

Ambient Conversion of Carbon Dioxide into Liquid Fuel by a Heterogeneous Synergetic Dual Single-Atom Catalyst

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Abstract:

Ambient conversion of carbon dioxide into various liquid fuels or chemicals is a potential economical solution for reducing CO₂ emissions, which may be responsible for recent climate change. Here, we report a highly active dual single-Pd-atom catalyst for ambient conversion of CO₂ to formic acid using a step-by-step catalyst design strategy by the density functional theory (DFT) method. The theoretically predicted catalyst is synthesized experimentally and verified to capture a significant amount of CO₂ (5.05 mmol/g, 273 K), and it can efficiently convert CO₂ to formic acid under ambient conditions (30 °C, 1 bar) with a turnover frequency (TOF) as high as 13.46 h⁻¹, which is the first such report in the field of heterogeneous catalysts. Two major factors contributing to this extraordinary catalytic activity include a pore enrichment effect of the microporous structures of the covalent triazine framework and a ternary synergetic effect among two neighbouring Pd atoms and rich nitrogen environment. Our work may aid the development of heterogeneous catalysts to produce other commonly used fuels from CO₂ under ambient conditions.

Main

With the unrestrained use of fossil energy, excessive emission of CO₂ has become one of the most concerning environmental problems in the world. The selective hydrogenation of CO₂ into useful liquid fuels is regarded as the most promising route to replace fossil feedstocks and realize CO₂ emission reduction.^{1, 2, 3} Hydrogenation of CO₂ to formic acid, one of the most basic liquid fuels, which is present as formate in practical production to shift thermodynamic equilibrium forward, has attracted increasing attention in recent years.^{4, 5, 6} Moreover, with the rapid development of formic acid dehydrogenation techniques, formic acid is expected to become an attractive hydrogen carrier in fuel cells with its great advantages of high volumetric hydrogen density (53 g H₂ per litre of HCOOH), high chemical stability, and low toxicity.^{6, 7, 8} Thus, developing an efficient catalyst system for CO₂ capture and conversion to formate without further energy input (ambient conversion) is highly desired and could result in a truly carbon-neutral liquid fuel.

Great efforts have been made to conduct CO₂ conversion to formate, including the use of homogenous organometallic complexes^{9, 10, 11}, immobilized organometallic complexes^{12, 13} and supported noble metal nanoparticles^{14, 15, 16}. Among them, homogeneous catalyst systems can achieve the target of ambient conversion of gaseous CO₂. For example, Fujita, Himeda *et al.*^{17, 18, 19, 20, 21} reported a series of half-sandwich Ir(III) complexes, which realized the formation of formate from CO₂ at 25 °C and 1 bar by modulating the electron donating effect of the ligands. Linehan *et al.*²² reported a noble-metal free molecular catalyst system for the production of formate from CO₂ and H₂ at room temperature and atmospheric pressure. However, the disadvantages of homogeneous catalytic systems, such as poor reaction continuity, poor stability, and difficulty in product separation, prevent their large-scale application. It is of great significance to develop a heterogeneous catalytic system for the conversion of gaseous CO₂ to formic acid under ambient conditions, which hasn't been reported in the literature. Single-atom catalysts (SACs),^{23, 24, 25, 26} a new frontier in heterogeneous catalysis, which have advantages of both homogeneous and

heterogeneous catalysts, are expected to be potential catalysts for the hydrogenation of CO₂ to formic acid under ambient conditions. Shao *et al.*²⁷ demonstrated that SACs are highly effective for the hydrogenation of CO₂ to formic acid by constructing an atomically dispersed Ir catalyst, which presented the best performance to date for heterogeneous conversion of CO₂ to formate under high temperature and pressure conditions. Unfortunately, even SACs cannot achieve ambient conversion of CO₂ to formic acid. Compared to SACs, dual single-atom catalysts with synergistic effects between adjacent metal atoms and tuneable electronic environments could further improve the intrinsic activity of the catalyst.^{28, 29, 30, 31, 32} However, these researches on CO₂ hydrogenation mainly focus on electrocatalysis^{32, 33, 34} or high temperature and high pressure operation conditions³¹. Therefore, rational design of highly efficient dual single-atom catalysts with multi- synergetic sites may realize ambient conversion of CO₂ to formic acid.

In this work, we realized ambient conversion of CO₂ to formic acid by a heterogeneous catalyst, which consists of dual Pd single atoms anchoring on a microporous layered 2,6-pyridinedicarbonitrile-derived covalent triazine framework (2,6-DCP-CTF). First, we screened seven noble metal SACs by using the DFT method and predicted Pd as the most active metal for the hydrogenation of CO₂ to formic acid among various noble metals. Furthermore, we found that the dual Pd atoms within nitrogen rich environment exhibited a much lower barrier for this reaction than that of the Pd single atom, indicating that a ternary synergetic effect among two neighbouring Pd atoms and rich nitrogen environment could further improve the intrinsic activity of Pd. The experimental results verified the predictions. By regulating the loading percentage of Pd, we obtained Pd/[2,6-DCP-CTF] with abundant dual Pd atoms, which achieved ambient conversion of CO₂ to formic acid. As a typical example of a theoretical prediction experiment, this work is expected to play an important role in the design of CO₂ conversion catalysts at room temperature and atmospheric pressure in the future.

Results and discussion

Theoretical screening of noble metal SACs

To save effort, we first carried out theoretical screening of noble metal SACs for the proof of concept. To simplify, 1,3,5-triazine,2-(2-pyridinyl) ligand-anchored single noble metal atoms were used as SAC models for CO₂ hydrogenation. It was previously reported that the first hydrogenation step is the rate-determining step for CO₂ hydrogenation to formate.^{12, 35} Thus, we chose the first hydrogenation step of CO₂ to formate as the criterion to explore the most active sites for CO₂ activation among seven different noble metal ions (Ru, Rh, Pd, Ir, Pt, Au, and Os) by using DFT method. We compared the adsorption energies of CO₂ on the above noble metal atoms and their corresponding ions. It was found that the absolute values of the adsorption energies on the metal atoms were much lower than those on their corresponding ions (Supplementary Fig. 1). Taking the adsorption configuration of Pd-based catalysts as an example, CO₂ is physically adsorbed on 2,6-DCP-CTF-[Pd⁰] with a Pd-O bond length of 3.1 Å, while its adsorption on 2,6-DCP-CTF-[Pd²⁺] is stronger with a Pd-O bond length of 2.2 Å (Supplementary Fig. 2). Therefore, the above seven kinds of noble metal ions dispersed on 2,6-DCP-CTF were adopted as active sites for CO₂ hydrogenation. The computational results of the energy barriers of the first hydrogenation step of CO₂ to formate on 2,6-DCP-CTF-[M^{δ+}] are shown in Fig. 1a and Supplementary Table 1. Fig. 1a shows that 2,6-DCP-CTF-[Pd²⁺] presents the lowest energy barrier of 1.37 eV, which indicates that Pd is the most effective metal for CO₂ activation among the seven noble metals assessed.

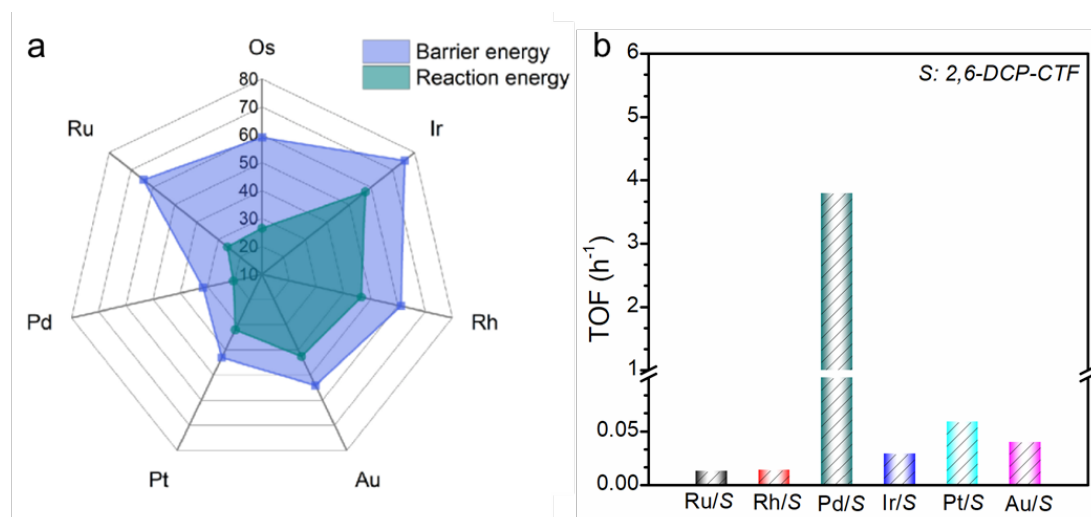


Fig. 1 Theoretical screening of noble metal SACs (a) and their corresponding catalytic activity for CO₂ hydrogenation to formate in experiment (b). Reaction conditions: 20 mg catalyst, 5 ml of 1 M NaHCO₃ solvent, 30 °C, 0.1 MPa, and 12 h.

Then, we chose six of the most commonly used noble metals (Ru, Rh, Pd, Ir, Pt, Au) as examples to confirm the above theoretical predictions. *2,6-DCP-CTF* was prepared by the traditional ionothermal method by trimerization of *2,6-DCP* in molten ZnCl₂ at 400 °C for 20 h and 600 °C for another 20 h (Fig. 2a).³⁶ The formation of the corresponding covalent triazine rings was confirmed by Fourier transform infrared spectroscopy (FT-IR). As shown in Fig. 2b, *2,6-DCP* possesses a clear cyano group absorption peak at 2245 cm⁻¹. This peak disappeared completely after the formation of *2,6-DCP-CTF*, and the characteristic absorption peaks of the triazine ring at 1540 cm⁻¹ and 1100 cm⁻¹ were visible, which indicated that the trimerization was complete. In addition, the porosity and elemental contents of *2,6-DCP-CTF* were determined. Specifically, the prepared *2,6-DCP-CTF* exhibits adsorption properties typical of microporous materials and has a specific surface area of 1964 m²/g, three types of pores with sizes of 0.57, 1.4, and 2.7 nm and a total pore volume of 1.54 cm³/g (Fig. 2c, Supplementary Table 2). The nitrogen content was estimated to be 8.01 wt.% (Supplementary Table 3), which is lower than the theoretical value (32.6%). This suggests that the material generates a considerable number of voids or defect sites during the trimerization process at high temperature. The morphological characteristics of *2,6-DCP-CTF* were detected by using scanning electron microscopy

(SEM) and transmission electron microscopy (TEM). As shown in Fig. 2d and Supplementary Fig. 3, *2,6-DCP-CTF* exhibited obvious layered properties, which is consistent with the schematic model in Fig. 2a. *M*/[*2,6-DCP-CTF*] (*M* = Ru, Rh, Pd, Ir, Pt, Au) catalysts were prepared by soaking the support powders into the corresponding aqueous noble metal salt solutions with a 1 wt.% theoretical loading percentage followed by filtration, washing, and drying after stirring for 12 h under a N₂ atmosphere.

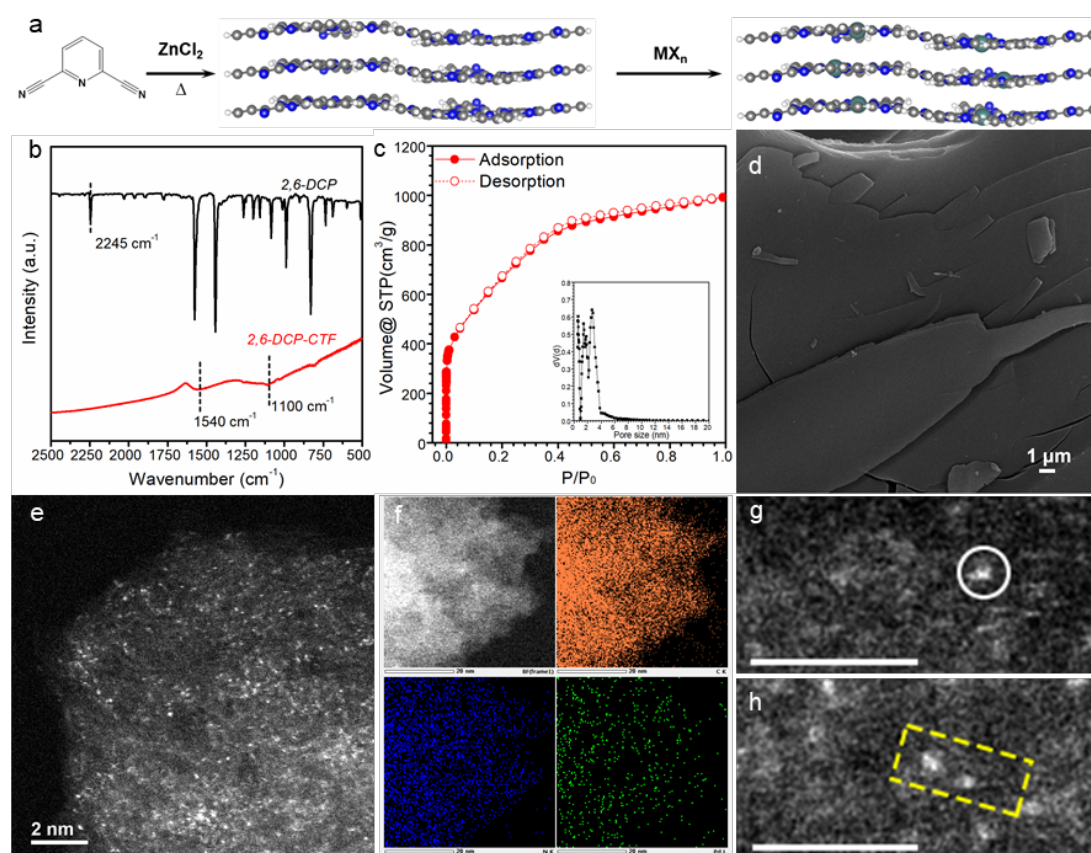


Fig. 2 Synthesis and structural characterizations of *2,6-DCP-CTF* and *Pd*/[*2,6-DCP-CTF*]. a, Schematic illustration of the fabrication procedure of the *2,6-DCP-CTF* and *M*/[*2,6-DCP-CTF*] catalysts. b, FT-IR spectra of the monomer *2,6-DCP* and *2,6-DCP-CTF* samples. c, N₂ adsorption-desorption isotherms (77 K) and DFT method pore size distribution of *2,6-DCP-CTF*. d, SEM images of *2,6-DCP-CTF*. e, Aberration-corrected STEM of *Pd*/[*2,6-DCP-CTF*]. f, EDS mapping results of *Pd*/[*2,6-DCP-CTF*]. g, h, Magnified HAADF-STEM image of *Pd*/[*2,6-DCP-CTF*] (the scale bar is 1 nm).

The catalytic performances of the as-prepared M/[2,6-DCP-CTF] catalysts for CO₂ hydrogenation were studied at 30 °C in a H₂/CO₂ mixture (0.1 MPa) with NaHCO₃ (1 M) as an additive in the liquid phase. After reaction for 12 h, formate was detected using high-performance liquid chromatography (HPLC). As shown in Fig. 1b and Supplementary Table 4, Pd/[2,6-DCP-CTF] exhibited the highest turnover frequency of 3.80 h⁻¹ among the six catalysts, which confirmed the predictions of the theoretical calculations. The catalytic activities of the six catalysts are in the order of Pd/[2,6-DCP-CTF] > Pt/[2,6-DCP-CTF] > Au/[2,6-DCP-CTF] > Ir/[2,6-DCP-CTF] > Rh/[2,6-DCP-CTF] > Ru/[2,6-DCP-CTF]. The above experiments verified the theoretical predictions that Pd is the most effective metal for the hydrogenation of CO₂ to formate. Based on the Pd/[2,6-DCP-CTF] catalyst, we explored the fine structure of Pd by using aberration-corrected STEM. As shown in Fig. 2e, Pd exhibited atomic dispersion on the support, and the white dots were identified as Pd species according to the contrast and EDS mapping analysis (Fig. 2f, Supplementary Fig. 4). In addition, there were two kinds of Pd species in the observation range: single- and dual-Pd-atom species (Figs. 2g and 2h).

Optimization of the Pd/[2,6-DCP-CTF] structure and performance

To distinguish which Pd species contribute to the hydrogenation of CO₂ into formic acid, we carried out theoretical calculations. Based on the experimental results, we rebuilt the theoretical model. As shown in Fig. 3a, 2,6-DCP-CTF, possessing a two-dimensional structure, consists of two types of pores. The initial periodic structure contains abundant nitrogen atoms with a weight loading of 32.6%. Under the ionothermal process at high temperature (600 °C) in the experiment, carbonation of the sample occurs. Most of the nitrogen atoms would be replaced by carbon atoms, leading to a low nitrogen weight loading of 8.01%. In addition, structural collapse makes many larger pores. Through-pores (in Fig. 3b) with enough nitrogen atoms in the framework structure of 2,6-DCP-CTF were necessary to anchor neighbouring Pd atoms in the framework. Moreover, we investigated the CO₂ uptake performance. As shown in Fig. 3c, the nitrogen-rich pores, which are good CO₂ adsorbents, have a high

CO₂ concentration at 303 K. The pore-enrichment effect favours CO₂ conversion and can increase the reaction rate.^{37, 38}

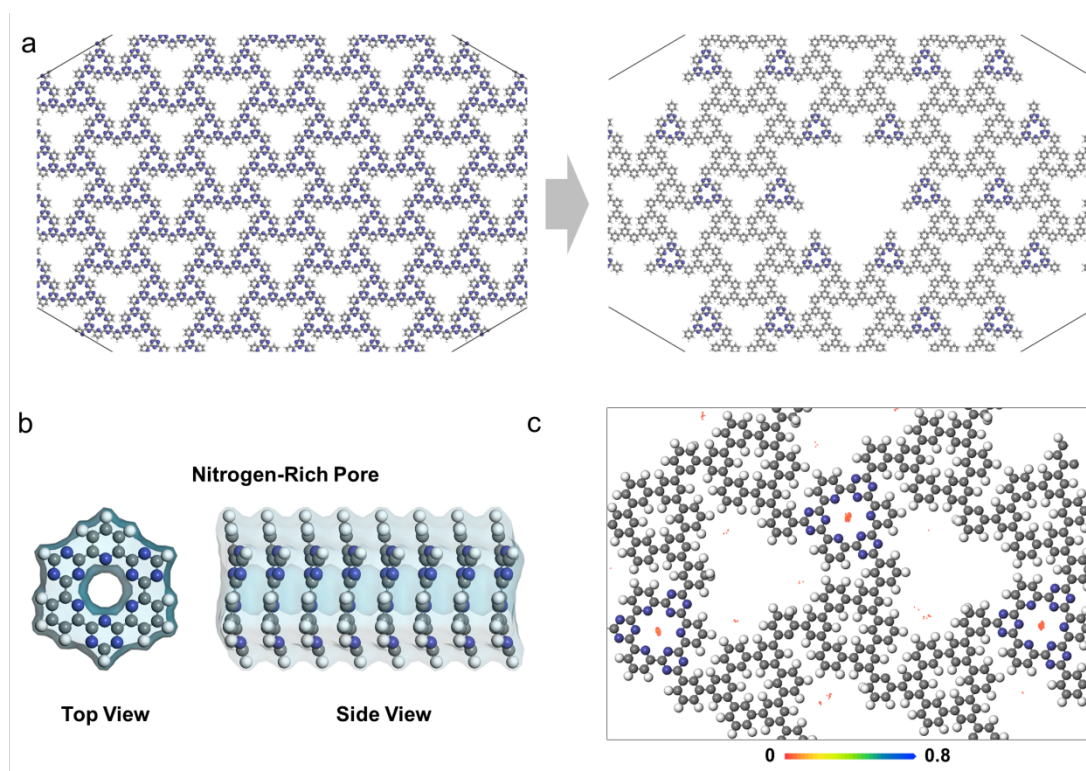


Fig. 3. Framework structure of 2,6-DCP-CTF. a. Schematic of structural changes before and after ionothermal processing at high temperature (600 °C). b. Schematic of a nitrogen-rich pore. c. CO₂ density map in the final framework structure of 2,6-DCP-CTF.

Based on the above understandings, the Pd/[2,6-DCP-CTF] dual single-atom model was built to evaluate the free energy barrier of CO₂ hydrogenation, in which two Pd²⁺ ions were anchored in the neighbouring layers through the Pd-N coordination bonds (Supplementary Fig. 5). Hydrogen dissociation was first investigated. As shown in Fig. 4a, the hydrogen molecule was easily dissociated with the help of the N atoms in the paratriazine ring. The free energy barrier of hydrogen dissociation was only 2.78 kcal/mol. The synergetic effect between Pd and N contributes to hydrogen dissociation under ambient conditions, providing abundant active hydrogen to further reaction. Two reaction pathways for CO₂ hydrogenation on Pd/[2,6-DCP-CTF] are shown in Figs. 4b and 4c. The pathway starting from the

configuration of hydrogen and CO₂ co-adsorbed on a single Pd atom is the Pd₁ pathway. For the Pd₂ pathway, CO₂ is adsorbed on one Pd atom, while hydrogen is adsorbed on another Pd atom. The intermediate structures of CO₂ adsorption and hydrogenation in the Pd₁ system and Pd₂ system are shown in Fig. 4c. The adsorption energies of hydrogen and CO₂ in these two systems are similar. However, there is an obvious energy barrier difference between the two reaction pathways. The free barrier energy in the Pd₁ pathway is 34.1 kcal/mol, while that in the Pd₂ pathway is 21.7 kcal/mol. The synergy of the neighbouring Pd²⁺ ions improved the activity of CO₂ hydrogenation in the Pd₂ pathway. In addition, we further calculated the reaction path of formate radical hydrogenation to formic acid. As shown in Supplementary Fig. 6, there are also two pathways for formate radical hydrogenation. The free energy barriers of these two paths are 2.2 kcal/mol and 9.1 kcal/mol, respectively. Thus, the rate-determining step of hydrogenation of CO₂ to formic acid is indeed the step of CO₂ hydrogenation.

Furthermore, we studied the mechanism of the high activity of the dual-atom system at the microscopic electron level. As shown in Fig. 4c, in the Pd₁ pathway, the adsorbed CO₂ and H in the initial state (IS) are far away, and the C-H bond length is 3.43 Å. While in the Pd₂ pathway, the C-H bond length is 2.60 Å. The interaction region indicator (IRI)^{39, 40} for the co-adsorption configurations of CO₂ and H in the two pathways were analysed. As shown in Fig. 4d, in the Pd₂ system, there is a vdW interaction between adsorbed H and CO₂. Thus, the H is easier to transfer to CO₂. Besides, the atom charges of H in the Pd₁ and Pd₂ pathways are 0.29 e and 0.15 e. In comparison, the atom charges of C atoms of CO₂ in both pathways are 0.87 e. Thus, H with a low charge is more easily transfer to the C atom of CO₂. Moreover, in addition to the bonding interaction between H and its adsorbing Pd²⁺ (Pd-I), the H atom was also attracted by the Pd²⁺ ion (Pd-II) in the neighbouring layer. The attraction of Pd-II to H weakens the adsorption interaction between H and Pd-I, which favours H to leave Pd and transfer to CO₂. Therefore, the dual-atom system shows better catalytic activity for the hydrogenation of CO₂ to formic acid.

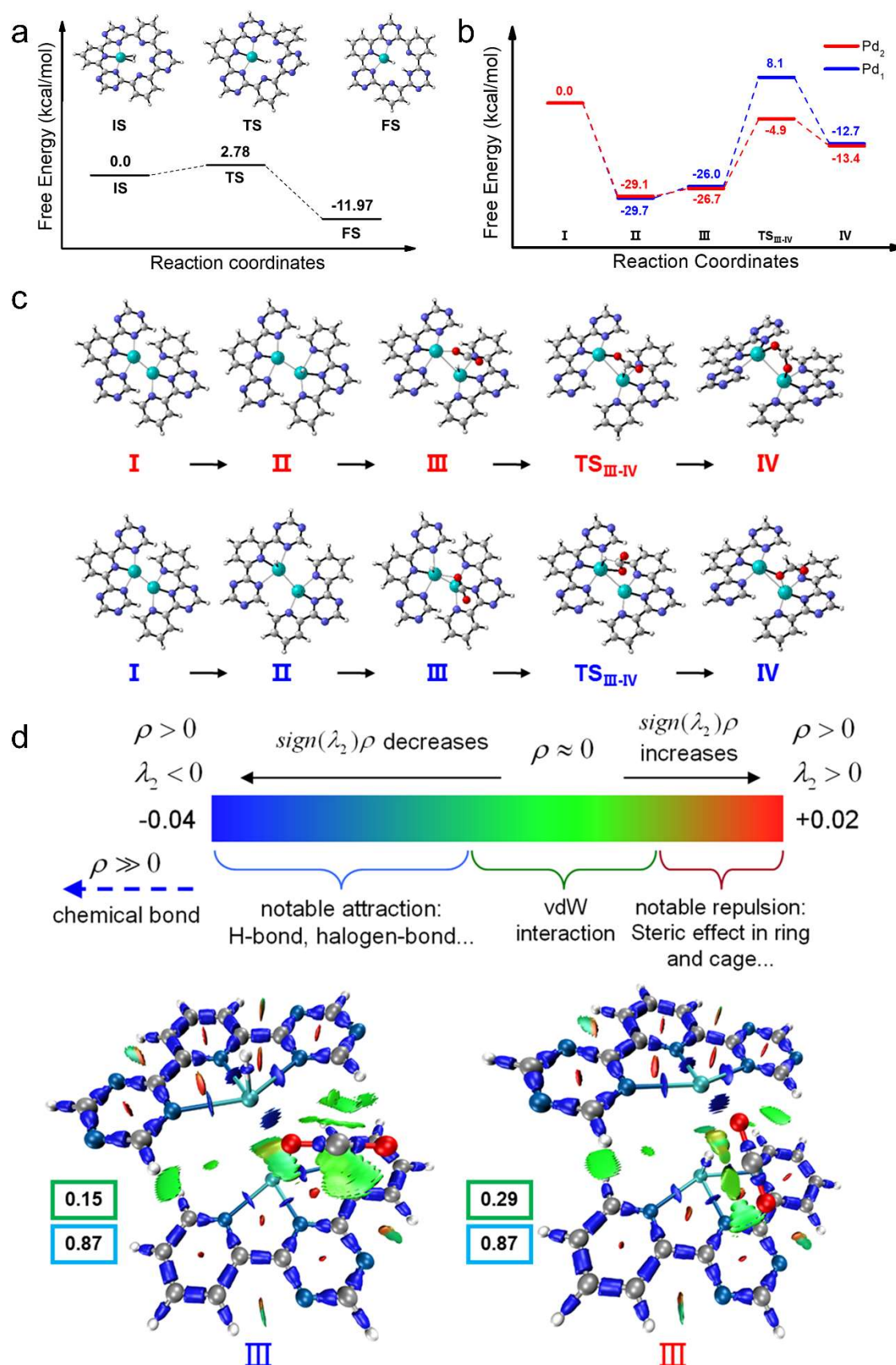


Fig. 4. DFT calculations. a, Hydrogen dissociation energy with the structures of the initial state (IS), transition state (TS), and final state (FS). b, Free energy profile of

CO₂ hydrogenation through the Pd₁ pathway and Pd₂ pathway c, Intermediate structures of CO₂ adsorption and hydrogenation in the Pd₁ system and Pd₂ system. d. Isosurface of the interaction region indicator (IRI) for the CO₂ and H co-adsorption configurations in the Pd₁ (left) and Pd₂ (right) system, respectively. The isosurface is mapped according to the function $IRI = 1.0 \text{ sign}(\lambda_2)\rho$. The values in the green and blue frames are the atom charges of adsorbed H and C atoms of CO₂, respectively.

Synthesis and catalytic evolution of Pd/[2,6-DCP-CTF] dual single-atom catalyst

According to the above theoretical model, we calculated the theoretical Pd loadings to be 4.76 wt.% for the ideal dual single-atom catalyst with Pd atom pairs distributed in two close layers. Thus, we tried to prepare Pd/[2,6-DCP-CTF] with abundant dual Pd atoms by increasing the initial Pd loading percentage to 4.0 wt.% and 5.0 wt.%. The actual metal loadings were determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES) to be 3.45 wt.% and 4.40 wt.%, and the corresponding samples were denoted as 3.45Pd/[2,6-DCP-CTF] and 4.4Pd/[2,6-DCP-CTF], respectively. The dispersions of Pd in the above samples were first investigated by TEM at low magnification. As shown in Supplementary Fig. 7a, 3.45Pd/[2,6-DCP-CTF] exhibited the typical morphology of the 2,6-DCP-CTF support without any Pd nanoparticles, which indicated that the Pd species were atomically dispersed. However, Pd nanoparticles appeared in 4.4Pd/[2,6-DCP-CTF] as the Pd loading percentage was close to saturation (Supplementary Fig. 7b). To reveal the fine structure information of Pd in 3.45Pd/[2,6-DCP-CTF], we performed aberration-corrected scanning transmission electron microscopy (AC-STEM) characterization. As shown in Fig. 5a, 3.45Pd/[2,6-DCP-CTF] exhibited abundant white dots, which were identified as Pd species according to the contrast and EDS mapping analysis (Fig. 5b). In the aberration-corrected STEM image at high magnification shown in Fig. 5c, most of the Pd species existed in the form of dual atoms, which were marked with yellow rectangles. In addition, there were few isolated and multiple Pd atoms because of the randomness of the Pd loading process and inhomogeneity of the support. We further quantified the percentage of dual Pd

atoms to be approximately 66% in this range (Fig. 5d). The X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) were measured to determine the electronic and coordination structures of Pd atoms in 3.45Pd/[2,6-DCP-CTF] catalysts. As shown in the Pd K-edge XANES profiles (Fig. 5e), the intensity of the white line of Pd in the 3.45Pd/[2,6-DCP-CTF] sample is higher than that of the Pd foil and close to that of PdO, suggesting that the Pd species carry positive charges.⁴¹ XPS was carried out to obtain deeper insight into the electronic properties of 3.45Pd/[2,6-DCP-CTF]. (Supplementary Fig. 8) The Pd 3d_{5/2} peak was located at 337.6 eV, indicating a near +2 valence state.⁴² The Fourier transform (FT) k³-weighted EXAFS spectrum in R space of the 3.45Pd/[2,6-DCP-CTF] sample (Fig. 5f) exhibits two obvious peaks. The fitting details are listed in Fig. 5 g and Supplementary Table 5. The first prominent peak at 1.75 Å corresponds to the Pd-N coordination path with a coordination number (CN) of 2.48 ± 0.88 . The second peak located at 2.91 Å is attributed to the Pd-Pd coordination path of dual Pd atoms with a CN of 1.75 ± 0.624 . The above parameters are in line with our DFT model (Fig 5 h). Overall, we synthesized Pd/[2,6-DCP-CTF] with abundant dual Pd atoms in the experiment as the theoretical predictions.

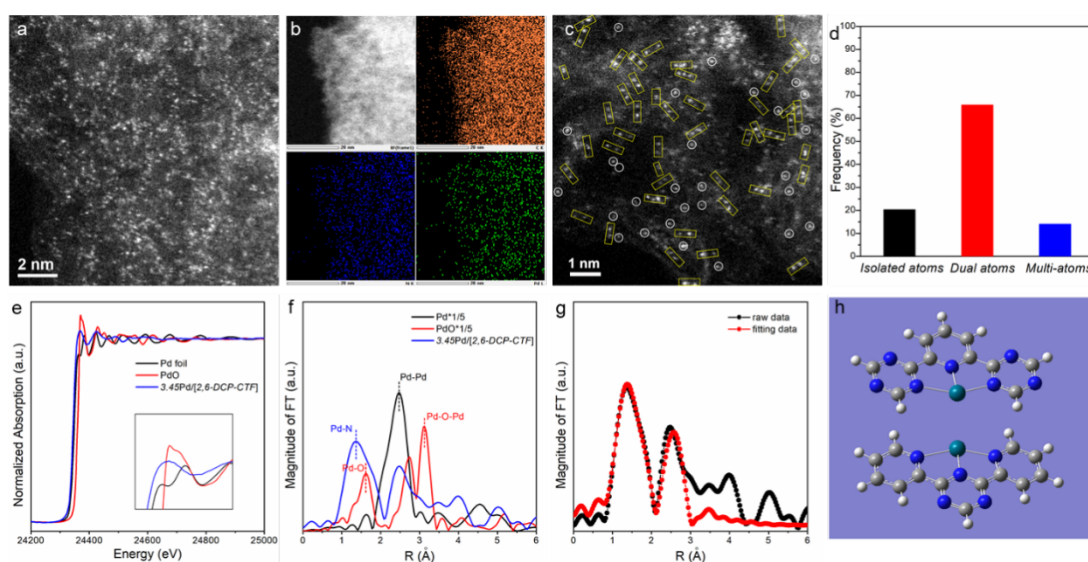


Fig. 5 Structural and electronic characterizations of Pd/[2,6-DCP-CTF]. a, Aberration-corrected STEM image of the 3.45Pd/[2,6-DCP-CTF] catalyst. b, EDS mapping results of 3.45Pd/[2,6-DCP-CTF]. c, Aberration-corrected STEM image at

high magnification. d, Histogram of the contents of isolated Pd atoms, dual Pd atoms, and multi-Pd atoms for 3.45Pd/[2,6-DCP-CTF]. e, Pd K-edge XANES spectra for 3.45Pd/[2,6-DCP-CTF]. Pd foil and PdO were used as the reference. f, Pd K-edge EXAFS in R space for 3.45Pd/[2,6-DCP-CTF]. Pd foil and PdO were used as the reference. g, R space fitting curve of 3.45Pd/[2,6-DCP-CTF]. h, Structural model of Pd/[2,6-DCP-CTF].

The CO₂ sorption properties of the catalysts were investigated using volumetric methods at 273 K and 303 K, and a commercial Pd/C catalyst was used as the reference. As shown in Fig. 6a, b, the CO₂ adsorption isotherms of both 3.54Pd/[2,6-DCP-CTF] and commercial Pd/C displayed reversible adsorption capacity. When the pressure approached 1 bar, the CO₂ uptake of 3.54Pd/[2,6-DCP-CTF] reached 5.05 mmol/g and 2.47 mmol/g at 273 K and 303 K, respectively, which were much higher than those of commercial Pd/C (2.92 mmol/g and 1.49 mmol/g). These results indicate that the rich microporous structure and abundant nitrogen content of 2,6-DCP-CTF contribute to the enrichment and capture of CO₂, which agrees well with the theoretical predictions (Fig. 3c). Furthermore, we compared the CO₂ adsorption capacities of our Pd/[2,6-DCP-CTF] catalyst with those of excellent CO₂ capture materials in the literature.³ As shown in Supplementary Table 6, our catalyst exhibits nearly the highest adsorption capacity under identical conditions. As an excellent CO₂ capture material with synergistic dual Pd atoms, the 3.45Pd/[2,6-DCP-CTF] sample is expected to achieve efficient conversion of carbon dioxide.

The catalytic properties of the as-obtained 3.45Pd/[2,6-DCP-CTF] catalyst were evaluated under the same conditions to explore the disparity in catalytic properties between different Pd species, isolated Pd atoms and dual atom pairs. As shown in Fig. 6c, the 3.45Pd/[2,6-DCP-CTF] sample was considerably more active than the 0.82Pd/[2,6-DCP-CTF] sample, indicating that dual Pd atoms exhibited much higher activity. To demonstrate our assumption, we synthesized a Pd/[2,6-DCP-CTF] sample with a much lower Pd loading (0.39 wt.%), where Pd existed mainly as isolated atoms

(Supplementary Fig. 9). As expected, the $0.39\text{Pd}/[2,6\text{-DCP-CTF}]$ sample only yielded 0.17 mM formate under ambient conditions (30 °C, 0.1 MPa) after 12 h, and its TOF was measured to be 0.09 h^{-1} . These results agree well with the theoretical predictions (Fig. 4). In addition, we compared the catalytic activity of our catalysts and a commercial Pd/C catalyst. The results showed that our catalyst exhibited a TOF nearly one order of magnitude higher than that of the commercial Pd/C catalyst. We further investigated the cumulative amount of HCOOH produced within 12 h. As shown in Fig. 6d, upon prolonging the reaction time from 2 h to 4 h, 6 h, 8 h, 10 h and 12 h, the yield of formate increased linearly from 0.14 mmol to 0.26 mmol, 0.37 mmol, 0.47 mmol, 0.56 mmol, and 0.68 mmol, and the TON of the most active catalyst reached 103.68. This indicates that product accumulation has little influence on the reaction and that the catalyst exhibits good stability during the reaction process. Furthermore, we optimized the activity of our catalysts by screening the additives. As shown in Supplementary Table 7, $3.45\text{Pd}/[2,6\text{-DCP-CTF}]$ exhibited much higher activity with 1 M Na_2CO_3 as the additive, and the TOFs reached 13.46 h^{-1} under ambient conditions (30 °C, 1 bar). In addition, we also investigated the direct hydrogenation of Na_2CO_3 and found that formate production was negligible without gaseous CO_2 in the reactant.

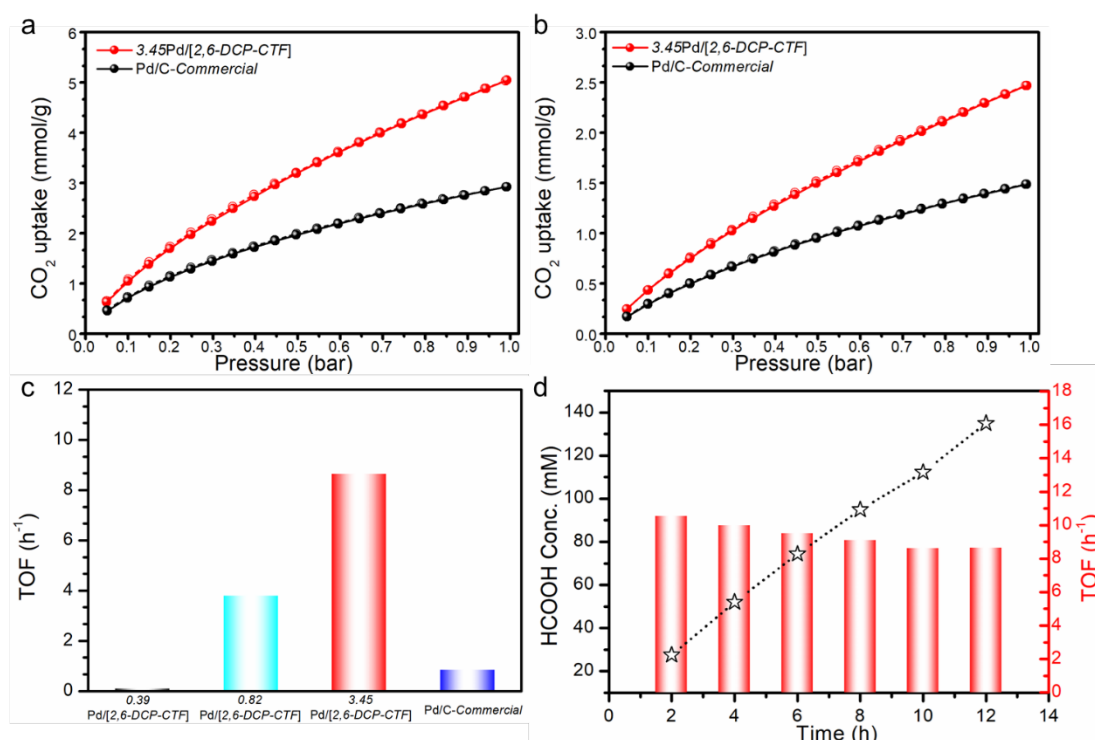


Fig. 6 Catalyst performance and CO₂ uptake data. a, b, CO₂ adsorption (solid symbols) and desorption (open symbols) isotherms of 3.45Pd/[2,6-DCP-CTF] and commercial Pd/C. c, TOF for the hydrogenation of CO₂ into formate over different catalysts. d, Formate yield during the hydrogenation of CO₂ over 3.45Pd/[2,6-DCP-CTF]. Reaction conditions: 20 mg catalyst, 30 °C, 1 bar (CO₂/H₂=1:1), 5 mL NaHCO₃ (1 M), 12 h.

Conclusion

In summary, we have realized effective hydrogenation of CO₂ to formate under ambient conditions on heterogeneous catalysts for the first time. Theoretical calculations based on the DFT method predicted the most active structure of the catalyst to be the ternary synergistic sites in the microporous material (2,6-DCP-CTF) with pore enrichment effect for CO₂. In details, Pd-N synergistic site is favorable for hydrogen dissociation, and Pd-Pd synergistic site for high efficient CO₂ hydrogenation. In experiments, we prepared Pd/[2,6-DCP-CTF] SACs with abundant dual Pd atom pairs derived from different layers of 2,6-DCP-CTF by

regulating the Pd loading percentage and demonstrated that synergistic dual Pd atoms on 2,6-DCP-CTF can capture a significant amount of CO₂ (5.05 mmol/g, 273 K) and efficiently convert CO₂ to formic acid under ambient conditions with a turnover frequency (TOF) as high as 13.46 h⁻¹. This work provides an effective strategy to generate excellent catalysts with high catalytic activity and may pave the way for converting CO₂ to many more liquid fuels under ambient conditions.

Methods

Sample preparation

2,6-DCP-CTF: 2,6-Pyridinedicarbonitrile-derived covalent triazine framework (2,6-DCP-CTF) samples were synthesized by the traditional ionothermal method. Specifically, 2,6-DCP (3 g) and anhydrous ZnCl₂ (15 g) were mixed in a glove box and then transferred into a Pyrex ampule under an inert atmosphere. The ampule was evacuated with a vacuum pump, sealed, and heated to 400 °C for 20 h and then 600 °C for 20 h. The ampule was then cooled to room temperature and opened carefully. The reaction mixture was subsequently ground and then washed thoroughly with large amounts of water to remove most of the ZnCl₂. Further stirring in diluted HCl (2 M) for 12 h was carried out to remove the residual salt. After this purification step, the resulting black powder was filtered, washed successively with water, and dried in vacuum at 150 °C for 12 h.

M/[2,6-DCP-CTF]: *M/[2,6-DCP-CTF]* catalysts (M = Ru, Rh, Pd, Ir, Pt, Au) were prepared by soaking 2,6-DCP-CTF support powder in aqueous solutions with 1 wt.% theoretical metal weight loadings of ruthenium chloride, rhodium chloride, palladium trifluoroacetate, chloroiridic acid, chloroplatinic acid and chloroauric acid (Shanghai Macklin Biochemical Co., Ltd) for 12 h with magnetic stirring under N₂ atmosphere. The suspensions were then filtered and washed with deionized water. The filter cake was dried at 80 °C for 12 h under vacuum. The samples were denoted as *M/[2,6-DCP-CTF]* (M = Ru, Rh, Pd, Ir, Pt, Au). Pd/[2,6-DCP-CTF] SACs with different Pd atom densities were prepared by varying the initial Pd loading percent.

The actual metal weight loadings were detected using inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis.

Characterization

The actual loadings of the noble metals were determined by using ICP-AES on an IRIS intrepid II XSP instrument (Thermo Electron Corporation).

Fourier transform infrared (FT-IR) spectra were collected on a Bruker VERTEX 70v spectrometer equipped with a DLATGS detector using KBr pellets and operated at a resolution of 4 cm⁻¹ for 32 scans.

Specific Surface areas were measured on a Quantachrome Autosorb-iQ using N₂ adsorption isotherms and the Brunauer-Emmett-Teller (BET) analysis method. The samples were degassed under vacuum at 260 °C for 8 h before the adsorption measurements.

CO₂ adsorption isotherms were measured on a Quantachrome Autosorb-iQ using CO₂ as the adsorbate. The samples were degassed under vacuum at 260 °C for 8 h before the adsorption measurements.

X-ray photoelectron spectroscopy (XPS) data were collected using a ThermoFisher ESCALAB 250Xi spectrometer with a monochromatized Al K α X-ray source (1486.6 eV) and an applied power of 150 W. C_{1s} (binding energy 284.8 eV) was used as the reference.

The X-ray absorption spectra (XAS) including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of the sample at K-edge was collected at the Beamline of TPS44A1 in National Synchrotron Radiation Research Center (NSRRC), Taiwan. A pair of channel-cut Si (111) crystals was used in the monochromator. The spectra were recorded at room temperature under the fluorescence mode with a solid-state detector. The Athena software package was used for the data analysis.

Transmission electron microscopy (TEM) analysis was performed by using a FEI

Tecnai G2 F20 operated at 200 keV with a specified point-to-point resolution of 0.27 nm. Aberration-corrected high angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX) images were obtained on a JEOL JEM-ARM200F STEM/TEM system with a guaranteed resolution of 0.08 nm. TEM specimens were prepared by depositing a suspension of the powdered sample on lacey carbon-coated copper grids.

Catalytic reactions

CO₂ hydrogenation to formic acid was performed at 30 °C and 1 bar (H₂:CO₂ = 1:1). In a typical hydrogenation experiment, 20 mg catalyst and 5 mL NaHCO₃ (1 M) were added to a three-necked bottle connected to a balloon. Then, the feed gas was introduced after purging the residual air in the system three times, and the reaction mixture was stirred at 30 °C for 12 h. Formic acid concentrations were determined using high-performance liquid chromatography (HPLC) with an Agilent 1260 II instrument and a Hi-Plex H column and UV detector (210 nm) using 0.005 M H₂SO₄ as the mobile phase.

Computational methods

The first hydrogenation step of CO₂ to formate was calculated using the program Gaussian16 for preliminary screening.⁴³ Calculations were performed by the M06l/6-31G* method for nonmetal elements and the M06l/LANL2DZ method for metal atoms.^{44, 45, 46} The metals were augmented with the corresponding LANL2DZ pseudopotential, which is acceptable in terms of both precision and time requirements. The SMD solvation model⁴⁷ was applied for the simulation in dual Pd systems. The vibrational frequencies of the optimized configurations were analysed to validate that these configurations correspond to a local minimum or transition state (TS). A TS with one imaginary frequency was found and verified by the intrinsic reaction coordinate (IRC) method.⁴⁸

The periodic structure was optimized using the classical molecular mechanical method using a universal force field⁴⁹. The grand canonical Monte Carlo (GCMC)

method and COMPASS force field⁵⁰ were used to predict the CO₂ uptake performance. In every GCMC simulation, 1,000,000 equilibration steps were used before the production stage of 3,000,000 Monte Carlo steps.

The calculation method was based on metal ions with a valence state of 2 or higher that are stably anchored on 2,6-DCP-CTF. 2,6-DCP-CTF has a periodic two-dimensional microporous structure. To reduce the computational complexity, part of 2,6-DCP-CTF was constructed as a catalytic unit, named 2,6-DCP-CTF-[M] ([M] = Ru³⁺, Rh³⁺, Pd²⁺, Ir³⁺, Pt²⁺, Au³⁺, Os⁴⁺).

Data availability

The data that support the findings of this study are available from the authors upon reasonable request.

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Author Contributions

W. -Q. D. conceived the concept and design research. G.- Q. R. designed and carried out the catalyst synthesis, characterization, and catalytic test. S.-L. Z. carried out the catalyst synthesis, characterization, and catalytic test. L. S., J.-K. S. and L. Y. executed the theoretical calculations. T. Y. carried out the TEM characterization. All authors were involved in the writing of the manuscript.

Competing interests

The authors declare no competing interests.