[Electronic Supplementary Information]

Hydrodeoxygenation of guaiacol over physically mixed Co/TiO_2 and WO_3/TiO_2 catalysts

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Table S1. Price per gram of noble and non-noble metals commonly used in HDO catalysts. The price was obtained from https://dailymetalprice.com at 2023.09.05 and 2023.09.06.

Metal		Price ($/g)
Noble	Pd	38.956
	Pt	29.276
	Ru	14.950
Non-noble	Co	0.03342
	Ni	0.02084
	Cu	0.008254
	Fe	0.0001190

Table S2. Summary of the literatures on guaiacol and alkyl substituted guaiacol HDO conducted by heterogeneous catalysts in batch reaction system.

Reactant	Catalyst	Composition	Solvent	Reaction conditions			Conv. / %	O-free HC Yield / %	Ref.
				T /°C	$P(H_2)$ /bar	t /h			
Guaiacol	Co/TiO_2 + WO_3/TiO_2	Co 10 wt.%, WO_3 10 wt.%	n-Octane	250	10	1	100	87	This work
Guaiacol	Co/TiO_2	Co 10 wt.%	n-Octane	250	10	1	100	6.4 (Cyclohexanol 83)*	This work
Guaiacol	$CoWO_x$/ TiO_2	Co 10 wt.%, WO_3 10 wt.%	n-Octane	250	10	1	0.5	0	This work
Guaiacol	Ru/ HZSM-5	Ru 5 wt.%	Water	240	2	1	100	96	[1]
Guaiacol	Ru/ SBA-15	Ru 5 wt.%	$[Bmim]PF_6$	150	20	6	>99.0	95	[2]
Guaiacol	Ru/CNT	Ru 5 wt.%	Water/ n-Dodecane	220	50	3	100	92	[3]
4-Propyl -guaiacol	Ru/C + Nb_2O_5	Ru 5 wt.%	Water (methanol additive)	250	6	2	36	10	[4]
4-Propyl -guaiacol	Ru/C + Nb_2O_5	Ru 5 wt.%	Water (methanol additive)	250	6	12	100	100	[4]
Guaiacol	Ru-WO_x/ SiAl	Ru 5 wt.%, WO_x 30 wt.%	Water	250	16	1.5	100	88	[5]
Guaiacol	Ru/WZr	Ru 5 wt.% W 10 wt.%	Water	270	40	1	96.8	55	[6]
4-Propyl -guaiacol	$RuCoW_x$/ NC	0.188 mmol Co and Ru	n-Dodecane	240	10	4	100	95.2	[7]
Guaiacol	Ru/TiO_2	Ru 2 wt.%	Octane	260	10	4	99.9	91	[8]
Guaiacol	Pt-WO_{3-x}	-	n-hexane	220	30	1	63.7	47	[9]
Guaiacol	Pt/HY	Pt 0.5 wt.% Si/Al = 2.6	Decane	250	40	2	82.9	56	[10]
Guaiacol	Pd/WO_x/ Al_2O_3	Pd 2 wt.%, W 32 wt.%	n-Decane	300	70	2.5	100	88	[11]
Guaiacol	Rh/ZrO_2	Rh 0.5 wt.%	n-Dodecane	300	70	3	100	88	[12]

Guaiacol	Re/SiO_2	Re 7 wt.%	n-Heptane	280	20	1	98	57	[13]
Guaiacol	Co/SiO_2	Co 20 wt.%	n-Tetradecane	300	10	1	100	93	[14]
Guaiacol	Co/SiO_2	Co 20 wt.%	n-Tetradecane	300	50	1	100	98	[14]
Guaiacol	Sulfided CoMo/ Al_2O_3	-	n-Tetradecane	300	50	1	100	31 (Phenol 61)*	[14]
Eugenol	Co/TiO_2	Co 10 wt.%	n-Dodecane	200	10	2	100	0 (Alcohol 99.9)*	[15]
Guaiacol	Co-MoO_2 @C	Co 4.71 wt.% Mo 16.10 wt.%	n-Hexane	340	8	4	97	61	[16]
Guaiacol	RANEY® Ni + Nafion/ SiO_2	13 wt.% Nafion/SiO_2	Water	300	40	2	100	84	[17]
Guaiacol	Ni-WO_x/ $NiAl_2O_4$	Ni 10 wt.%, W 15 wt.%	Dodecane	250	50	4	97.8	82	[18]
Guaiacol	Ni/ Beta-12.5	Ni 15.7 wt.%	No solvent	250	40	3.3	99.5	70	[19]
Guaiacol	Ni/Nb_2O_5	Ni 20 wt.%	Water	200	25	5	93.6	0.3 (Alcohols 92)*	[20]
Guaiacol	Ni/Nb_2O_5	Ni 20 wt.%	Water	300	25	5	100	98	[20]
Guaiacol	Ni5Cu/ SZ-3	Ni 10 wt.%, Cu 5 wt.%	Dodecane	300	50	8	100	93	[21]

* Yield of main products where oxygen is not fully removed.

Table S3. Comparison of the conversion and product yields for guaiacol HDO catalyzed by Co(10)/TiO_2(R) physically mixed with WO_3(10)/TiO_2(R) and pristine TiO_2(R). Reaction conditions: Catalyst 1 0.1 g, Catalyst 2 0.1 g, Guaiacol 2 mmol, *n*-octane 20 mL, 250 ℃, H_2 10 bar, 1 h.

Entry	Catalyst 1	Catalyst 2	Conversion (%)	Product Yield (%)				
				1	2	3	4	5
8	Co(10)/TiO_2(R)	WO_3(10)/TiO_2(R)	100	25.4	59.1	1.3	0	0
11	Co(10)/TiO_2(R)	TiO_2(R)	100	0.9	3.3	0.2	87.8	7.0

Table S4. Atomic content of the Co(10)/TiO_2(R) and WO_3(10)/TiO_2(R) fresh and AR catalysts obtained from ICP-AES. The number in parentheses represent the wt.% content of WO_3.

Catalyst		Content (wt.%)	
		Co	W (WO_3)
Co(10)/TiO_2(R)	Fresh	10.6	0
	AR	9.5	0.7 (0.8)
WO_3(10)/TiO_2(R)	Fresh	0	8.1 (10.2)
	AR	0.2	7.9 (9.9)

Table S5. Carbon content of fresh, AR, and AR_400C of WO_3(10)/TiO_2(R)_400C catalysts obtained elemental analysis.

WO_3(10)/TiO_2(R)	C content (wt.%)
Fresh	0.113 ± 0.033
AR	0.399 ± 0.002
AR_400C	0.076 ± 0.023

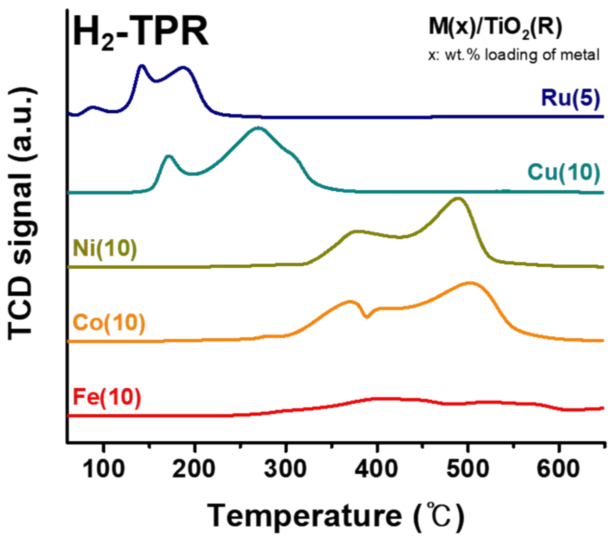

Figure S1. H_2-TPR profiles of metal loaded rutile TiO_2 catalysts after calcination at 400 °C (M = Ru, Cu, Ni, Co, and Fe, x = wt.% loading of metal).

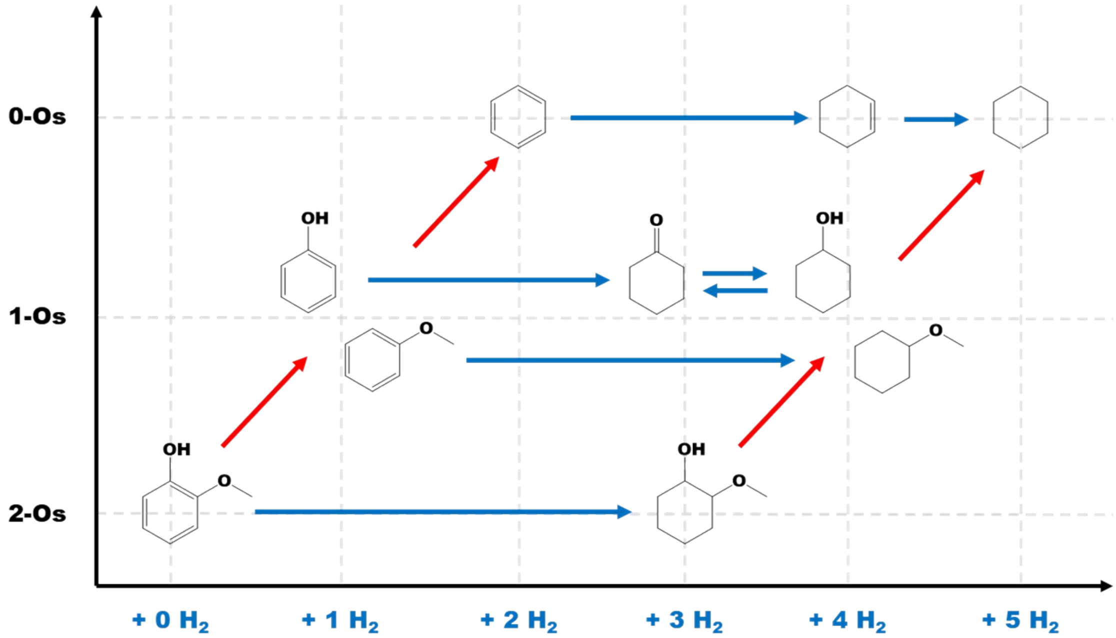

Figure S2. Simplified reaction pathway of guaiacol HDO.

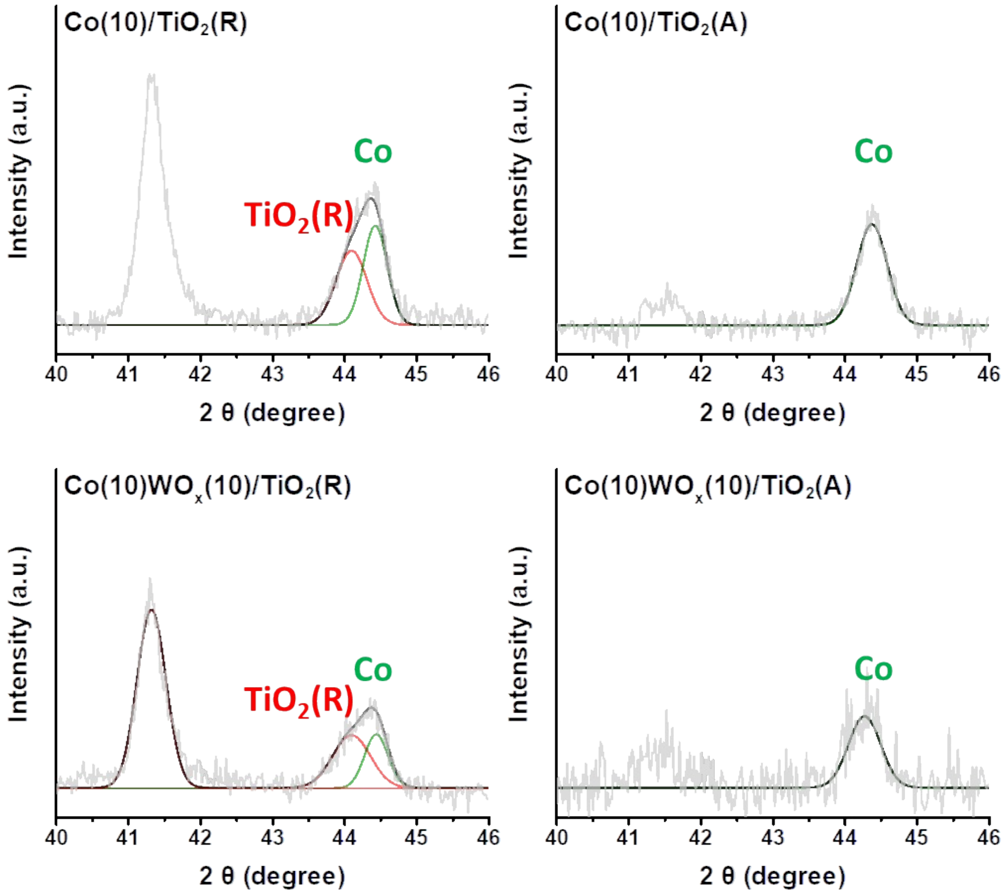

Figure S3. XRD patterns of the Co and W loaded catalysts.

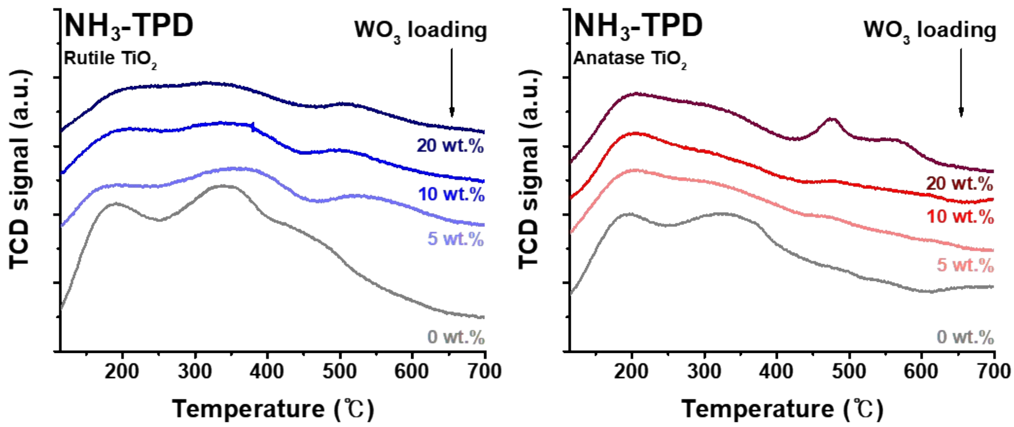

Figure S4. NH_3-TPD profiles of the WO_3 loaded rutile and anatase TiO_2 catalysts with various WO_3 loadings.

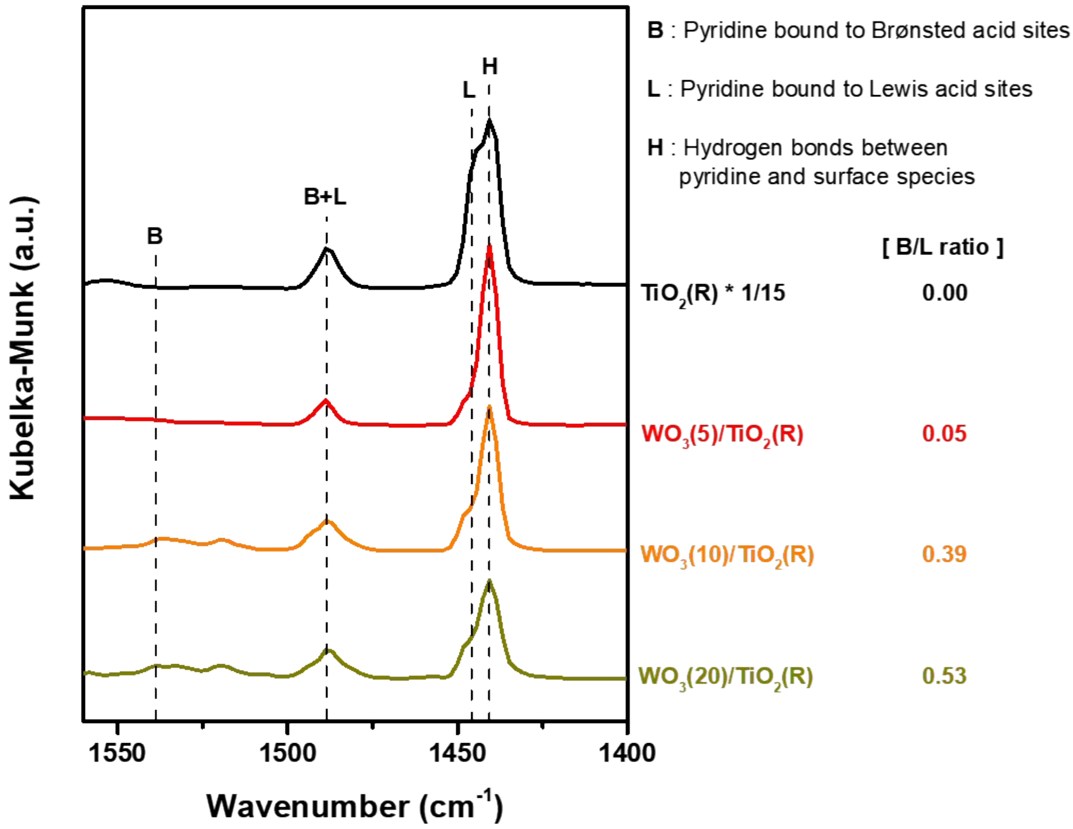

Figure S5. FTIR spectra of adsorbed pyridine over pristine TiO_2(R) and WO_3 loaded TiO_2(R) catalysts and corresponding B/L ratios. The deconvoluted peak areas of Lewis acid sites (1445 cm^{-1}) and Brønsted acid sites (1540 cm^{-1}) were used to quantify the B/L ratio, and molar extinction coefficients of 1.67 and 2.22 μmol^{-1} were used for Brønsted and Lewis acid sites (J. Catal., 141 (1993) 347), respectively.

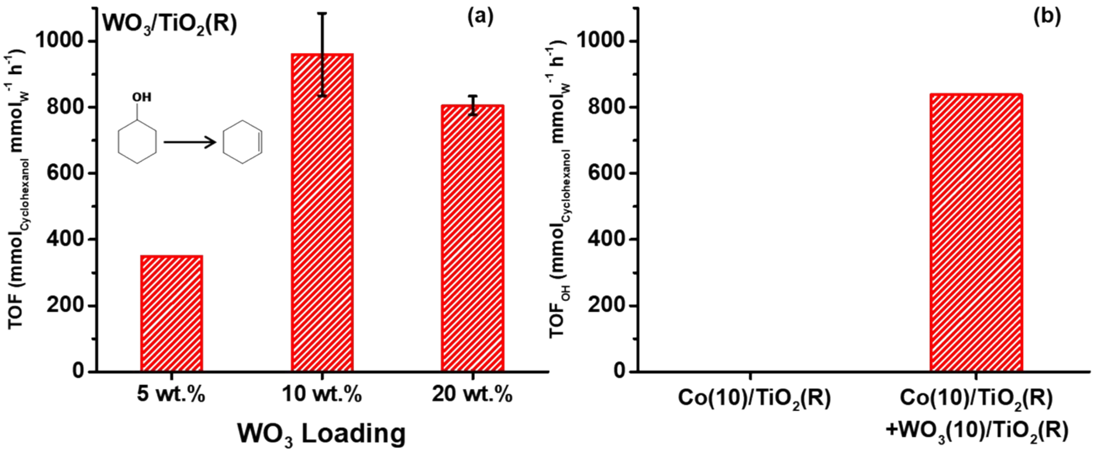

Figure S6. Turnover frequencies (TOFs) of (a) rutile TiO_2 catalysts with different WO_3 loadings and (b) Co loaded rutile TiO_2 and PM catalyst in cyclohexanol dehydration reaction (The TOF_{OH} of Co(10)/TiO_2(R) catalyst was calculated based on the amount of Co instead of W). Reaction condition: Cyclohexanol 2 mL, Catalyst 0.005 g each, *n*-octane 18 mL, 250 ℃, H_2 10 bar, 1 h.

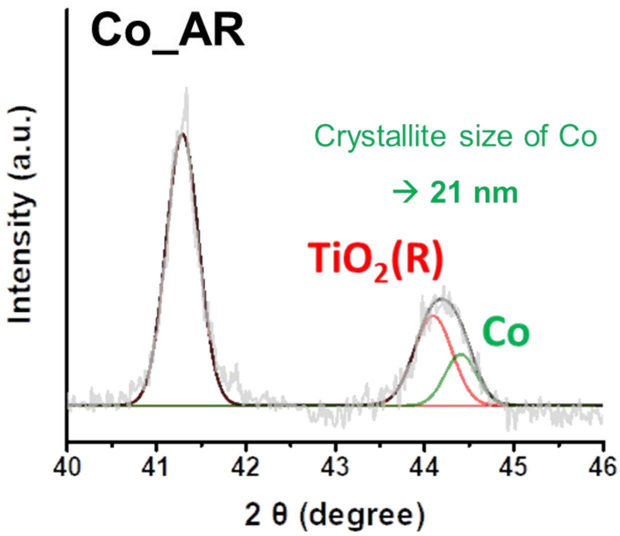

Figure S7. XRD pattern and crystallite size of metallic Co calculated from Scherrer equation of the Co_AR catalyst.

Figure S8. Photographs of fresh, AR, and AR_400C of WO_3(10)/TiO_2(R) catalyst.

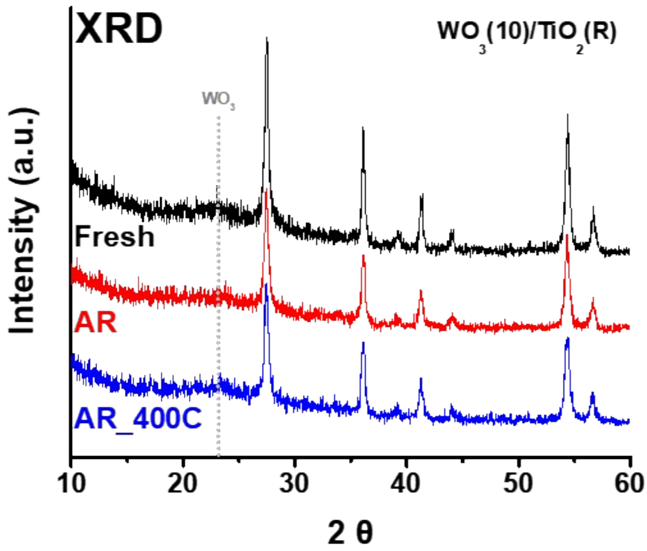

Figure S9. XRD patterns of fresh, AR, and AR_400C of WO_3(10)/TiO_2(R) catalyst.

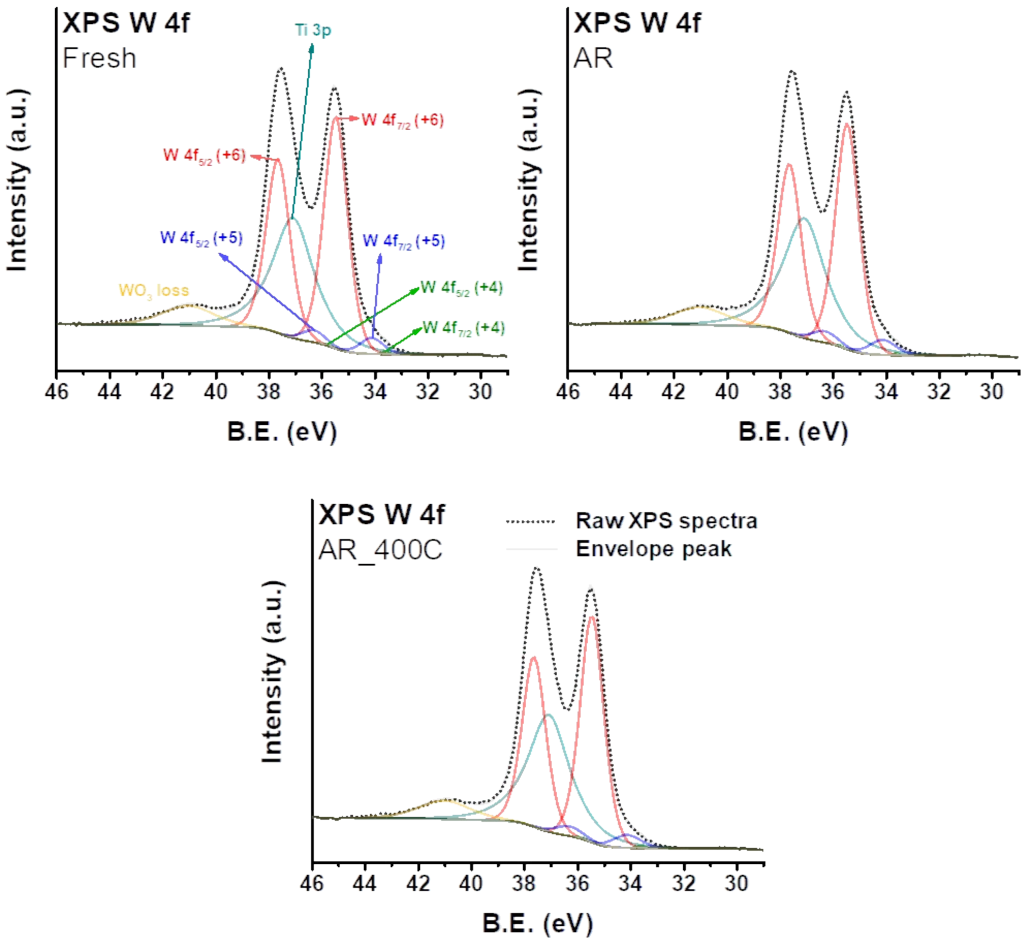

Figure S10. XPS W 4f spectra of fresh, AR, and AR_400C of WO_3(10)/TiO_2(R)_400C catalyst.

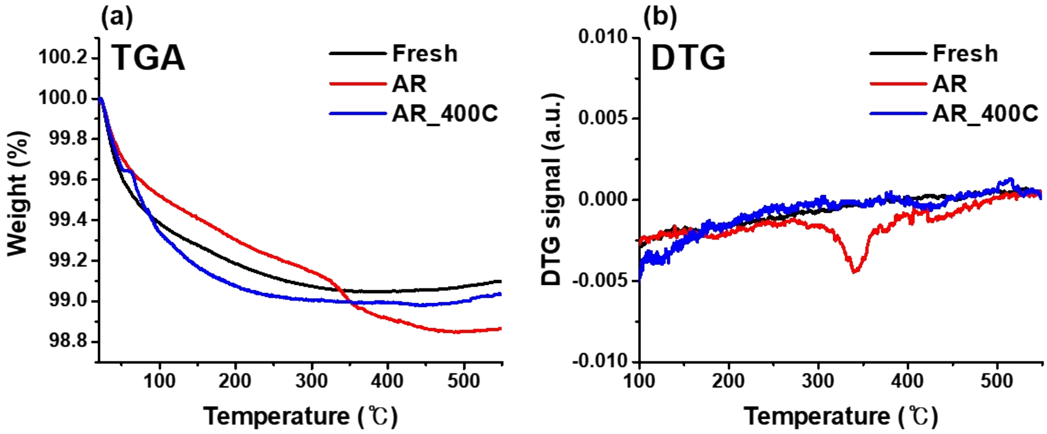

Figure S11. (a) TGA profiles and (b) DTG curves obtained from fresh, AR, and AR_400C of WO_3(10)/TiO_2(R) catalyst.

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