Supporting Information

Experimental and Theoretical Insights into the Active Sites on WO_x/Pt(111) Surfaces for Dehydrogenation and Dehydration Reactions

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1. Method for Estimating Tungsten Coverage on Pt(111)

Shown below is the method we used to estimate the W coverages on Pt(111). The W coverages estimated from the peak areas of CO TPD experiments were correlated to the measured AES peak-to-peak ratios of W (38 eV) and Pt (168 eV). It should be pointed out that the accurate sensitivity factor for the W (38 eV) peak is difficult to obtain, and that the Pt substrate is screened by the WOx overlayer. Therefore, the peak-to-peak ratios instead of the atomic ratios were used to correlate with the peak areas from CO TPD experiments. The data was fitted by a linear equation, which was used in later experiments to estimate W coverages from AES measurements.

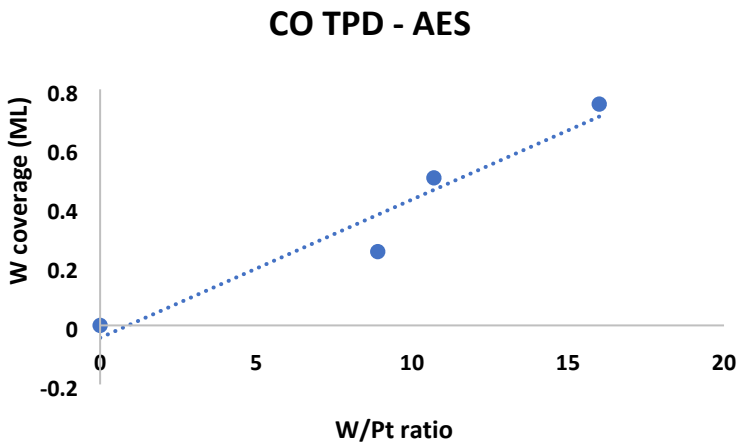

Figure S1. Correlation of W(38 eV)/Pt(168 eV) peak-to-peak ratios with W coverages estimated from the peak areas of CO TPD experiments.

Table S1. W(38 eV)/Pt(168 eV) AES ratios at WO_x coverages estimated by CO TPD experiments.

WO_x coverage (ML)	**W (38 eV)/Pt (168 eV) ratio**
0.00	0.00
0.25	8.90
0.50	10.70
0.75	16.00

2. IPA Desorption of Surfaces Modified by Different Coverages of Tungsten

Shown in Figure S2 is the desorption spectra of IPA (45 amu). Two types of IPA desorption peaks were observed. For surfaces modified with WO_x, the peaks centered at 161 K were contributed from weakly bonded IPA, while the peaks centered at 206 K were contributed from strongly bonded IPA. For Pt(111), the strongly bonded peak appeared at 223 K. The fraction of IPA reacted is shown in Table S2. The quantification results were based on the desorption peaks of strongly bonded IPA. Clearly, on surfaces with 0.6 ML W or less, most of the IPA (greater than 85 %) desorbed. As the W coverage was increased, more IPA underwent reactions instead of desorbing. On above 1 ML W/Pt(111), only 21% of IPA desorbed, while 79% reacted.

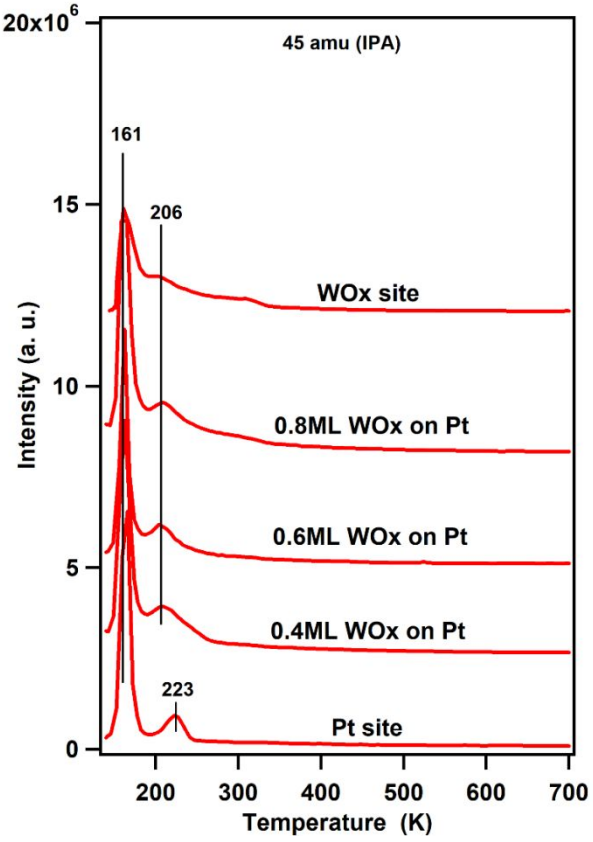

Figure S2. Desorption spectra of IPA (45 amu) after an exposure of 5 L IPA on Pt(111) surfaces modified by different coverages of WO_x.

Table S2. Activities of Different Reaction Pathways and IPA Desorption (Molecules per Metal Atom) on Corresponding Surfaces with the Percentage of IPA Desorbed Shown in Parenthesis

WO_x coverage	Dehydrogenation	Dehydration	IPA desorption	% IPA reacted
0 ML	0.011	0.000	0.208 (95%)	5%
0.4 ML	0.006	0.002	0.048 (86%)	14%
0.6 ML	0.000	0.002	0.023 (93%)	7%
0.8 ML	0.000	0.009	0.012 (59%)	41%
Above 1 ML	0.000	0.011	0.003 (21%)	79%

3. Additional TPD Figures after Exposing the Corresponding Surfaces to IPA

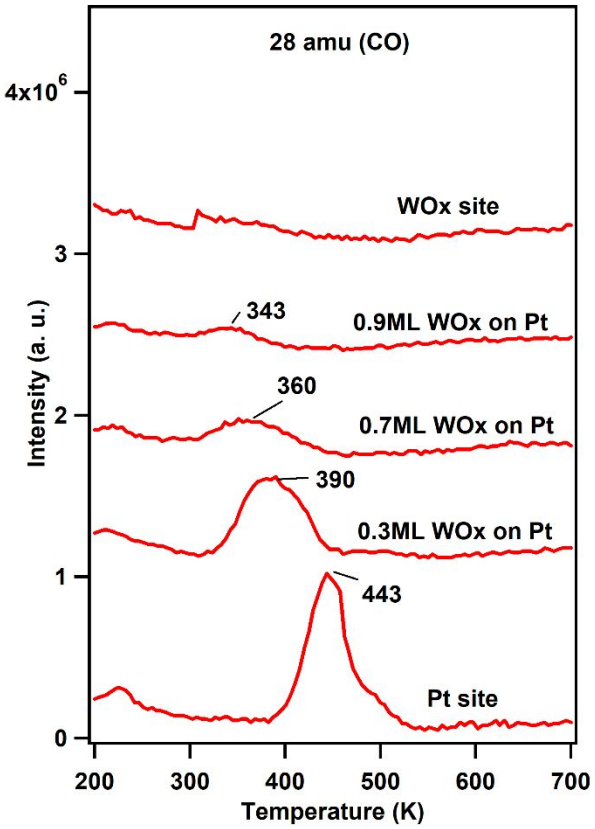

Figure S3. Desorption spectra of CO (28 amu) from Pt(111) surfaces modified by different coverages of WO_x after an exposure to 5L IPA.

4. W/Pt, O/Pt, O/W AES Peak-to-Peak Ratios as a Function of WO_x Coverage

Table S3. W/Pt, O/Pt, O/W AES Peak-to-Peak Ratios as a Function of WO_x Coverage

WO_x coverage	W/Pt	O/Pt	O/W
0ML	0.00	0.00	N/A
0.4ML	10.5	6.00	0.57
0.6ML	13.3	10.0	0.75
0.8ML	17.5	10.8	0.62
Above ML	28.6	17.1	0.60

5. Quantification Results of CO TPD and IRRA Spectra of CO Adsorption on Pt(111) and As-synthesized WO_x/Pt(111) Surfaces

Table S4. CO Activity (Molecules per Metal Atom) as a Function of WO_x Coverage

WO_x coverage	CO activity
0.00 ML	0.445
0.75 ML	0.334
0.50 ML	0.220
0.00 ML	0.000

Show in Figure S4 below is the CO IRRA spectra on the Pt(111) and as-synthesized WO_x/Pt(111) surfaces. The CO vibrational frequency on WO_x/Pt(111) was 2102 cm^{-1}, as compared to 2083 cm^{-1} on Pt(111). This indicated that CO bonded to WO_x/Pt(111) less strongly than Pt(111), consistent with the CO TPD data shown in the Manuscript (Figure 1). This also suggested that WO_x modified Pt(111) electronically.

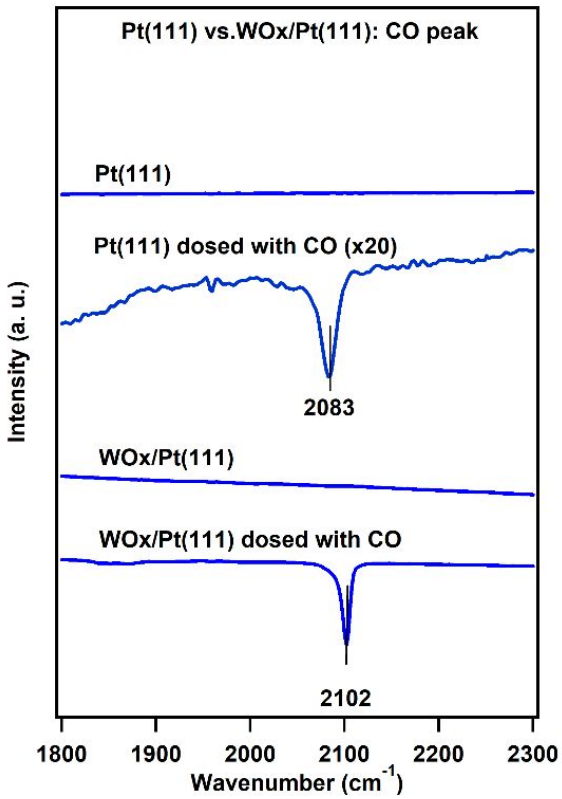

Figure S4. IRRA spectra of CO adsorption on Pt(111) and as-synthesized WO_x/Pt(111).

6. Quantification Results for H_2 and H_2O Desorption after Exposing the Corresponding Surfaces to IPA

The quantification results are shown in Table S5. On surfaces with less than 0.6 ML WO_x, H_2 that desorbed came from both the H_2 produced by the dehydrogenation reaction, as well as the background H_2 adsorbed on the surface. When there were more than 0.6 ML WO_x on the surface, H_2 could not adsorb. In contrast, H_2O desorption followed the same trend as that of the dehydration pathway (propylene desorption), because H_2O was produced by the dehydration reaction.

Table S5. Activities (Molecules per Metal Atom) of Dehydrogenation, Dehydration, H_2 Desorption, and H_2O Desorption

WO_x coverage	Dehydrogenation	Dehydration	**H_2 Desorption**	**H_2O Desorption**
0 ML	0.011	0.000	0.106	0.000
0.4 ML	0.006	0.002	0.023	0.002
0.6 ML	0.000	0.002	0.006	0.002
0.8 ML	0.000	0.009	0.000	0.007
Above 1 ML	0.000	0.011	0.000	0.011