Supporting Information

Table S1 The comparison of the catalytic results of our sample 4 and the other reported catalysts in literature for methanol synthesis from CO_2 hydrogenation

Catalyst	Pressure (MPa)	Temperature (°C)	Methanol selectivity	Methanol Yield ($g_{methanol}/g_{active\ metal}$*h)	Ref.
A commercial Hi fuel R120 catalyst (Cu wt% 50%)	2	270	2.4%	0.1	This work
Cu/ZnO (Cu wt% 50%)	5	250	42.1%	1.0	1, 2
Cu/ZnO/Al_2O_3 (Cu wt% 50%)	5	250	52.3%	1.4	1, 2
Cu/ZnO/Ga_2O_3 (Cu wt% 50%)	5	250	53.2%	1.5	1, 2
Pd/ZnO (Pd wt% 10%)	5	250	37.5%	3.3	3
Pd/Ga_2O_3 (Pd wt% 10%)	5	250	51.5%	6.4	3
Ag/ZnO/Al_2O_3 (Ag wt% 10%)	5	250	75.0%	0.8	4
Ga modified Ag/ZnO/Al_2O_3 (Ag wt% 10%, Ga wt% 2%)	5	250	82.6%	1.3	4
Au/ZnO/TiO_2 (Au wt% 5%)	5	300	21.2%	0.8	5
Sample 4 (Pd wt% 5%)	2	250	70.5%	4.3	This work
Sample 4 (Pd wt% 5%)	2	270	67.3%	6.1	This work
Sample 4 (Pd wt% 5%)	4.5	250	77.6%	8.3	This work
Sample 4 (Pd wt% 5%)	4.5	270	64.9%	12.0	This work

Table S2 The comparison in catalytic performance of the fresh (Test 1) and retested sample 4 (Test 2) at 250 °C, under 2 MPa, 4.5 MPa

Sample 4	Test 1 （2.0 MPa）	Test 2 （2.0 MPa）	Test 1 （4.5 MPa）	Test 2 （4.5 MPa）
Methanol selectivity (%)	67.7	70.5	77.6	74.5
CO_2 conversion (%)	6.7	7.9	11.3	9.3

Note: the used sample 4 was collected after the catalysis testing (Test 1) and then pre-reduced with pure H_2 at 280 °C for 2h before the second testing (Test 2). The lost catalyst powder during its collection after Test 1 was normalized to 100mg for comparison in Test 2.

As shown in Table S2, no obvious deactivation is observed for the repeated testing catalyst within experimental errors, which indicates the good stability of the catalyst.

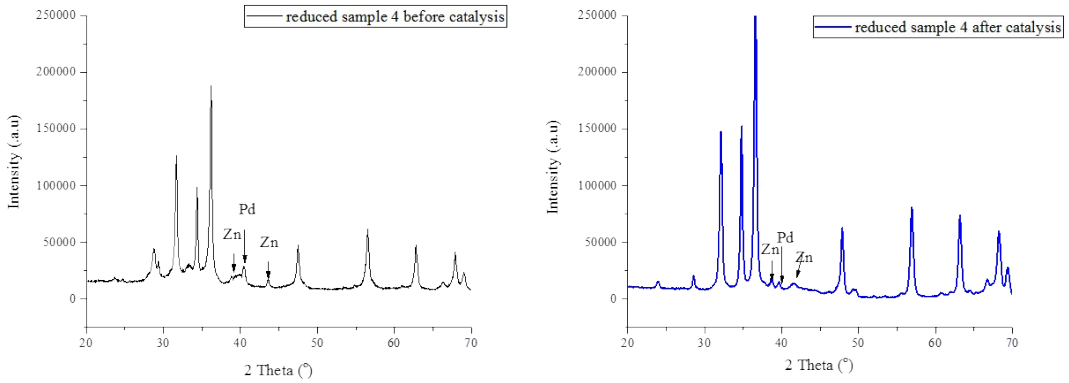
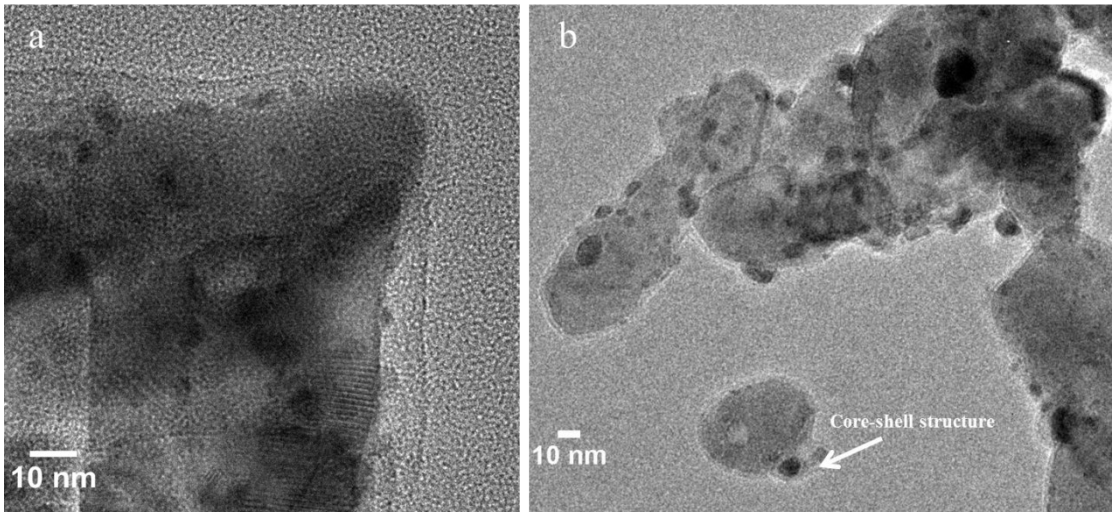


Fig. S1 The comparison of XRD patterns of reduced sample 4 before and after the catalysis reaction

From the XRD patterns of reduced sample 4, the diffraction peaks assigned to metallic Zn and Pd (as labelled in Fig. S1) are evident after the catalysis, which indicates the maintenance of the PdZn bimetallic structure.



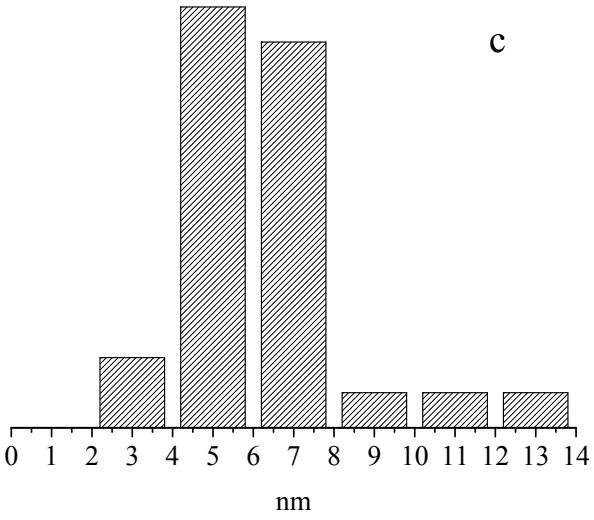
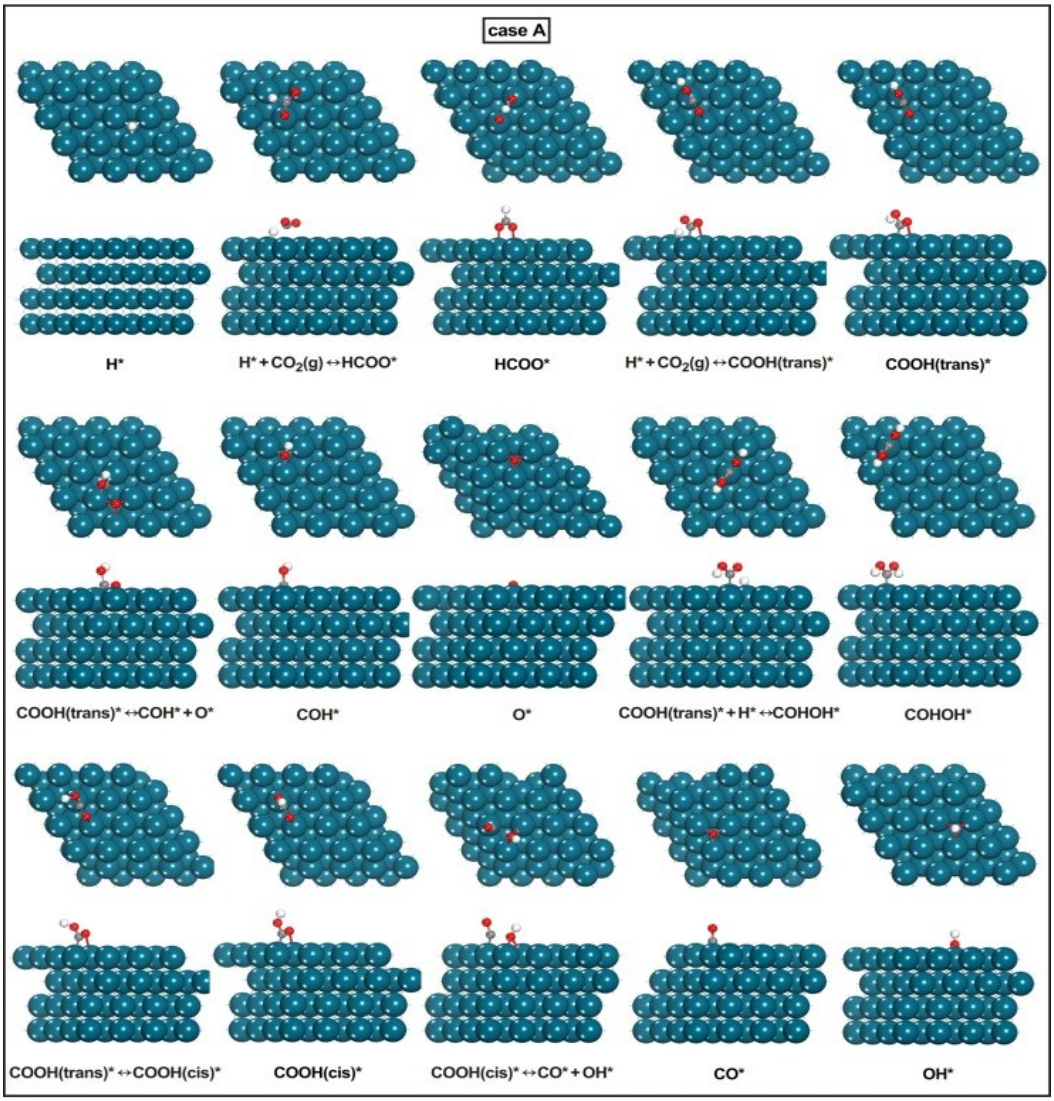


Fig. S2 (a, b) The TEM images of sample 4 after catalytic testing; (c) size distribution of Pd-based particles after catalytic testing

Comparing with the fresh sample, the average size of Pd-based particles in sample 4 slightly grows from 3-5 nm to 4-7nm, indicating some degree of metal sintering after the testing. However, the core-shell structure of Pd@Zn is clearly observable in the used sample.


case A
H*
H* + CO2(g) ↔ HCOO*
HCOO*
H* + CO2(g) ↔ COOH(trans)*
COOH(trans)*
COOH(trans)* ↔ COH* + O*
COH*
O*
COOH(trans)* + H* ↔ COHOH*
COHOH*
COOH(trans)* ↔ COOH(cis)*
COOH(cis)*
COOH(cis)* ↔ CO* + OH*
CO*
OH*

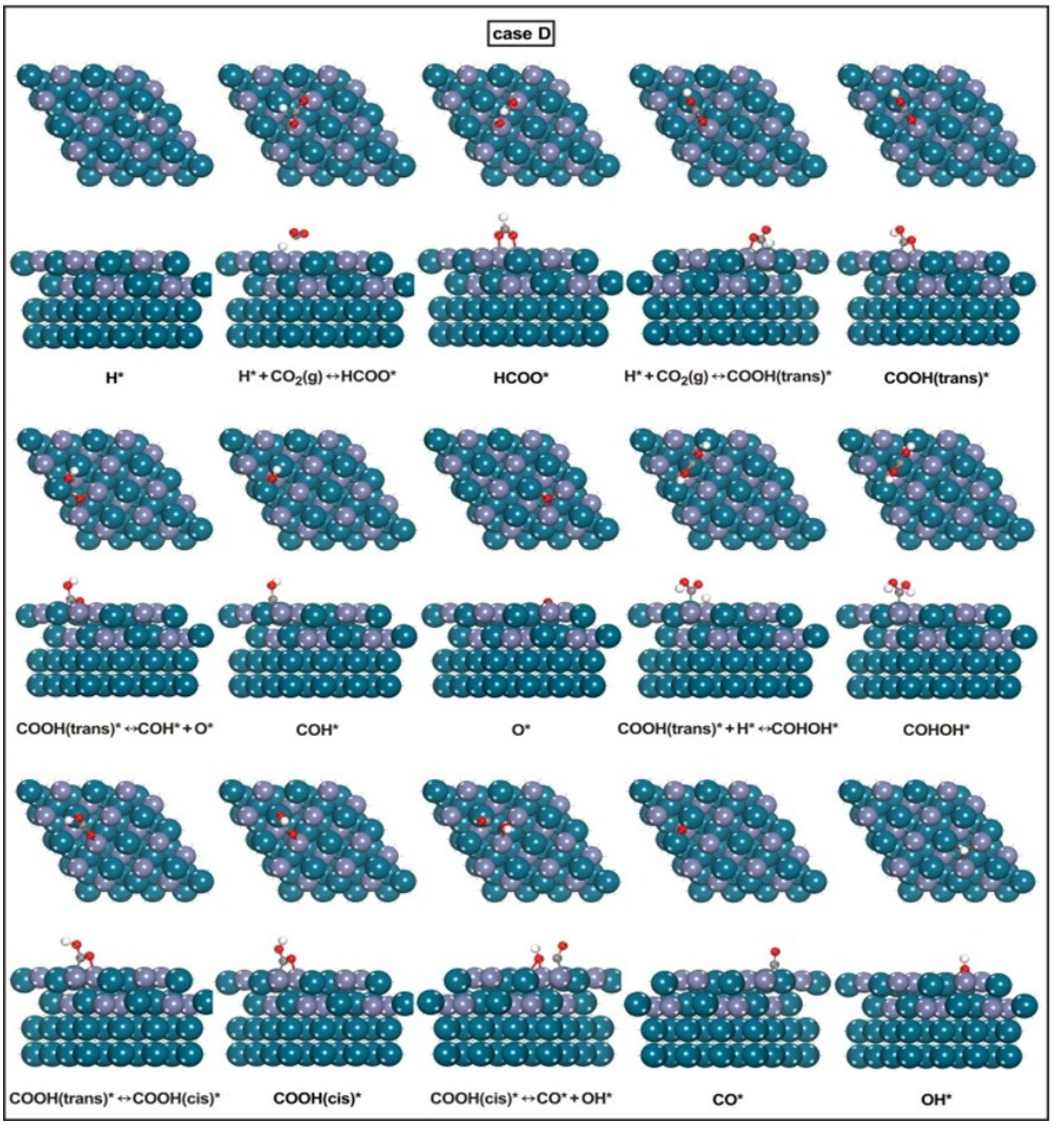


Fig. S3 Corresponding structures of adsorbed species shown in Fig. 11 and Fig. 12. Pd, Zn, H, C and O atoms are in cyan, purple, white, grey and red, respectively. Note: adsorbed COOH reported in the main text represents the trans-COOH species in the calculation.

References:

1. T. Fujitani, M. Saito, Y. Kanai, M. Takeuchi, K. Moriya, T. Watanabe, M. Kawai and T. Kakumoto, *Chem. Let.* 1993, **6**, 1079-1080.

2. T. Fujitani, M. Saito, Y. Kanai, T. Kakumoto, T. Watanabe, J. Nakamura and T. Uchijima, *Catal. Lett.* 1994, **25**, 271-276.

3. T. Fujitani, M. Saito, Y. Kanai, T. Watanabe, J. Nakamura and T. Uchijima, *Appl. Catal. A: General* 1995, **125** , L199-202.

4. S. Sugawa, K. Sayama, K. Okabe and H. Arakawa, *Energy Convers. Mgmt* 1995, **36**, 665-670.

5. H. Sakurai and M. Haruta, *Appl. Catal. A: General* 1993, **127**, 93-105.