



Catalytic Nanoparticles in MOFs

The Effect of N-Containing Supports on Catalytic CO Oxidation Activity over Highly Dispersed Pt/UiO-67

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Abstract: Investigations of the effects of the support on catalytic properties are important for heterogeneous systems. Herein, we report the preparation of highly dispersed Pt nanoparticles (NPs) in three isomorphous UiO-67-type metal–organic frameworks (MOFs), namely, pristine UiO-67, N-UiO-67, and NH₂-UiO-67. Structural measurements revealed that the sizes of the Pt NPs were 4.5 nm for Pt/UiO-67 and 2.5 nm for N-UiO-67 and NH₂-UiO-67. The dominant influences on the sizes of the

Introduction

In recent decades, supported noble-metal catalysts (NMCs)^[1] have received enormous interest because of their envisioned catalytic performances in practical chemical engineering applications, including selective oxidation^[2] and hydrogenation^[3] as well as carbon-carbon bond coupling.^[4] Essentially, the supports play some important roles both geometrically and electronically. On the one hand, through the functional groups on the surface or matrix of the supports, catalysts can be effectively confined to a specific size and generate unique polyhedral configurations that expose enough highly active crystal planes, and this confinement offers a way to improve the catalytic activity and stability. On the other hand, chemical interactions between the catalyst and the support can adjust the electronic structures of the catalyst (such as d-band offset) and support surface to form a unique interface effect between them.^[5] This effect usually induces different adsorption interactions between the substrate and the catalysts and support and, thereby, endows high catalytic selectivity.^[6] Therefore, investigations of the effects of the support are important for supported heterogeneous systems.

As one new type of periodically porous material, metalorganic frameworks (MOFs),^[7] which are built from the connections between secondary building units (SBUs, such as metal

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Pt NPs are the functional groups of the support and the pore size of the MOF. Furthermore, CO catalytic oxidations were performed as a model reaction. Interestingly, the catalytic performance sequence is 5 % Pt/N-UiO-67 > 5 % Pt/UiO-67 > 5 % Pt/ NH₂-UiO-67. A combination of experimental measurement and DFT calculation revealed that the catalytic properties depend on not only the size of the Pt NPs but also the nature of the support.

clusters and metal ions) and rigid organic ligands, possess high surface areas and readily adjustable pores. Therefore, such advantages make them a possible ideal support in heterogeneous catalysts. Many chemists have been motivated by this belief, and their research efforts in the past decade have resulted in several noble-metal-supported MOF catalysts consisting of various MOFs (e.g., MOF-74,^[8] ZIF-8,^[9] MIL-101,^[10] MOF-177,^[11] etc.)^[12] and single or binary metal clusters. Owing to the abundant functional groups of their organic linkers, MOF supports have the potential to manipulate catalytic properties either geometrically or electronically. Although other supports (e.g., carbon,^[13] metal oxides,^[6,14] and zeolites) have been studied widely,^[15] the effects of the support on NMC/MOFs have not been reported until now.

Herein, we report the synthesis and catalytic properties of several Pt/UiO-67 MOFs and focus on the effect of the N-containing functional groups in the MOF support on the catalytic performance, as determined through experimental measurements and theoretical calculations.

Results and Discussion

The UiO-67^[16] MOF is a three-dimensional porous framework, which is constructed through the connection of biphenyl-4,4'dicarboxylic acid (H₂BPDA) linkers and $Zr_6O_4(OH)_4(CO_2)_{12}$ SBUs. In the SBU, each Zr^{IV} ion is linked to the adjacent ones through carboxyl bridges to generate regular octahedra. The connection of the SBUs through organic linkers results in a three-dimensional framework. Generally, owing to the robust Zr–O coordination bonds, UiO-67 MOFs show high thermal and chemical stabilities as well as large specific surface areas. For the compar-

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ison of the MOF support, we used three UiO-67-type MOFs s(labelled as UiO-67, N-UiO-67, and NH₂-UiO-67), in which the organic linkers are H₂BPDA, 5(4'-carboxyphenyl)picolinic acid (N-H₂BPDA) with a pyridine nitrogen atom, and 2-aminobiphenyl-4,4'-dicarboxylic acid (NH₂-H₂BPDA) with an amine nitrogen atom. The three MOFs were prepared by one-step hydrothermal reactions of mixtures of ZrCl₄, the organic ligand, and a modulator (such as acetic or benzoic acid) in N,N-dimethylformamide (DMF). In this regard, in the same molar quality, acetic acid is more effective than benzoic acid for the promotion of N-UiO-67 crystallinity. The XRD pattern of N-UiO-67 modulated by the addition of 3 equiv. of acetic acid shows the sharpest peaks among all the materials (Figure S1), because complexes can form between the zirconium cations and the 3 equiv. of acetic acid and retain the most suitable balance with the SBUs for N-UiO-67 growth. As shown in the SEM images (Figure 1a-d), N-UiO-67 and UiO-67 display typical octahedral microcrystals consisting of eight triangular surfaces of 200 nm, whereas beautiful sea-urchin-like microcrystals were found for NH₂-UiO-67 (Figures 1e-f and S2). This morphology difference is governed by the intrinsic Lewis base characteristics of the organic linkers (e.g., NH₂-H₂BPDA) in the crystallization process. Pt/N-UiO-67 materials of different loadings (1, 3, and 5 %) were prepared. To identify the effect of the support, 5 % Pt on N-UiO-67, UiO-67, and NH₂-UiO-67 were also prepared. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed to verify the actual Pt contents, which were 0.75, 1.82, 3.74, 4.32, and 3.54 % for 1 % Pt/N-UiO-67, 3 % Pt/N-UiO-67, 5 % Pt/N-UiO-67, 5 % Pt/NH2-UiO-67, and 5 % Pt/ UiO-67 (Table S1), respectively. The lower Pt contents measured by ICP-OES in comparison with the theoretical contents can be attributed to the loss of Pt during the loading process.



Figure 1. SEM images of (a and b) N-UiO-67, (c and d) UiO-67, and (e and f) $\rm NH_2\text{-}UiO\text{-}67.$

The transmission electron microscopy (TEM) images showed the morphologies and structures of Pt/N-UiO-67, Pt/UiO-67, and Pt/NH₂-UiO-67. The 5 % Pt/N-UiO-67 material was selected as

an example for the investigation of the morphology and structure. As shown in Figure 2a and b, the Pt nanoparticles (NPs) were highly dispersed on the N-UiO-67 surface without any clear aggregation, which implies that most Pt NPs were confined on N-UiO-67. From the high-resolution TEM (HRTEM) images (Figure 2c), the Pt NPs show clear lattice fringes with a lattice spacing of 2.30 Å, which fits well with the interplanar spacing of the (111) planes in face-centered cubic (FCC) Pt. The size of ca. 2.5 nm (Figure 2d) for the Pt NPs, which was obtained from the statistical results of more than 100 particles, suggests that some of the Pt NPs lie on the surfaces or edges of the MOF pores. The energy-dispersive X-ray spectroscopy (EDS) spectra confirmed the presence of C, Zr, and Pt in the MOFs (see Figure S7, S9, and S10). The similar structures and platinum size distributions of 1 % Pt/N-UiO-67 and 3 % Pt/N-UiO-67 are shown in Figure S6 and S8, respectively. Both of them exhibit similarly sized Pt NPs to those of 5 % Pt/N-UiO-67. A reduced loading value is not beneficial for the size of the Pt NPs. This phenomenon can be attributed to the confining effect of the MOFs. The Pt NPs are also distributed evenly on the surfaces of NH₂-UiO-67 and UiO-67 with sizes of ca. 2.5 and 4.5 nm, respectively (see Figures S8 and S10), and the EDS spectra also confirmed the presence of C, Zr, and Pt in these MOFs (see Figures S9 and S11). On the one hand, in spite of their similar pore sizes, N-UiO-67 and UiO-67 load different-sized Pt NPs. A possible reason for this is that the interactions between the pyridine N atoms and Pt are more favorable than the C-Pt interactions, and this leads to a confining environment for highly dispersed Pt NPs. The pyridine N atom can provide an anchor site for the immobilization of Pt NPs and restrict the size of the Pt NPs size. This phenomenon is supported by the TEM and X-ray photoelectron spectroscopy (XPS) results. On the other hand, such differences between UiO-67 and NH₂-UiO-67 are related to their different pore sizes.



Figure 2. (a–c) TEM images and (d) Pt NP distribution curve for 5.0 % Pt/N-UiO-67.

The powder XRD (PXRD) results for the as-synthesized Pt/N-UiO-67 match well with the simulated pattern of N-UiO-67 (Figure 3a); this implies that the integrity of the N-UiO-67 framework is maintained after Pt modification. No clear peaks of the Pt NPs were observed in the PXRD pattern because of





the short-range order of the Pt NPs, and this is in good agreement with the TEM results. Similarly, the whole frameworks of NH₂-UiO-67 and UiO-67 (see Figures S12 and S13) also remained robust after the loading of Pt NPs. An inspection of the XPS peaks is particularly informative regarding the electronic structure of Pt/N-UiO-67. As shown in Figure 3b, the specific peaks of C 1s, N 1s, O 1s, Zr 3d, and Pt 4f were found in the full XPS spectrum. Furthermore, the high-resolution C 1s spectrum (Figure S14a) shows four peaks, which correspond to the carbon atoms of C-N (281.59 eV), C-C (282.50 eV), C-O (284.00 eV), and C-Pt (285.63 eV) bonds. In comparison to that of N-UiO-67 (Figure S15b), the N 1s binding energy changes slightly (399.1 to 399.9 eV) for 5 % Pt/N-UiO-67 owing to the Pt-N interactions. In addition, the Pt 4f XPS spectra for 5 % Pt/ UiO-67 and 5 % Pt/NH₂-UiO-67 also support the presence of Pt. The Pt 4f signal of 5 % Pt/N-UiO-67 (Figure S14d) can be divided into two single peaks at binding energies of 71.91 and 75.24 eV, which can be well matched with two Pt 4f_{7/2} (71.20 eV) and Pt 4f_{5/2} (74.53 eV) peaks and, therefore, reveal the electronic structure of Pt⁰. The slight offset of the main peaks is clearly relevant to the Pt coordination environment, such as the carbon, pyridine nitrogen, and amine nitrogen atoms (Figures S16d and S17c). Therefore, it is concluded that the functional groups of the organic linker can affect the electronic structure of the Pt NPs. Moreover, the thermal stabilities of Pt/N-UiO-67 and N-UiO-67 were measured by thermogravimetric analysis (TGA). As shown in Figure 3c, the initial weight loss (ca. 20%) can be

attributed to the removal of solvent molecules and modulator. Both N-UiO-67 and Pt/N-UiO-67 maintained their original frameworks until above 300 °C. As displayed in Figure 3d, the Brunauer-Emmett-Teller (BET) surface areas before and after the loading of the Pt NPs were measured by N₂ physisorption measurements at 77 K. The specific surface areas for N-UiO-67, 1 % Pt/N-UiO-67, 3 % Pt/N-UiO-67, and 5 % Pt/N-UiO-67 were 619, 212, 175, and 158 m²/g, respectively. The specific surface areas gradually decreased as the Pt loading increased, as the Pt NPs occupied the holes or covered the cavities. The Pt/N-UiO-67 structure was further verified by FTIR spectroscopy. As shown in Figure S18, the Zr–O, Zr–O–Zr, and carboxyl stretches^[12d] were observed at $\tilde{v} = 459$, 658, and 1415 cm⁻¹, respectively. All of the peaks are the same for N-UiO-67 and Pt/N-UiO-67, and this also indicates the stability of Pt/N-UiO-67. The similar IR peaks also observed for NH2-UiO-67, Pt/NH2-UiO-67, UiO-67, and Pt/ UiO-67 (Figure S19) suggest that the MOF frameworks remained intact after Pt loading.

The catalytic oxidation of CO is an important reaction in new energy and environmental chemistry. CO oxidation was chosen as a model reaction to identify the effect of the support on the catalytic properties. Herein, we specifically take the uniformly dispersed Pt/N-UiO-67 as an example for discussion. Firstly, the catalytic activity of pristine N-UiO-67 as a blank was measured. As shown in Figure 4a, the pure MOF support has no catalytic activity over the temperature range 60 to 180 °C. Subsequently, much attention was paid to the effect of the loading value of



Figure 3. (a) PXRD patterns of N-UiO-67, 1.0 % Pt/N-UiO-67, 3.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; (b) XPS spectra of N-UiO-67, 5.0 % Pt/N-UiO-67, 5.0 % Pt/N-UiO-67, and 5.0 % Pt/UiO-67; (c) TGA curves of N-UiO-67, 1.0 % Pt/N-UiO-67, 3.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; and (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67, 1.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67, 1.0 % Pt/N-UiO-67; (d) nitrogen adsorption isotherms of N-UiO-67; (d) nitrogen ads







Figure 4. (a) CO conversion of N-UiO-67, 1.0 % Pt/N-UiO-67, 3.0 % Pt/N-UiO-67, and 5.0 % Pt/N-UiO-67; (b) endurance test of CO oxidation with 5 % Pt/N-UiO-67.

the Pt NPs on the catalytic activity. The 5 %, 3 %, and 1 % Pt/N-UiO-67 exhibited good catalytic activities with light-off temperatures of 80, 90, and 110 °C, respectively. The temperatures for 100 % (50 %) conversion of CO were approximately 120 (100), 130 (110), and 150 (130) °C, respectively. Generally, 5 % Pt/N-UiO-67 displayed the best catalytic activity for CO oxidation among the three different samples, and the superior activity can be ascribed to the increased amount of active Pt NPs because of the high loading. Furthermore, 5 % Pt/N-UiO-67 maintained 100 % CO conversion for 4000 min at 120 °C (see Figure 4b). Moreover, not only better catalytic activity but also better stability was shown for 5 % Pt/N-UiO-67 compared to those of other MOF-supported precious-metal catalysts.^[9b,12q,12r] In particular, to the best of our knowledge, the stability of 5 % Pt/N-UiO-67 for CO oxidation is better than those of most other MOF-based catalysts. The powder XRD xpatterns (see Figure S20) exhibited no loss of crystallinity after the CO oxidation reaction, which implies that 5 % Pt/N-UiO-67 was stable during CO oxidation. Furthermore, according to the TEM results (see Figure S21), the Pt particles were dispersed uniformly with an average diameter of 2.5 nm after CO oxidation, the ICP Pt content of 3.52 % for 5 % Pt/N-UiO-67 was similar to that of the catalyst before the reaction. The stability was further confirmed by the IR spectra of 5 % Pt/N-UiO-67 before and after the CO oxidation reaction (see Figure S22). In addition, the recycling of the 5.0 % Pt/N-UiO-67 catalyst was also evaluated; it was reused after an initial CO oxidation reaction, and the results indicated that the catalyst kept nearly 100 % conversion for CO oxidation in the additional runs (see Figure S23) and, therefore, exhibited excellent catalyst stability for CO oxidation. On the basis of these results, we determined the catalytic properties of 5 % Pt/UiO-67 and 5 % Pt/NH₂-UiO-67 for comparison with those of 5 % Pt/N-UiO-67. As shown in Figure 5, the light-off temperatures were 90 °C for 5 % Pt/UiO-67 and 140 °C for 5 % Pt/NH₂-UiO-67, and the temperatures for 100 % (50 %) CO conversion were approximately 140 (130) and 150 (145) °C, respectively. Therefore, 5 % Pt/N-UiO-67 shows better catalytic activity than 5 % Pt/UiO-67 and 5 % Pt/NH₂-UiO-67. For supported catalysts, both NMC particle size and support play essential roles in determining the catalytic properties. On the basis of the structures of three catalysts, two effects

can be identified: (1) Owing to their high ratio of active crystal planes, the smaller Pt NPs in N-UiO-67 are responsible for the difference between 5 % Pt/N-UiO-67 (ca. 2.5 nm) and 5 % Pt/UiO-67 (ca. 4.5 nm). (2) Interestingly, although the Pt NPs in N-UiO-67 and NH₂-UiO-67 are nearly the same size and have similar exposed crystal planes, the catalytic performance of 5 % Pt/N-UiO-67 is much better than that of 5 % Pt/NH₂-UiO-67. This result can be attributed to the effect of the MOF support on the catalytic properties.



Figure 5. CO conversion of 5 % Pt/N-UiO-67, UiO-67, and NH₂-UiO-67.

Although it is difficult to investigate the adsorption structure of 2.5-4.5 nm Pt NPs in complex periodical MOFs, the exploration of the electronic structure can provide some help to understand the effect of the support on the catalytic properties. DFT calculation results revealed the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbital (LUMOs), as shown in Figure 6. An inspection of the HOMOs and LUMOs reveals that the LUMOs of UiO-67, N-UiO-67, and NH₂-UiO-67 all feature the same characteristics of local π -type phenyl antibonding orbitals. The three HOMOs exhibit different distributions: Firstly, that of UiO-67 involves π -type phenyl bonding orbitals. Secondly, in addition to π -type phenyl bonding orbitals on one end, that of N-UiO-67 consists of π -type bonding orbitals and local dangling orbitals of N atoms on the other end. Thirdly, the LUMO of NH₂-UiO-67 exhibits larger differences and is composed mainly of π -type aniline bonding





orbitals and the dangling local orbitals of N (-NH₂) atoms on one end. Furthermore, the Mulliken charge population results reveal that the local charge of the biphenyl moiety can be arranged on the pyridine N atom or electron-donating -NH₂ group (see Table S1). In view of the molecular orbital mode, the pyridine N and amine N atoms exhibit different hybridization modes, namely, sp² for the pyridine N atom and sp³ for the amine N atom. The pyridine N atom is preferable to the amine N atom for the generation of a conjugate system with the phenyl group. Thus, the N-containing functional group can effectively adjust the electronic structure of UiO-67, consistent with previous computational results.^[17] The transformation of the electronic properties may generate an interface effect and, thereby, exert a critical effect on the catalytic properties of the Pt NPs loaded in UiO-67-type MOFs.



Figure 6. HOMOs (left) and LUMOs (right) of (a–b) UiO-67, (c–d) N-UiO-67, and (e–f) NH_2 -UiO-67.

Conclusions

We successfully loaded three UiO-67-type MOFs (pristine UiO-67, N-UiO-67, and NH₂-UiO-67) with Pt NPs. Structural characterizations indicate that the Pt NPs are highly dispersed in the MOFs with specific sizes of 4.5 nm for Pt/UiO-67 and 2.5 nm for Pt/N-UiO-67 and Pt/NH₂-UiO-67. The size of the Pt NPs is controlled by the functional group of the organic linker as well as the pore size of the MOF. Catalytic tests with different Pt loadings and supports revealed that 5 % Pt/N-UiO-67 possesses the best catalytic properties in terms of the light-off temperature and 100 % conversion temperature. Furthermore, 5 % Pt/N-UiO-67 maintained 100 % CO conversion for 4000 min at 120 °C. The excellent catalyst activity and stability can be attributed to the synergetic effect of the 2.5 nm Pt NPs and N-UiO-67. Therefore, it is concluded that the catalytic properties of Pt NP/MOFs rely on the support as well as the particle size of the Pt NPs.

Experimental Section

Materials: ZrCl₄ (98 %), biphenyl-4,4'-dicarboxylic acid (97 %), and NaBH₄ (98 %) were obtained from Aladdin. 5-(4'-Carboxyphenyl)-picolinic acid (95 %) and potassium tetrachloroplatinate(II) were

purchased from Jinan Camolai Trading Company and J&K, respectively. We synthesized 2-aminobiphenyl-4,4'-dicarboxylic acid (95 %) ourselves. All solvents were received from commercial suppliers and employed without further purification.

Characterization: The PXRD patterns of the Zr MOFs were recorded with a Panalytical X-Pert pro diffractometer equipped with a Cu- K_{α} radiation source. The morphologies of the materials and elemental mappings were measured by TEM (Tecnai G2 F30). The thermal stabilities were determined with a thermal gravimetric analyzer (SDT Q600, TA Instruments Co.) with samples heated at a rate of 10 °C min⁻¹ from room temperature to 800 °C in an N₂ atmosphere. The XPS measurements were performed with a Kratos AXIS Ultra DLD instrument with 300 W Al- K_{α} radiation and the C 1s peak at a binding energy of 284.5 eV as an internal standard. The specific surface areas were determined through the measurement of nitrogen adsorption/desorption isotherms at –73 °C with a surface properties analyzer (3Flex, Micromeritics). The FTIR spectra were recorded with a Nicolet 6700 FTIR spectrometer (Thermo).

N-UiO-67: ZrCl₄ (23.3 mg), 5-(4'-carboxyphenyl)picolinic acid (24.3 mg, 0.1 mmol), DMF (3 mL), and acetic acid (18 μ L for 3 equiv., 24 μ L for 4 equiv., 30 μ L for 5 equiv., and 60 μ L for 10 equiv. with respect to ZrCl₄) or benzoic acid (36.6 mg for 3 equiv. with respect to ZrCl₄, 73.2 mg for 6 equiv. with respect to ZrCl₄) were added to a vessel, which was capped, sealed, heated to 120 °C for 24 h, and cooled for 24 h in a preheated oven. The product was further purified by filtration, washed with DMF and diethyl ether several times, and dried under vacuum at 80 °C for 4 h.

Pt/N-UiO-67: Firstly, the as-prepared N-UiO-67 (0.10 g) was dissolved in DMF (8 mL) through sonication for 10 min. Different amounts of potassium tetrachloroplatinate(II) (2.22 mg for 1 % Pt/ N-UiO-67, 6.67 mg for 3 % Pt/N-UiO-67, 11.44 mg for 5 % Pt/N-UiO-67) were dispersed in DMF (4 mL) in a 25 mL beaker by stirring. Then, both solutions were mixed in a flask and stirred for a further 4 h. NaBH₄ (2 mg for 1 % Pt/N-UiO-67, 6 mg for 3 % Pt/N-UiO-67, 10 mg for 5 % Pt/N-UiO-67) was added dropwise to the mixture. Finally, the color of the solution changed from yellow to gray (Figure S24). The product was collected by filtration and washed with DMF and diethyl ether several times. The resultant products were dried under vacuum at 80 °C for 4 h.

Pt/UiO-67: UiO-67 was prepared the same way as N-UiO-67, except biphenyl-4,4'-dicarboxylic acid (24.3 mg, 0.1 mol) was used in place of 5-(4'-carboxyphenyl)picolinic acid. 5 %Pt/UiO-67 was synthesized by the same procedure as that described above for the preparation of 5 % Pt/N-UiO-67 but with UiO-67 instead of N-UiO-67.

2-Aminobiphenyl-4,4'-dicarboxylic Acid: First, biphenyl-4,4'-dicarboxylic acid dimethyl ester (27 g, 0.1 mol) and concentrated sulfuric acid (100 mL) were mixed and cooled to 5 °C in a 250 mL three-necked flask, and a mixture of nitric acid (69 %, 9.13 g, 0.1 mol) and concentrated sulfuric acid (30 mL) was added over 30 min. After 30 min, the mixture was added to an ice-cold water bath with stirring and extracted with ethyl acetate, the organic phase was washed with water, a saturated solution of sodium carbonate and saturated brine, dried with anhydrous sodium sulfate, and concentrated to afford 2-nitrobiphenyl-4,4'-dicarboxylic acid dimethyl ester (28 g). Second, 2-nitrobiphenyl-4,4'-dicarboxylic acid dimethyl ester (28 g, 0.09 mol), Pd/C (10 %, 3 g), dichloromethane (300 mL), and methanol (300 mL) were mixed in a 1000 mL threenecked flask and stirred overnight under a H₂ atmosphere. The solution was filtered, and the mother liquor was concentrated and dried to afford a solid (20 g). Third, the previous solid, KOH (1 M, 33.67 g, 0.6 mol), and tetrahydrofuran (THF, 200 mL) were added to a





1000 mL three-necked flask and heated to 70 °C and then under reflux for 5 h. The solution was concentrated by removal of the THF, and the PH was adjusted to 2–3 with hydrochloric acid solution. The solid was collected by filtration and dried to afford solid 2-aminobiphenyl-4,4'-dicarboxylic acid as faint yellow (15 g, 58 % yield). As shown in Figures S25 and S26, the structure of 2-aminobiphenyl-4,4'-dicarboxylic acid was further confirmed by ¹H and ¹³C NMR spectroscopy.

Pt/NH₂-UiO-67: NH₂-UiO-67 was initially synthesized from the hydrothermal reaction of $ZrCl_4$ (70.6 mg) and 2-aminobiphenyl-4,4'-dicarboxylic acid (77.1 mg) in DMF (5 mL) at 120 °C for 48 h. 5 % Pt/NH₂-UiO-67 was prepared by the same procedure as that described above for the synthesis of 5 % Pt/N-UiO-67 with NH₂-UiO-67 instead of N-UiO-67.

CO Oxidation Measurement: CO oxidation was performed with a fixed-bed plug-flow reactor system (diameter 4 mm, length 400 mm) made of quartz. The catalyst (50 mg) mixed with quartz sand (>300 µm, 100 mg) was put into the middle of the reactor and then preheated in Ar at 100 °C for 1 h before the test. The reaction gas consisted of CO (1 vol.-%), O₂ (20 vol.-%), and Ar (balance, 79 vol.-%) with a space velocity (SV) of 120000 mL $h^{-1} g_{cat}^{-1}$ (flow rate 100 mL min⁻¹). The CO reaction temperature ranged from room temperature to the 100 % conversion temperature and was monitored by a thermocouple with a ramp rat of 0.5 °C min⁻¹. The tail gas was analyzed with a FuLi 9790 II GC instrument with a TDX-01 column (3 m length), for which the temperatures of the column (80 °C), injection (150 °C), and thermal conductivity detector (TCD, 110 °C) were programmed. The gas retention times were measured by comparison with those of authentic samples. The CO conversion was typically calculated with Equation (1):

$$X_{\rm CO} = (1 - X\alpha/X_0) \times 100 \%$$
 (1)

where $X_0 = 1 \% X$ represents the peak area content of CO after the reaction, and α is a correction factor.

The catalyst stability tests were performed under the same reaction conditions as those described above, except the catalyst after the CO oxidation reaction was used without reduction, and the temperature was 120 $^{\circ}$ C.

Supporting Information (see footnote on the first page of this article): SEM and TEM images and structural characterization of Pt/UiO-67, N-UiO-67, and NH2-UiO-67; EDS analysis results, XPS spectra, IR spectra, and PXRD patterns of Pt/UiO-67, N-UiO-67, and NH2-UiO-67; DFT computational details.

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Catalytic Nanoparticles in MOFs

☐ The Effect of N-Containing Supports on Catalytic CO Oxidation Activity over Highly Dispersed Pt/UiO-67



The effects of metal–organic framework (MOF) supports on catalytic activity were uncovered for highly dispersed Pt nanoparticles (NPs) loaded in UiO-67.

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