Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Catalytic deoxygenation of C_{18} fatty acid over supported metal Ni catalyst promoted by the basic sites of $ZnAl_2O_4$ spinel phase

Guangci Li,[*,a] Lei Chen,[a] Ruikun Fan,[a] Di Liu,[b] Song Chen,[a] Xuebing Li,[*,a] and Keng H. Chung[a]

[a] *Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266101, PR China*

[b]*College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, P.R. China.*

[*] Corresponding authors.
E-mail addresses: ligc@qibebt.ac.cn (G. Li), lixb@qibebt.ac.cn (X. Li).

Experimental section

All chemicals were purchased from commercial suppliers and used as received without further purification: $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, urea, SiO_2, and decalin (Sinopharm, AR standard), oleic acid, stearic acid, and 1-octadecanol (Aladdin, AR standard), *n*-octadecane (Aladdin, ≥ 99.5% GC standard).

Preparation of $ZnAl_2O_4$ support

$ZnAl_2O_4$ support was prepared via a hydrothermal synthesis process followed by a thermal treatment. Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (2 mmol), $Al(NO_3)_3 \cdot 9H_2O$ (4 mmol), and urea (48 mmol) were dissolved into deionized water (40 mL) to form a colorless solution. The solution was then transferred into 100 mL Teflon-lined stainless autoclave and heated at 180 °C for 3 h to produce Zn-Al oxide precursor. After that, the autoclave was cooled naturally to room temperature, and the white precursor was collected by filtration, washed with deionized water to get a neutral pH, and then dried in air at 80 °C overnight. The dried material was then calcined at 750 °C for 4 h to produce the final composite oxide.

Preparation of $Ni/ZnAl_2O_4$ and Ni/SiO_2

The preparation procedure for the two Ni-based catalysts is the same as described in Section 2.2 in the text.

Table S1. Textural properties of the Zn-Al composite oxides.

Catalyst	BET specific surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
S-120	87.8	0.17	3.9
S-140	86.1	0.22	5.1
S-160	104.2	0.20	3.8
S-180	76.5	0.19	5.0
S-200	77.1	0.20	5.1

Table S2. XPS data for Zn $2p_{3/2}$ spectra of different Ni-based catalysts.

Catalysts	$ZnAl_2O_4$		ZnO	
	BE (eV)	At. (%)	BE (eV)	At. (%)
C-120	1021.6	46.8	1021.2	53.2
C-140	1021.9	50.0	1021.3	50.0
C-160	1022.2	55.1	1021.5	44.9
C-180	1022.7	58.9	1021.7	41.1
C-200	1022.7	64.8	1021.6	35.2

Table S3. The Ni content of different Ni-based catalysts and Ni species distribution.

Catalysts	Ni content (wt.%) [a]	Surface Ni content (wt.%) [b]	Ni^{2+}		Ni^{0}	
			BE (eV)	At. (%)	BE (eV)	At. (%)
C-120	10.8	9.2	855.3	92.1	851.9	7.9
C-140	11.0	9.2	855.6	86.1	852.1	13.9
C-160	10.5	13.5	855.7	82.2	852.5	17.8
C-180	10.6	18.0	856.2	78.1	853.5	21.9
C-200	10.3	19.6	856.2	75.0	853.1	25.0

[a] The value is determined by ICP-OES analysis.

[b] The value is determined by XPS analysis.

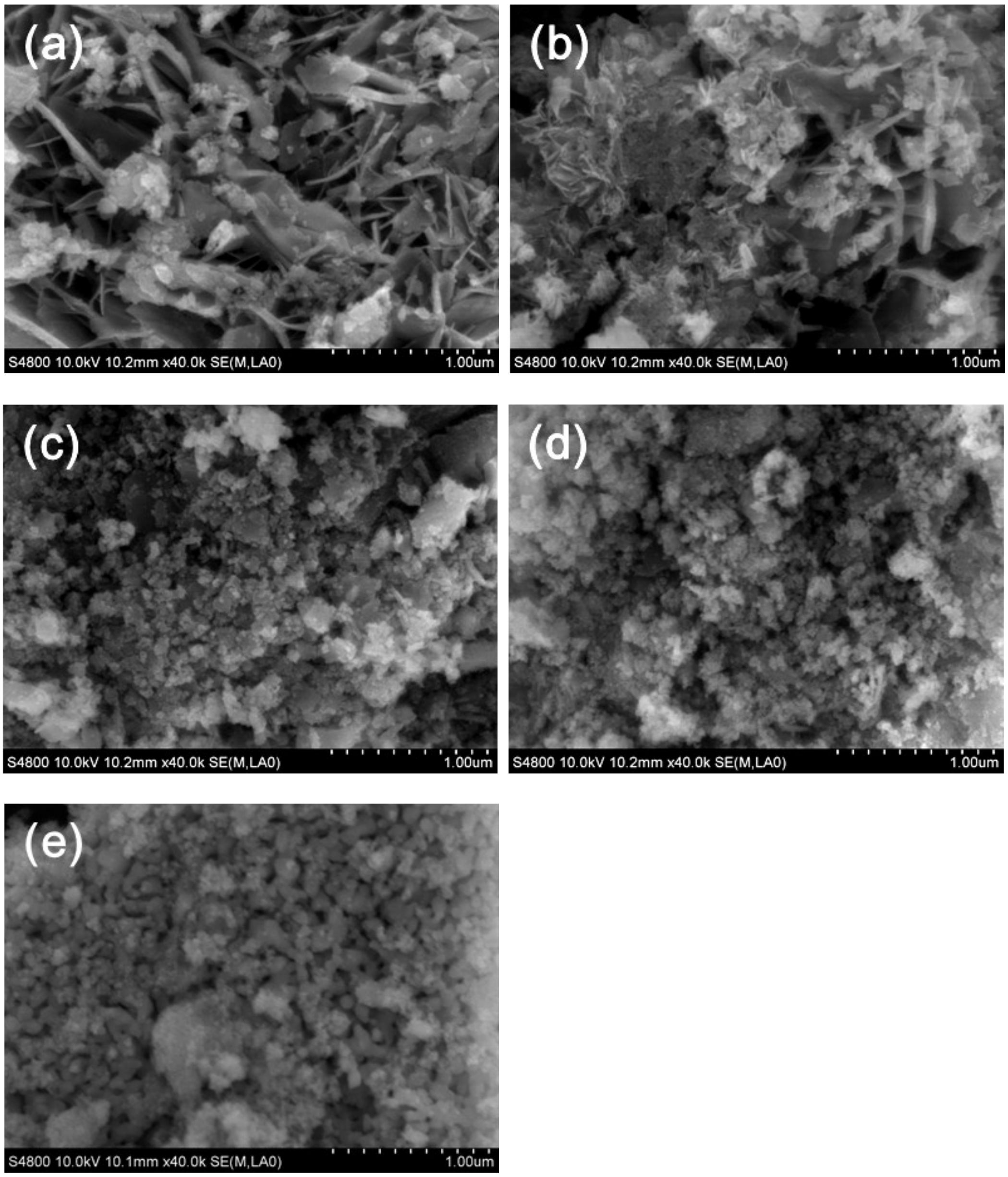

Fig. S1. SEM images of Zn-Al composite oxides: (a) S-120, (b) S-140, (c) S-160, (d) S-180, and (e) S-200.

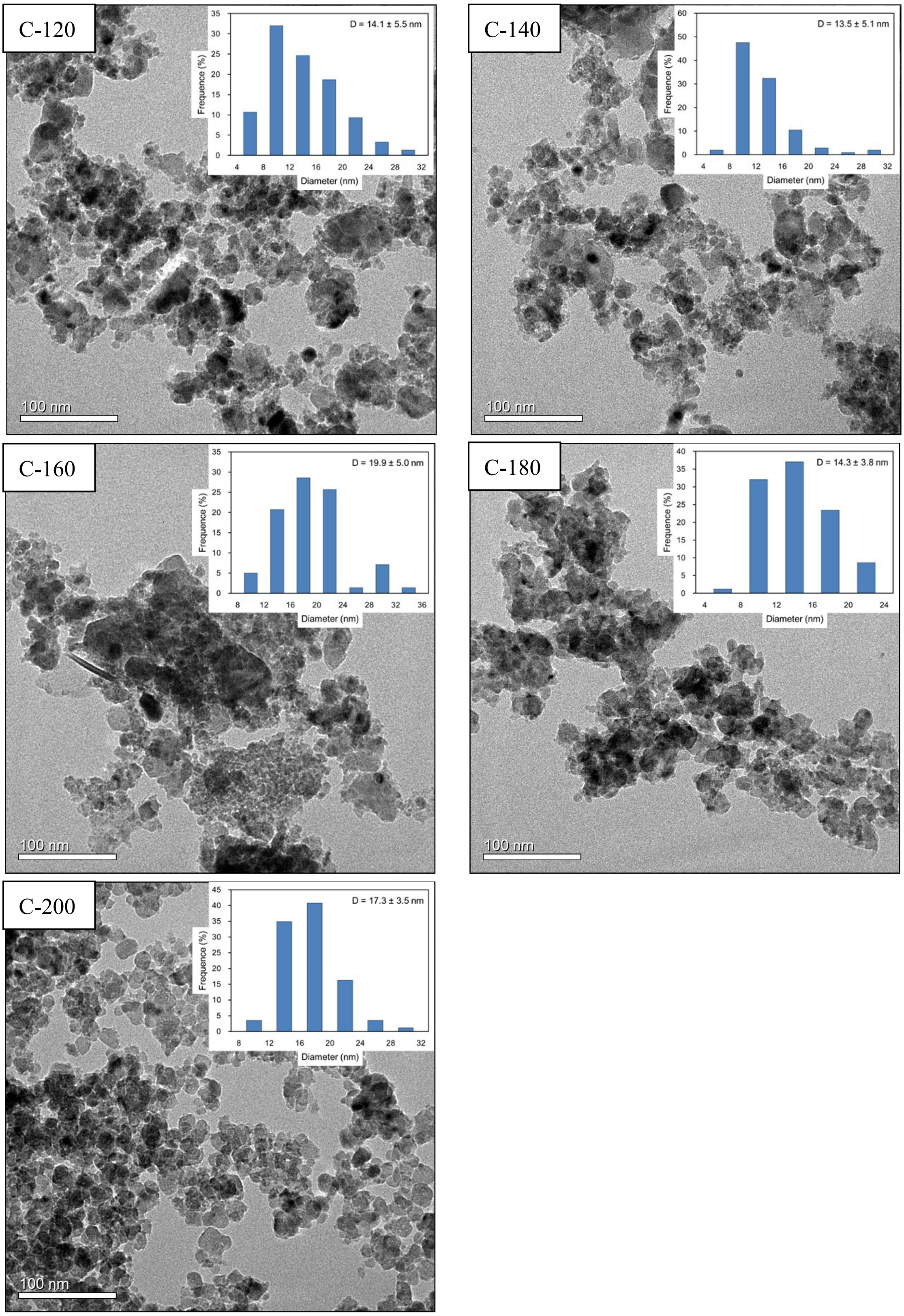

Fig. S2. TEM images of the reduced Ni-based catalysts and their histograms of Ni particle size distribution (inset).

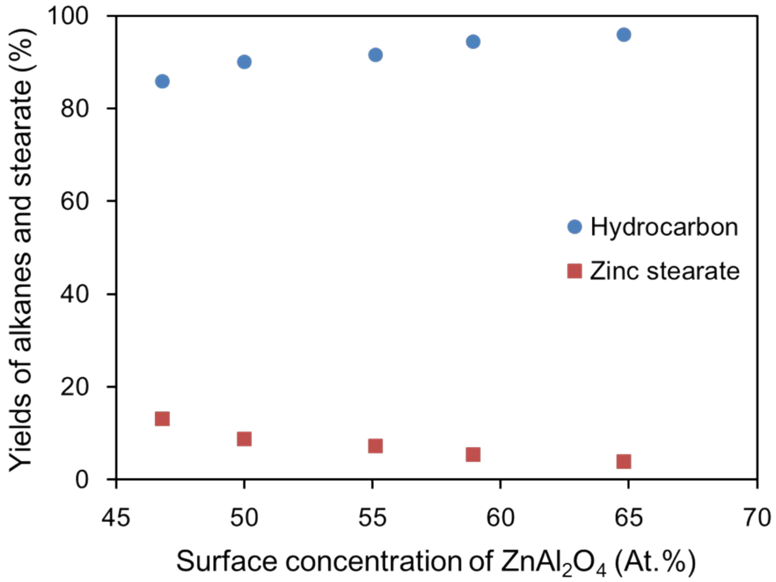

Fig. S3. Yields of heptadecane and zinc stearate as a function of surface concentration of $ZnAl_2O_4$ on Ni-based catalysts.

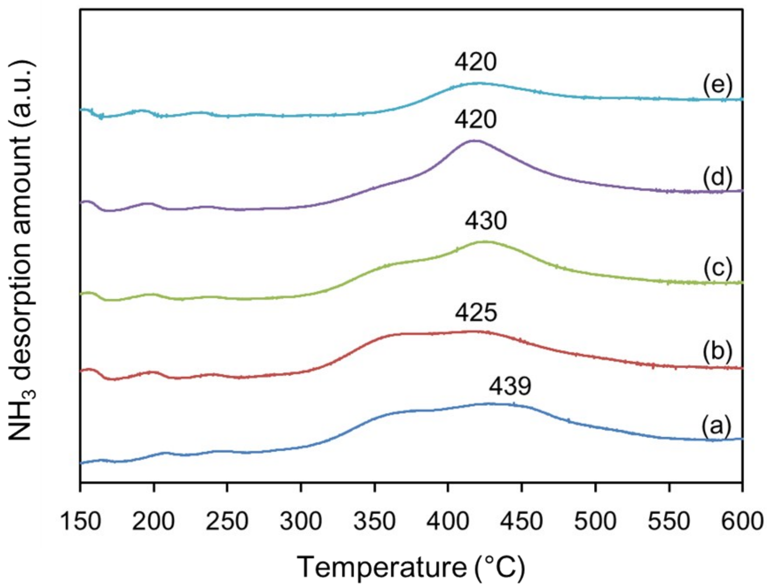

Fig. S4. NH_3-TPR profiles of Zn-Al composite oxides: (a) S-120, (b) S-140, (c) S-160, (d) S-180, and (e) S-200.

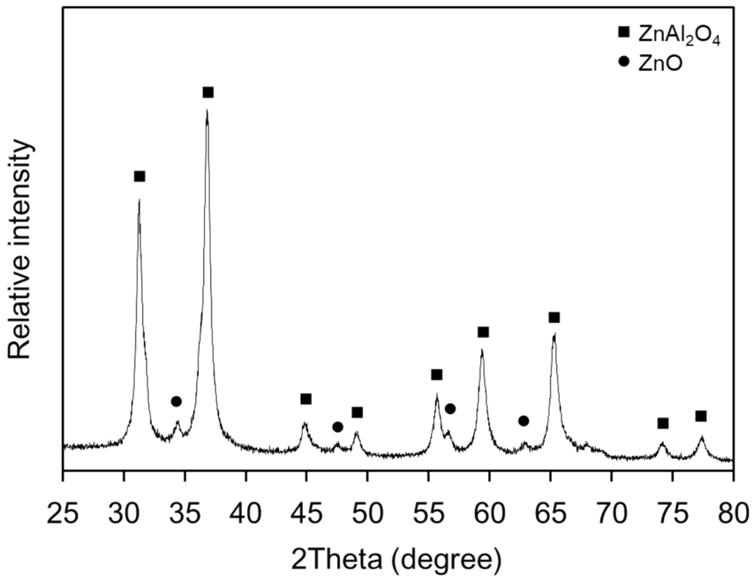

Fig. S5. XRD pattern of $ZnAl_2O_4$ support.

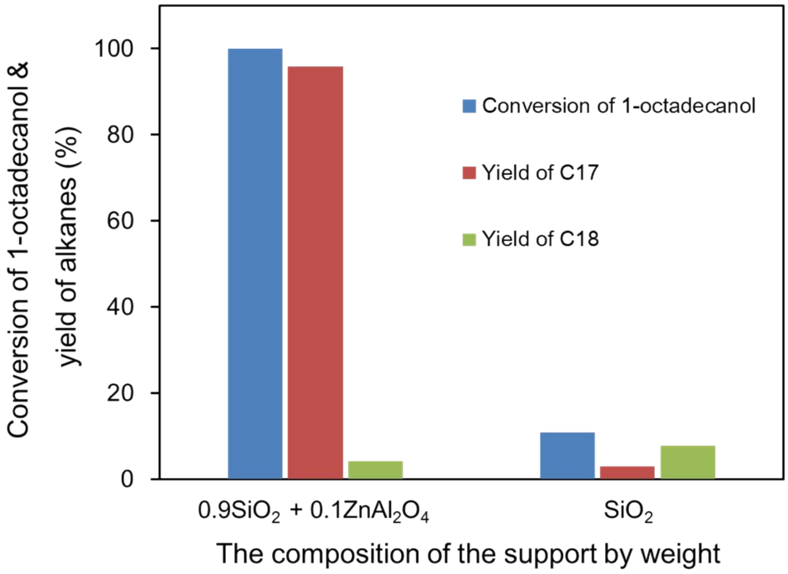

Fig. S6. The effect of addition amount of $ZnAl_2O_4$ on the catalytic deoxygenation of 1-octadecanol. Reaction conditions: 1-octadecanol (2.0 g), decalin (30.0 g), catalyst (0.2 g), temperature (280 °C), H_2 pressure (2.5 MPa), and stirring at 600 r/min for 6 h.

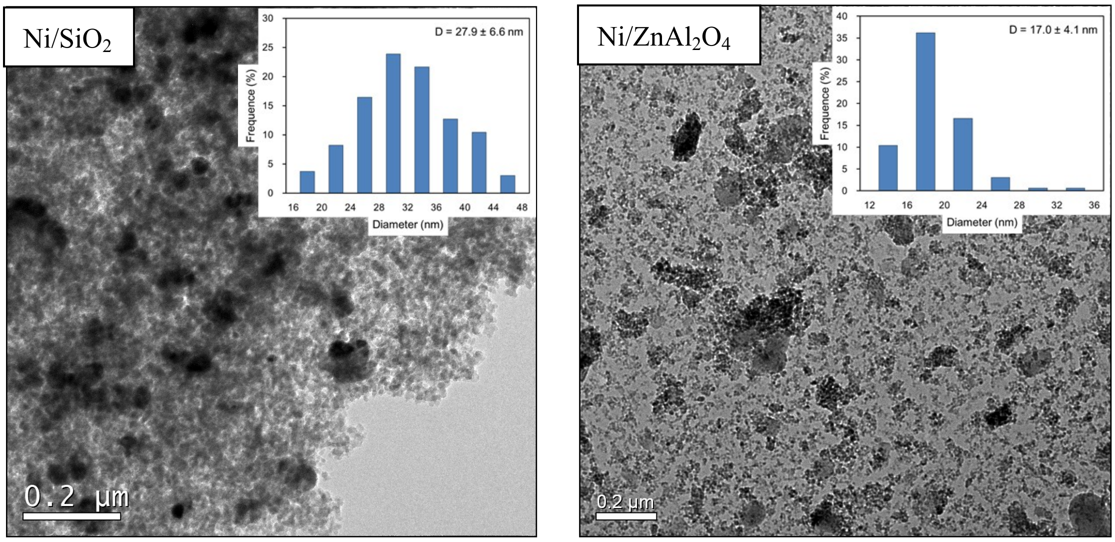

Fig. S7. TEM images of the reduced Ni-based catalysts and their histograms of Ni particle size distribution (inset).

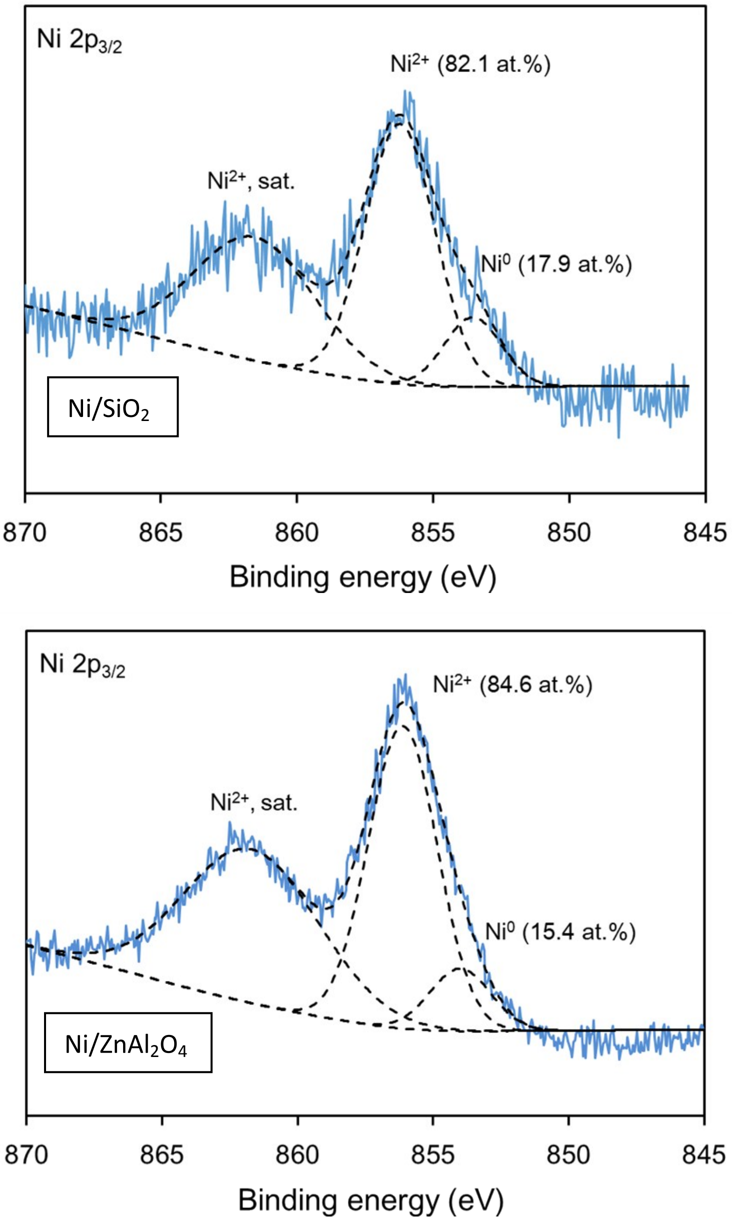

Fig. S8. Ni $2p_{3/2}$ XPS spectra of Ni/SiO_2 and $Ni/ZnAl_2O_4$ catalysts.