Supporting Information

Enhanced Lattice Oxygen Reactivity Over Ni Modified WO_3-Based Redox Catalysts for Chemical Looping Partial Oxidation of Methane

Sai Chen, Liang Zeng, Hao Tian, Xinyu Li, and Jinlong Gong*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology; Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China.

* Corresponding author. Fax: +86-22-87401818; Email address: jlgong@tju.edu.cn.

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Table S1 XRD derived characteristics of various oxygen carriers.

Oxygen Carriers	Crystal Phase/Size	WO_3	WO_3/Al_2O_3	$Ni_{0.3}W_1O_x/Al_2O_3$	$Ni_{0.5}W_1O_x/Al_2O_3$	$Ni_1W_1O_x/Al_2O_3$	NiO/Al_2O_3
Fresh	Phase	WO_3	$Al_2(WO_4)_3$, Al_2O_3	WO_3, $Al_2(WO_4)_3$, $NiWAlO_x$, Al_2O_3	WO_3, Al_2O_3	$NiWO_4$	—
	Size (nm)	>100[a]	54[b]	43[a]	32[a]	60[c]	—
after reduction	Phase	$WO_{2.96}$, $WO_{2.72}$, WO_2	WO_2, Al_2O_3, $WO_{2.72}$	WO_2, W, WC, Ni, Al_2O_3	WO_2, W, Ni, Al_2O_3	WC, Ni, Al_2O_3	Ni, Al_2O_3
	Size (nm)	—	—	12[d], 15[e]	9[d], 13[e]	14[d], 20[f]	16[d], —
after 1st cycle	Phase	WO_3	$Al_2(WO_4)_3$, Al_2O_3	WO_3, $NiWO_4$, Al_2O_3	WO_3, $NiWO_4$, Al_2O_3	$NiWO_4$, Al_2O_3	—
	Size (nm)	>100[a]	60[b]	45[a]	35[a]	63[c]	—
after 10th cycle	Phase	—	—	—	WO_3, $NiWO_4$, Al_2O_3	—	—
	Size (nm)	—	—	—	40[a]	—	—

[a] Determined by the Scherrer equation from the (001) plane of WO_3, [b] Determined by the Scherrer equation from the (031) plane of $Al_2(WO_4)_3$ and [c] Determined by the Scherrer equation from the (-111) plane of $NiWO_4$ in XRD patterns.

[d] Determined by the Scherrer equation from the (111) plane of Ni, [e] Determined by the Scherrer equation from the (210) plane of W and [f] Determined by the Scherrer equation from the (100) plane of WC in XRD patterns.

Table S2 Data derived from ICP-OES for the fresh samples.

Samples	WO_3/Al_2O_3	$Ni_{0.3}W_1O_x/Al_2O_3$	$Ni_{0.5}W_1O_x/Al_2O_3$	$Ni_1W_1O_x/Al_2O_3$
Ni/W	0	0.29	0.52	1.1

Table S3 Data derived from XPS of $Ni_{0.5}W_1O_x/Al_2O_3$ after one and ten cycles.

Oxygen Carriers	OI/(OII+OIII)	W^{6+}/W^{5+}	Ni/W
1^{st} cycle	2.2	5.8	0.26
10^{th} cycle	4.2	2.9	0.18

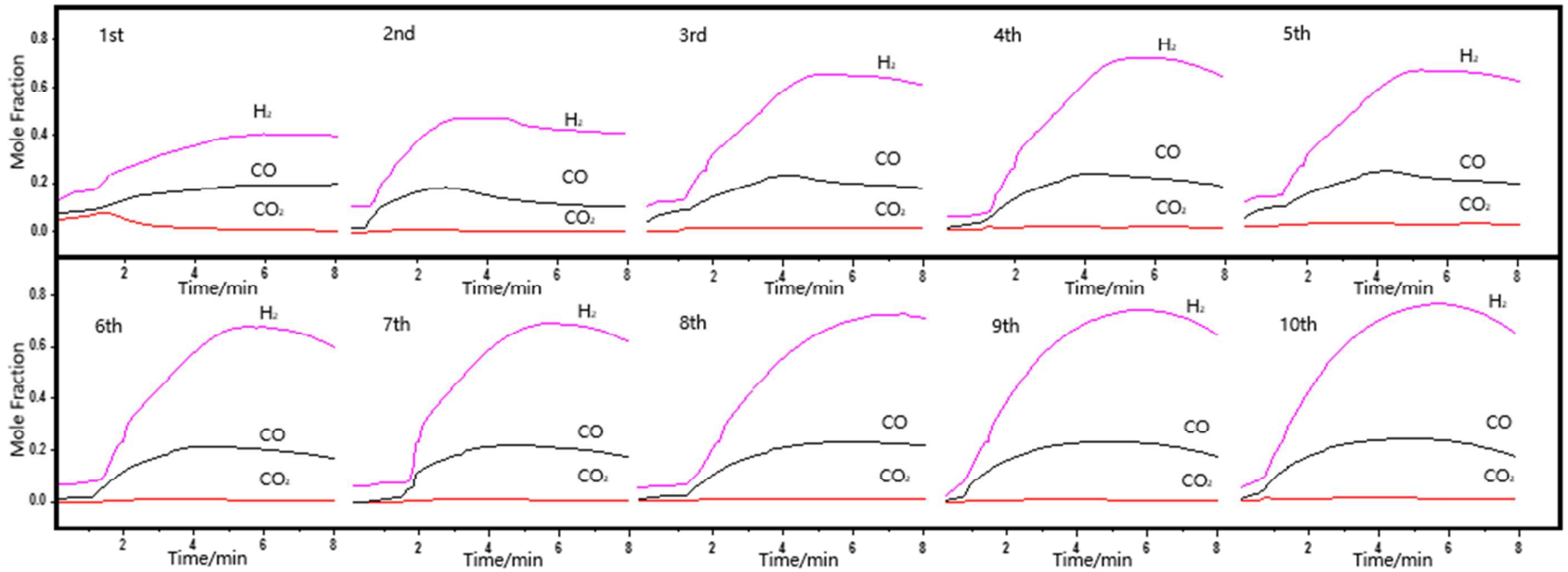

Figure S1. Molar fractions of CO, CO_2, and H_2 from reduction on $Ni_{0.5}W_1O_x/Al_2O_3$ during 10 redox cycles (The purple, black and red lines respectively represent H_2, CO and CO_2).

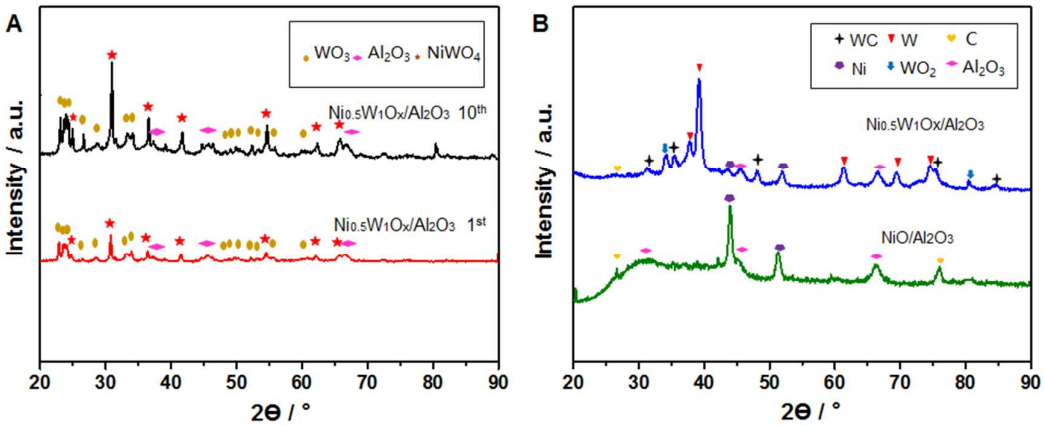

Figure S2. XRD patterns of (A) $Ni_{0.5}W_1O_x/Al_2O_3$ after the first and tenth cycle, (B) $Ni_{0.5}W_1O_x/Al_2O_3$ and NiO/Al_2O_3 after reduction in the first cycle.

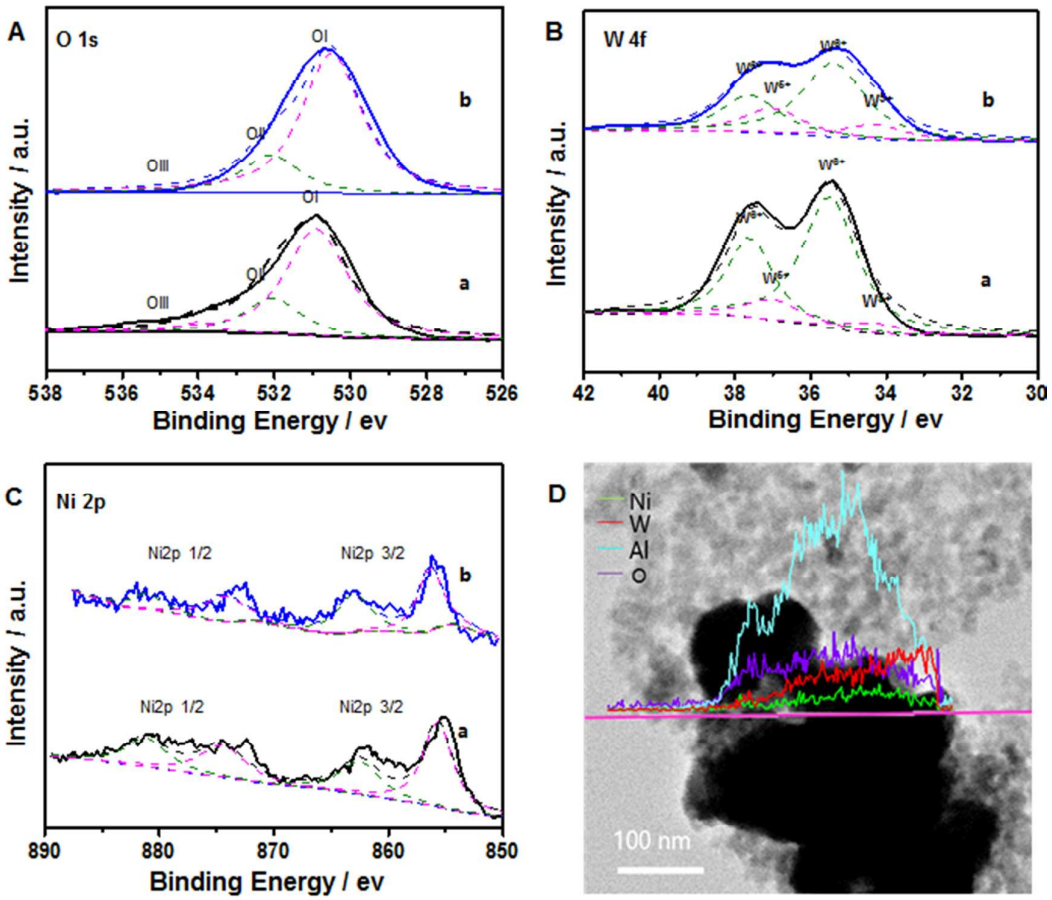

Figure S3. (A) O 1s, (B) W 4f and (C) Ni 2p XPS spectra of $Ni_{0.5}W_1O_x/Al_2O_3$ after (a) one and (b) ten cycles, (D) EDS line scan of $Ni_{0.5}W_1O_x/Al_2O_3$ after one cycle.

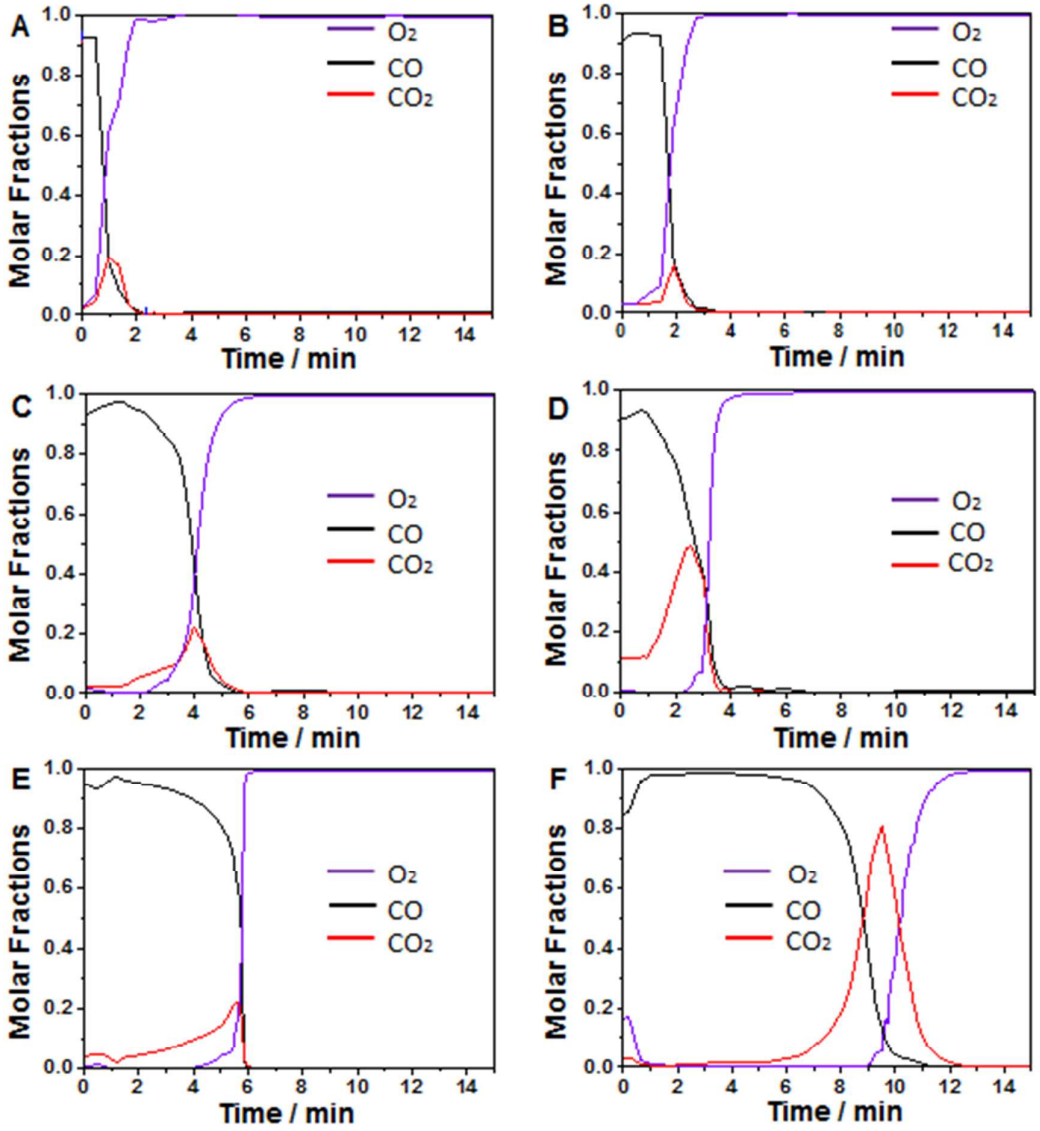

Figure S4. Molar fractions of CO, CO_2 and O_2 from oxygen oxidation of (A) WO_3, (B) WO_3/Al_2O_3, (C) $Ni_{0.3}W_1O_x/Al_2O_3$, (D) $Ni_{0.5}W_1O_x/Al_2O_3$, (E) $Ni_1W_1O_x/Al_2O_3$ and (F) NiO/Al_2O_3 at 800 °C in the first cycle.

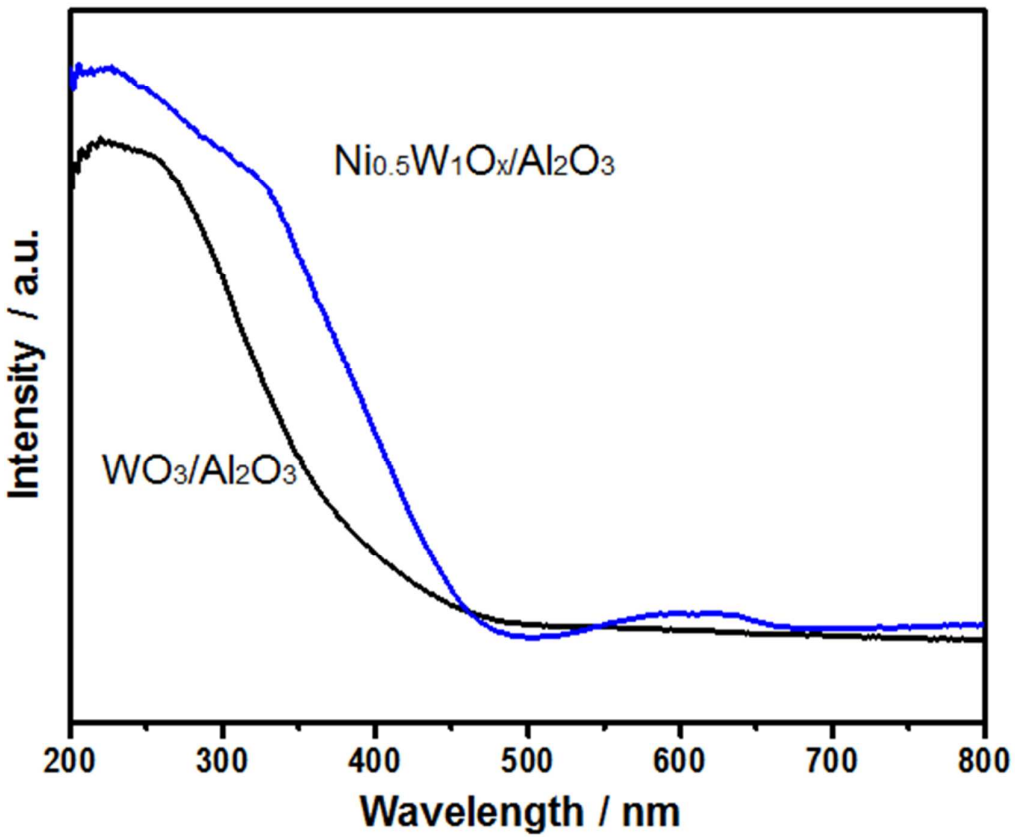

Figure S5. UV−Vis reflectance spectra of fresh WO_3/Al_2O_3 and $Ni_{0.5}W_1O_x/Al_2O_3$.