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An ultra-low Pd loading nanocatalyst with high activity and stability for CO oxidative coupling to dimethyl oxalate[†]

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A Pd/α -Al₂O₃ nanocatalyst with ultra-low Pd loading exhibits high activity and stability for CO oxidative coupling to dimethyl oxalate, which was prepared by a Cu²⁺-assisted *in situ* reduction method at room temperature. The small size and high dispersion of Pd nanoparticles facilitated by Cu²⁺ ions are responsible for the excellent catalytic activity.

Dimethyl oxalate (DMO) is widely used in syntheses of various significant chemical products, such as the hydrolyzation of DMO to oxalate acid, the ammonolysis of DMO to oxamide, and especially important application of the hydrogenation of DMO to ethylene glycol (EG).¹⁻⁶ EG is a crucial chemical raw material with a global demand of about 25 million tons each year, which is usually produced from ethylene oxidation.^{7,8} However the cost of production is very high due to the soaring price of crude oil and the depletion of petroleum resources. Hence, a new EG synthesis technology called coal to ethylene glycol (CTEG) (Fig. S1, ESI⁺)^{9,10} developed by our institute has been successfully applied to industrialization (Fig. S2, ESI⁺).

CTEG is a promising green and favorable economic technology.¹⁰ CO oxidative coupling to DMO is the crucial step in the realization of the conversion of inorganic C1 to organic C2 in CTEG,¹¹ and it is considered to be one of the most important applications in C1 chemistry.¹² This chemical process is an environmentally friendly technology with mild reaction conditions and low energy consumption. In addition, CO oxidative coupling to DMO can not only sufficiently utilize the CO exhausts from plants to produce valuable chemicals, but also effectively reduce environmental pollution. Pd based catalysts supported on α -Al₂O₃ have been proved to be promising and effective catalysts for CO oxidative coupling to oxalate.^{12–17} However, the Pd loading of industrial catalysts for CO oxidative coupling to DMO is relatively high at 2 wt% (the state of the art), resulting in a great increase in the cost of production. Moreover, the shortage of noble metal resources is more and more serious in the world along with their large consumption in various industrial catalysts and the jewelry industry. Our previous intensive research showed that the exposed (111) facets of Pd nanocatalysts are active planes for CO oxidative coupling to DMO.¹⁷ Therefore, the design of efficient Pd nanocatalysts with the exposed (111) facets and low Pd loading is a great challenge.

Herein, we report an ultra-low Pd loading (*ca.* 0.1 wt%) Pd/ α -Al₂O₃ nanocatalyst, which was synthesized *via* a Cu²⁺-assisted *in situ* reduction approach at room temperature. This nanocatalyst exhibits unprecedented catalytic activity and excellent stability for CO oxidative coupling to DMO. Cu²⁺ ions have been found to play a key role in the formation of this highly efficient nanocatalyst structure with the assistance of polyvinylpyrrolidone (PVP) and citric acid.

Two types of catalysts (denoted **C1** and **C2**, respectively) have been synthesized under the same conditions except that catalyst **C1** was obtained upon the addition of Cu^{2+} ions in the precursors (see ESI[†] for details). The evaluation of catalytic performance for CO oxidative coupling to DMO was carried out in a home-made catalytic evaluation device. The catalytic performances of **C1** and **C2** are presented in Table 1, which were evaluated under the same reaction conditions as those used for industrial catalysts. The Pd loading of **C1** measured using inductively coupled plasma (ICP) is only 0.13 wt%, which is about 1/3 and 1/15 those of **C2** and industrial

 Table 1
 CO oxidative coupling to DMO on different catalysts^a

Catalysts	Pd content (wt%)	Conversion ^b (%)	Selectivity ^c (%)	$\begin{array}{c} \operatorname{STY}^d \\ (\operatorname{g} \operatorname{L}^{-1} \operatorname{h}^{-1}) \end{array}$
C1 ^e	0.13	62	97	1332
$\mathbf{C2}^{f}$	0.37	32	97	687
Industrial catalyst	2	34	95	750

^{*a*} Reaction conditions: 200 mg of catalyst, 3000 h⁻¹ of gas hourly space velocity (GHSV), reactants CO/CH₃NO volume ratio 1.4, 0.1 MPa, 130 °C (for more details see ESI). ^{*b*} Conversion of CO. ^{*c*} Selectivity to DMO. ^{*d*} STY represents the space-time yield, grams of DMO per liter of catalyst per hour (g L⁻¹ h⁻¹). ^{*e*} C1 prepared with the addition of Cu²⁺ ions under the preparation conditions. ^{*f*} C2 prepared without the addition of Cu²⁺ ions under the preparation conditions.

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Fig. 1 (a) Conversion of CO (C1 ● and C2 \bigcirc) and selectivity to DMO (C1 ▲ and C2 \checkmark) for CO oxidative coupling to DMO at different reaction temperatures, respectively. (b) Conversion of CO (\blacksquare) and selectivity to DMO (\Box) of C1 (200 mg) at 130 °C for 100 h.

catalysts, respectively. Nevertheless, the conversion of CO and the space-time yield (STY) of DMO at 130 °C demonstrate that the activity of C1 is almost double that of C2 and 80% higher than that of the industrial catalyst. The temperature dependence of CO conversion and DMO selectivity (Fig. 1a) indicates that the reaction temperature greatly influences the activities of catalysts for CO oxidative coupling to DMO. The conversions of CO for both the catalysts increase gradually along with the increase in the reaction temperature between 90 and 150 °C, but catalyst C1 always shows much better activity than C2. Meanwhile, the selectivity of C1 to DMO is higher than 95% at 90-150 °C, which is also superior to that of C2. Moreover, catalyst C1 displays very high catalytic activity at 150 °C. The conversion of CO can reach up to 69.1%, close to the theoretical maximum value of 71.4%. It implies that methyl nitrite was almost completely consumed, which can be verified using gas chromatography (Fig. S4, ESI⁺). The long-term stability of the catalyst is very important for CO oxidative coupling to DMO from both academic and industrial viewpoints. The lifetime evaluation of C1 is shown in Fig. 1b, which shows that the high activity and selectivity of C1 can be maintained up to 100 h. This highly efficient and longlived nanocatalyst may have a potential industrial application.

Fig. 2 illustrates the *in situ* DR-FTIR spectra for the reaction of CO with methyl nitrite to DMO. The band at 1774 cm^{-1} is attributed to the C—O stretching vibrations of the DMO product. It is obvious to note that the intensity of the band at 1774 cm^{-1} in the spectrum of C1 is much stronger than that in the spectrum of C2 and has not been shown to decrease in the whole time range, which demonstrates the superior catalytic activity of C1 relative to C2, consistent with the results of catalytic activity evaluation. In addition, the bands at 1627 and 1675 cm⁻¹ are assigned to the N—O vibrations of methyl nitrite, and the bands at 2178 and 2116 cm⁻¹ are ascribed to CO in the gaseous state.

All these results demonstrate that catalyst **C1** exhibits much higher catalytic activity for CO oxidative coupling to DMO in comparison with **C2**. What causes the large difference in catalytic activities between the two catalysts?

TEM images presented in Fig. 3a and c reveal that the Pd nanoparticles (NPs) of C1 are highly dispersed on the α -Al₂O₃ support, while the Pd NPs of C2 are somewhat aggregated into large NPs during the catalyst preparation process. HRTEM images (Fig. 3b and d) of both catalysts show that the interval between two lattice fringes of Pd NPs is *ca.* 0.226 nm, corresponding to the interplanar distance of the (111) plane of the face-centered cubic (fcc) Pd.¹⁷⁻¹⁹ On the basis of the size distribution histograms shown in the insets

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Fig. 2 The *in situ* DR-FTIR spectra for the reaction of CO and methyl nitrite to DMO on C1 (a) and C2 (b) at 130 $^\circ$ C, respectively.



Fig. 3 TEM images of C1 (a) and C2 (c) with the corresponding size distributions of Pd NPs (insets), and HRTEM images of C1 (b) and C2 (d), respectively.

of Fig. 3, the average size of Pd NPs of C1 is 2.7 nm, which is much smaller than that of C2 (11.6 nm), and the size distribution of Pd NPs of C1 becomes much narrower and more uniform compared with that of C2. In addition, the results in Table 2 show marked differences in the dispersion and the specific surface area of active component Pd NPs between the two catalysts. The dispersion of Pd for C1 is 19.8% and the specific surface area is 91.8 m² g⁻¹, whereas the dispersion and the specific surface area of Pd for C2 are much

 $\ensuremath{\text{Table 2}}$ The dispersion and the specific surface area of Pd obtained from CO chemisorption

Catalysts	Pd dispersion (%)	Pd specific surface area $(m^2 g^{-1})$
C1	19.8	91.8
C2	5.4	24.0



smaller (5.4% and 24.0 m² g⁻¹), respectively. Therefore, catalyst C1 with much smaller particle size, much higher dispersion and specific surface area of Pd can easily account for the higher catalytic activity. The TEM image and the size distribution (Fig. S12, ESI[†]) of C1 after the durability test for 100 h are nearly similar to those of the fresh catalyst, implying that neither aggregation nor sintering of the Pd NPs for C1 occurred during the test.

Based on the above experimental facts, we can infer that the introduction of Cu²⁺ ions into the reaction system has a great influence on the reduction of PdCl₄²⁻ species, significantly increases the dispersion and the specific surface area of active component Pd, and also decreases the ensemble size of Pd NPs over the Pd/ α -Al₂O₃. Herein, we suggest a plausible Cu²⁺assisted growth mechanism of Pd NPs over catalysts, as shown in Scheme 1. $PdCl_4^{2-}$ is firstly reduced by L-ascorbic acid to form Pd nuclei at room temperature. It is well known that Cu underpotential deposition (UPD) occurs on the Pd surface, and the redox potential of the Pd(111)/Cu(UPD) is around 0.60 V, 20,21 which is close to the reduction potential of PdCl₄²⁻ (0.62 V). Therefore, Cu^{2+} ions can be reduced to metallic Cu^{0} , which leads to an underpotentially deposited Cu monolayer on the Pd surface. Two weak binding peaks appear at 931.7 and 951.7 eV in the XPS spectrum (Fig. S8b, ESI⁺), which are assigned to the metallic state Cu^{0,22} The weak peaks of Cu 2p in the XPS spectrum imply that the amount of Cu is very low. The trace amount of Cu confirms the UPD of Cu on the Pd surface. On the other hand, the potential of $Cu^{2+/0}$ (0.34 V) is lower than the reduction potential of $PdCl_4^{2-}$. $PdCl_4^{2-}$ may be reduced to Pd by the galvanic replacement reaction (GRR),²² leading to the growth of Pd NPs, and Cu atoms are reoxidized to Cu²⁺ ions. However, as the interference of Cu²⁺ ions, the growth rate of Pd NPs should be lower than that without Cu²⁺ ions. The reduction of PdCl₄²⁻, Cu UPD, and GRR will finally reach equilibrium as the precursors are consumed to a certain level. This can be verified by the more incomplete consumption of $PdCl_4^{2+}$ for preparation of C1 after enough time (Table S1 and Fig. S7, ESI⁺). Thus, the introduction of Cu²⁺ ions into the

reaction system can inhibit the reduction of $PdCl_4^{2-}$ and change the growth kinetics of Pd NPs, which results in the formation of the small and homogeneous Pd NPs on an α -Al₂O₃ support. In contrast, uneven Pd NPs are formed without the assistance of Cu²⁺ ions. Small and uniform Pd NPs (Fig. S13, ESI†) as expected were also obtained when the same molar amount of Cu(NO₃)₂·3H₂O was used instead of CuCl₂·2H₂O.

In summary, an ultra-low Pd loading Pd/α -Al₂O₃ nanocatalyst with high activity and stability for CO oxidative coupling to DMO was successfully synthesized *via* a Cu²⁺-assisted *in situ* reduction approach at room temperature. Cu²⁺ ions contribute to the small size and high dispersion of Pd NPs on an α -Al₂O₃ support, which leads to the excellent catalytic activity. Due to its facile synthesis and low Pd loading, this highly efficient and long-lived nanocatalyst may have a good prospect of industrial application. Importantly, this synthesis method should be universal for designing other supported noble metal nanocatalysts with high dispersion and small NPs.

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