



Supplementary Materials

Facile synthesis of microporous carbons from biomass waste as high performance supports for dehydrogenation of formic acid

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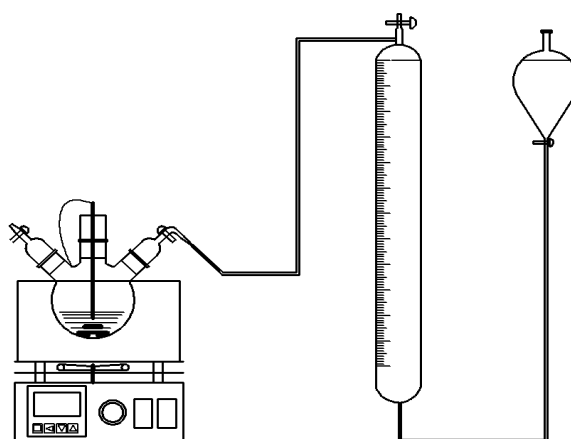


Figure S1. Experimental apparatus of H₂ generation from the FA dehydrogenation.

The average particles sizes were estimated from XRD by Debye-Scherrer. Equation (S1):

$$D = K\lambda / BCOS\theta \quad (1)$$

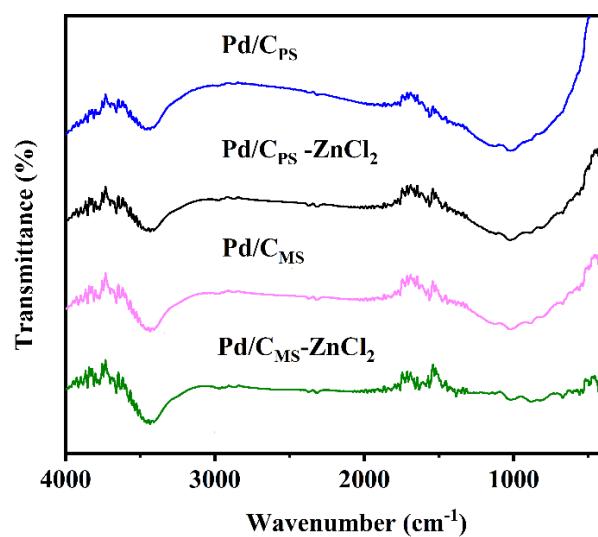


Figure S2. The spectrum of various catalysts.

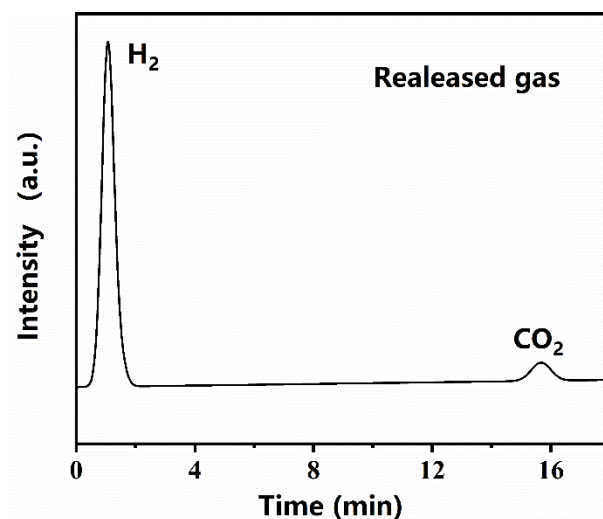


Figure S3. GC spectrum using TCD for the gas from FA over $\text{Pd/C}_{\text{MS}}\text{-ZnCl}_2$.

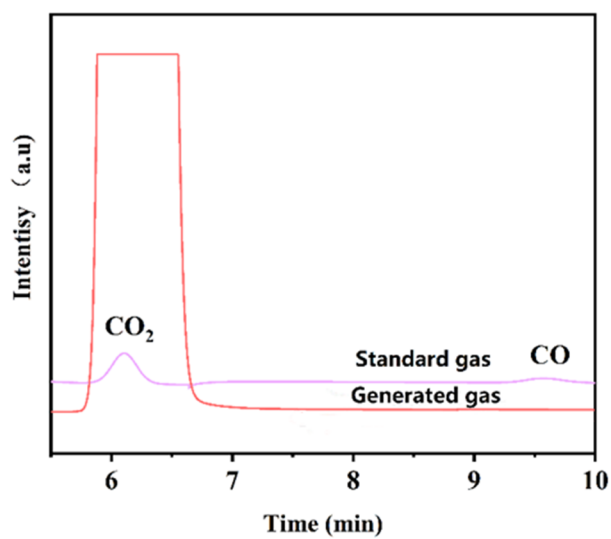


Figure S4. GC spectrum using PDHID for the standard gas and the gas from FA over $\text{Pd/C}_{\text{MS}}\text{-ZnCl}_2$.

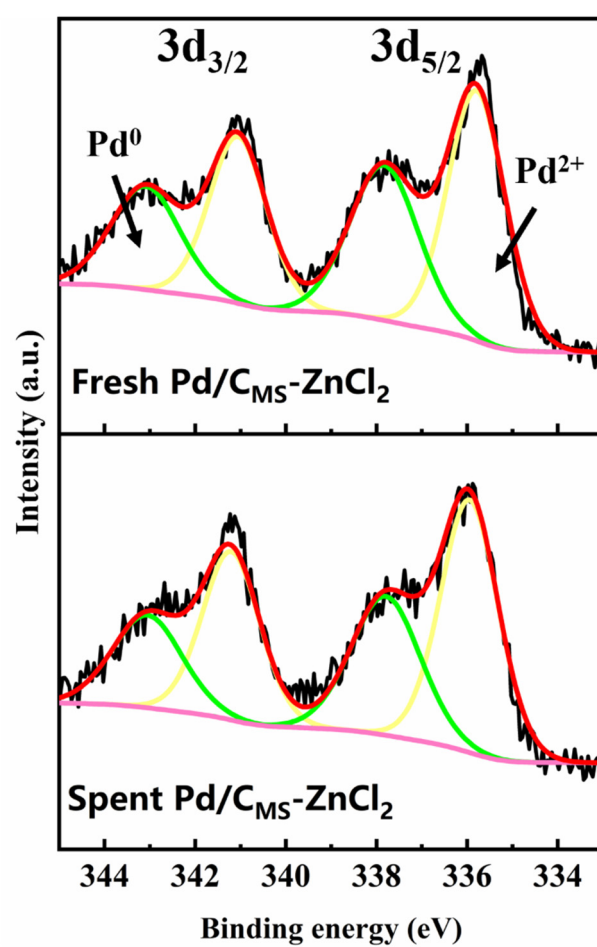


Figure S5. XPS patterns of Pd 3d of Pd/C_{MS}-ZnCl₂ before and after reaction.

Table S1. O content of various catalysts (at %).

| Catalysts | O | O1 | O2 | O3 | O4 |
|---------------------------------------|-------|------|------|------|------|
| Pd/C _{PS} | 6.30 | 0.36 | 2.31 | 3.30 | 0.33 |
| Pd/C _{PS} -ZnCl ₂ | 10.26 | 0.40 | 4.92 | 4.44 | 0.50 |
| Pd/C _{MS} | 8.06 | 0.29 | 3.03 | 4.30 | 0.44 |
| Pd/C _{MS} -ZnCl ₂ | 12.50 | 0.44 | 5.98 | 5.73 | 0.35 |

Table S2. C content and Ash of various catalysts.

| Catalysts | XPS (at.%) | | | | Ash (wt%) |
|---------------------------------------|------------|-------------------|------------|---------------------------|-----------|
| | C | C=C aromatic C | phenolic C | aliphatic carboxylic C | |
| Pd/C _{PS} | 89.17 | 70.19 | 14.86 | 4.12 | 4.38 |
| Pd/C _{PS} -ZnCl ₂ | 85.10 | 67.67 | 13.84 | 3.59 | 3.19 |
| Pd/C _{MS} | 87.47 | 69.76 | 14.08 | 3.63 | 0.60 |
| Pd/C _{MS} -ZnCl ₂ | 83.00 | 61.74 | 17.34 | 3.92 | 0.21 |

Table S3. Pd content of various catalysts.

| Catalysts | XPS (at.%) | | | ICP (wt%) |
|---------------------------------------|------------|-----------------|------------------|-----------|
| | Pd | Pd ⁰ | Pd ²⁺ | Pd |
| Pd/C _{PS} | 4.53 | 2.99 | 1.54 | 4.76 |
| Pd/C _{PS} -ZnCl ₂ | 4.64 | 2.96 | 1.68 | 4.78 |
| Pd/C _{MS} | 4.47 | 2.91 | 1.56 | 4.67 |
| Pd/C _{MS} -ZnCl ₂ | 4.50 | 2.90 | 1.60 | 4.70 |

Table S4. FA dehydrogenation catalyzed by various catalysts.

| Catalysts | TON _x | | | |
|---------------------------------------|------------------|-------|-------|-------|
| | 1 | 5 | 60 | 120 |
| Pd/C _{PS} | 5.3 | 43.5 | 108.8 | 130.6 |
| Pd/C _{PS} -ZnCl ₂ | 19.0 | 92.3 | 387.4 | 462.5 |
| Pd/C _{MS} | 5.6 | 54.4 | 141.5 | 168.5 |
| Pd/C _{MS} -ZnCl ₂ | 28.3 | 103.3 | 413.5 | 484.3 |