

## Supplementary Information

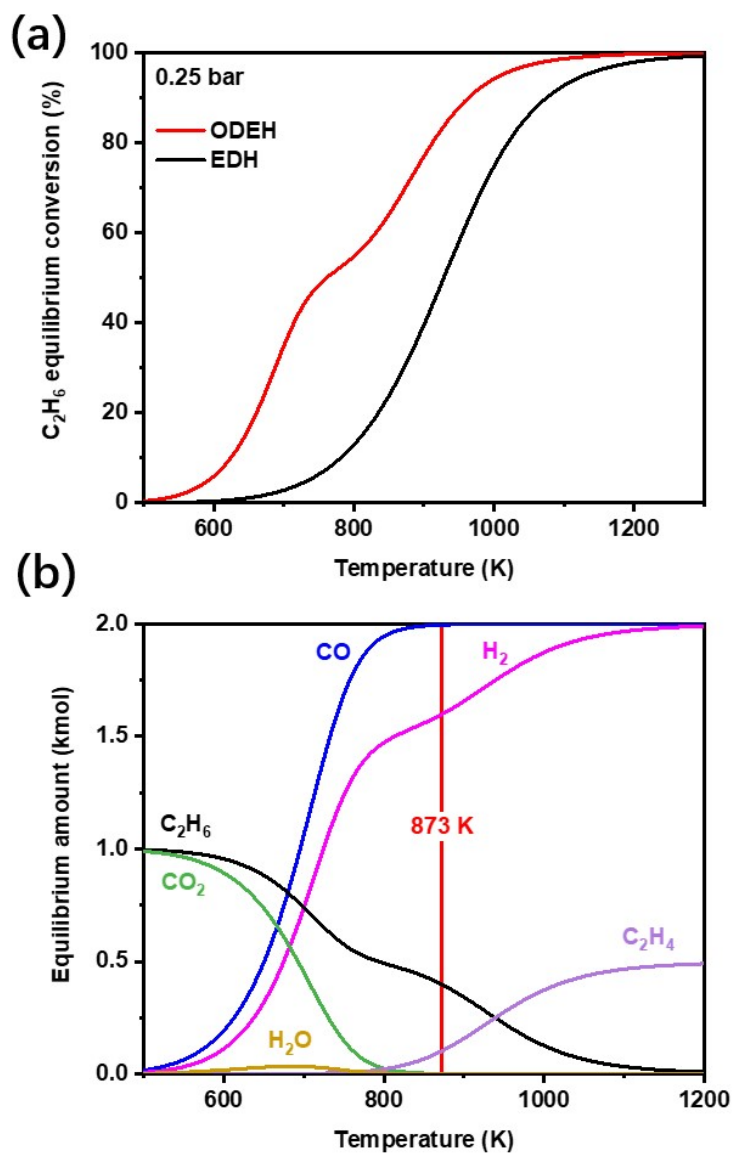
### **A stable Pt modified cobalt tungstate catalyst for CO<sub>2</sub>-assisted oxidative dehydrogenation of ethane**

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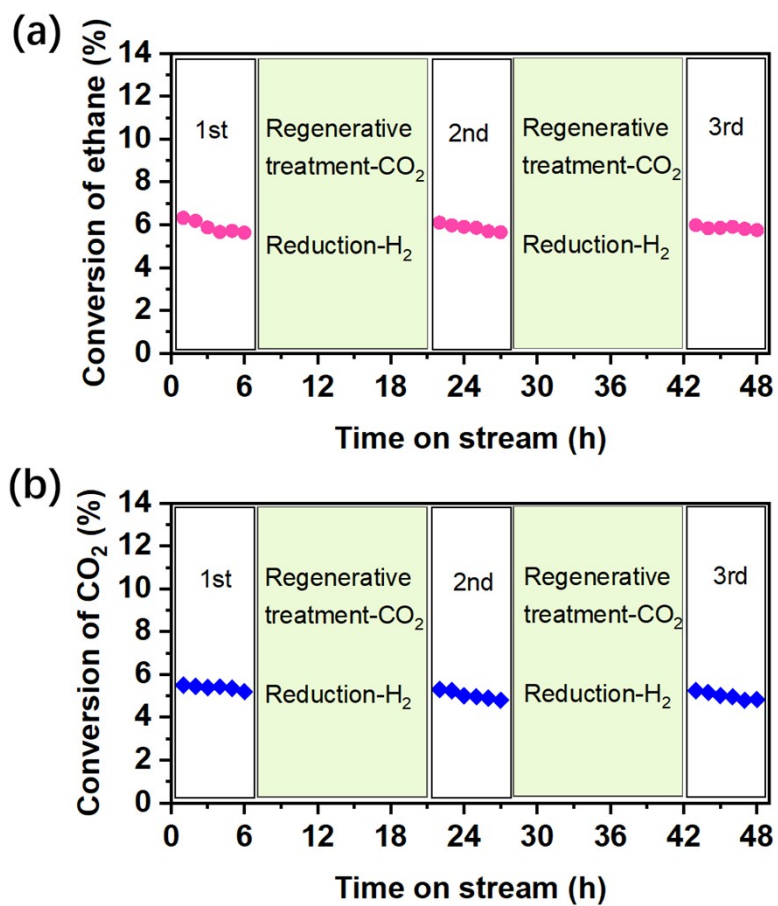
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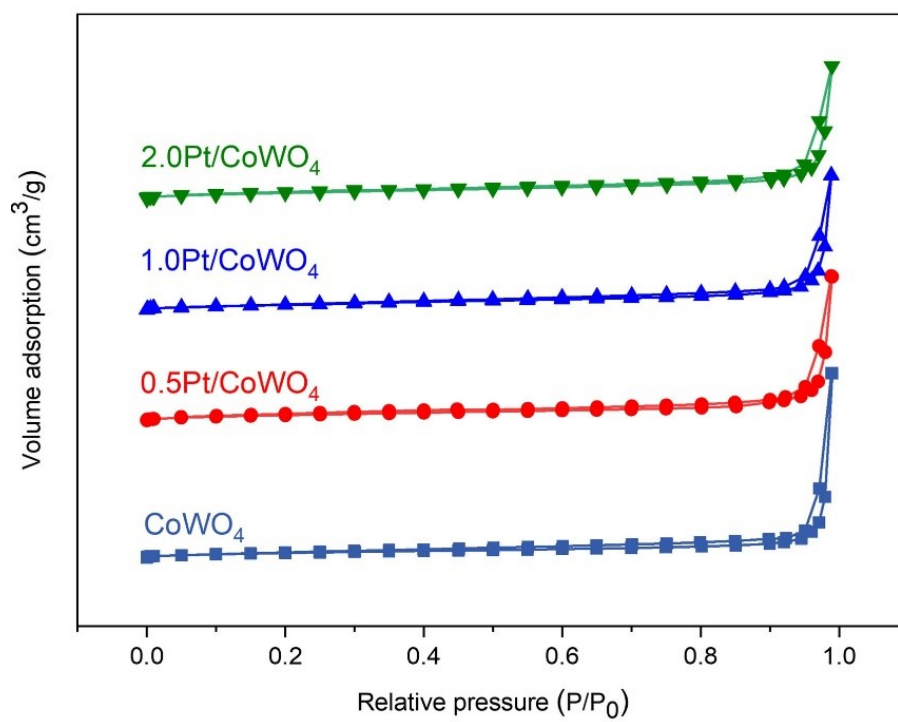
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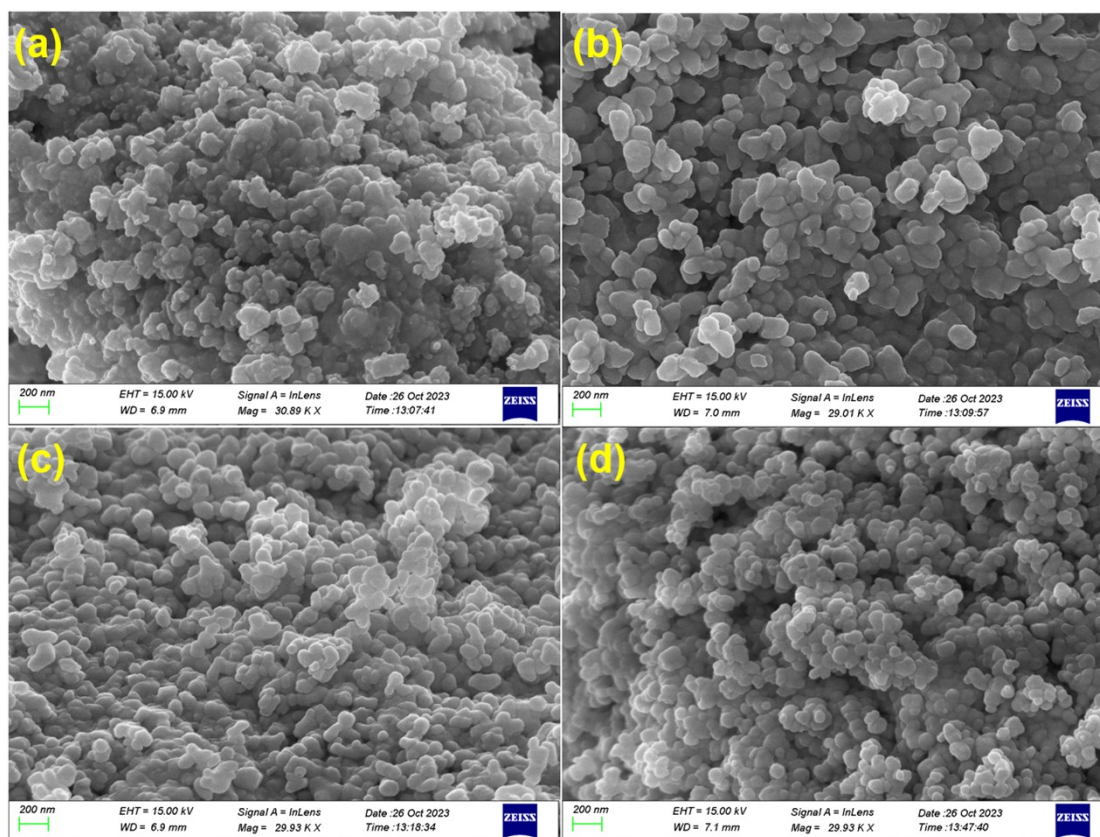
**Fig S1.** Thermodynamic equilibrium plots. Equilibrium calculations were performed through HSC Chemistry 6.0 software, which utilizes a Gibbs free energy minimization algorithm. (a) product amounts for  $CO_2+C_2H_6$  system. (b)  $C_2H_6$  equilibrium conversion with 25 vol% ethane for  $CO_2$ -ODEH and direct dehydrogenation of ethane.



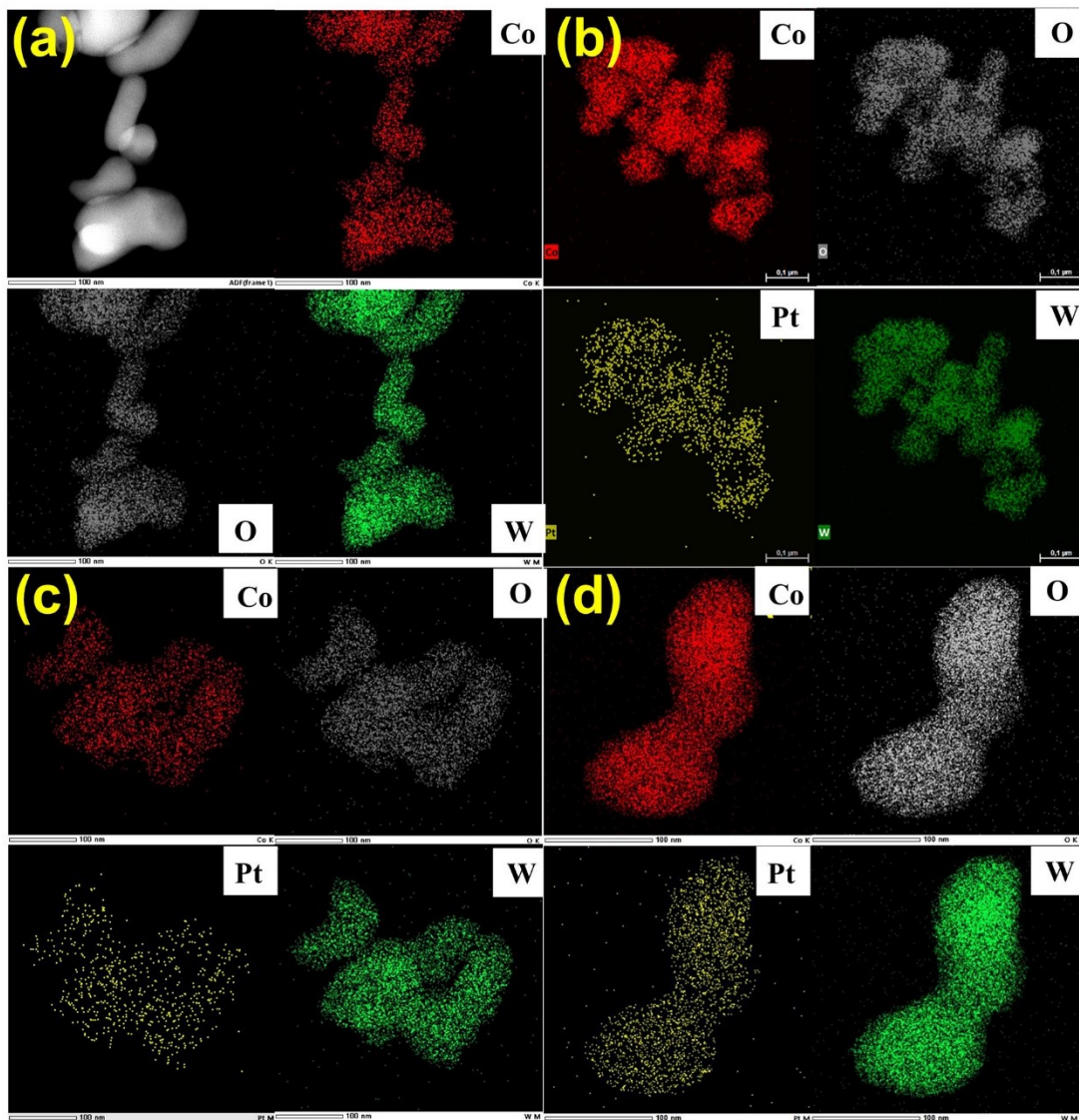
**Fig S2.** Catalytic stability of 1.0Pt/CoWO<sub>4</sub> in CO<sub>2</sub>-ODH after regeneration in CO<sub>2</sub> atmosphere.



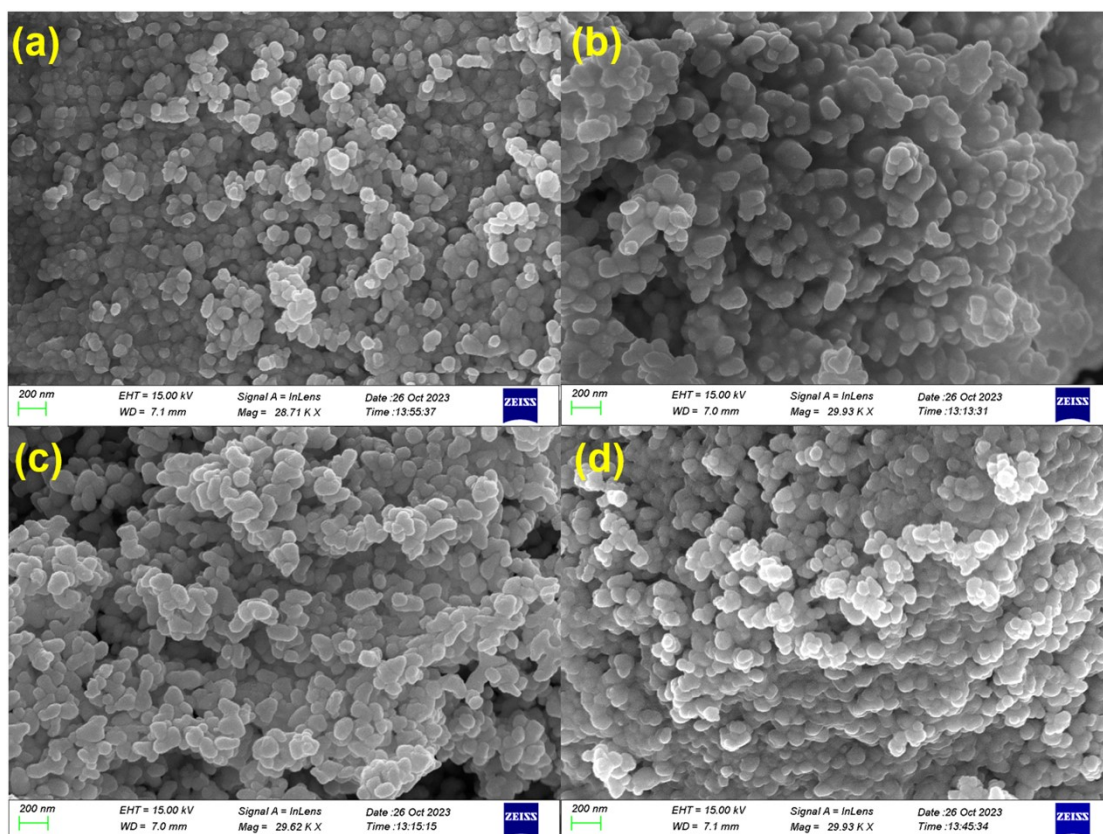
**Fig S3.** N<sub>2</sub> adsorption-desorption isotherm of different catalysts.



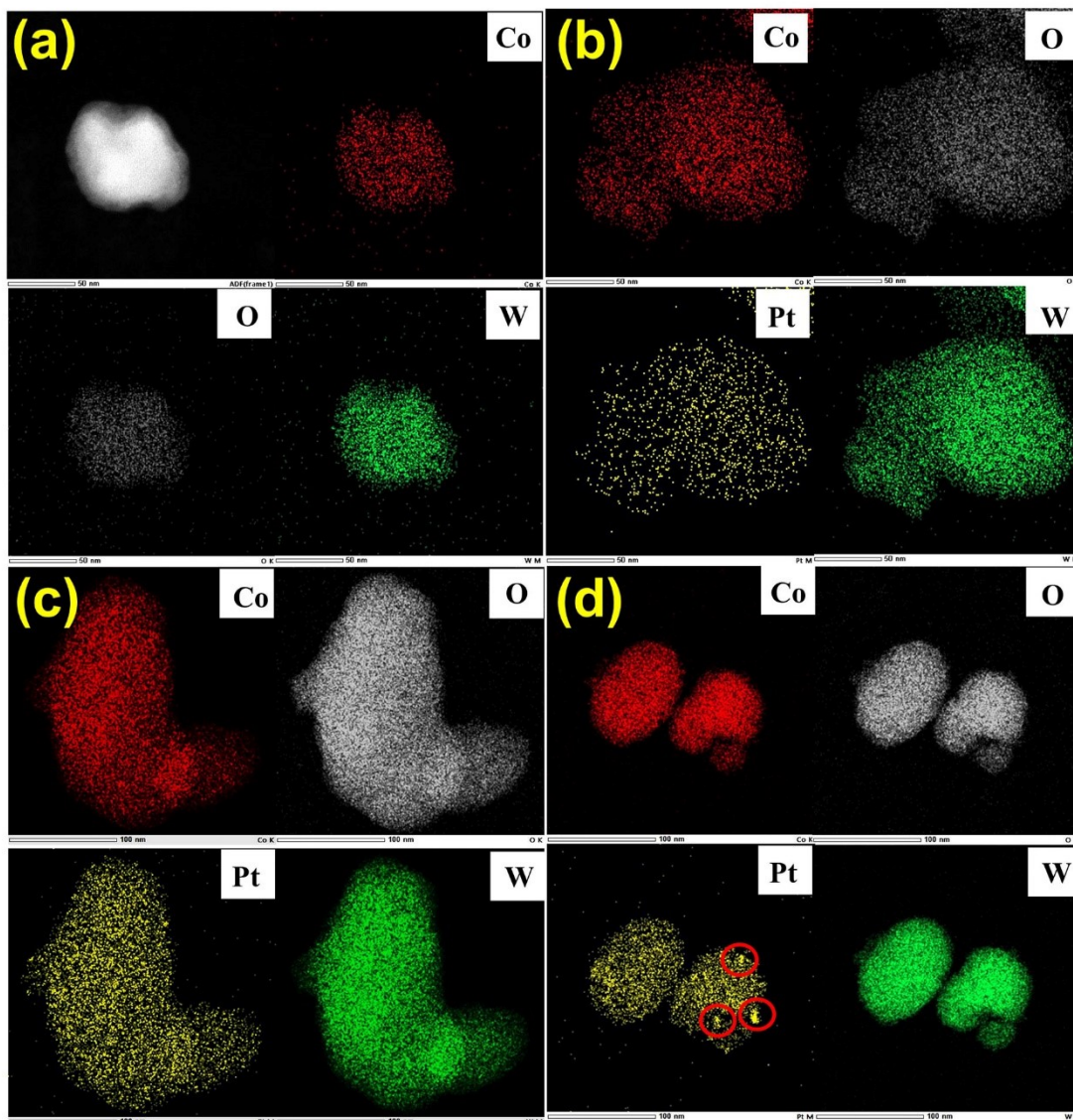
**Fig S4.** SEM images of reduced catalysts before reaction. (a)  $\text{CoWO}_4$ , (b)  $0.5\text{Pt}/\text{CoWO}_4$ , (c)  $1.0\text{Pt}/\text{CoWO}_4$  and (d)  $2.0\text{Pt}/\text{CoWO}_4$  samples.



**Fig S5.** Elemental mappings of reduced catalysts before reaction. (a)  $\text{CoWO}_4$ , (b)  $0.5\text{Pt}/\text{CoWO}_4$ , (c)  $1.0\text{Pt}/\text{CoWO}_4$  and (d)  $2.0\text{Pt}/\text{CoWO}_4$  samples.

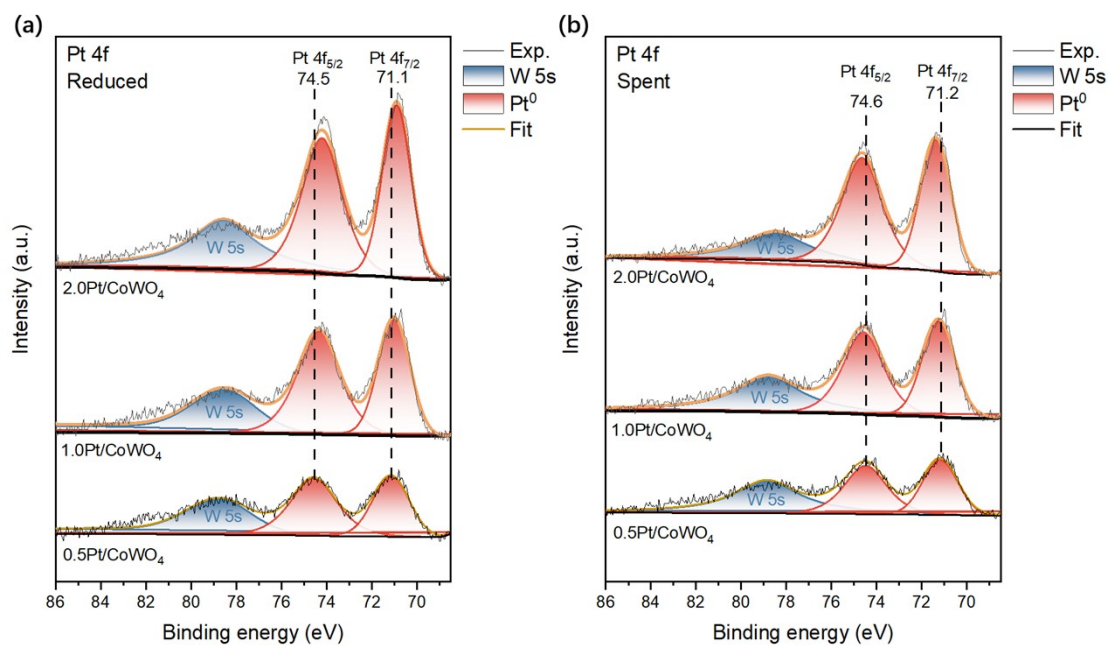


**Fig S6.** SEM images of spent catalysts after CO<sub>2</sub>-ODH reaction. (a) CoWO<sub>4</sub>, (b) 0.5Pt/CoWO<sub>4</sub>, (c) 1.0Pt/CoWO<sub>4</sub> and (d) 2.0Pt/CoWO<sub>4</sub> samples.

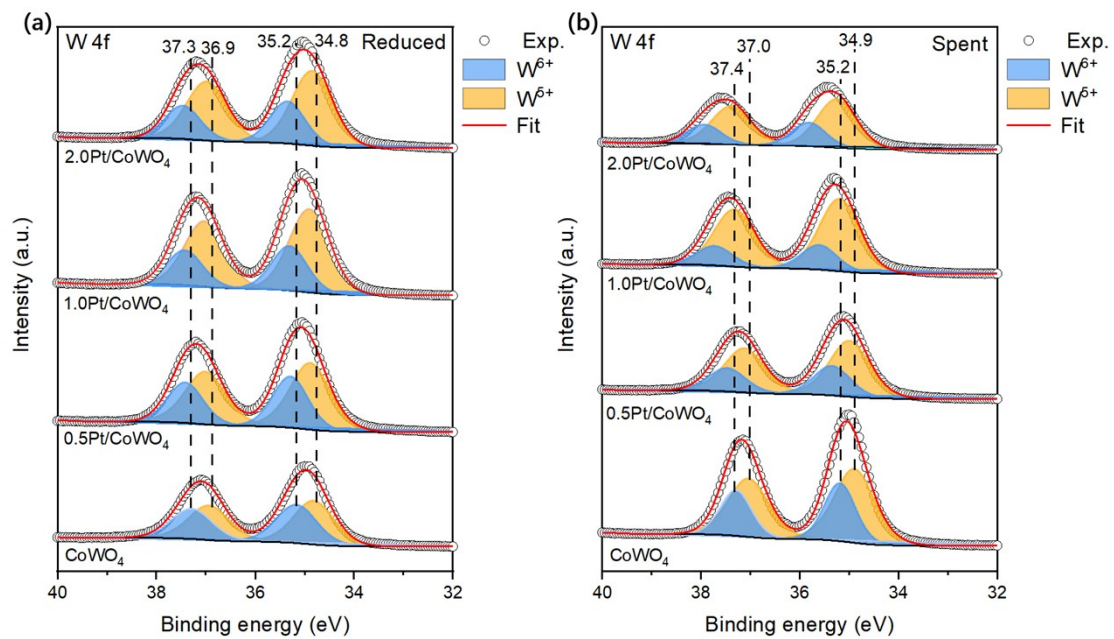


**Fig S7.** Elemental mappings of spent catalysts after  $\text{CO}_2$ -ODH reaction. (a)  $\text{CoWO}_4$ , (b)  $0.5\text{Pt}/\text{CoWO}_4$ , (c)  $1.0\text{Pt}/\text{CoWO}_4$  and (d)  $2.0\text{Pt}/\text{CoWO}_4$  samples.

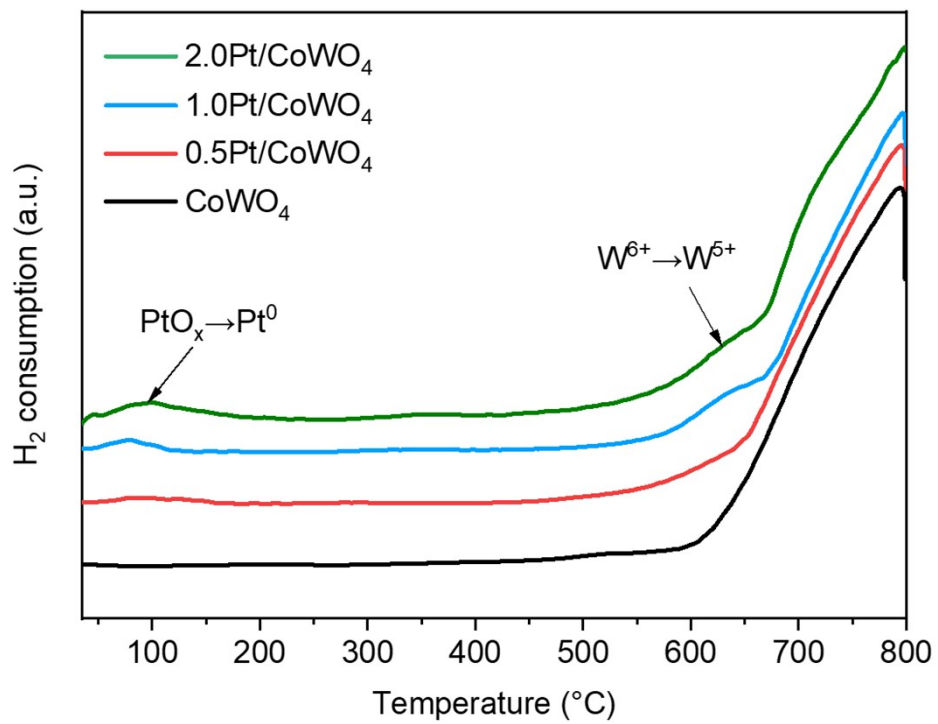




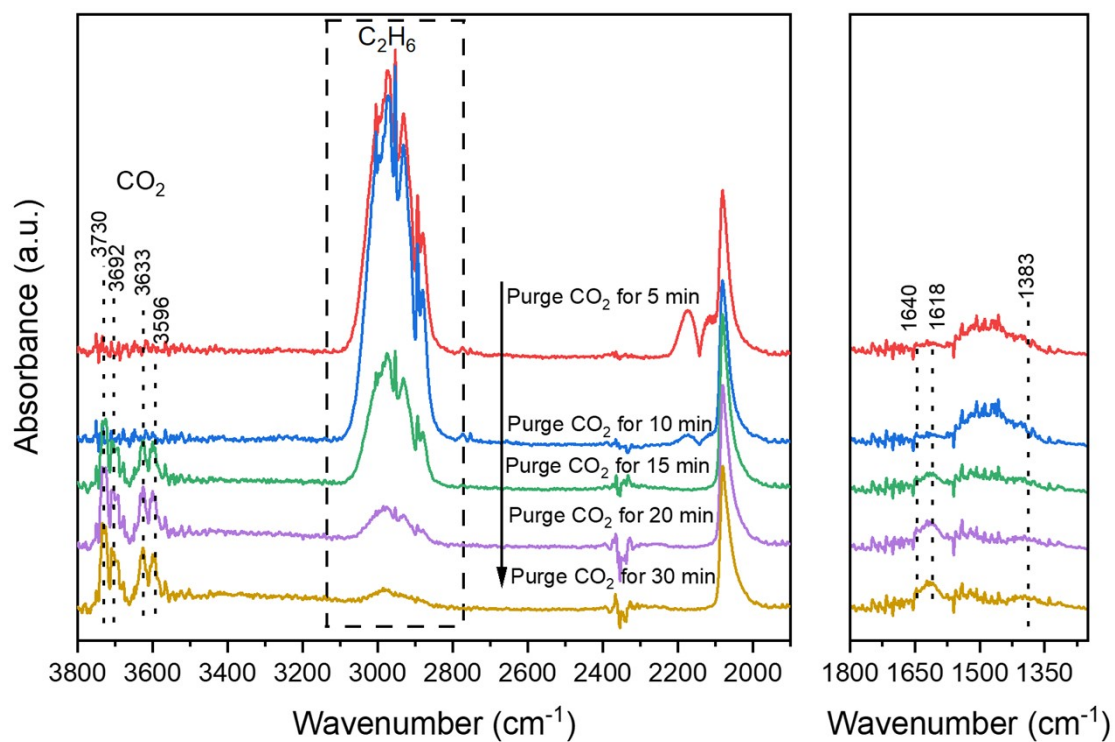
**Fig S8.** The deconvoluted Pt 4f XPS spectra of xPt/CoWO<sub>4</sub> (x=0.5, 1.0, 2.0) catalysts (a) before and (b) after ODH reaction.



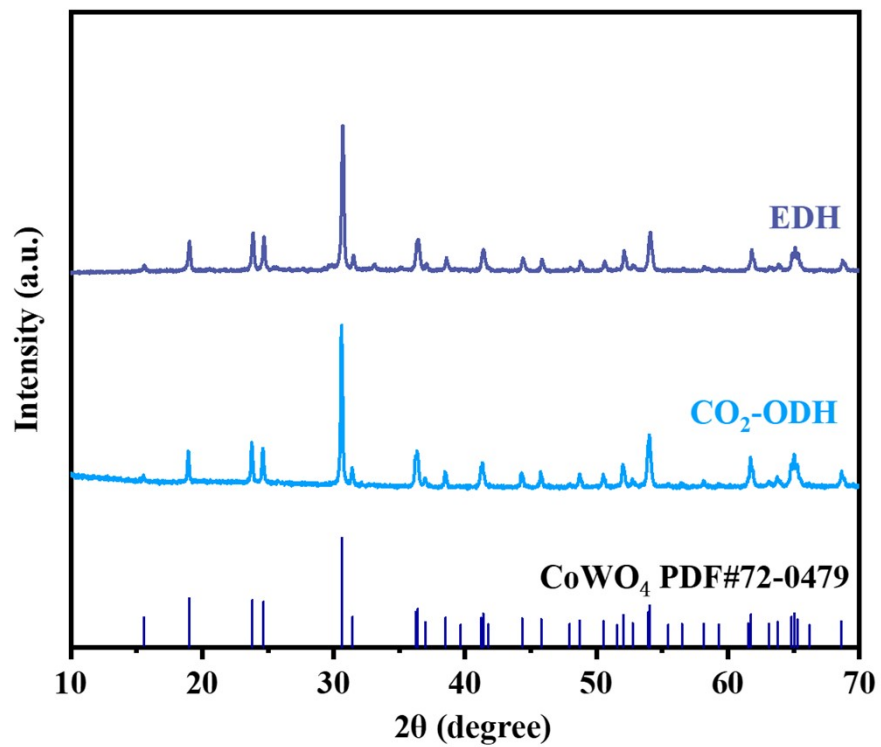
**Fig S9.** The deconvoluted W 4f XPS spectra of CoWO<sub>4</sub> and xPt/CoWO<sub>4</sub> (x=0.5, 1.0, 2.0) catalysts (a) before and (b) after CO<sub>2</sub>-ODH reaction.



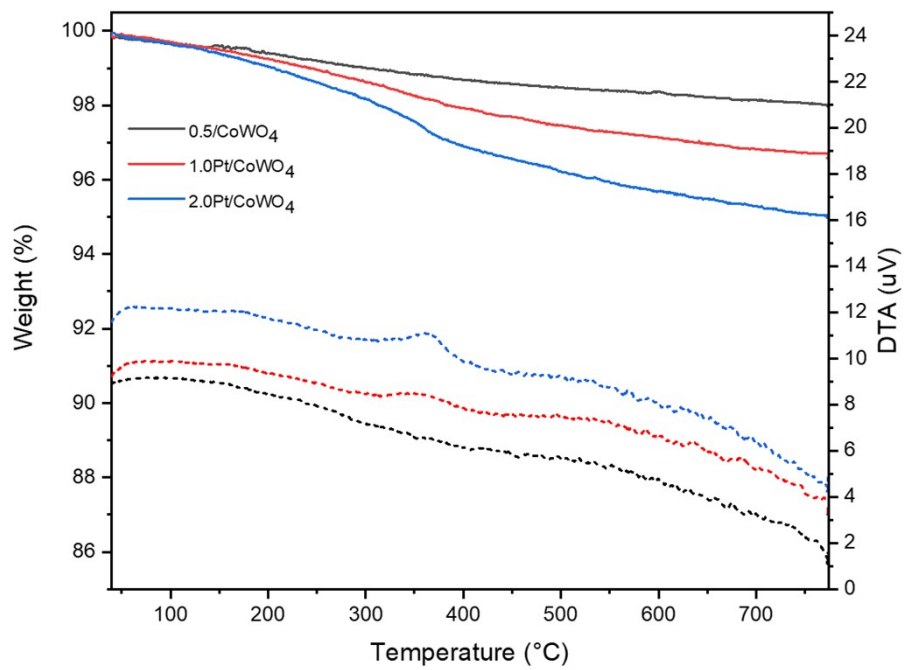
**Fig S10.** H<sub>2</sub>-TPR spectra of various catalysts.



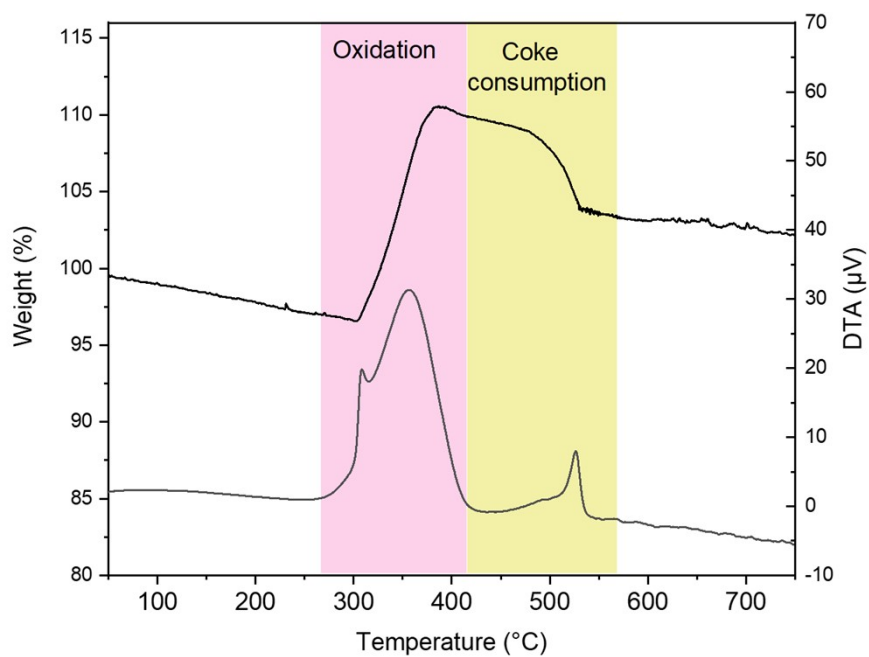
**Fig S11.** The *in situ* DRIFT spectra collected after 5 vol%  $\text{CO}_2$  (10 mL/min) was introduced into the cell and reacted with ethane before temperature raised.



**Fig S12.** XRD patterns of spent 1.0Pt/CoWO<sub>4</sub> catalyst with (CO<sub>2</sub>-ODH reaction) and without CO<sub>2</sub> cofed (EDH reaction).



**Fig S13.** TG-DTA curves of various catalysts after ODH reactions.



**Fig S14.** TG-DTA curves of 1.0Pt/CoWO<sub>4</sub> catalysts after EDH reaction.

**Table S1.** Ethane/CO<sub>2</sub> conversion and ethene/CO/CH<sub>4</sub> selectivity as a function of time on stream (TOS) over various xPt/CoWO<sub>4</sub> (x = 0, 0.5, 1.0, 2.0) catalysts.

| Catalysts               | Reactions | C <sub>2</sub> H <sub>6</sub> <sup>a</sup><br>Conv. (%) | CO <sub>2</sub> <sup>a</sup><br>Conv.<br>(%) | Sel. (%) |                   |                               |
|-------------------------|-----------|---|--|----------|-------------------|-------------------------------|
|                         |           |   |  | CO       | CH <sub>4</sub>   | C <sub>2</sub> H <sub>4</sub> |
| CoWO <sub>4</sub>       | ODH       | 1.25  | 1.20   | 46.53    | 0.39              | 53.08                         |
| 0.5Pt/CoWO <sub>4</sub> | ODH       | 4.85  | 4.07   | 40.26    | 0.76              | 58.98                         |
| 1.0Pt/CoWO <sub>4</sub> | ODH       | 6.47  | 5.65   | 46.03    | 0.56              | 53.41                         |
|                         | EDH       | 0.44 <sup>b</sup>                                       | -  | -        | 1.16 <sup>b</sup> | 98.84 <sup>b</sup>            |
| 2.0Pt/CoWO <sub>4</sub> | ODH       | 6.65  | 6.79   | 55.56    | 3.11              | 41.33                         |

<sup>a</sup> Reaction conditions: 0.1 g of catalyst mixed with 0.3 g quartz sand, atmosphere pressure, C<sub>2</sub>H<sub>6</sub>:CO<sub>2</sub>:N<sub>2</sub>:Ar = 25:25:47:3, 12000 mL/(g·h), 600 °C.

<sup>b</sup> Reaction conditions: 0.1 g of catalyst mixed with 0.3 g quartz sand, atmosphere pressure, C<sub>2</sub>H<sub>6</sub>:N<sub>2</sub>:Ar = 25:72:3, 12000 mL/(g·h), 600 °C.

**Table S2.** Co 2p XPS quantitative analysis results of CoWO<sub>4</sub> and xPt/CoWO<sub>4</sub> (x=0, 0.5, 1.0, 2.0) catalysts before and after reaction.

| Catalyst                | Status | Co species (%)  |                  |                  | Co <sup>2+</sup> /Co <sup>3+</sup> |
|-------------------------|--------|-----------------|------------------|------------------|------------------------------------|
|                         |        | Co <sup>0</sup> | Co <sup>2+</sup> | Co <sup>3+</sup> |                                    |
| CoWO <sub>4</sub>       | Fresh  | -               | 38.4             | 61.6             | 0.62                               |
|                         | ODH    | -               | 41.7             | 58.3             | 0.72                               |
| 0.5Pt/CoWO <sub>4</sub> | Fresh  | -               | 42.1             | 57.9             | 0.73                               |
|                         | ODH    | -               | 43.0             | 57.0             | 0.75                               |
| 1.0Pt/CoWO <sub>4</sub> | Fresh  | -               | 45.8             | 54.2             | 0.86                               |
|                         | ODH    | -               | 47.7             | 52.3             | 0.91                               |
|                         | EDH    | 59              | 29.5             | 11.44            | 2.58                               |
| 2.0Pt/CoWO <sub>4</sub> | Fresh  | 3.8             | 43.3             | 52.9             | 0.82                               |
|                         | ODH    | 4.0             | 44.0             | 52.0             | 0.85                               |



**Table S3.** The surface Pt of fresh samples from the XPS data.

| Catalyst                | Binding energy (eV) |                   |                      |                   |
|-------------------------|---------------------|-------------------|----------------------|-------------------|
|                         | Fresh Pt            | Used Pt           | Fresh                | Used Pt           |
|                         | 4f <sub>5/2</sub>   | 4f <sub>5/2</sub> | Pt 4f <sub>7/2</sub> | 4f <sub>7/2</sub> |
| 0.5Pt/CoWO <sub>4</sub> | 71.1                | 71.2              | 74.5                 | 74.6              |
| 1.0Pt/CoWO <sub>4</sub> | 71.0                | 71.3              | 74.3                 | 74.7              |
| 2.0Pt/CoWO <sub>4</sub> | 70.9                | 71.4              | 74.2                 | 74.7              |

**Table S4.** W 4f XPS fitting results for the CoWO<sub>4</sub> and xPt/CoWO<sub>4</sub> (x=0, 0.5, 1.0, 2.0) catalysts before and after reaction.

| Catalyst                | Status | W species (%)   |                 |
|-------------------------|--------|-----------------|-----------------|
|                         |        | W <sup>6+</sup> | W <sup>5+</sup> |
| CoWO <sub>4</sub>       | Fresh  | 46.6            | 53.4            |
|                         | ODH    | 37.1            | 62.9            |
| 0.5Pt/CoWO <sub>4</sub> | Fresh  | 39.6            | 60.4            |
|                         | ODH    | 31.8            | 68.2            |
| 1.0Pt/CoWO <sub>4</sub> | Fresh  | 32.0            | 68.0            |
|                         | ODH    | 22.8            | 77.2            |
| 2.0Pt/CoWO <sub>4</sub> | Fresh  | 32.7            | 67.3            |
|                         | ODH    | 29.5            | 70.5            |