Iodide-Coordinated Single-Site Pd Catalysts for Alkyne Dialkoxy carbonylation

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Abstract:

Heterogeneous single-metal-site catalysts (HSMSCs) have attracted considerable interest, but most studies have focused on the metal atoms in the active site while ignoring the key role of ligands. The unique coordination environment of a single-site catalyst is crucial for realizing its potential. Constructing this kind of catalyst via a feasible and practical fabrication method is challenging. Herein, a single-site Pd catalyst with iodide ligands supported on activated carbon (Pd\(_{1}/\)AC) was successfully fabricated by atomic dispersion of large Pd nanoparticles (NPs). Intermediate I• radicals were detected during the atomic dispersion process of Pd NPs by \textit{in situ} imaging photoelectron photoion coincidence spectroscopy (\textit{in situ} iPEPICO) with vacuum ultraviolet synchrotron radiation. The molecular structure of the single-site Pd was established as \([\text{Pd(CO)}I_4(O=\text{AC})]^{2-}\) through combined characterization. Alkyne dialkoxy carbonylation with high selectivity toward 1,4-dicarboxylic acid esters (> 94%) and high acetylene conversion (> 99%) was achieved. A sulfonic promoter on the Pd\(_{1}/\)AC catalyst for alkyne dialkoxy carbonylation was avoided because of the iodide ligand. Good durability and a broad substrate scope were successfully achieved.

Keywords: Single-site Pd\(_{1}/\)AC catalyst; Atomic dispersion of nanoparticles; Radical process; Alkyne dialkoxy carbonylation; Coordination environment.
1. Introduction

Developing a metal catalyst with 100% atom efficiency is the holy grail of academic and industrial catalysis research. Heterogeneous single-metal-site catalysts (HSMSCs) have attracted considerable attention since their emergence\cite{1,2}. The unique coordination environment of a single-site catalyst is crucial to achieving excellent performance\cite{3-6}. Constructing this kind of catalyst via a feasible and practical fabrication method is challenging. Atomic dispersion of nanoparticles (NPs) is used not only to prepare HSMSCs but also to redisperse agglomerated or sintered metal NPs\cite{7-9}. One of the most pressing challenges is overcoming the Ostwald ripening process\cite{10-13}, which is manifest as the growth of large particles at the expense of smaller particles. Dispersants or inducers are critical, providing coordinative ligands to inhibit reagglomeration of atomically dispersed metal ions and, more importantly, providing an appropriate active center environment to realize the potential of single metal ions. Moreover, a support decorated with abundant N-, O-, P-, and/or S-containing groups with lone-pair electrons is essential to anchor and accommodate a mononuclear complex, to prevent their further diffusion, and to achieve the complete atomic dispersion of metal NPs.

Generally, the larger the metal NPs are, the more difficult it is for these materials to disintegrate, and the more energy is needed to prevent smaller particles from reaggregating\cite{14-15}, according to Monte Carlo models\cite{10,13,16}. Ding et al. reported that Rh NPs with a size of approximately 5 nm can be dispersed into isolated Rh mononuclear complexes on an active carbon support\cite{8}, while Ir NPs larger than approximately 6 nm
are difficult to disperse due to strong Ir-Ir bonds and the resulting kinetic stability of Ir NPs. Au particles larger than 10 nm were also very difficult to disperse. In addition, some molecules with lone-pair electrons such as CO, O₂, and NO could coordinate with the surface metal ions of NPs, reducing their specific energy and weakening their interaction with the parent matrix during the atomic dispersion of NPs. Furthermore, chlorination, oxychlorination, and halogenated hydrocarbon treatment for the redispersion of metal NPs have been discussed previously. However, urgent issues remain, including the high energy consumption, particle size limitation, and subsequent recoalescence of the exfoliated metal atoms, especially after removing the dispersants or induced species. Supported Pd catalysts were efficient in versatile catalytic reactions. Nevertheless, active Pd(II) species can be easily transformed to large Pd(0) NPs or even completely inactive palladium black due to the stable outer electron structure of Pd(0)([Kr]4d¹⁰). Therefore, the quest for a stable heterogeneous single-site Pd catalyst is still ongoing.

Alkyne alkoxy carbonylation is a well-known reaction to synthesize α,β-unsaturated carboxylic acids and their derivatives. Acetylene alkoxy carbonylation to synthesize methyl acrylate was first conducted by Reppe and coworkers in 1939 using a homogeneous Pd(OAc)₂ catalyst assisted by 2-PyPPh₂ (Py = pyridine) and sulfonic acid promoters. Various sulfonic acids were essential to promote this homogeneous catalysis. In addition to the low recyclability, the homogeneous catalytic system suffers from complicated separation and metal leaching. These
problems inspired numerous attempts to anchor single-metal active complexes onto supports. A Pd₁/POP catalyst supported on a copolymer and polymerized from vinyl-functionalized ligands containing P, N, and benzene sulfonic acid has exhibited excellent activity\textsuperscript{37}. However, the synthesis of this copolymer was quite demanding.

Herein, a single-site Pd catalyst with an iodide ligand and 5 wt% loading on an activated carbon (Pd₁/AC) support was successfully fabricated by atomic dispersion of large Pd nanoparticles (NPs). Key intermediate I⁻ radicals were detected during the atomic dispersion of Pd NPs by \textit{in situ} imaging photoelectron photoion coincidence spectroscopy (\textit{in situ} iPEPICO) with vacuum ultraviolet synchrotron radiation. The molecular configuration of the single-site Pd was established as [Pd(CO)I₄(O=AC)]\textsuperscript{2⁻}, where O=AC represents the carbonyl groups on the surface of AC, by utilizing a combination of characterization techniques, such as high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), \textit{in situ} diffuse reflectance infrared Fourier transform spectroscopy (\textit{in situ} DRIFT), X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure spectroscopy (EXAFS).

The single-site Pd catalyst Pd₁/AC with the unique molecular structure of [Pd(CO)I₄(O=AC)]\textsuperscript{2⁻} was applied in the alkyne dialkoxycarbonylation reaction, and the I ligands were necessary both as part of the active center and for stabilization of single-site Pd atoms. An unexpectedly high dialkoxycarbonylation selectivity of 1,4-dicarboxylic acid esters (> 94%) was achieved with excellent acetylene conversion (>
99%). The need for a sulfonic promoter during alkyne carbonylation on the Pd₁/AC catalyst was avoided because of the iodide ligand. Good durability over at least seven recycling tests and a broad substrate scope, including some alcohols and alkynes, were also achieved.

2. Experimental Section

2.1 Catalyst preparation

Preparation of a supported Pd NP catalyst (Pd/AC). First, coarse coconut shell activated carbon (AC) of 40–60 mesh was washed with deionized water (353 K) until the electrical conductivity of the washings was less than 20 μS/cm, and then the samples were dried at 393 K for 12 h. Second, 0.85 g PdCl₂ with 58.7 wt% Pd was dissolved in an aqueous hydrochloric acid solution (5 mL 36% HCl and 10 mL deionized water). Then, 10 g washed AC was added to the precursor solution and dried at 363 K in a water bath. Furthermore, the obtained sample was dried overnight at 393 K and calcined at 573 K for 2 h under a flow of argon (110 mL/min) in a tubular quartz reactor. Finally, the sample was treated with H₂ at 573 K for 2 h to obtain a fresh approximately 5 wt% Pd NP catalyst (denoted as Pd/AC).

A single-site Pd catalyst (Pd₁/AC) was prepared from Pd NPs (Pd/AC) using a top-down NP atomic dispersion strategy. The dispersion of Pd/AC was conducted in a quartz tube reactor. First, the Pd/AC was heated from room temperature to 573 K under a N₂ flow (60 mL/min). Then, the gas flow was switched to a mixture of CO and CH₃I at a flow rate of 30 mL/min. CO was manipulated by passing through a bottle filled
with CH₃I at 298 K for 1 h. Finally, the sample was cooled to room temperature under a flow of CO. The obtained catalyst was denoted as Pd₁/AC.

2.2 Catalyst characterization

X-ray diffraction (XRD) measurements were performed using a PANalytical X’Pert Pro X-ray diffractometer with a Cu Kα X-ray source at a wavelength of 1.5045 Å. X-ray photoelectron spectroscopy (XPS) characterization was performed on a Thermo Scientific ESCALAB 250Xi equipped with an Al Kα radiation X-ray source. High-resolution transmission electron microscopy (HR-TEM) images of the samples were obtained with a JEOL JEM-2100 equipped with an energy-dispersive spectrometer (EDS). The particle size distribution was evaluated based on the statistical results with the aid of a Nano Measure based on HR-TEM images. Aberration-corrected high-angle annular dark-field (HAADF-STEM) images were recorded on a JEOL JEM-ARM200F STEM/TEM instrument with a CEOS probe corrector working at 200 kV to guarantee a resolution of 0.08 nm.

CO temperature-programmed desorption mass spectroscopy (CO-TPD MS) of Pd₁/AC was performed by means of an AMI-300 chemisorption analyzer from 3P Instruments. A 100 mg sample was first treated at 303 K for 1 h in a flow of helium (30 mL/min) to remove the physisorbed species. After stabilization of the baseline, TPD data were collected using a thermal conductivity detector (TCD) and a mass spectrometer at a heating rate of 10 K/min to 1273 K. For quantification of the total desorbed CO, the peak area of the TCD signal was calibrated with pulsed sampling
using a standard gas of 10% CO/He. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed using a PerkinElmer ICP-OES 7300DV. A mixture of H₂O₂ and concentrated HNO₃ was employed to dissolve the samples at high temperature and pressure in a sealed test bottle. Aqua regia (HCl/HNO₃ = 3/1 vol) was then added to dissolve the residues.

*In situ* diffuse reflection infrared Fourier transform spectroscopy (*in situ* DRIFT) of the Pd/AC atomic dispersion was conducted on a Bruker VERTEX 80v FTIR spectrometer with a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. The catalysts were loaded into a PIKE high-temperature reaction chamber (ZnSe windows). Mass flow controllers were employed to control the gas flow rates across the reactor bed. The temperature of the catalyst was increased to 513 K in He (20 mL/min). CO was bubbled through CH₃I at 298 K at a flow rate of 20 mL/min. After the atomic dispersion of Pd/AC, desorption was conducted at 303 K with helium purging to decrease the influence of reactants, and the DRIFT spectra were recorded in the wavenumber range of 800–4000 cm⁻¹ by averaging 64 scans at a resolution of 4 cm⁻¹ to improve the signal-to-noise ratio.

*In situ* imaging photoelectron photoion coincidence spectroscopy (*in situ* iPEPICO) was conducted at the VUV synchrotron radiation beamline of Swiss Light Source to investigate the radicals and intermediates in the gas phase during the atomic dispersion of Pd NPs. CO (2 mL/min), argon (18 mL/min), and CH₃I (0.1 mL/min) gases were supplied by a set of digital mass flow controllers to a resistively heated SiC
tubular microreactor placed in the source vacuum chamber\textsuperscript{39}. The granular samples were placed directly into a microreactor with an internal diameter of 1 mm. The pressures at the reactor inlet and the source chamber were 20 kPa and 2 mPa, respectively. The central part of the molecular beam leaving the reactor was skimmed and fed into the analysis chamber. Synchrotron radiation was monochromatized, and photon energies in the range of 10–14 eV were used to ionize the formed species. The photon energies were chosen so that the mass spectrometric signal of the species of interest was not perturbed by dissociative photoionization of heavier species. The signals of CH\textsubscript{3}\textperiodcentered and CH\textsubscript{3}I were recorded at a photon energy of 10 eV. The mass spectral peak of I\textperiodcentered was recorded at a photon energy of 11 eV. That of CO was recorded at photon energy of 14 eV. The signals of CH\textsubscript{3}CH\textsubscript{3} and I\textsubscript{2} were recorded at photon energies of 12.0 eV and 10.0 eV, respectively. All the signals were normalized based on the gas input of CH\textsubscript{3}I.

Extended X-ray absorption fine structure (EXAFS) measurements of the Pd K-edge were carried out on the BL14W1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF). The data were recorded in fluorescence mode with an electrolyte detector. The original EXAFS data were analyzed with the Demeter software package. Fourier transformation was applied to process the \(k^3\)-weighted raw data. The theoretical scattering amplitude and phase-shift functions of the paths for fitting the EXAFS data were calculated with the FEFF6 code.

\textbf{2.3 Catalytic evaluation}
Alkyne dialkoxy carbonylation was performed in a stainless steel autoclave (50 mL) with a magnetic stirrer and an automatic temperature controller. The autoclave was equipped with a snuffle valve at 12.0 MPa, and the ratio of acetylene was controlled below 15% for safety. The catalysts and substrates such as methanol and acetylene were added in sequence. Subsequently, CO and air were added. The detailed reaction conditions are listed with the reaction data. After adding a certain amount of the Pd\textsubscript{i}/AC catalyst, CH\textsubscript{3}OH, CO, air, and alkynes were added sequentially, and the autoclave was pressurized at room temperature. After the reaction, the liquid products removed from the autoclave were quantitatively analyzed offline using an Agilent 7890B gas chromatograph equipped with a DB-WAX column and flame ionization detector. The tail gas product was analyzed using an Agilent 7890B gas chromatograph equipped with a Porapak-Q column and a TCD. Taking acetylene as an example, its conversion and product selectivity were calculated as follows:

\[
Con_{C_2H_2} = \frac{n_{MA} + n_{DMS} + n_{DMM} + n_{DMF}}{n_{C_2H_2}} \times 100\% \tag{1}
\]

\[
Sel_{MA} = \frac{n_{MA}}{n_{MA} + n_{DMS} + n_{DMM} + n_{DMF}} \times 100\% \tag{2}
\]

\[
Sel_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{MA} + 2n_{DMS} + 2n_{DMM} + 2n_{DMF}} \times 100\% \tag{3}
\]

\[
n_{CO_2} = \frac{A_t \times w_0 \% \times \frac{P_i}{P_0} \times \frac{V}{22.4}}{A_0} \tag{4}
\]

\[
TOF = \frac{n_{C_2H_2} \times Con_{C_2H_2}}{n_{pd} \times t} \tag{5}
\]
where \( Con \) is the conversion of acetylene, \( Sel \) is the selectivity, \( t \) denotes the reaction time (h), \( n \) represents moles of the products, \( Ai \) represents the peak area in the gas products, \( A_0 \) represents the peak area in the gas products in the standard gas, \( w_0 \% \) represents the percentage composition, \( P_r \) is the pressure of autoclave after reaction, \( P_0 \) is the atmospheric pressure, and \( V \) is the volume of the autoclave. MA, DMSu, DMM, and DMF denote methyl acrylate (\( H_2C=CHCOOCH_3 \)), dimethyl succinate (\( \text{H}_2\text{C}_3\text{COOCH}_3 \)), dimethyl maleate (\( Z \)) (\( \text{H}_2\text{C}_3\text{COOCH}_3 \)) and dimethyl fumarate (\( E \)) (\( \text{H}_2\text{C}_3\text{COOCH}_3 \)), respectively. TOF is the turnover frequency.

### 3. Results and Discussion

The Pd NP catalyst supported on AC (Pd/AC) with a loading of 5 wt% was first prepared via the reduction of pure \( H_2 \) at 573 K for 2 h. As expected, the surface of the AC was decorated with Pd NPs with an average size of \(~16\) nm, as seen in the HR-TEM image in Figure 1a. Pd/AC was obtained after treatment with CO/CH\(_3\)I at 513 K for 1 h. Bright- and dark-field HAADF-STEM images confirmed the isolated single Pd ions on the surface of the AC, while no Pd NPs were observed (Figures 1b and S1), suggesting that the Pd NPs with a diameter of \(~16\) nm were atomically dispersed. A single-site Pd catalyst with an iodide ligand supported on activated carbon (Pd\(_i\)/AC) was successfully fabricated by atomic dispersion of large Pd NPs. The CO-TPD MS experiment showed that the CO/Pd molar ratio was 0.84 for Pd\(_i\)/AC, indicating that a single Pd-CO bond was probably formed in Pd\(_i\)/AC (Figure S2). Importantly, only
slight loss of metal loading occurred during the atomic dispersion of Pd NPs, as confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Table S1).

X-ray photoelectron spectroscopy (XPS) of Pd 3d₅/₂ indicated the presence of 83% Pd⁰ and 17% Pd⁴⁺ (PdO₂ layer passivated by 1% O₂) in the Pd/AC, while 100% Pd²⁺ species was observed in the Pd₁/AC (Figure 1d), suggesting that the Pd NPs (Pd⁰) were completely atomically dispersed from a metal valence perspective. EXAFS analysis of the Pd K-edge was conducted (Figures S3-S4)⁴⁰. A Pd-Pd bond with a length of 2.72 Å and a coordination number (CN) of 8.22 was detected in the Pd/AC sample (Figure 1d and Table 1), while instead of a Pd-Pd bond, a Pd-I bond with a length of 2.61 Å and a CN of 4.08 was observed in the Pd₁/AC sample. Furthermore, a Pd–CO bond with a length of 2.20 Å and a CN of 0.98 could also be fitted, which agrees well with the CO–TPD result. Moreover, wavelet transform (WT) contour plots of the Pd/AC and Pd₁/AC samples also confirmed the backscattering of Pd NPs with k values concentrated at 10.0 Å⁻¹ in the Pd/AC catalyst and the single Pd ions in the Pd₁/AC catalyst with k values concentrated at 11.4 Å⁻¹ in both radial distance and k-space resolution (Figure S5)⁴¹-⁴². Therefore, the atomically dispersed Pd ions were assigned a molecular configuration of [Pd(CO)I₄(O=AC)]²⁻, where (O=AC) represents carbonyl groups on the surface of the AC support⁶,⁴³. Compared with Ir or Au NPs, for which NPs larger than 10 nm were very difficult to disperse⁹,¹⁷-¹⁸, large Pd NPs with a size of approximately 16 nm were surprisingly readily dispersed.
Table 1. EXAFS fitting of standard samples of PdO and Pd foil as well as of Pd/AC and PdI/AC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>$N$</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (10$^{-3}$ Å$^2$)</th>
<th>$\Delta E_0$ (eV)</th>
<th>$R$-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdO</td>
<td>Pd-O</td>
<td>4.0</td>
<td>2.02±0.01</td>
<td>2.3±1.2</td>
<td>5.3±1.3</td>
<td>0.005</td>
</tr>
<tr>
<td>Pd foil</td>
<td>Pd-Pd</td>
<td>12.0</td>
<td>2.74±0.00</td>
<td>5.3±0.0</td>
<td>2.2±0.3</td>
<td>0.005</td>
</tr>
<tr>
<td>Pd/AC</td>
<td>Pd-O</td>
<td>0.5±0.2</td>
<td>1.95±0.02</td>
<td>2.3±0.0</td>
<td>0.3±0.5</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>Pd-Pd</td>
<td>8.2±0.5</td>
<td>2.72±0.00</td>
<td>7.7±0.4</td>
<td>0.3±0.5</td>
<td></td>
</tr>
<tr>
<td>PdI/AC</td>
<td>Pd-CO</td>
<td>1.0±0.3</td>
<td>2.03±0.03</td>
<td>3.0±0.0</td>
<td>3.2±0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd- (O=AC)</td>
<td>1.0±0.0</td>
<td>2.20±0.02</td>
<td>2.3±0.0</td>
<td>3.2±0.4</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Pd-I</td>
<td>4.1±0.3</td>
<td>2.61±0.00</td>
<td>3.5±3.2</td>
<td>3.2±0.4</td>
<td></td>
</tr>
</tbody>
</table>

5 wt% Pd/AC, $R$ range: 1.3~3.1 Å; $k$ range: 2.8~14.1 Å$^{-1}$. 5 wt% PdI/AC, $R$ range: 1.2~2.9 Å; $k$ range: 2.6~14.7 Å$^{-1}$. $N$ is the coordination number, $R$ is the distance between the absorber and the backscatterer, $\sigma^2$ is the Debye–Waller factor; standard sample Pd foil, amp 0.815, $k$-weight = 1, 2, 3, $\Delta E_0$, energy shift. Feff calculations: single scattering, Pd-O, reference CIF: PdO, COD: 4124668, $R_{\text{eff}}$ = 2.011; Pd-Pd, reference CIF: Pd, Fm-3m, COD: 1011112, $R_{\text{eff}}$ = 2.734 Å; Pd-CO, reference CIF: (NH$_4$)$_2$(PdCl$_4$(CO)$_2$), COD: 1532523, $R_{\text{eff}}$ = 2.000 Å; Pd-I, reference CIF: PdI$_2$, COD: 1539344, $R_{\text{eff}}$ = 2.619 Å; Pd-(O=AC), first quick shell path, $R_{\text{eff}}$ = 1.925 Å.
To evaluate the atomic dispersion of Pd NPs at different reaction times, systematic characterizations, including XRD, TEM, HAADF-STEM, XPS, *in situ* DRIFT, and *in situ* iPEPICO spectroscopy, were performed. As indicated in Figure S6, the diffraction peaks at 40°, 47°, 68°, and 82° were attributed to the (111), (200), (220) and (311) lattice planes, respectively, of cubic Pd particles in Pd/AC (see the PDF card: 00-005-0681). The calculated average crystal particle size determined by XRD was 13 nm (Figure 1a). The number of large Pd NPs decreased dramatically after treatment with CO/CH$_3$I for just 2 min, as shown in Figure 2a, consistent with the change in the XRD patterns in Figure S6. Moreover, Pd NPs surrounded by iodide species were unambiguously observed in the HAADF-STEM image and the corresponding EDS mapping in Figure 2b-c. After treatment with CO/CH$_3$I for 5 min, no Pd X-ray diffraction peaks could be discerned in the XRD patterns in Figure S6, and almost all Pd NPs were dispersed into (Pd)$_n$ clusters, as shown in the HAADF-STEM image (Figure 2d). Furthermore, single Pd ions dominated by uniform I dopants were observed in the HAADF-STEM images and the corresponding EDS mapping after treatment for 15 min (Figure 2e-f). The XPS results revealed the valence change of Pd 3d during atomic dispersion (Figure S7), where Pd$^0$ gradually disappeared while Pd$^{2+}$ gradually increased. Pd$^{2+}$, which was originally absent, reached an abundance of 63% after 2 min, 87% after 5 min, and 100% after 15 min, confirming the Pd NP atomic dispersion process from an electronic perspective.
In situ DRIFT experiments were also employed. A monocarbonyl complex with Pd\(^{2+}\)-CO was detected at 2145 cm\(^{-1}\), showing the coordination of CO with Pd\(^{2+}\) (Figure S8)\(^{44-45}\). Furthermore, the peaks at 1237 cm\(^{-1}\) and 1263 cm\(^{-1}\) were attributed to CH\(_3\)-I, while the peaks at 2962 cm\(^{-1}\) and 2986 cm\(^{-1}\) were ascribed to CH\(_3\)CH\(_3\), implying homolytic cleavage of the CH\(_3\)I bond and recombination of CH\(_3\)\(\cdot\) radicals to form CH\(_3\)CH\(_3\). In situ iPEPICO \(^9,46-48\) was further applied to investigate the radicals and intermediates in the gaseous phase during the atomic dispersion of Pd NPs (Figure 3). The in situ-formed I\(\cdot\) (m/z=127) radical was clearly distinguished from CO (m/z=28), C\(_2\)H\(_6\) (m/z=30), CH\(_3\)I (m/z=142), and I\(_2\) (m/z=254). The I\(\cdot\) radical signal at m/z=127 emerged and increased gradually as the temperature increased from 638 K to 985 K and then decreased slightly, while the signal attributed to CH\(_3\)I decreased gradually as the temperature increased from 594 K to 985 K and then remained stabilized. The CH\(_3\)\(\cdot\) signal at m/z=15 was negligible, and the C\(_2\)H\(_6\) (m/z=30) and I\(_2\) (m/z=254) peaks increased as the temperature increased from 594 K (Figure S9), indicating that the CH\(_3\)\(\cdot\) and I\(\cdot\) radicals generated by CH\(_3\)I homolysis quickly recombined in the atomic dispersion of Pd NPs. CH\(_3\)I (m/z=142) decomposed at 1173 K in the blank experiment without a catalyst (Figure S10) at a temperature much higher than 594 K in the presence of the Pd catalyst. The reaction started at a higher temperature in the iPEPICO microreactor because of the high dilution of the feed gas, the low residence time (10~100 μs) and the low pressure (1~4 kPa) inside the microreactor\(^{49}\).
Based on the above experimental data, CH$_3$I was adsorbed on the surface of Pd NPs and homolyzed into CH$_3$· and I· radicals. However, the CH$_3$· and I· radicals either were more strongly bound and severely recombined on the surface to CH$_3$CH$_3$ and I$_2$ or were too short-lived to be detected after desorption. Some I· radicals escaped in the gaseous phase and were detected, while others participated in a redox reaction, capturing an electron from Pd and oxidizing it to Pd(II) during the atomic dispersion process. As shown by in situ DRIFT, CO-TPD, XPS, and EXAFS, ambient CO coordinated to Pd$^{2+}$, simultaneously forming [Pd(CO)I$_4$]$^{2-}$, which was bound by the surface carbonyl sites of AC as [Pd(CO)I$_4$(O=AC)]$^{2-}$.

In this work, alkyne dialkoxy carbonylation was investigated using characterized Pd NPs (Pd/AC with a loading of 4.76%) and a single-site catalyst (Pd$_1$/AC with a loading of 0.84%) (Figure 4a and Table S2) without sulfonic acid as a promoter. The catalytic performance of Pd/AC with different dispersion times (0 min, 2 min, 5 min, and 15 min) was also evaluated. As shown in Table S2, the acetylene conversion increased from 0.0% to 96.5% as the dispersion time increased, demonstrating the direct relationship between Pd catalyst activity and the single atomic centers. In addition, a high conversion (> 99%) and a high selectivity (> 94%) were achieved for the acetylene substrate and 1,4-dicarboxylic acid esters (dimethyl succinate, dimethyl maleate (Z), and dimethyl fumarate (E)), respectively, as indicated in Figure 4b and Table 2 for the Pd$_1$/AC catalyst. The CO pressure and temperature were found to play a major role and correlated almost linearly with the acetylene conversion (Figure 4b, Figure S11a, and
Table S3-S4). A high air pressure increased the selectivity toward 1,4-dicarboxylic acid esters, although it slightly decreased the acetylene conversion (Figure S11b and Table S5). Notably, the Pd/AC catalyst could be recycled at least seven times without substantial loss of activity, showing excellent stability (Figure 4c). The conversion of acetylene stabilized at ~88% after the 2nd cycle, and the selectivity of 1,4-dicarboxylic acid esters remained at above 95% during the seven tests. Unexpectedly, the selectivity of CO2 in this system was only approximately 1.0% based on the carbon source of CO. Negligible metal leaching was observed by ICP-OES after the 7th cycle in the case of the Pd/AC catalyst compared with the fresh catalyst (Table S6). A hot filtration experiment was also conducted, and no increase in activity was detected, indicating that the dialkoxy carbonylation of acetylene occurred on the surface of the Pd/AC catalyst. (Figure S12).

Table 2. Activity comparison of different catalysts for acetylene dialkoxy carbonylation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>Sel. (%)</th>
<th>TOF (h⁻¹)</th>
<th>Reference</th>
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<tr>
<td></td>
<td></td>
<td>MA</td>
<td>DMSu</td>
<td>DMM+DMF</td>
<td></td>
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<tr>
<td>1</td>
<td>¹Pd/AC</td>
<td>99.1</td>
<td>3.3</td>
<td>2.7</td>
<td>94.0</td>
</tr>
<tr>
<td>2</td>
<td>²Pd/POPs</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>3</td>
<td>³Pd/NaY+CH₃I</td>
<td>23.7</td>
<td>0.0</td>
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<td>98.1</td>
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<tr>
<td>4</td>
<td>³Pd/NaY</td>
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<tr>
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<td>⁴Pd/PIP</td>
<td>53.3</td>
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</tr>
<tr>
<td>6</td>
<td>⁴Pd/AC</td>
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<tr>
<td>7</td>
<td>⁴Pd/AC + I₂</td>
<td>58.1</td>
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</tr>
<tr>
<td>8</td>
<td>⁵Pd/g-C₃N₄</td>
<td>trace</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>No.</td>
<td>Catalyst</td>
<td>Conv. (%)</td>
<td>Selectivity (%)</td>
<td></td>
<td>( \text{CO} )</td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------</td>
<td>-----------</td>
<td>-----------------</td>
<td>-----</td>
<td>----------------</td>
</tr>
<tr>
<td>9</td>
<td>( ^5 \text{Pd/MgO} )</td>
<td>trace</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>10</td>
<td>( ^5 \text{Pd/CeO}_2 )</td>
<td>8.0</td>
<td>100.0</td>
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<td>0</td>
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<tr>
<td>11</td>
<td>( ^5 \text{Pd/Al}_2\text{O}_3 )</td>
<td>10.2</td>
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<tr>
<td>12</td>
<td>( ^5 \text{Pd/SiO}_2 )</td>
<td>12.6</td>
<td>49.4</td>
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<tr>
<td>13</td>
<td>( ^5 \text{Pd/AC} )</td>
<td>21.9</td>
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<tr>
<td>14</td>
<td>( ^5 \text{Pd/AC(nanosheet)} )</td>
<td>43.8</td>
<td>100.0</td>
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<tr>
<td>15</td>
<td>( ^6 \text{Pd/Fe}_2\text{O}_3+\text{KI} )</td>
<td>80.0</td>
<td>78.0</td>
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<tr>
<td>16</td>
<td>( ^7 \text{Homo. Pd+Cu} )</td>
<td>86.0</td>
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Reaction conditions: 1 Catalyst (0.3 g Pd/AC, 0.84 wt% Pd), acetylene (9.0 mmol), \( \text{CH}_3\text{OH} \) (10.0 g), \( P_{\text{CO}} = 4.2 \text{ MPa} \), \( P_{\text{Air}} = 3.0 \text{ MPa} \), 343 K, 5.0 h. 2 Catalyst (0.3 g Pd/POPs, 1 wt% Pd), acetylene (9.0 mmol), \( \text{CH}_3\text{OH} \) (10.0 g), \( P_{\text{CO}} = 3.2 \text{ MPa} \), \( P_{\text{Air}} = 2.0 \text{ MPa} \), 373 K, 12 h. 3 Catalyst (0.8 g Pd/NaY molecular sieve, 0.2 wt% Pd), acetylene (9.0 mmol), \( \text{CH}_3\text{OH} \) (10.0 g), \( P_{\text{CO}} = 3.2 \text{ MPa} \), \( P_{\text{Air}} = 2.0 \text{ MPa} \), 363 K, 12 h. 4 Catalyst (0.3 g Pd/AC, 1 wt% Pd; 0.3 g Pd/PIPs, 1 wt% Pd), acetylene (9.0 mmol), \( \text{CH}_3\text{OH} \) (10.0 g), \( P_{\text{CO}} = 2.2 \text{ MPa} \), \( P_{\text{Air}} = 3.0 \text{ MPa} \), 373 K, 3.0 h. 5 Ref. 54. \( T = 353 \text{ K} \); 0.05 g catalyst; \( P_{\text{CO}} = 4.55 \text{ MPa} \), \( P_{\text{O}_2} = 0.45 \text{ MPa} \); t = 10 h. 6 Ref. 55. \( T = 353 \text{ K} \), 0.05 g catalyst, 10 mmol of \text{C}_2\text{H}_2, \text{O}_2 + \text{CO} \) (1:10, 5 \text{ MPa}) , and KI as a promoter for 5 h. 7 Ref. 56. Conv. (%) is the conversion of acetylene, MA denotes methyl acrylate, and Sel. (%) is 1,4-dicarboxylic acid esters including DMSu, DMM and DMF.

In contrast, single-site Pd catalysts with different coordination environments were prepared according to the references\(^{51-53}\). Single-site Pd catalysts are supported on a porous organic polymer, porous ionic polymer, and NaY molecular sieve carriers (Pd\(_1/\text{POPs}, \text{Pd}_1/\text{PIPs}, \text{or Pd}_1/\text{NaY}). Unexpectedly, the Pd\(_1/\text{AC} \) catalyst exhibited higher
activity than the Pd/POPs, Pd/PIPs, Pd/NaY, Pd/AC catalysts and other reported Pd NPs or homogeneous Pd catalysts (Table 2). More interestingly, the Pd/POPs, Pd/NaY, and Pd/AC catalysts showed little activity because they lacked iodine species, indicating the essential role of the iodide coordination configuration in [Pd(CO)I₄(O=AC)]²⁻ during alkyne dialkoxy carbonylation. To the best of our knowledge, this is the first report on the role of the iodine ligand. This stabilized structure is thus an important candidate for alkyne dialkoxy carbonylation catalysis, as it relies on an iodine ligand instead of a sulfonic acid promoter. Furthermore, it exhibited broad adaptability for different alkyne substrates, such as 1-hexyne and phenylacetylene instead of acetylene, as well as ethanol, n-propanol, n-butanol, and cyclohexanol instead of methanol. The Pd/AC catalyst achieved exemplary conversion of alkyynes and selectivity to the corresponding 1,4-dicarboxylic acid esters across a broad spectrum of reactants (Figures S13-14, Tables S7-S10).

4. Conclusions

An excellent heterogeneous single-site Pd/AC catalyst was fabricated by a facile atomic dispersion of Pd NPs with an average particle size of approximately 16 nm within only 5~15 min. The large Pd NP size was found to not inhibit dispersion. In situ PEPICO and DRIFT measurements showed that the nascent iodine radicals, formed by homolytic C-I bond breaking in iodomethane, were first adsorbed on the surface of the Pd NPs, and then Pd⁰ was oxidized to Pd²⁺; ambient CO coordinated with the resulting
Pd$^{2+}$ to diffuse the newly formed mononuclear complex to the surface of the AC, where it was finally captured by the surface carbonyl groups of the AC. Based on the combined CO-TPD, HAAD-STEM, XPS, and EXAFS results, the resulting single-site Pd$_1$/AC catalyst was determined to have a molecular configuration of [Pd(CO)$_4$(O=AC)]$^{2-}$. Alkyne dialkoxy carbonylation was achieved on the Pd$_1$/AC catalyst without sulfonic acid promotion, thanks to the iodide coordination in [Pd(CO)$_4$(O=AC)]$^{2-}$, which resulted in high acetylene conversion (> 99%) and selectivity for 1,4-dicarboxylic acid esters (> 94%, CH$_3$OOCCHCHCOOCH$_3$). The catalyst was durable and could be recycled at least seven times without a loss of activity. It was also active for a broader spectrum of substrates. This study is expected to provide a new reference case for the preparation and application of single-site Pd catalysts at the molecular level from the view of heterogeneously coordinative catalysis.

**Associated Content**

The Supporting Information is available free of charge at XXXXX.

More details about the experiments, including a HAADF-STEM image of fresh Pd$_1$/AC; CO-TPD results for Pd/AC and Pd$_1$/AC; EXAFS fitting in q space and k space of Pd/AC and Pd$_1$/AC; wavelet transform contours of Pd/AC and Pd$_1$/AC; XRD patterns of Pd/AC treated for different times; XPS results of Pd/AC treated for different times; *in situ* DRIFT during atomic dispersion of Pd nanoparticles; *in situ* PEPICO spectra during atomic dispersion of Pd nanoparticles; hot filtration tests of the Pd$_1$/AC catalyst
for acetylene dicarbonylation; ICP-OES data for Pd/AC, Pd1/AC, and spent Pd1/AC after the first and 7th tests; catalytic activity evaluation of the Pd/AC catalyst with different dispersion times; effects of temperature, CO pressure and air pressure on the catalytic activity of Pd1/AC and dialkoxy carbonylation of various alcohols and alkynes.

Notes

The authors declare no competing financial interest.

Acknowledgements

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References:


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Figure 1. (a) HR-TEM image of Pd/AC, (b) HAADF-STEM image of Pd/AC, (c) Pd 3d XPS of Pd/AC and Pd/AC, (d) EXAFS fit of the Pd k-edge in R space for Pd/AC and Pd/AC.
Figure 2. HAADF-STEM images of samples treated with CO/CH$_3$I for (a, b) 2 min, (d) 5 min, and (e) 15 min and (c, f) EDS maps corresponding to (b) and (e). The green dots represent I atoms, and the brownish red dots represent Pd atoms.
Figure 3. *In situ* PEPICO signals for (a) CH$_3$I, (b) I*, (c) CH$_3$• and (d) CO during the atomic dispersion of Pd/AC NPs as a function of reactor temperature. Photon energies at which the respective species’ signal was obtained are given.
**Figure 4.** (a) Schematic diagram of acetylene dialkoxy carbonylation. (b) The effect of CO pressure on the catalytic activity of the Pd/AC catalyst for acetylene dialkoxy carbonylation. Conditions: Catalyst (0.3 g Pd/AC, 0.84 wt% Pd), acetylene (9.0 mmol), CH$_3$OH (10.0 g), $P_{\text{air}} = 3.0$ MPa, 343 K, 5.0 h. (c) Reaction stability test of the Pd/AC catalyst for acetylene dialkoxy carbonylation. Conditions: Catalyst (0.6 g Pd/AC, 0.84 wt% Pd), acetylene (8.0 mmol), CH$_3$OH (10.0 g), $P_{\text{air}} = 2.5$ MPa, $P_{\text{CO}} = 2.6$ MPa, 353 K, 1.0 h. Conv.% is the acetylene conversion, and Sel.% is the selectivity of alkyne dialkoxy carbonylation, including DMSu, DMM and DMF.