

## Supporting Information

### Synergetic Effect between $\text{Pd}^{2+}$ and $\text{Ir}^{4+}$ Species Promoting Direct Ethane Dehydrogenation into Ethylene over Bimetallic $\text{PdIr/AC Catalysts}$

#### The synthesis of $\text{Pd7Ir2/AC-B-N}$

In order to evaluate the nano-particles' catalytic activity, we prepared  $\text{Pd7Ir2/AC-B-N}$  mainly possessing nano-particles without atomically dispersed Pd/Ir species. Firstly, 0.2 g AC-B support and equal weight of (3-aminopropyl)triethoxysilane (APTES) were dispersed in 20 mL water and sonicated for 30 min at RT, and then 1.40 mL Pd (0.1 M,  $\text{Na}_2\text{PdCl}_4$  from Aladdin) and 0.24 mL Ir (0.1 M,  $\text{H}_2\text{IrCl}_6$  from Aladdin) were added into the solution with fiercely stirring. After 4 hrs agitation, the solution was filtrated by distilled water and then the filter cake was dried by freeze dryer and calcined under  $\text{N}_2$  at 500 °C for 1 h. The ICP results presented the Pd and Ir contents were 6.0% and 1.5%. The morphology of this sample was shown in Fig. S12.

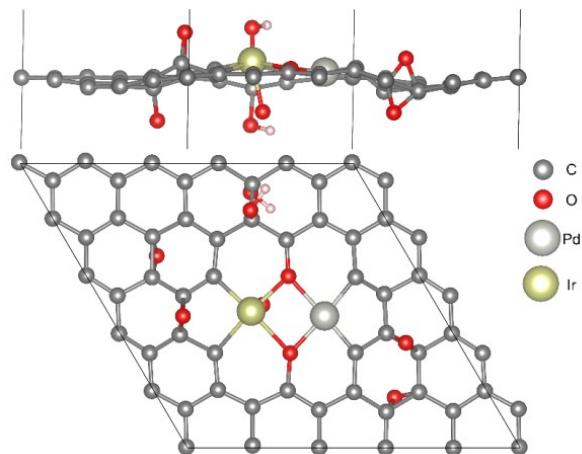


Figure S1. Side and Top view of Pd-Ir/AC with O species

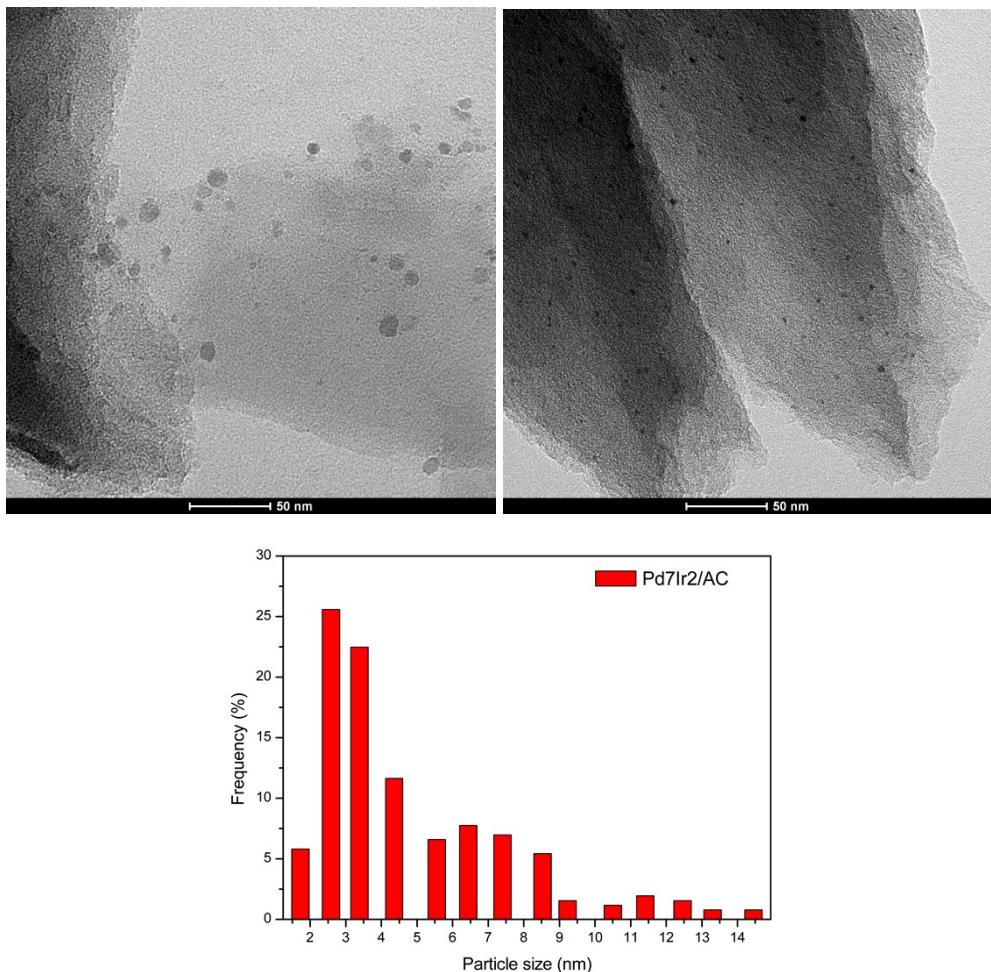


Figure S2 TEM images of Pd7Ir2/AC with the corresponding particle size distributions

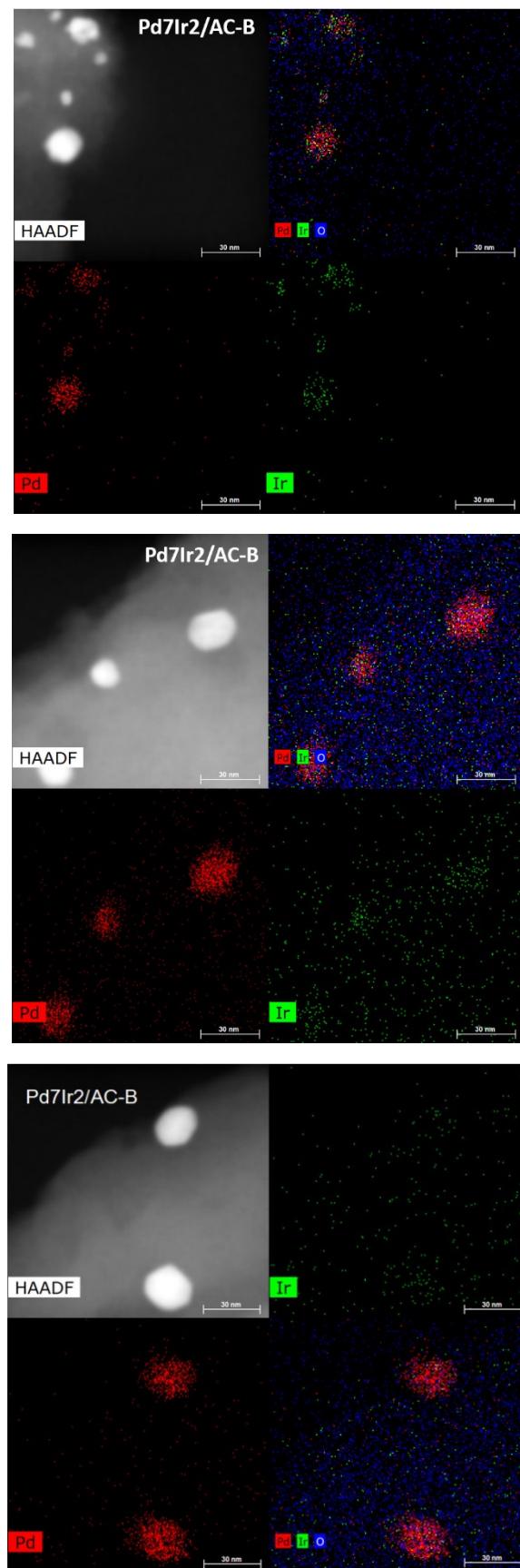


Figure S3 STEM images of Pd, Ir and O mapping over fresh Pd7Ir2/AC-B

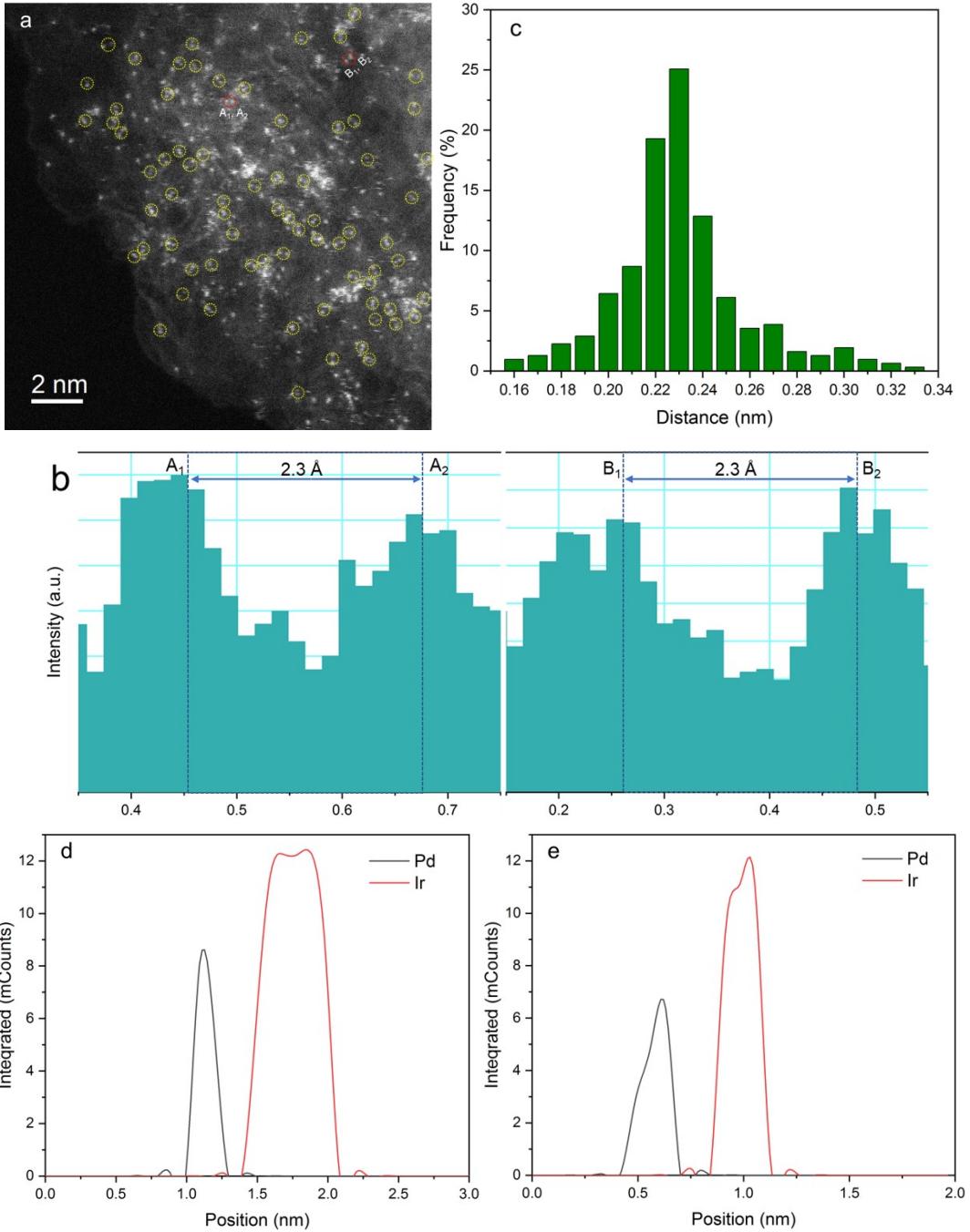


Figure S4 (a) Atomic-resolution HAADF-STEM image of Pd<sub>7</sub>Ir<sub>2</sub>/AC-B. (b) the corresponding Z-contrast analysis of region A and B in Fig. a. (c) Statistical distribution of dual single-atom distance. (d) and (e) EDS line scan spectra of dual single-atom in region A and B.

In this work, we further utilized the EDS spectra through line scanning method to identify the Pd-Ir pairs on Pd<sub>7</sub>Ir<sub>2</sub>/AC-B in Fig. S4. In Fig. S 4a, the bright spots were the atomically dispersed Pd and Ir atoms, and we highlighted the dual single-atom with yellow circle and the atom distance was calculated as 2.3 Å in Fig. S 4b according to the model in Fig. S1. Fig. S 4c listed the thorough statistical distribution

of interatomic distance, which mainly located nearby 2.3 Å by Z-contrast analysis. Furthermore, we chose two pairs of dual single-atom in region A and B labelled by red circles for EDS line scanning, and the spectra in Fig. S4 d and e proved the adjacent atom pairs were Pd-Ir atoms. It was worthy to mention that the atoms distance in Fig. S4 d and e was not 2.3 Å, which might be induced by the sample shift during the line scanning process.

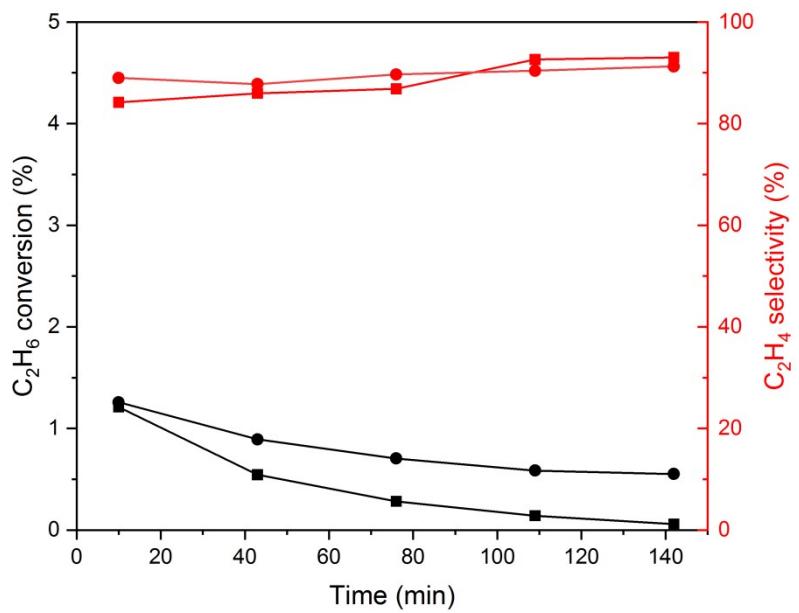


Figure S5 the C<sub>2</sub>H<sub>6</sub> conversion and C<sub>2</sub>H<sub>4</sub> selectivity over pristine AC support (circle symbol) and AC-B support (square symbol) at 500 °C .

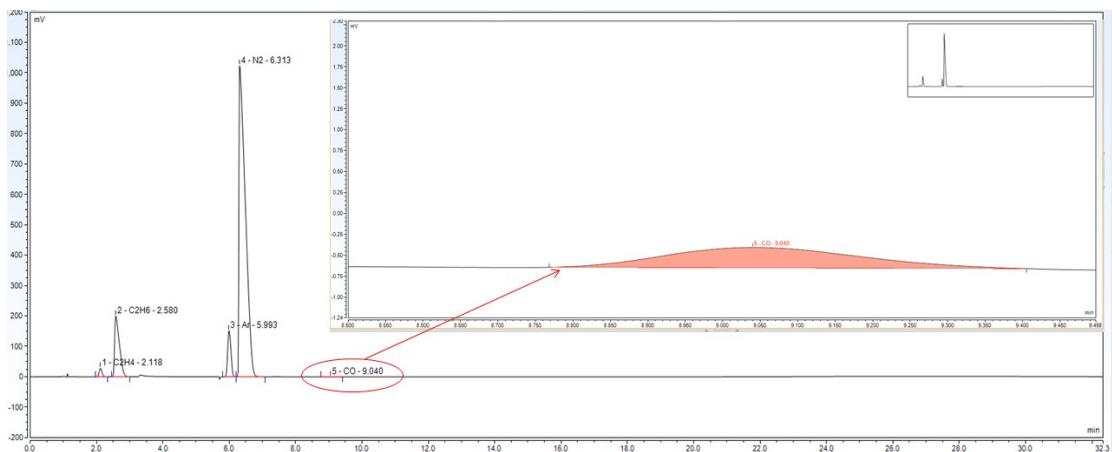


Figure S6 the gas-chromatography spectrum (TCD) of EDH over Pd7Ir2/AC after 1 h at 500 °C

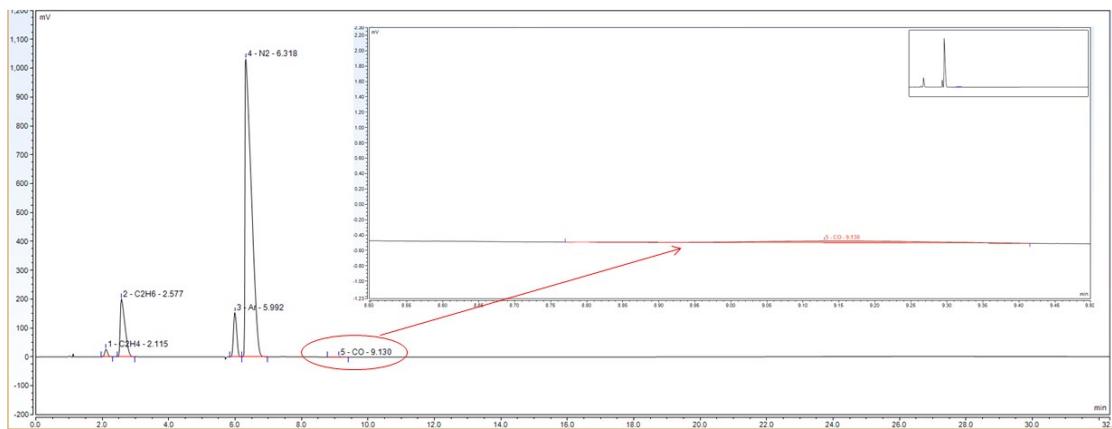


Figure S7 the gas-chromatography spectrum (TCD) of EDH over Pd7Ir2/AC-B after 1 h at 500 °C

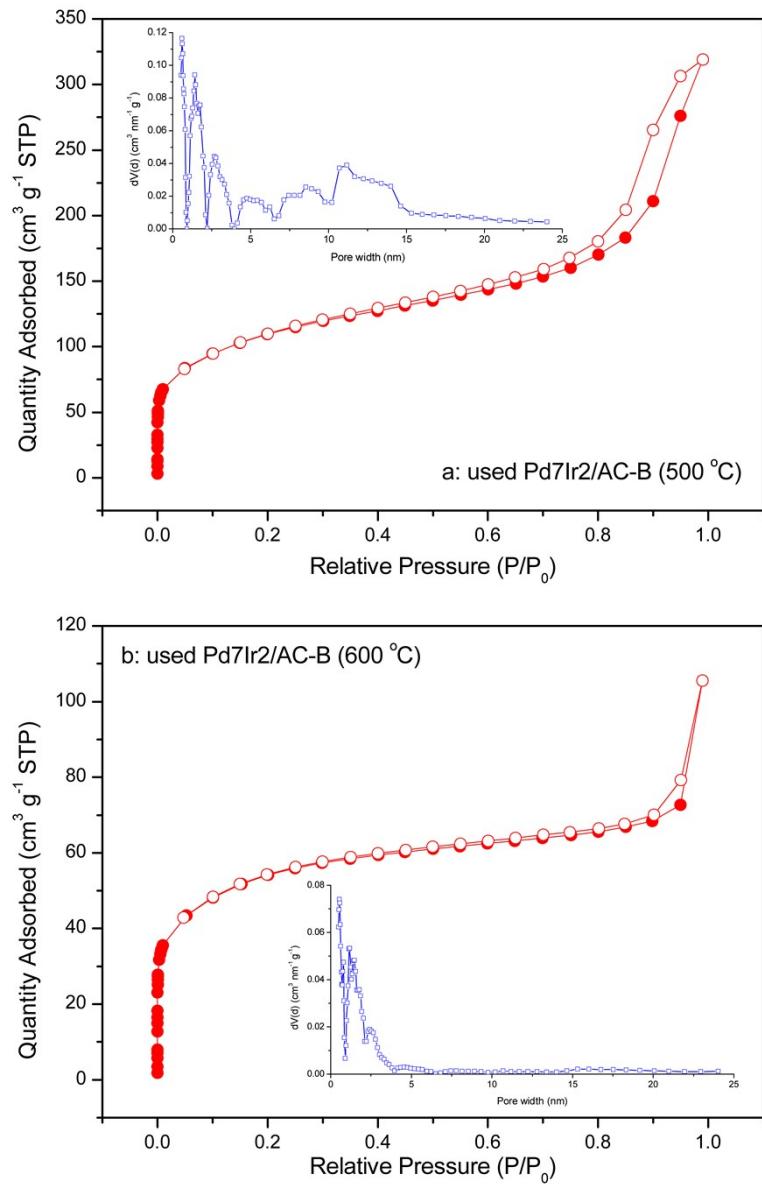


Figure S8 N<sub>2</sub> adsorption-desorption isotherm and pore distribution of used Pd<sub>7</sub>Ir<sub>2</sub>/AC-B at 500 °C

(a) and 600 °C (b) after 340 min EDH reaction.

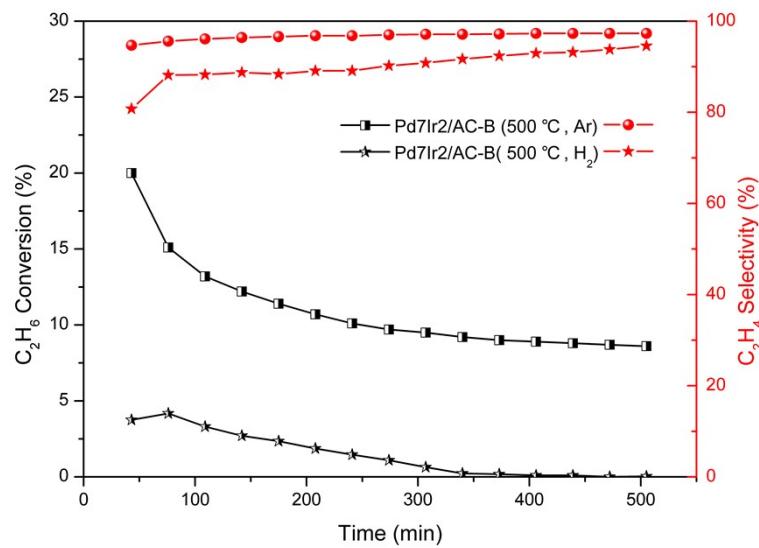
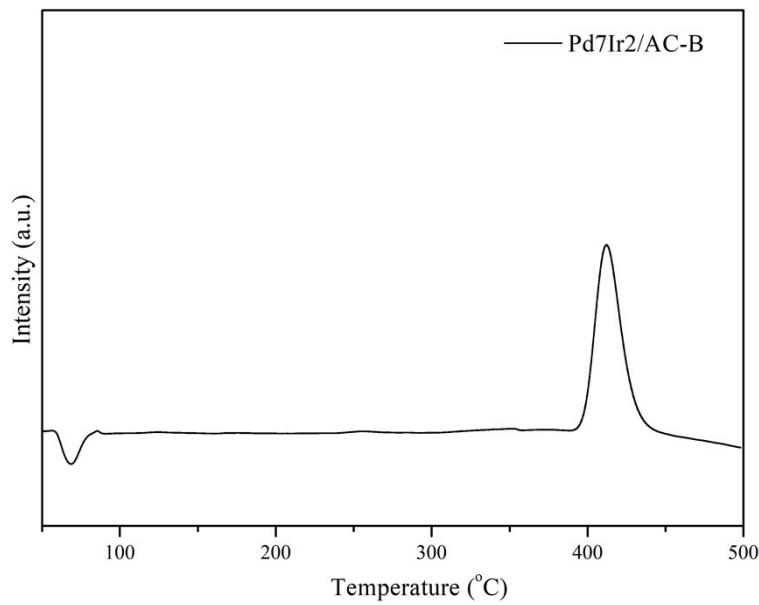


Figure S10 the EDH activity comparison over Pd7Ir2/AC-B after Ar or H<sub>2</sub> pretreatment from RT to 500 °C, respectively.

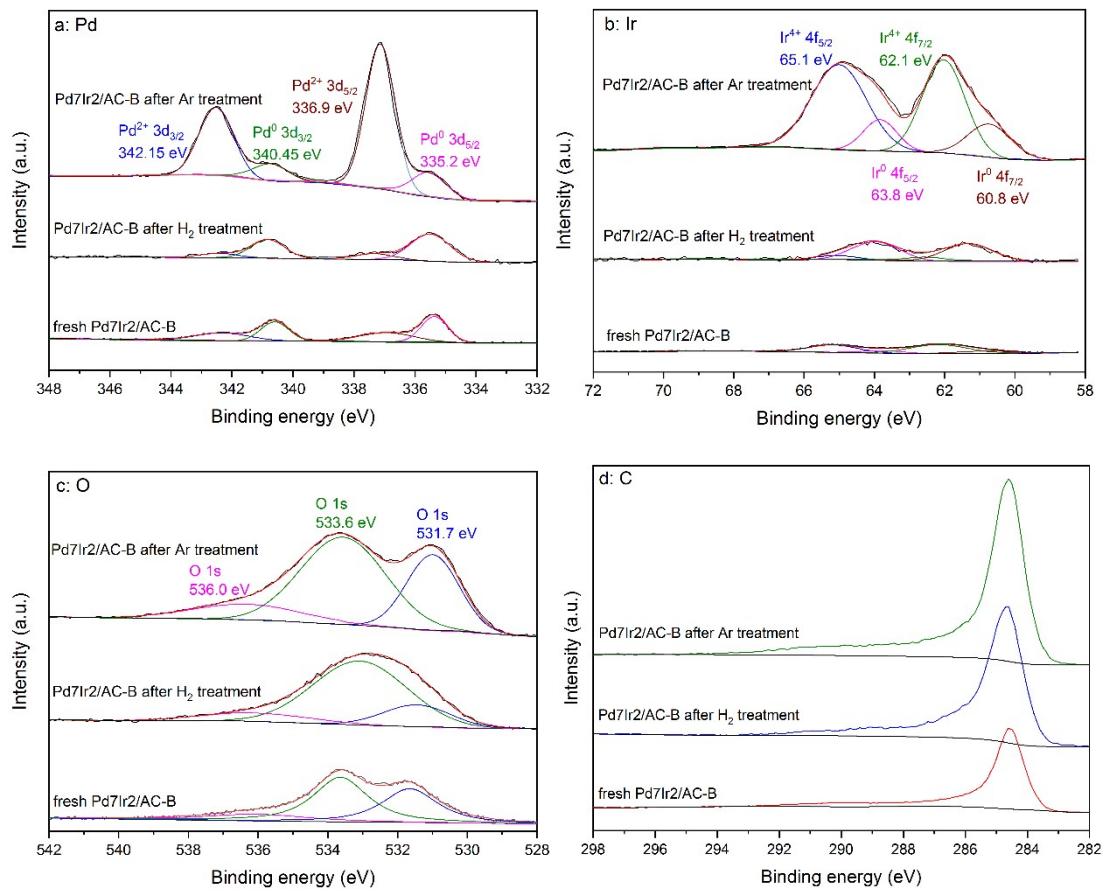


Figure S11 XPS spectra of (a) Pd 3d, (b) Ir 4f, (c) O 1s and (d) C1s over fresh Pd7Ir2/AC-B and Pd7Ir2/AC-B after H<sub>2</sub> or Ar pretreatment at 500 °C.

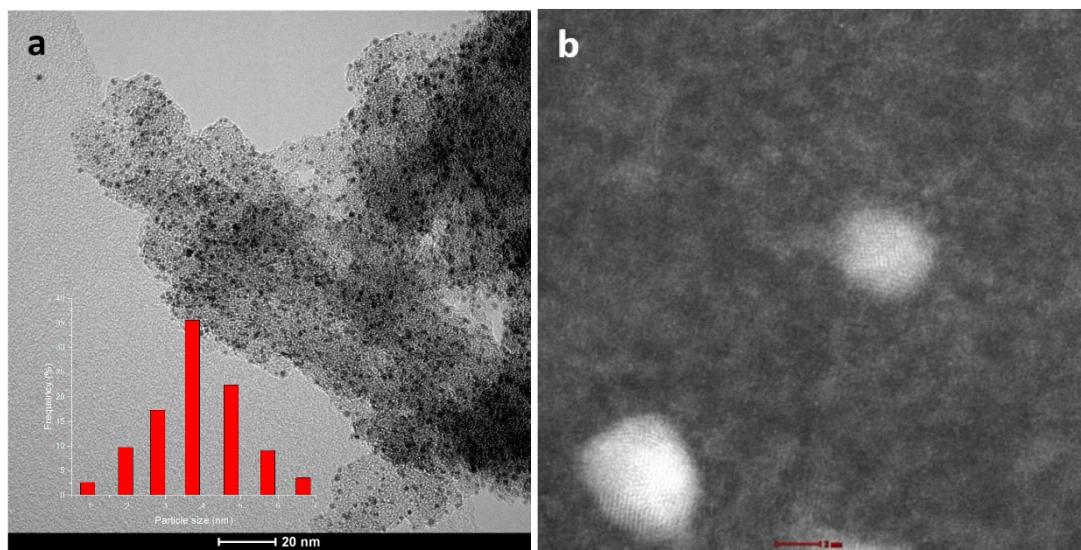


Figure S12 TEM image (scale bar 20 nm) (a) and atomic-resolution HAADF-STEM image (scale bar 2 nm) (b) of Pd7Ir2/AC-B-N

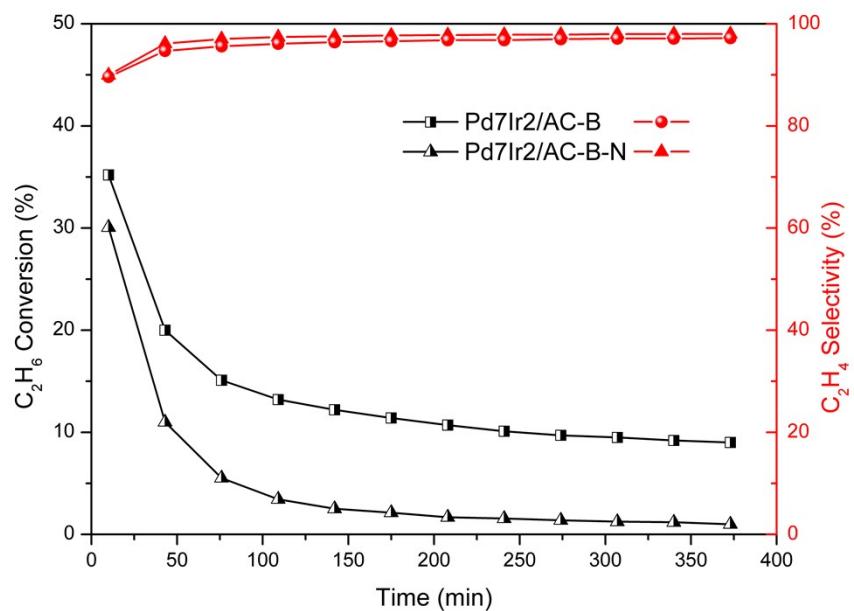


Figure S13 the EDH activity over Pd7Ir2/AC-B-N with Ar pretreatment from RT to 500 °C, respectively.

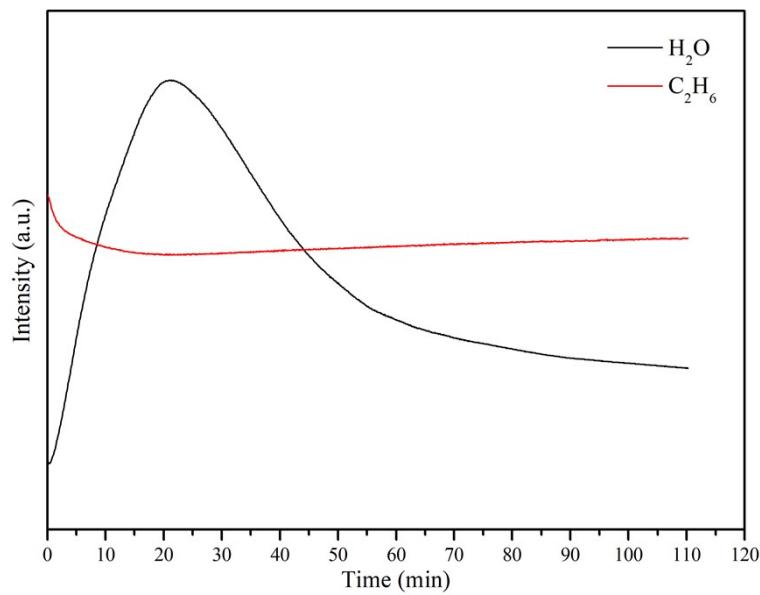


Figure S14 MS results of  $\text{C}_2\text{H}_6$  and  $\text{H}_2\text{O}$  concentration profiles during EDH process over Pd7Ir2/AC-B at 500 °C. Prior to the activity test, the catalyst was pretreated by Ar from RT to 500 °C.

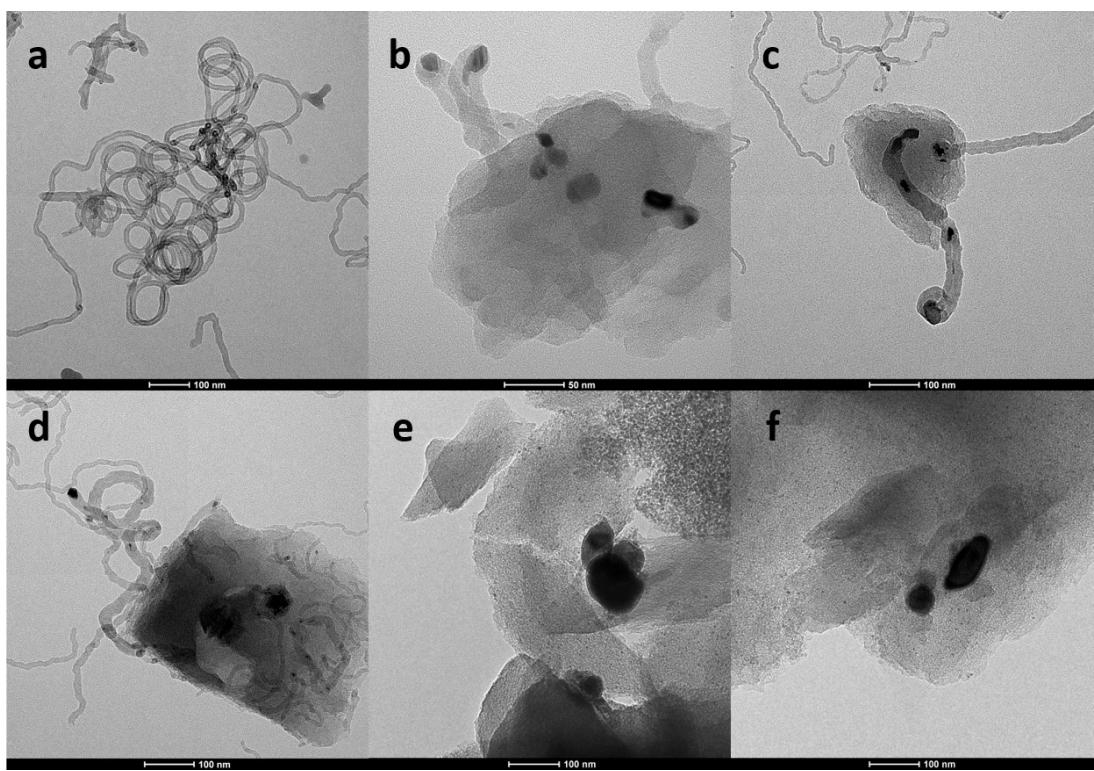


Figure S15 (a) and (b): TEM images of used Pd7Ir2/AC-B under 600 °C reaction; (c) and (d): TEM images of used Pd7Ir2/AC-B under 500 °C reaction; (e) and (f): TEM images of used Ir/AC-B under 500 °C reaction.

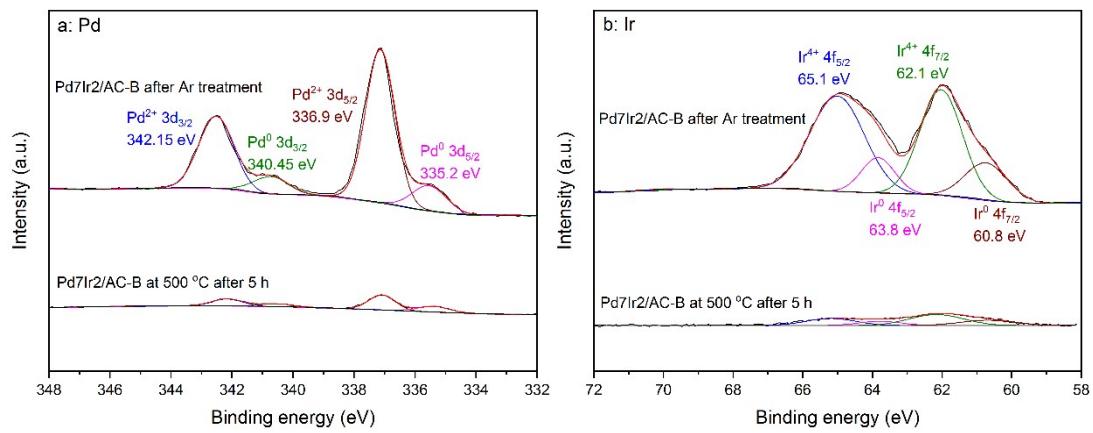


Figure S16 XPS spectra of (a) Pd 3d and (b) Ir 4f over Pd7Ir2/AC-B after Ar treatment prior to EDH activity test and after 5 h reaction at 500 °C.

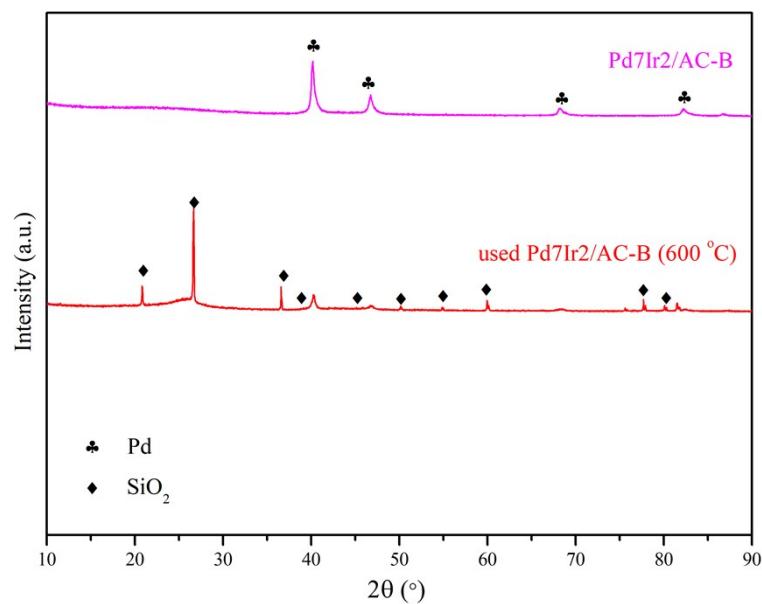


Figure S17 XRD profile of used Pd7Ir2/AC-B sample

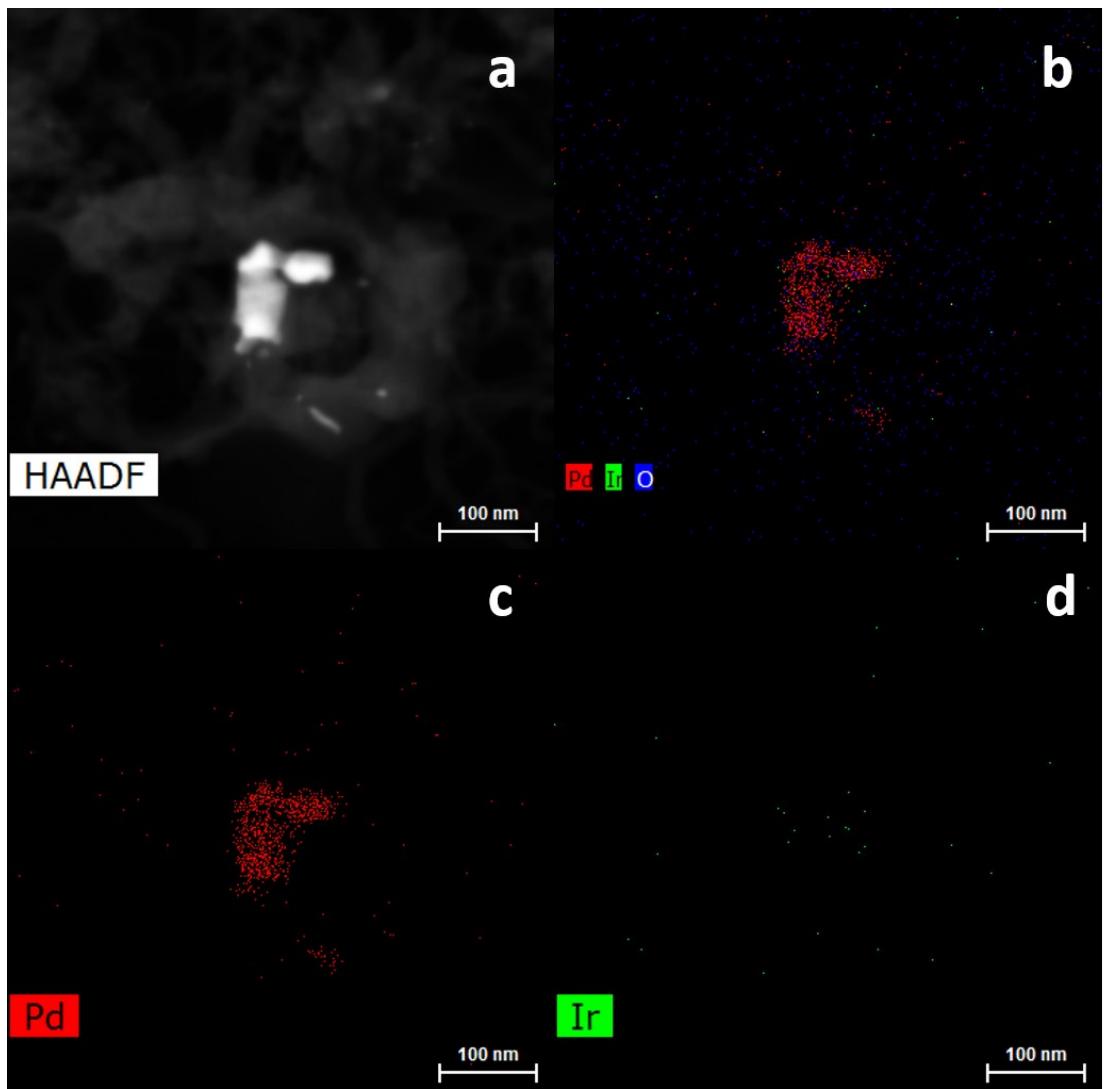


Fig. S18 STEM images of Pd, Ir and O mapping over used Pd<sub>7</sub>Ir<sub>2</sub>/AC-B after 600 °C reaction

Table S1 the comparison of direct EDH activity over various catalysts

Reaction conditions	Sample in references	Reaction activity	this work
600 °C	2 wt% Fe/ZSM-5 <sup>1</sup>	0.324 mmol <sub>C2H6</sub> ·g <sub>Fe</sub> <sup>-1</sup> ·s <sup>-1</sup> /270 min	2.88 mmol <sub>C2H6</sub> ·g <sub>PdIr</sub> <sup>-1</sup> ·s <sup>-1</sup> /340 min
600 °C	0.8 wt% Fe-silicalite-1 <sup>2</sup>	0.86 mol <sub>C2H4</sub> ·g <sub>Fe</sub> <sup>-1</sup> ·h <sup>-1</sup> /340 min	8.58 mol <sub>C2H4</sub> ·g <sub>PdIr</sub> <sup>-1</sup> ·h <sup>-1</sup> /340 min
600 °C	Pt-In(0.7) <sup>3</sup>	R <sub>C2H6</sub> :5.3 s <sup>-1</sup> (initial)	R <sub>C2H6</sub> :2.25 s <sup>-1</sup> (10 min)
550 °C	PtSn/Mg(x-Ga)AlO <sup>4</sup>	R <sub>C2H6</sub> :0.25 s <sup>-1</sup>	R <sub>C2H6</sub> :0.802 s <sup>-1</sup> (500 °C) <sup>a</sup>
650 °C	0.4 wt%Pt-meso-GaZSM-5 <sup>5</sup>	R <sub>C2H6</sub> :0.46 s <sup>-1</sup>	R <sub>C2H6</sub> :2.25 s <sup>-1</sup> (600 °C)
510 °C	1 wt% Pt-ETS-2 <sup>6</sup>	R <sub>C2H6</sub> :0.009 s <sup>-1</sup> per Pt	R <sub>C2H6</sub> :0.244 s <sup>-1</sup> per PdIr (500 °C)
600 °C	2.2 wt% Pt <sub>3</sub> Ga/SiO <sub>2</sub> <sup>7</sup>	R <sub>C2H6</sub> :0.032 s <sup>-1</sup> per Pt	R <sub>C2H6</sub> :0.328 s <sup>-1</sup> per PdIr (600 °C)
650 °C	0.8Cr/MFI <sup>8</sup>	R <sub>C2H6</sub> :4.1 s <sup>-1</sup> (initial)	R <sub>C2H6</sub> :2.25 s <sup>-1</sup> (600 °C)
600 °C	PtIn <sub>2</sub> <sup>7</sup>	R <sub>C2H6</sub> :1.3 s <sup>-1</sup>	R <sub>C2H6</sub> :2.25 s <sup>-1</sup> (600 °C)
600 °C	Pd-In-2.0 <sup>9</sup>	R <sub>C2H6</sub> :0.26 s <sup>-1</sup>	R <sub>C2H6</sub> :2.25 s <sup>-1</sup> (600 °C)

a: this data was based on Pd7Ir2/AC-B sample in Fig. 5 and Fig. 10.

Table S2 Rate of C<sub>2</sub>H<sub>6</sub> conversion normalized by active Pd+Ir species <sup>a</sup>

Sample	Time/min	Reaction rate/h <sup>-1</sup>	Time/min	Reaction rate/h <sup>-1</sup>
n				
Pd/AC-B	10	7345.8	340	863.0
Ir/AC-B	10	2724.5	340	584.4
Pd7Ir2/AC-B	10	2887.2	340	779.2
Pd7Ir2/AC-B (600 °C)	10	8087.3	340	1181.1

a: the EDH activity results were utilized from Fig. 5 and Fig. 10.

Table S3 the mole ratios of Pd<sup>2+</sup>:Pd<sup>0</sup> and Ir<sup>4+</sup>:Ir<sup>0</sup> after various pretreatments, the results was normalized by XPS peaks area from Fig. S11.

Sample	Pretreatment method	Pd <sup>2+</sup> :Pd <sup>0</sup>	Ir <sup>4+</sup> :Ir <sup>0</sup>
Pd7Ir2/AC-B	fresh sample	1:1.26	7:1
Pd7Ir2/AC-B	Ar treatment at 500 °C	5:1	2.9:1
Pd7Ir2/AC-B	H <sub>2</sub> treatment at 500 °C	1:4.7	1:6

## References:

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