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Electronic Supporting Information (ESI)

Confinement of subnanometric PdZn at defect enriched ZnO/ZIF-8 interface for efficient and selective CO₂ hydrogenation to methanol

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1. Supplementary figures



Fig. S1. High resolution TEM image of rod-like ZnO.

It reveals a d-spacing of 0.26 nm along the rod, which can be assigned to the characteristic (002) facet. This clearly suggest that the growth of the ZnO crystal follows the anisotropic growth along [001] direction.



Fig. S2. The size distribution histograms of (a) ZnO, (b) Z@Z8-0.5, (c) Z@Z8-1, (d) Z@Z8-2 and (e) Z@Z8-4.



Fig. S3. TGA curves of a series of Z@Z8-x samples compared with pure ZnO and ZIF-8.

Fig. S4 shows the TGA curves of all samples. ZnO hardly loses weight under the tested temperature region of below 600 °C, while ZIF-8 loses its 60% weight (slightly lower than the theoretical mass loss: 62.8%) due to the complete conversion of ZIF-8 to ZnO at above 320 °C. As expected, the weight loss of ZnO@ZIF-8 increases as the etching time increases. The weight content of ZIF-8 in different ZnO@ZIF-8 samples can be calculated to be 6.71%, 10.62%, 29.49% and 39.02% for the etching time at 0.5, 1, 2 and 4 h, respectively (Table S1).



Fig. S4. BET surface area of a series of Z@Z8-x samples compared with pure ZnO and ZIF-8 from N_2 sorption isotherms.

The increased content can be also indexed by the BET surface area (SA) measured from N₂ sorption curves (Fig. S5). Pure ZIF-8 has a much larger SA than ZnO (1400.1 vs 18.1 m² g⁻¹). For the four ZnO@ZIF-8 samples, as the etching time increases, the SA grows from 93.1 to 153.3, 412.2 and 553.9 m² g⁻¹. Based on an assumption that the contribution from ZnO is negligible compared to porous ZIF-8, the content of ZIF-8 shell can be calculated. The weight content of ZIF-8 in different Z@Z8-x samples can be calculated to be 6.65%, 11.0%, 29.4% and 39.4% for the etching time at 0.5, 1, 2 and 4 h, respectively (Table S1). The estimated values are very close to those from TGA analysis.

Fig. S5. Zn 2p XPS spectra of ZnO, ZIF-8 and different Z@Z8-x samples.

A gradual shift of Zn 2p peak towards higher binding energy reveals that more and more ZnO convert to ZIF-8 with the etching time going on.

Fig. S6. Representative TEM images and the corresponding size distribution (inset) of (a) Pd-

Z@Z8-0.5, (b) Pd-Z@Z8-2, (c) Pd-Z@Z8-4 and (d) Pd-ZIF-8.

Discussion on the catalytic activity of physical mixture of Pd-ZnO and ZIF-8

Fig. S7. Catalytic performance of Pd-ZnO and Pd-ZnO-Z8 in methanol synthesis from CO_2 hydrogenation. (a) CO_2 conversion, (b) methanol selectivity and (c) methanol STY at different reaction temperatures from 523 to 563 K.

We have supplemented the catalytic test of the physical mixture of Pd-ZnO with ZIF-8. Briefly, Pd-ZnO and ZIF-8 powders were mixed by using the pestle and mortar at the weight ratio of 1:1, denoted as Pd-ZnO-Z8. The catalytic measurements of Pd-ZnO-Z8 were taken under the same conditions with the other catalysts. The catalytic results of Pd-ZnO-Z8 together with Pd-ZnO were showed in **Fig. S7**. The addition of ZIF-8 powders decreased both the CO₂ conversion rate and methanol selectivity, resulting in a great drop in the STY of methanol. The reason could be that ZIF-8 powder, an inactive material to CO₂ hydrogenation to methanol, has a large specific surface area and partially encased the Pd-ZnO samples. Reactants cannot contact with Pd-ZnO efficiently, leading to a poor activity. The experiments give evidence the poor activity of Pd-ZnO-Z8.

Discussion on the STY_{Pd}

The STY_{Pd} was calculated by using the amount of Pd in catalysts (ω_{Pd}) obtained from ICP-AES to divide the methanol space time yield per gram of catalysts (STY_{cat}):

$$STY_{Pd} = \frac{STY_{cat}}{\omega_{Pd}}$$

Fig. S8. Methanol STY per gram of Pd (STY_{Pd}) at different reaction temperatures from 523 to 563 K.

As the contents of Pd in all catalysts were well controlled at the same level, STY_{Pd} shows the similar trend with STY_{cat} (Figure 6 in the main text).

Discussion on the apparent activation energy (E_a)

Fig. S9. Arrhenius plots of methanol STY over Pd-ZnO and different Pd-Z@Z8-x samples.

Tabl	le S4.	The ca	lculated E	$_{a}$ val	lues over	: Pd	-ZnO	and	different	Pd-Z	.@Z8-х	samples
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Sample	$E_a (kJ \cdot mol^{-1})$
Pd-ZnO	36.51
Pd-Z@Z8-0.5	29.79
Pd-Z@Z8-1	30.68
Pd-Z@Z8-2	29.46
Pd-Z@Z8-4	34.85

To calculate the apparent activation energy (E_a), the Arrhenius plots for methanol formation over different catalysts were displayed in Fig. S9. We found that the E_a decreased by about 6 kJ·mol⁻¹ on the catalysts with relatively thinner ZIF-8 shell in contrast to Pd-ZnO, and increased by about 5 kJ·mol⁻¹ when the ZIF-8 shell become too thick in Pd-Z@Z8-4. The trend of Ea shows an anti-volcanic relationship with the increasing of ZIF-8 thickness. It could probably be related to the volcanic relationship between methanol yield and ZIF-8 thickness. The three samples (Pd-Z@Z8-0.5, -1 and -2) show very close E_a (29.5~30.7 kJ mol-1) when considering the measurement errors. This suggests that a proper balance between PdZn alloy and surface defects are favored for methanol synthesis reaction.

Fig. S10. Multiple circular reaction test for the stability test of Pd-Z@Z8-1. (a) CO_2 conversion and (b) methanol selectivity in the reaction performed at 523K, 543K and 563K successively for 2 h in each cycle.

Fig. S11. TEM images of spent Pd-Z@Z8-1 after the time-on-stream test and the corresponding size distribution of Pd nanoparticles.

Discussion on the possible reaction pathway with the catalyst's structure model

Fig. S12. The possible reaction pathway with the catalyst's structure model.

The possible reaction pathway with the catalyst's structure model is showed in Fig. S11. The volcano-like behavior of catalytic activity is a compromise between the need for abundant defects on ZnO (achieved by increasing etching time) and PdZn alloy sites (achieved with shorter etching time). The fabrication of ZIF-8 shell in the Pd-Z@Z8-x catalysts can lead to two advantages and one disadvantage towards the catalytic activity. The two advantages are: a) fabricating more oxygen defects on the surface of ZnO nanorods; b) decreasing the size of Pd nanoparticles and leading to subnanometric PdZn alloys. The two advantages have synergetic impacts on improving the activity of the catalysts. However, the ZIF-8 shell is not always beneficial, especially when it grows too thick. There comes a disadvantage along with the growth of ZIF-8 shell. It could prevent the effective contacts between Pd nanoparticles and ZnO surface, thus disfavoring the formation of PdZn alloys which are regarded as the active sites for methanol synthesis. The combined actions of the two advantages and one disadvantage result in the volcanic relationship between methanol yield and ZIF-8 thickness. The best activity over Pd-Z@Z8-1 is the optimized balance. In Pd-Z@Z8-1, there are more oxygen defects as a result of the fabrication of ZIF-8 shell, and at the same time, the thickness of ZIF-8 shell is not enough to prevent the fabrication of subnanometric PdZn alloys.

Discussion on the clarity of Pd-N species

It is known that the binding energy (BE) would shift to a higher value when the electron cloud density of Pd decreases. We ascribed the peak at around 337.9 eV to the partial ionization of surface $Pd^{\delta+}$ atoms when coordinated by 2-methylimidazole via Pd 4d/N 2p charge transfer and Pd (4d)/Pd (5s,5p) rehybridization [Chem. Rev. 86 (1986) 1049-1109]. It is possibly similar to the Zn^{2+} atoms coordinated by 2-methylimidazole (ZIF-8 backbone). In our previous work, the Pd 3d5/2 XPS spectrum of Pd@ZIF-8 (denoted as PZ8) also showed a Pd^{$\delta+$} peak at 337.9 eV (*Appl. Catal. B-Environ.* **2018**, 234, 143– 152). At first, we thought it is may be due to the partial oxidation of Pd to PdO when exposed in air prior to XPS test. However, a series of Pd-Z@Z8 samples with different ZIF-8 thickness show a very close particle size of Pd (1.4~1.7 nm), which would give very similar oxidation degree for all ZIF-8 containing samples when exposed in air. But our XPS results show that the peak intensity and proportion of this high-valance peak gradually increases with the growth of ZIF-8 shell. So the assignment of PdO species can be ruled out. Therefore, we believe the high valance peak is from coordinative Pd^{δ^+} -N species which may cause an incomplete reduction to metallic Pd (Micropor. Mesopor. Mat. 2017, 243, 16-21.).

In the literature, bimetallic PdZn alloy has been generally regarded as the active sites for methanol synthesis rather than the monometallic Pd species. In this work, the Pd@ZIF-8 sample and Pd-Z@Z8-4 with a thicker ZIF shell show very poor activity and selectivity to methanol. Only when ZIF-8 was converted to ZnO and then form PdZn with Pd, the activity can be greatly enhanced (*Appl. Catal. B-Environ.* **2018**, 234, 143–152). So we believe that the Pd^{$\delta+$}-N species are not active sites for methanol synthesis.

2. Supplementary tables

<u>Complete</u>	Average	т /т	ZIF-8 content by	ZIF-8 content by	
Samples	width (nm)	I _{ZIF-8} /I _{ZnO}	TGA (%)	BET (%)	
Z@Z8-0.5	28.1	0.034	6.71	6.65	
Z@Z8-1	28.8	0.065	10.62	11.0	
Z@Z8-2	30.0	0.227	29.49	29.4	
Z@Z8-4	30.4	0.381	39.02	39.4	

Table S1. Evaluation of the formation of ZIF-8 layer on ZnO.

 Table S2. Pd content calculated from the data of ICP-AES in Pd-ZnO, Pd-ZIF-8 and different

Pd-Z@Z8-x samples.

Samples	Pd content (wt%)				
Pd-ZnO	2.93				
Pd-ZIF-8	3.11				
Pd-Z@Z8-0.5	2.91				
Pd-Z@Z8-1	2.97				
Pd-Z@Z8-2	3.07				
Pd-Z@Z8-4	3.12				

	Р	T (K)	CH ₃ OH	CO_2	GSHV	CH₃OH	Methanol	
Catalysts	(MPa)		select.	conv.	(ml h^{-1}	STY (g	yield (g	Ref.
	(IVIFa)		(%)	(%)	g-1)	$g_{cat}^{-1} h^{-1}$)	$g_{Pd}^{-1} h^{-1}$)	
$16\%Pd_{0.1}Zn_1/$	3	523	99	6.3	1800	0.04	0.9	
CNTs(h-type)								1
5% Pd/ZnO, SI	2	523	60	10.5	3600	0.08	1.6	2
5% Pd-ZnO,								
Wet	3.9	523	51	11.45	13800	0.29	5.8	3
impregnation								
5% Pd:Zn	2	500	40	10.0	2(00	0.00	1.0	4
(1:5)/TiO ₂	2	523	40	10.0	3600	0.06	1.2	4
5 wt%	2	402	4.5	0.2	2(00	0.05	1	F
Pd/ZnO/Al ₂ O ₃	3	493	45	9.3	3600	0.05	1	5
1 wt% Pd/β-		522	52	1 7	00000	0.05	25	C
Ga ₂ O ₃	3	523	52	1./	80000	0.25	25	6
5% Pd@Zn	4.5	543	65	14.0	18000	0.60	12.0	7
PZ8-400	4.5	543	56	14.7	21600	0.65	14.4	8
	28-1 4.5	523	79	6.6	19200	0.36	12.1	this
Pd-Z@Z8-1								work
	4.5	543	74	9.3	19200	0.47	15.7	this
Pd-Z@Z8-1								work

Table S3. Comparison of activities over our Pd-Z@Z8-1 catalyst with other reported Pd catalysts in the literature in CO_2 hydrogenation reaction.

Discussion on the effect of pressure and contact time

In CO_2 hydrogenation to methanol, the main competitive reaction is the reverse water gas shift (RWGS) process to give CO:

$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \qquad \Delta H_{298K} = -49.5 \text{kJ/mol}$$
(1)
$$CO_2 + H_2 \leftrightarrows CO + H_2O \qquad \Delta H_{298K} = 41.2 \text{ kJ/mol}$$
(2)

Thermodynamically, increasing the pressure could enhance both CO_2 conversion rate and methanol selectivity. Increasing the contact time of the reactants and catalysts could also enhance the CO_2 conversion rate. However, longer contact time always means lower flow rate of reactants (lower GSHV), leading to lower methanol STY. Table S3 only shows part of reported results of Pd-based catalysts in CO_2 hydrogenation to methanol.

It should be pointed that different catalysts have different optimized conditions. The reactor parameters such as reactor diameter and catalyst loading are normally different from each other, which would also effect the final activity. So it is very hard to achieve a precise and perfectly fair comparison.

Sample	$E_a (kJ \cdot mol^{-1})$				
Pd-ZnO	36.51				
Pd-Z@Z8-0.5	29.79				
Pd-Z@Z8-1	30.68				
Pd-Z@Z8-2	29.46				
Pd-Z@Z8-4	34.85				

Table S4. The calculated E_a values over Pd-ZnO and different Pd-Z@Z8-x samples.

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