	220	10	THF	3	>99	71.1	[20]
21	CuZnO(P)-r2 (ox)	220	5	dioxane	3	100.0	94.0	[21]
22	$Co_5Zn_1O_x$	180	12	THF	3	99.0	93.7	This work

Table S2. ICP-OES results of different catalysts.

Entry	Catalysts	Calculated[a]	ICP-OES tested
1	$Co_1Zn_3O_x$	$Co_1Zn_3O_x$	$Co_1Zn_{2.91}O_x$
2	$Co_1Zn_5O_x$	$Co_1Zn_5O_x$	$Co_1Zn_{4.6}O_x$
4	$Co_1Zn_1O_x$	$Co_1Zn_1O_x$	$Co_1Zn_{0.93}O_x$
5	$Co_3Zn_1O_x$	$Co_3Zn_1O_x$	$Co_{2.84}Zn_1O_x$
6	$Co_5Zn_1O_x$	$Co_5Zn_1O_x$	$Co_{4.91}Zn_1O_x$
7	$Co_7Zn_1O_x$	$Co_7Zn_1O_x$	$Co_{6.79}Zn_1O_x$

[a] Calculated from the feed amount of precursor salts.

BET data for catalysts

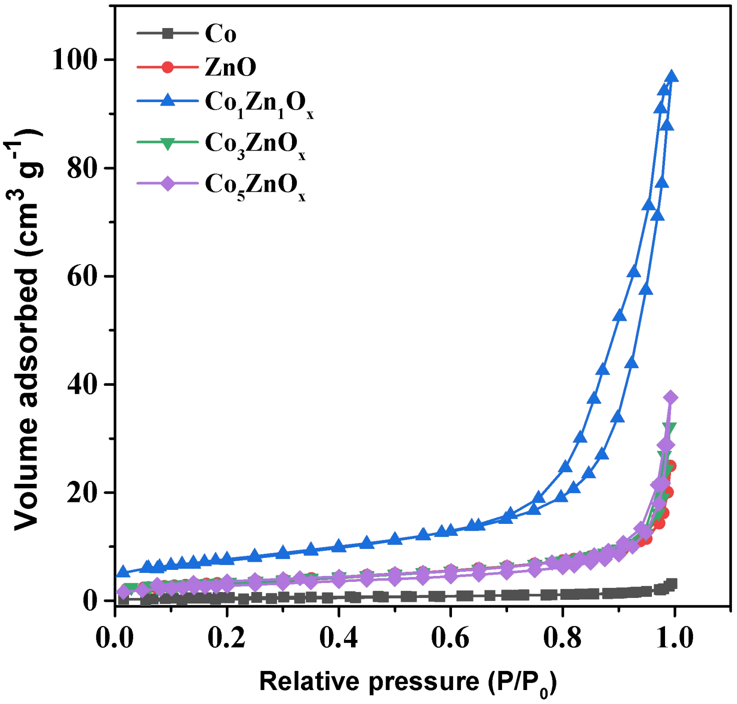

Fig. S1 N_2 adsorption/desorption isotherms of catalysts.

Table S3. The analysis results of N_2 adsorption/desorption isotherms for catalysts.

Catalysts	BET surface area (m^2/g)	C_{BET}	Pore size (nm)	Pore volume (cm^3/g)
Pure Co	2	91	7	0.01
ZnO	12	73	14	0.04
$Co_1Zn_1O_x$	28	129	19	0.15
$Co_3Zn_1O_x$	12	133	19	0.05
$Co_5Zn_1O_x$	10	64	25	0.06

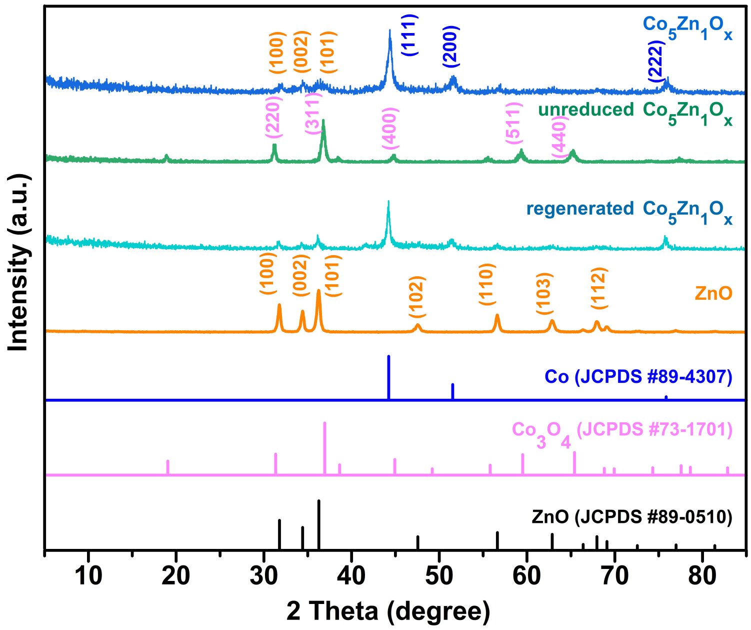

Fig. S2 XRD of $Co_5Zn_1O_x$ (blue), unreduced $Co_5Zn_1O_x$ (green), regenerated $Co_5Zn_1O_x$ (cyan) and ZnO (orange).

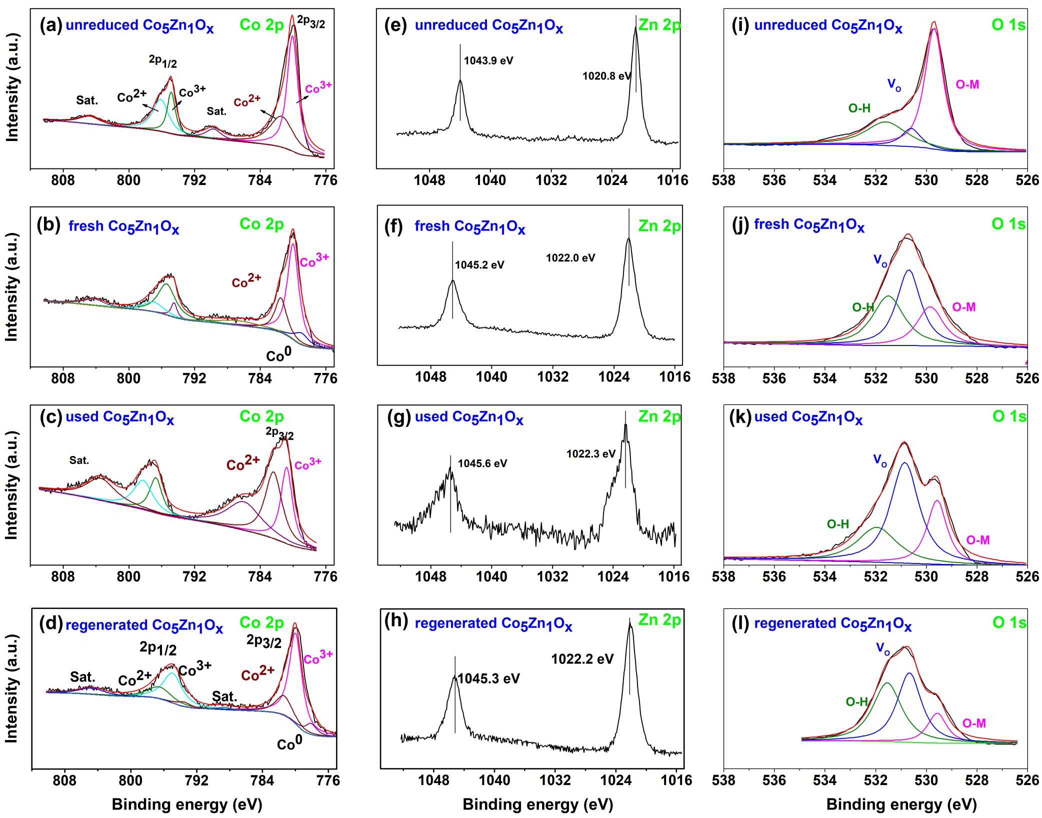

Fig. S3 XPS spectra of unreduced $Co_5Zn_1O_x$ (a Co 2p, e Zn 2p, and i O 1s), fresh $Co_5Zn_1O_x$ (b Co 2p, f Zn 2p, and j O 1s), the $Co_5Zn_1O_x$ catalyst after three times of use (c Co 2p, g Zn 2p, and k O 1s) and the regenerated $Co_5Zn_1O_x$ catalyst (d Co 2p, h Zn 2p, and l O 1s), respectively.

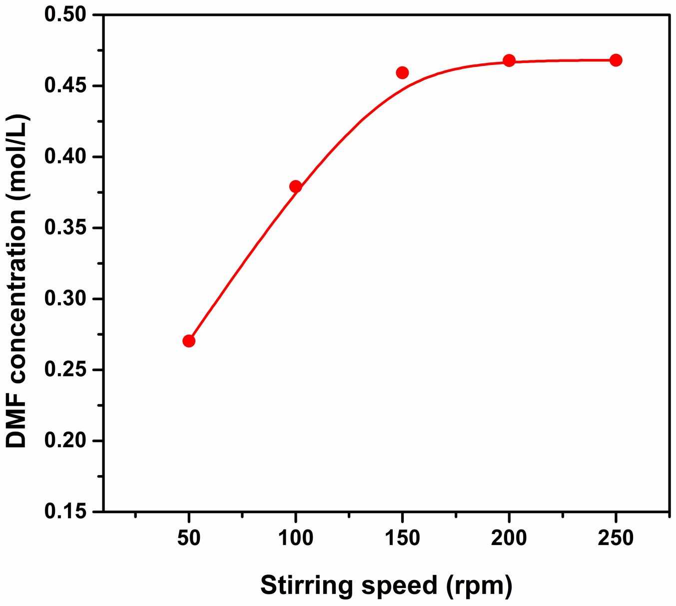

Fig. S4 Effect of stirring speed on the obtained DMF concentration in HDO of 5-HMF to DMF. The errors of conversion and selectivity were ± 2%. The reaction conditions were the same as those of entry 4 in Table 1.

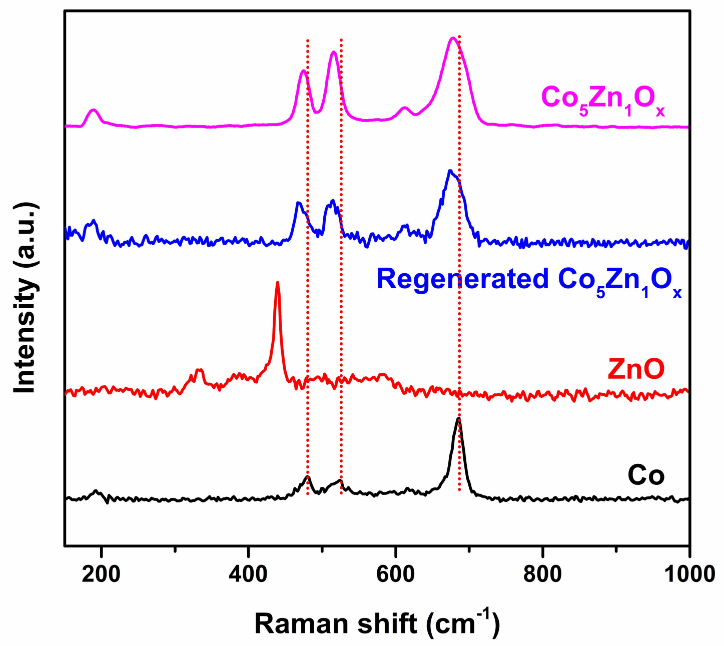

Fig. S5 Raman spectra of Co (black), ZnO (red), $Co_5Zn_1O_x$ (pink) and regenerated $Co_5Zn_1O_x$ (blue), respectively.

References

[1] N. Siddiqui, A.S. Roy, R. Goyal, R. Khatun, C. Pendem, A.N. Chokkapu, A. Bordoloi, R. Bal, *Sustain. Energ. Fuels*, 2018, **2**, 191−198.

[2] T. Thanatthanachon, T.B. Rauchfuss, *Angew. Chem. Int. Ed.*, 2010, **49**, 6616−6618.

[3] B. Saha, C.M. Bohn, M.M. Abu-Omar, *ChemSusChem*, 2014, 7, 3095−3101.

[4] P. Yang, Q. Cui, Y. Zu, X. Liu, G. Lu, Y. Wang, *Catal. Commun.*, 2015, **66**, 55−59.

[5] M. Chidambaram, A.T. Bell, *Green Chem.*, 2010, 12, 1253−1262.

[6] X. Kong, Y. Zhu, H. Zheng, F. Dong, Y. Zhu, Y.-W. Li, *RSC Adv.*, 2014, **4**, 60467−60472.

[7] S. De, S. Dutta, B. Saha, *ChemSusChem*, 2012, **5**, 1826−1833.

[8] L. Yu, L. Ye, J. Chen, J. Zheng, L. Ye, H. Lin, Y. Yuan, *ChemCatChem*, 2015, **7**, 1701−1707.

[9] G. Bottari, A.J. Kumalaputri, K.K. Krawczyk, B.L. Feringa, H.J. Heeres, K. Barta, *ChemSusChem*, 2015, **8**, 1323−1327.

[10] B. Chen, F. Li, Z. Huang, G. Yuan, *Appl. Catal. B- Environ.*, 2017, **200**, 192−199.

[11] B. Seemala, C.M. Cai, C.E. Wyman, P. Christopher, *ACS Catal.*, 2017, **7**, 4070−4082.

[12] P. Priecel, N.A. Endot, P.D. Cara, J.A. Lopez-Sanchez, *Ind. Eng. Chem. Res.*, 2018, **57**, 1991−2002.

[13] Z. Gao, C. Li, G. Fan, L. Yang, F. Li, *Appl. Catal. B-Environ.*, 2018, **226**, 523−533.

[14] A.J. Kumalaputri, G. Bottari, P.M. Erne, H.J. Heeres, K. Barta, *ChemSusChem*, 2014, **7**, 2266−2275.

[15] J. Zhang, J. Chen, *ACS Sustain. Chem. Eng.*, 2017, **5**, 5982−5993.

[16] R.J. Chimentão, H. Oliva, J. Belmar, K. Morales, P. Mäki-Arvela, J. Wärnå, Y. Murzin, J.L.G. Fierro, J. Llorca, D. Ruiz, *Appl. Catal. B- Environ.*, 2019, **241**, 270−283.

[17] Y. Zu, P. Yang, J. Wang, X. Liu, J. Ren, G. Lu, Y. Wang, *Appl. Catal. B- Environ.*, 2014, **146**, 244−248.

[18] G.-H. Wang, J. Hilgert, F.H. Richter, F. Wang, H.-J. Bongard, B. Spliethoff, C. Weidenthaler, F. Schüth, *Nature Mat.*, 2014, **13**, 293−300.

[19] Z. Zhang, C. Wang, X. Gou, H. Chen, K. Chen, X. Lu, P. Ouyang, J. Fu, *Appl. Catal. A-Gen.*, 2019, **570**, 245-250.

[20] J. Li, Z. Song, Y. Hou, Z. Li, C. Xu, C.-L. Liu, W.-S. Dong, *ACS Appl. Mater. Inter.*, 2019, **11**, 12481−12491.

[21] M. Brzezińska, N. Keller, A.M. Ruppert, *Catal. Sci. Technol.*, 2020, **10**, 658-670.