Supporting information

Synthesis of W-modified CeO_2/ZrO_2 catalysts for selective catalytic reduction of NO with NH_3

Chenglong Li[a], Zhitao Han[a]*, Yuqing Hu[a], Tingjun Liu[a], Xinxiang Pan[a b]

a. Marine Engineering College, Dalian Maritime University, Dalian 116026, China;

b. School of Electronic and Information Technology, Guangdong Ocean University, Zhanjiang 524088, China

Correspondence information: Dr. Zhitao Han, Dalian Maritime University, No.1, Linghai Road, Dalian 116026, China, hanzt@dlmu.edu.cn.

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Table. S1 Comparison of the performance over $Ce_{0.4}/W_{0.1}ZrO_x$ catalyst with related literatures.

Catalysts	Preparation method	Reaction mixture	$T_{80\%}$, ºC	Ref
$Ce_{0.4}/W_{0.1}ZrO_x$	Co-precipitation ($W_{0.1}ZrO_x$) Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. % N_2 as balance, GHSV = 60,000 h^{-1}	226-446 (NO_x)	This work
WO_3/CeO_2-ZrO_2	Incipient wetness impregnation	[NO] = [NH_3] = 550 ppm, [O_2] = 6 vol. % [CO_2] = 10 vol. %, [H_2O] = 10 vol. % N_2 as balance, GHSV = 90,000 h^{-1}	290-500 (NO)	1
$WO_3/Ce_{0.65}Zr_{0.35}O_2$	Wet impregnation	[NO] = [NH_3] = 0.1 %, [O_2] = 5 vol. % [H_2O] = 10 vol. %, Ar as balance GHSV = 30,000 h^{-1}	245-450 (NO_x)	2
WO_3/ZrO_2-$Ce_{0.6}Zr_{0.4}O_2$	Incipient wetness impregnation Solution combustion method	[NO] = [NH_3] = 1000 ppm, [O_2] = 10 vol. % [H_2O] = 10 vol. %, N_2 as balance GHSV = 50,000 h^{-1}	270-510 (NO_x)	3
WO_3/Ce-Zr (40-60)	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 10 vol. % [CO_2] = 10 vol. %, [H_2O] = 10 vol. % N_2 as balance, WHSV = 200 h^{-1}	250-500 (NO_x)	4
WO_3-$Ce_{0.75}Zr_{0.25}O_2$	Citric-aide sol-gel ($Ce_{0.75}Zr_{0.25}O_2$) Incipient wetness impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. % N_2 as balance, GHSV = 30,000 h^{-1}	290-400 (NO_x)	5

W-CeZr (SO_2-treatment)	Wet impregnation	[NO] = 900 ppm, [NO_2] = 100 ppm [NH_3] = 1000 ppm, [SO_2] = 100 ppm [O_2] = 6 vol. %, N_2 as balance WHSV = 300 h^{-1}	295-500 (NO_x)	6
CeO_2-ZrO_2-WO_3	Hydrothermal synthesis Incipient impregnation Co-precipitation Sol-gel	[NO] = [NH_3] = 600 ppm, [O_2] = 5 vol. % N_2 as balance, GHSV = 60,000 h^{-1}	185-450 (NO) 245-450 (NO) 190-430 (NO) 225-450 (NO)	7
CeO_2/ZrO_2-S	Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. % N_2 as balance, GHSV = 30,000 h^{-1}	235-500 (NO)	8
$Ce_{0.75}Zr_{0.25}O_2$-PO_4^{3-} (SO_2 + 10%H_2O treatment)	Sol-gel ($Ce_{0.75}Zr_{0.25}O_2$) Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. % N_2 as balance, GHSV = 30,000 h^{-1}	235-470 (NO_x)	9
NbO_x/$Ce_{0.75}Zr_{0.25}O_2$	Sol-gel ($Ce_{0.75}Zr_{0.25}O_2$) Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. % [CO_2] = 10 vol. %, N_2 as balance GHSV = 300,000 h^{-1}	190-450 (NO_x)	10
MoO_3/CeO_2-ZrO_2	Hydrothermal synthesis (CeO_2-ZrO_2) Impregnation	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. % He as balance, GHSV = 98,000 h^{-1}	245-430 (NO_x)	11
NiO-CeO_2-ZrO_2	Sol-gel	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol. % [CO_2] = 10 vol. %, N_2 as balance GHSV = 300,000 h^{-1}	250-450 (NO_x)	12

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Fig. S1

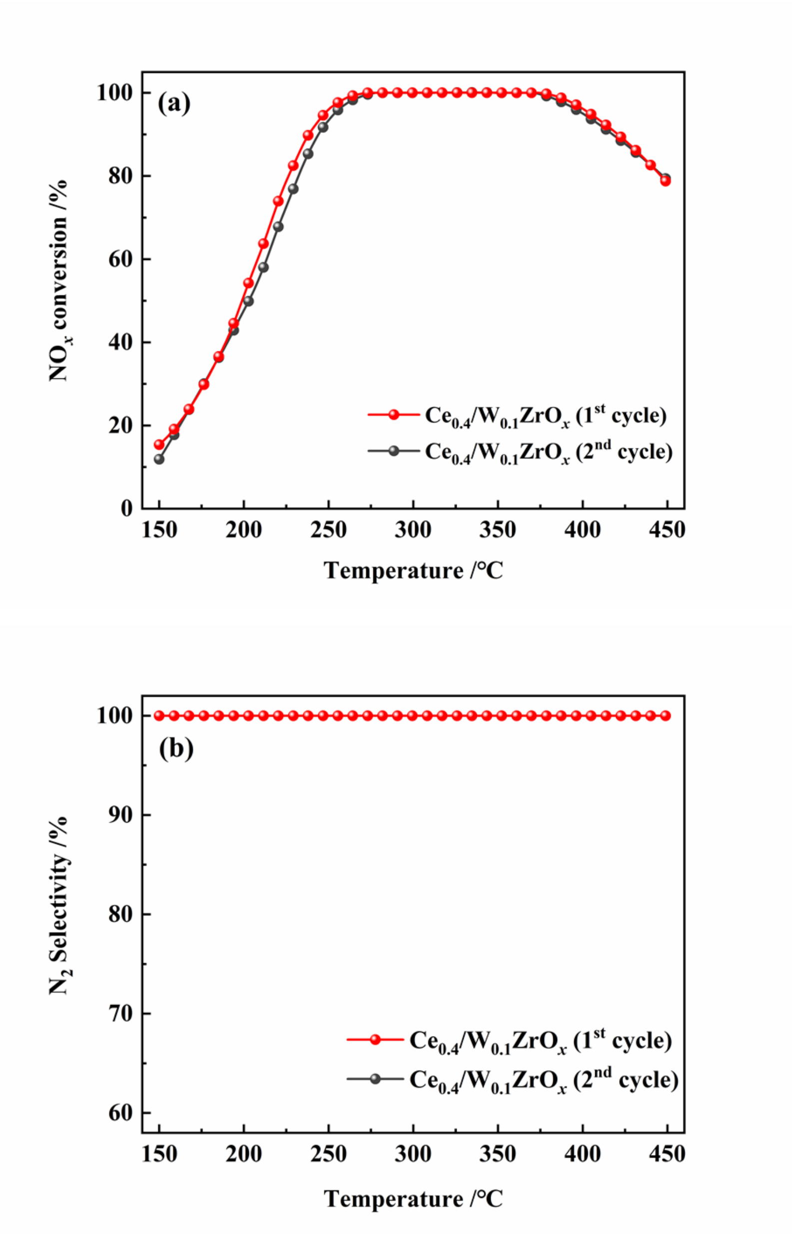

Fig. S1. SCR performance test results of $Ce_{0.4}/W_{0.1}ZrO_x$ (1st cycle) and $Ce_{0.4}/W_{0.1}ZrO_x$ (2nd cycle) catalyst: (a) NO_x conversion and (b) N_2 selectivity.

(Reaction conditions: 0.5 mL catalyst, [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol.%, balance with N_2, total flow rate = 500 mL·min^{-1} and GHSV =60,000 h^{-1})

Fig. S2

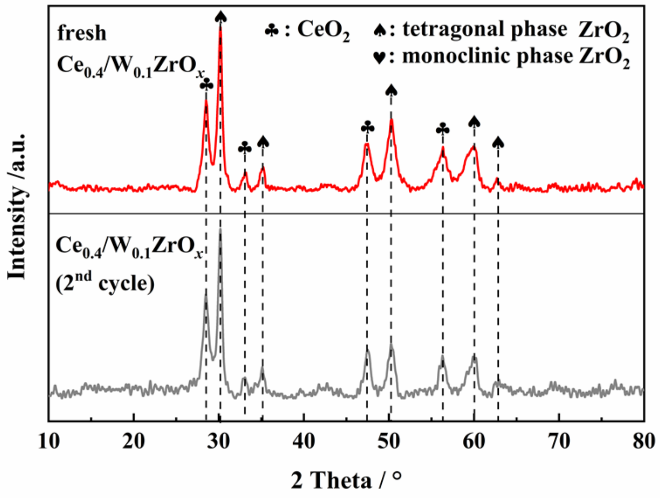

Fig. S2. XRD patterns of fresh $Ce_{0.4}/W_{0.1}ZrO_x$ and used $Ce_{0.4}/W_{0.1}ZrO_x$ (2^{nd} cycle) catalysts

To investigate the effect of stability reaction on the structure over $Ce_{0.4}/W_{0.1}ZrO_x$ catalyst, the structures of fresh $Ce_{0.4}/W_{0.1}ZrO_x$ and used $Ce_{0.4}/W_{0.1}ZrO_x$ (2^{nd} cycle) catalysts were characterized by XRD. It could be seen from Fig. S2 that the intensities of CeO_2 and ZrO_2 peaks did not change significantly before and after the SCR reaction. Moreover, no new peaks were detected on the XRD curve of $Ce_{0.4}/W_{0.1}ZrO_x$ (2^{nd} cycle) catalyst compared to the fresh $Ce_{0.4}/W_{0.1}ZrO_x$ catalyst. It was demonstrated that the structure of $Ce_{0.4}/W_{0.1}ZrO_x$ catalyst with better stability during the SCR reactions.

Fig. S3

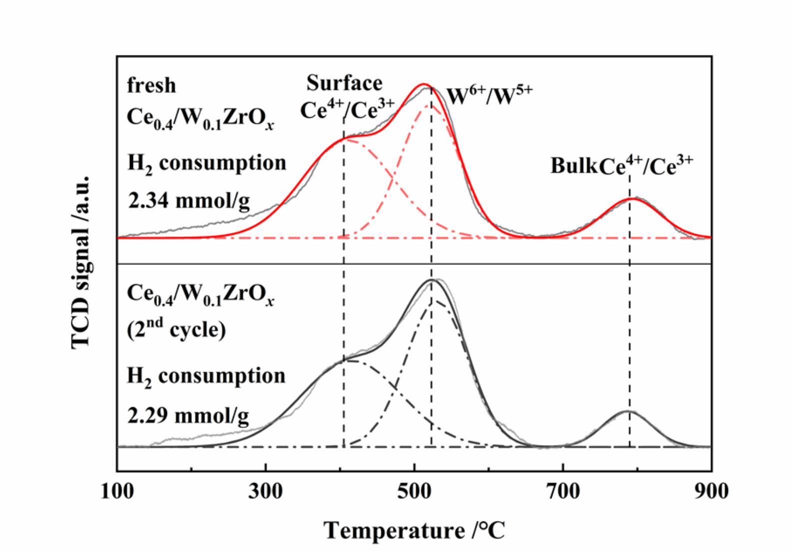

Fig. S3. H_2-TPR profiles of fresh $Ce_{0.4}/W_{0.1}ZrO_x$ and used $Ce_{0.4}/W_{0.1}ZrO_x$ (2^{nd} cycle) catalysts in the range of 100-900 ºC.

As shown in Fig. S3, intensities of the three reducing peaks over $Ce_{0.4}/W_{0.1}ZrO_x$ (2^{nd} cycle) catalyst did not decrease significantly compared to the fresh catalyst. In addition, the total H_2 consumption of the fresh $Ce_{0.4}/W_{0.1}ZrO_x$ catalyst only decreased by 0.05 mmol/g after cycling two times. It was indicated that $Ce_{0.4}/W_{0.1}ZrO_x$ catalyst still maintained a good redox property after the SCR reactions.

Fig. S4

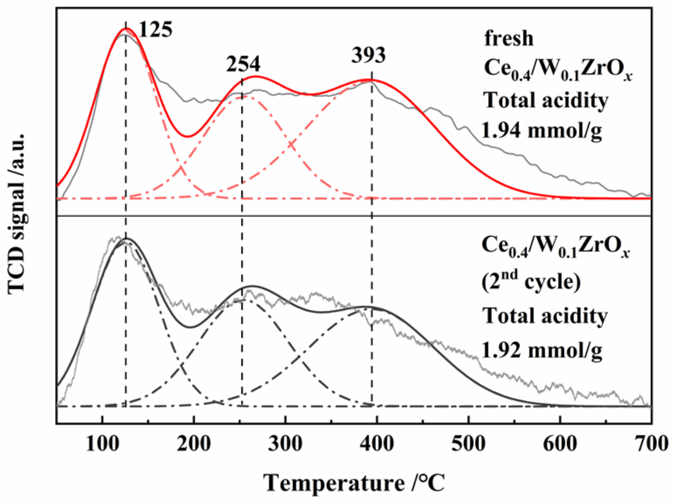

Fig. S4. NH_3-TPD curves of fresh $Ce_{0.4}/W_{0.1}ZrO_x$ and used $Ce_{0.4}/W_{0.1}ZrO_x$ (2nd cycle) catalysts in the range of 50-700 ºC.

The surface acidities of two catalysts were also investigated by NH_3-TPD characterization technique. It could be seen from Fig. S4 that NH_3-TPD profiles of the fresh $Ce_{0.4}/W_{0.1}ZrO_x$ and used $Ce_{0.4}/W_{0.1}ZrO_x$ (2nd cycle) catalysts both exhibited three desorption peaks, which intensities of the corresponding peaks were similar. In other words, there was no obvious damage in the surface acidity over $Ce_{0.4}/W_{0.1}ZrO_x$ catalyst after the SCR reactions.

Fig. S5

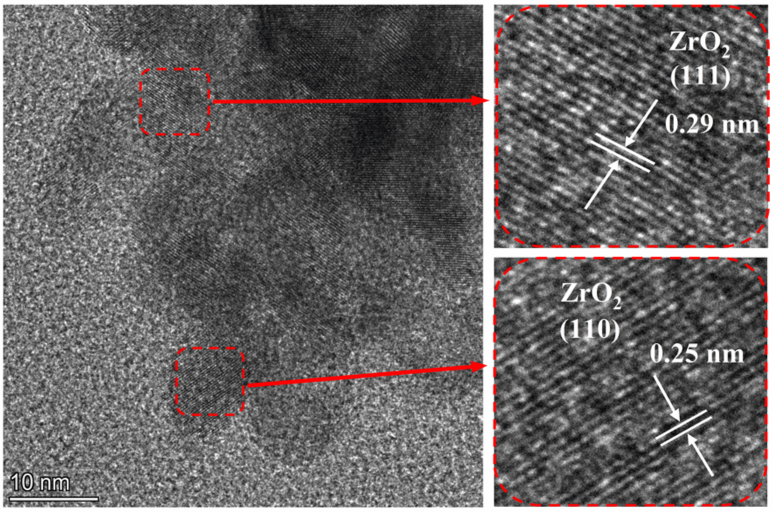

Fig. S5. TEM pattern of $W_{0.1}ZrO_x$ sample

Fig. S6

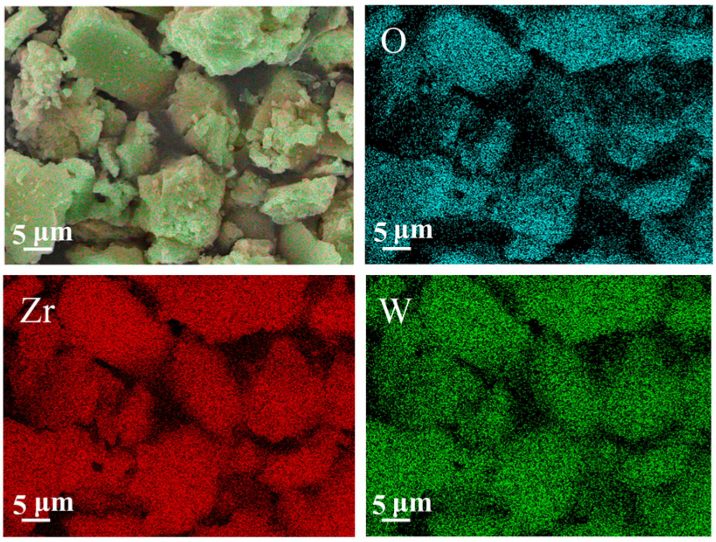

Fig. S6. EDS pattern over $W_{0.1}ZrO_x$ sample

To further investigate the dispersion of W, Zr and O elements over $W_{0.1}ZrO_x$ sample, EDS mapping was conducted and the results showed that the tungsten species were well dispersed on the support, as presented in Fig. S6.