

Guaiacol to Aromatics: Efficient Transformation over In Situ-Generated Molybdenum and Tungsten Oxides

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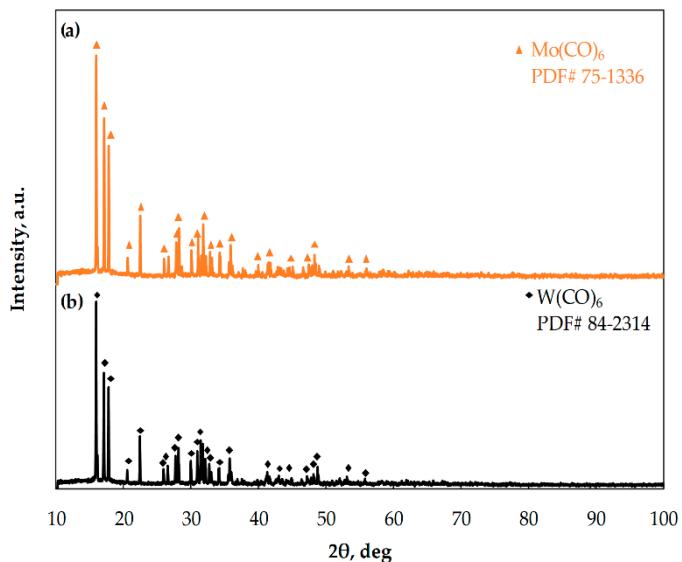


Figure S1. X-ray diffractograms of (a) molybdenum and (b) tungsten carbonyls – the precursors of the catalysts.

Table S1. Oxidation states (Mo 3d, W 4f regions) on the surface of the catalysts, identified by the XPS.

Temperature, °C	Catalyst	State	Region	Binding energy (eV)	Content (%)
120	MoO _x	Mo ⁵⁺	3d _{5/2}	231.8	6
			3d _{3/2}	234.8	4
		Mo ⁶⁺	3d _{5/2}	232.5	48
			3d _{3/2}	235.7	42
	WO _x	W ⁴⁺	4f _{7/2}	34.7	2
			4f _{5/2}	35.5	2
		W ⁶⁺	4f _{7/2}	35.9	50
			4f _{5/2}	38.0	46
240	MoO _x	Mo ⁴⁺	3d _{5/2}	230.5	3
			3d _{3/2}	231.9	2
		Mo ⁵⁺	3d _{5/2}	230.6	20
			3d _{3/2}	234.0	12
	WO _x	Mo ⁶⁺	3d _{5/2}	232.7	34
			3d _{3/2}	235.5	30
		W ⁴⁺	4f _{7/2}	34.7	2
			4f _{5/2}	35.3	2
360	MoO _x	W ⁶⁺	4f _{7/2}	35.7	49
			4f _{5/2}	37.8	47
		Mo ⁴⁺	3d _{5/2}	230.5	12
			3d _{3/2}	232.3	7
	WO _x	Mo ⁶⁺	3d _{5/2}	232.8	47
			3d _{3/2}	235.5	34
		W ⁴⁺	4f _{7/2}	34.3	5
			4f _{5/2}	35.4	4
	W ⁶⁺	W ⁶⁺	4f _{7/2}	35.9	47
			4f _{5/2}	37.8	43

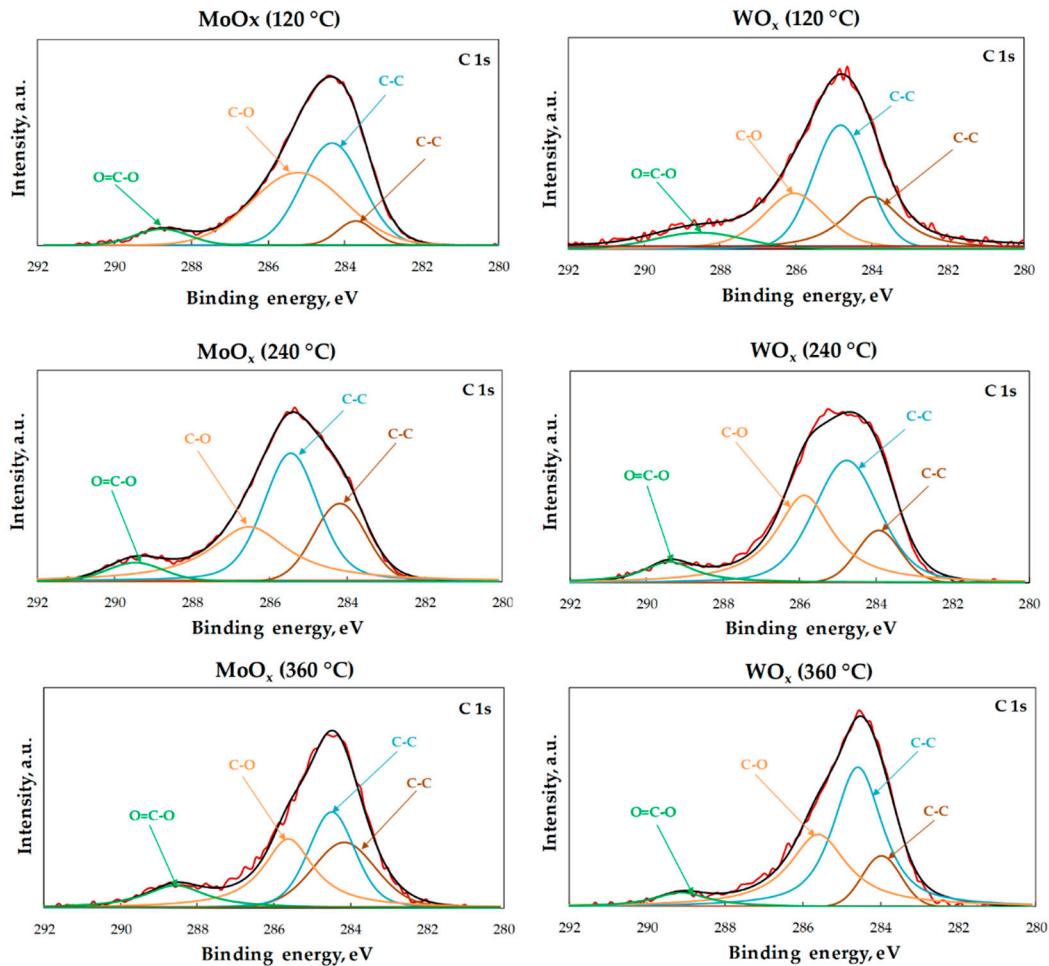


Figure S2. The XPS spectra in C 1s region of the catalysts obtained at different temperatures.

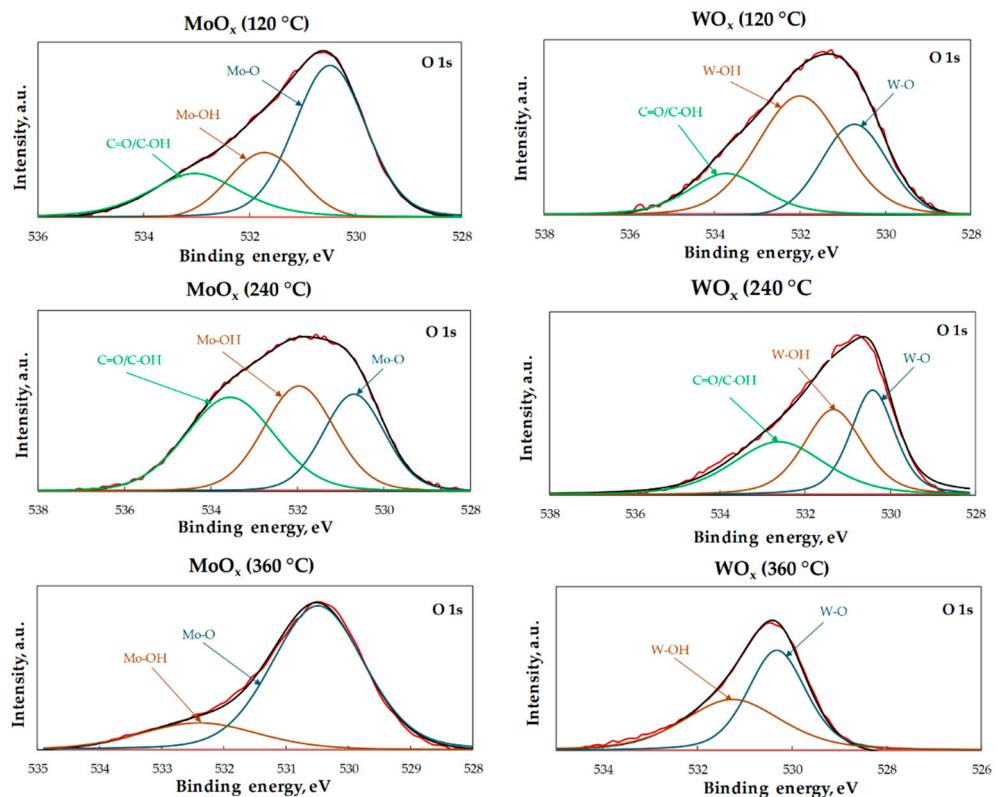


Figure S3. The XPS spectra in O 1s region of the catalysts obtained at different temperatures.

Table S2. Oxidation states (C 1s region) on the surface of the catalysts, identified by the XPS.

Temperature, °C	Catalyst	State	Binding energy (eV)	Content (%)
120	MoO _x	C-C	283.7	6
		C-C	284.3	42
		C-O	285.2	6
		O=C-O	288.8	46
240	WO _x	C-C	284.0	25
		C-C	284.8	41
		C-O	286.1	25
		O=C-O	288.5	9
360	MoO _x	C-C	284.2	21
		C-C	285.5	41
		C-O	286.5	32
		O=C-O	289.5	6
240	WO _x	C-C	283.9	12
		C-C	284.8	44
		C-O	285.9	36
		O=C-O	289.4	8
360	MoO _x	C-C	284.2	27
		C-C	284.5	30
		C-O	285.6	31
		O=C-O	288.6	12
360	WO _x	C-C	284.0	11
		C-C	284.6	49
		C-O	285.6	34
		O=C-O	289.1	6

Table S3. Oxidation states (O 1s region) on the surface of the catalysts, identified by the XPS.

Temperature, °C	Catalyst	State	Binding energy (eV)	Content (%)
120	MoO _x	Mo-O	530.5	55
		Mo-OH	531.7	22
		C=O/C-OH	533.0	23
	WO _x	W-O	530.7	29
		W-OH	532.0	53
		C=O/C-OH	533.7	18
240	MoO _x	Mo-O	530.7	28
		Mo-OH	532.0	34
		C=O/C-OH	533.6	38
	WO _x	W-O	530.4	32
		W-OH	531.3	35
		C=O/C-OH	532.6	34
360	MoO _x	Mo-O	530.5	80
		Mo-OH	532.4	20
	WO _x	W-O	530.5	53
		W-OH	531.7	47

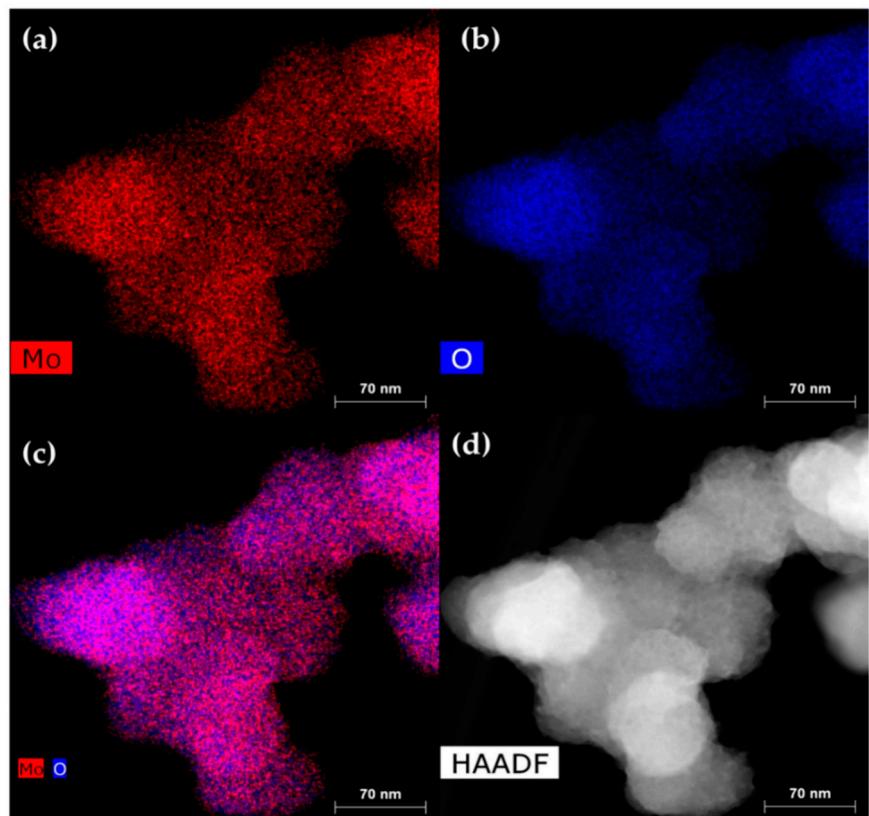


Figure S4. The elemental mapping of MoO_x . Maps are assigned to (a) molybdenum, (b) oxygen, (c) molybdenum and oxygen, and (d) the HAADF image.

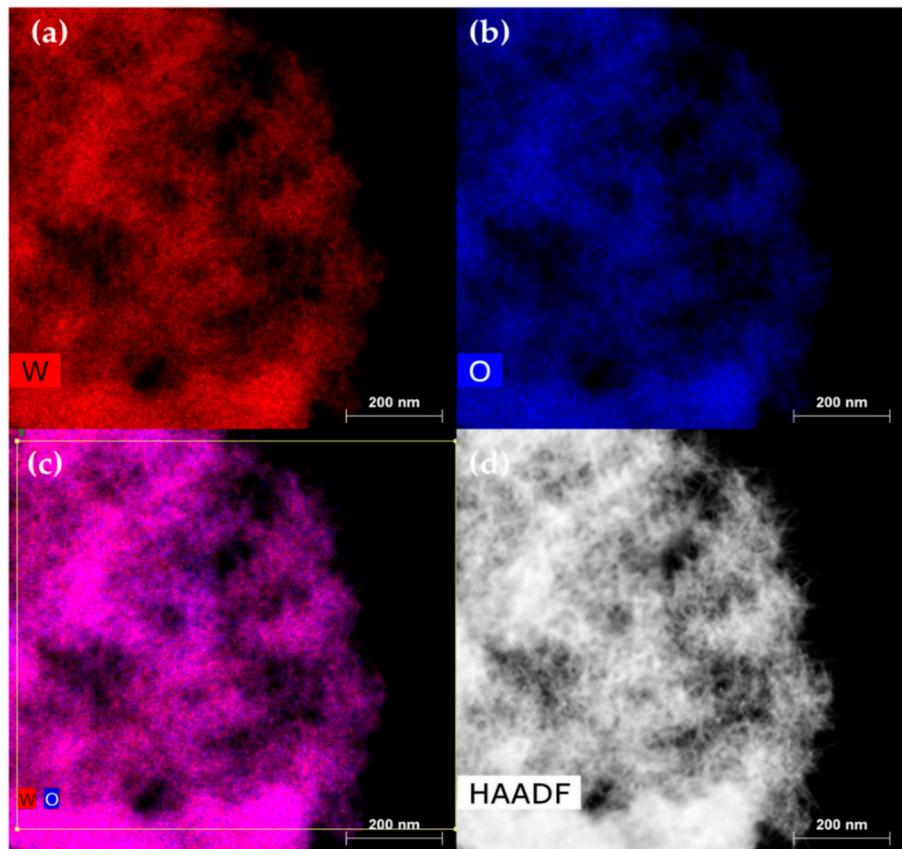


Figure S5. The elemental mapping of WO_x . Maps are assigned to (a) tungsten, (b) oxygen, (c) tungsten and oxygen, and (d) the HAADF image.

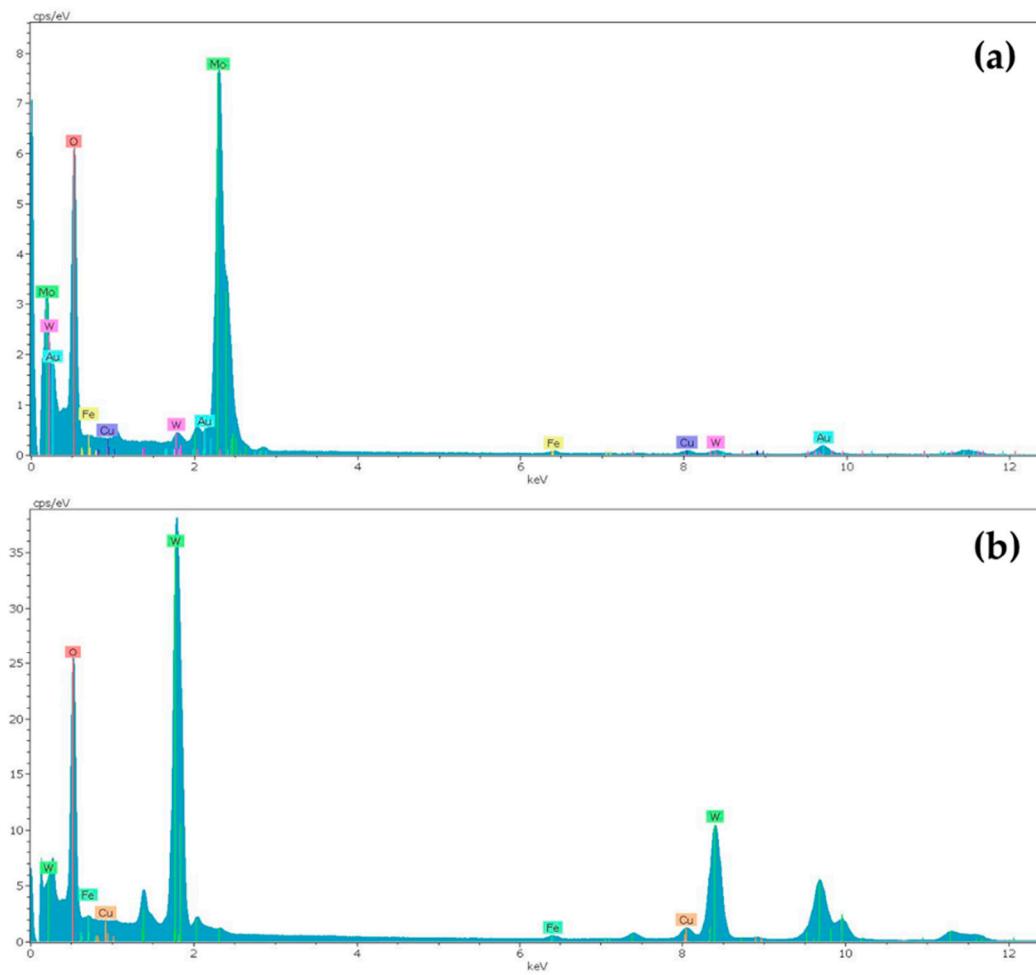


Figure S6. The EDX spectra of the catalysts: (a) MoO_x (b) WO_x .

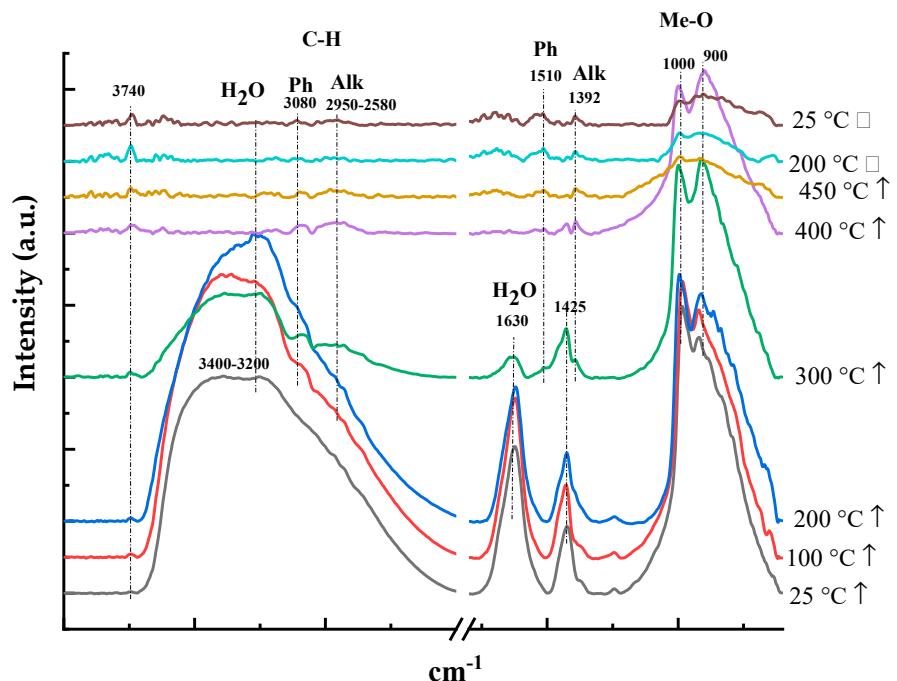


Figure S7. The DRIFT spectra of MoO_x in a range of 4000–600 cm^{-1} .

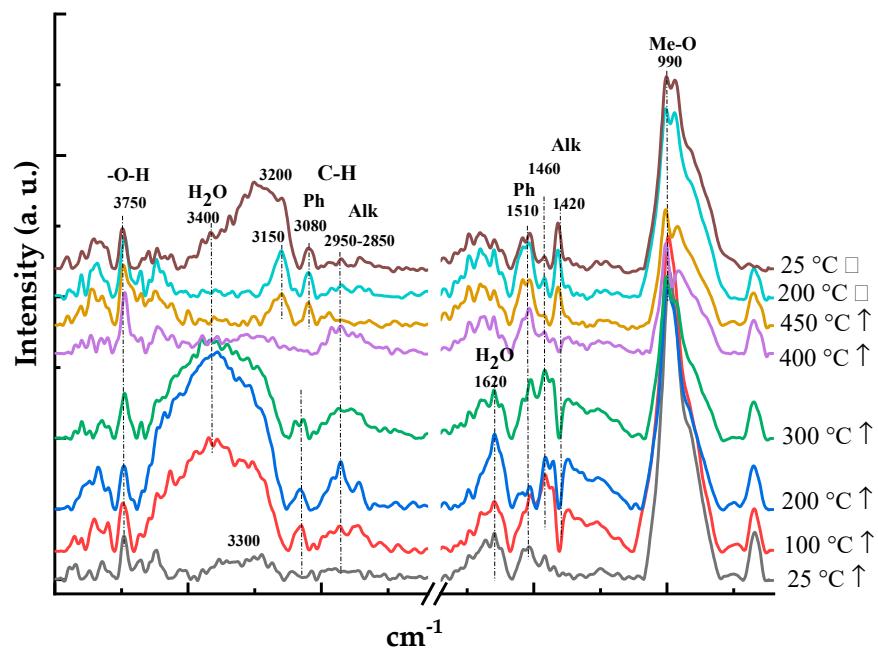


Figure S8. The DRIFT spectra of WO_x in a range of 4000–600 cm^{-1} .

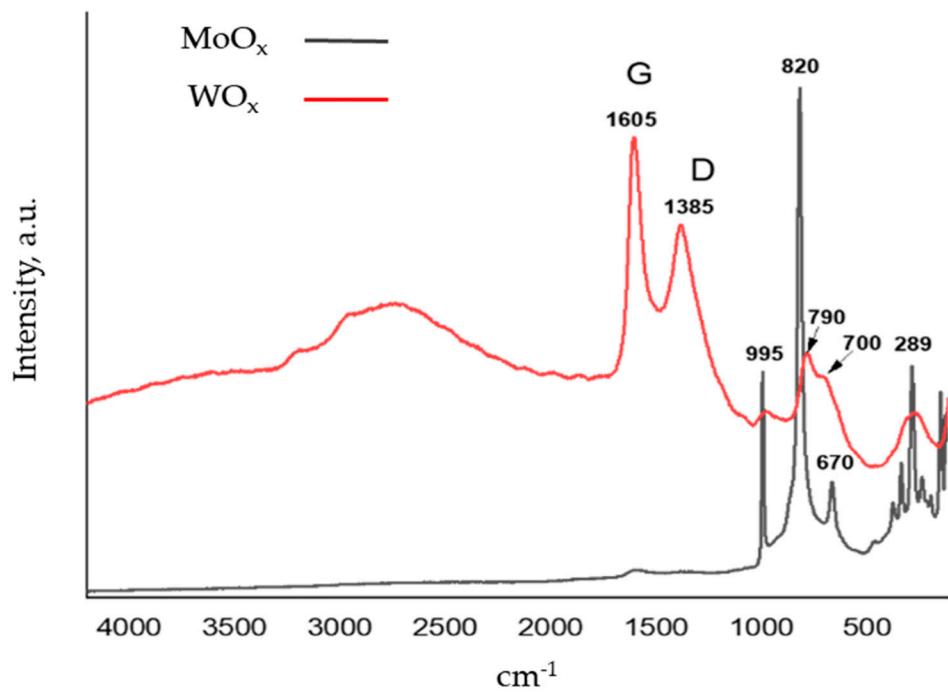


Figure S9. The Raman spectra of MoO_x and WO_x .

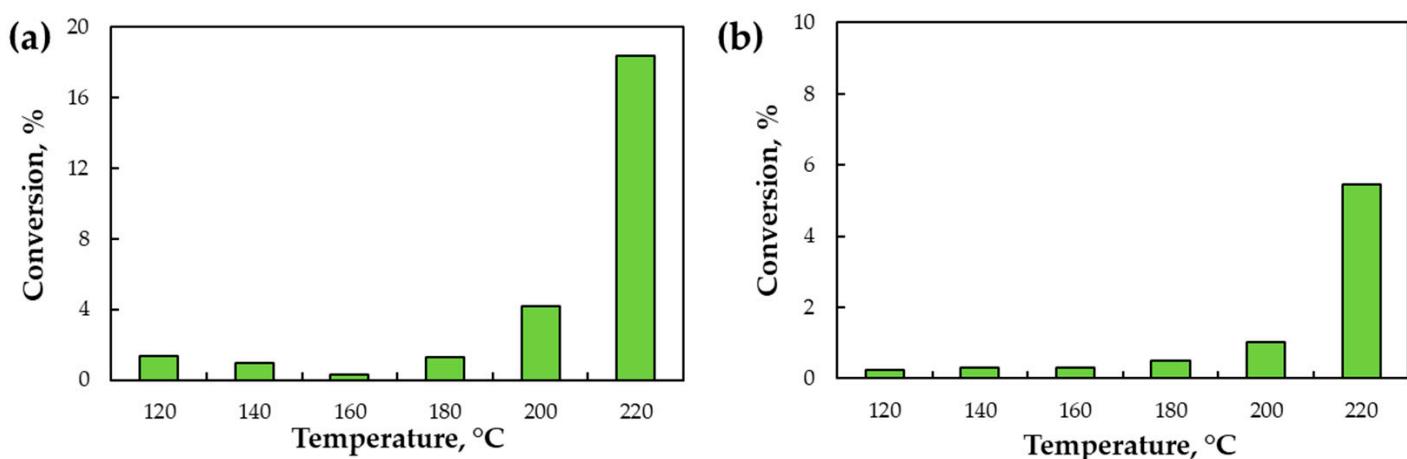


Figure S10. The results of the guaiacol HDO over in situ-formed (a) MoO_x (b) WO_x. Reaction conditions: 120–220 °C, 5 MPa H₂, 6 h; 10 wt. % guaiacol in toluene solution.

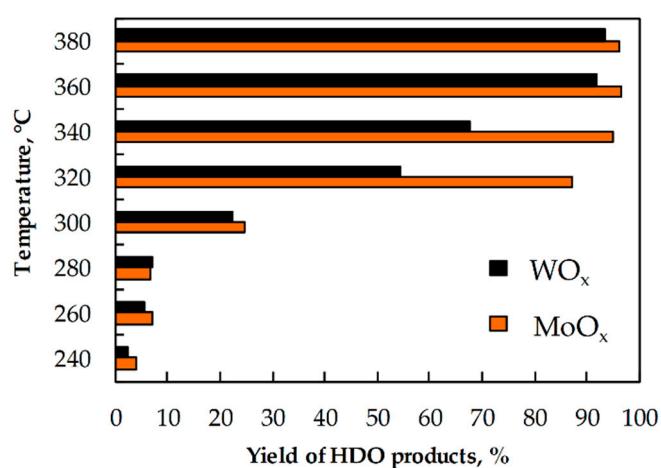


Figure S11. The yield of HDO products over in situ-formed MoO_x and WO_x. Reaction conditions: 240–380 °C, 5 MPa H₂, 6 h; 10 wt. % guaiacol in toluene solution.

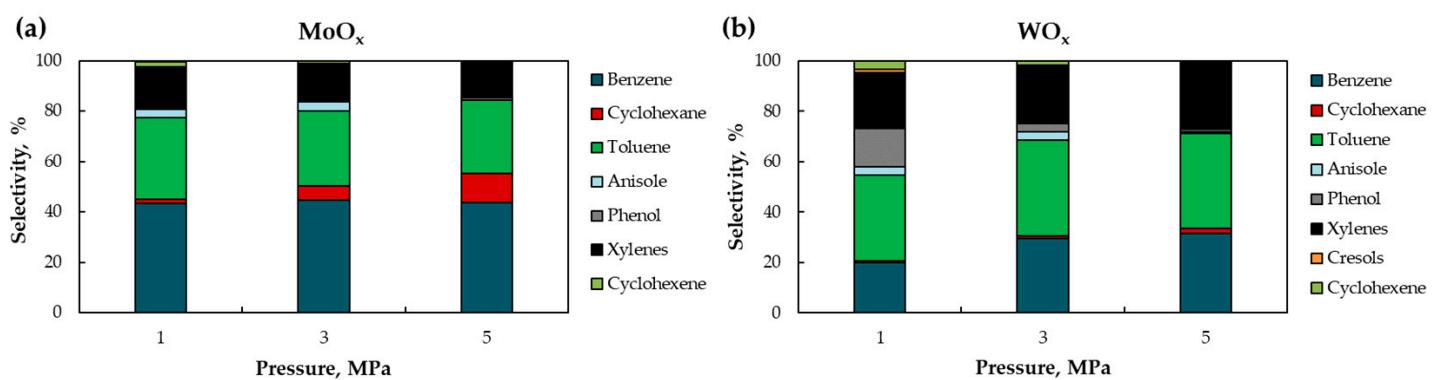


Figure S12. The results of guaiacol HDO over in situ-formed (a) MoO_x (b) WO_x. Reaction conditions: 380 °C, 1–5 MPa H₂, 6 h; 10 wt. % guaiacol in dodecane solution.

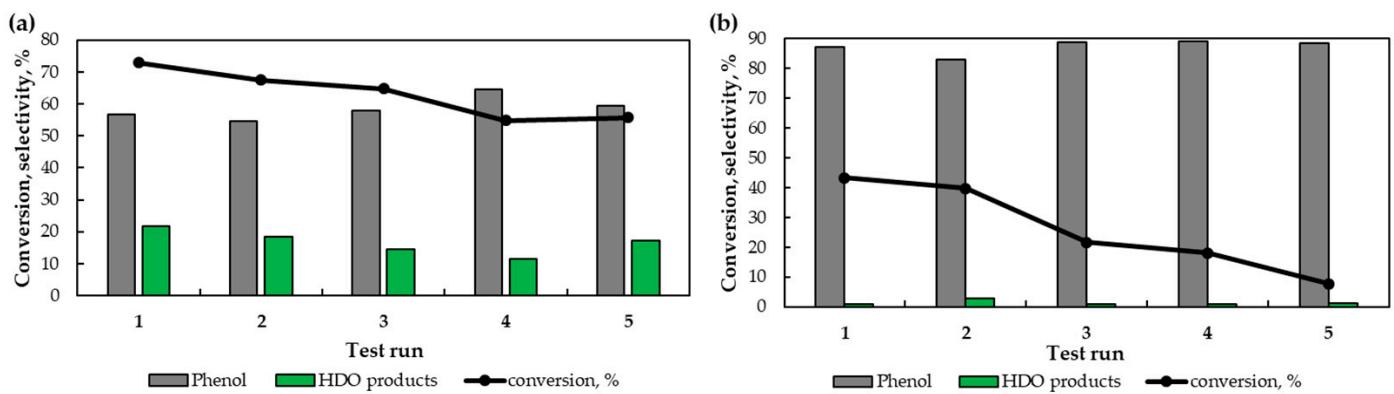


Figure S13. The recycling test runs of (a) MoO_x (b) WO_x. Reaction conditions: 320 °C, 5 MPa H₂, 1 h; 10 wt. % guaiacol in dodecane solution.