SPECIAL TOPIC: Single-atom Catalysts

Pd₁/CeO₂ single-atom catalyst for alkoxycarbonylation of aryl iodides

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ABSTRACT Heterogenization of the homogeneous catalysis has been studied for almost 50 years. Single-atom catalysis has the advantages of both homo- and heterogeneous catalysis. It has been proposed, and subsequently experimentally verified that single-atom catalysis is able to bridge homo- and heterogeneous catalysis, thus providing a new avenue to realize the heterogenization of homogeneous catalysis. Alkoxycarbonylation of aryl halides is an effective method for the direct synthesis of carboxylic acid derivatives, and is commonly catalyzed by Pd-based homogeneous complexes with N/P-containing ligands and organic/inorganic base. Herein, we firstly reported that Pd₁/CeO₂ single-atom catalyst showed good performance in the alkoxycarbonylation of aryl iodides reaction. Under base-free and ligand-free conditions, Pd₁/CeO₂ single-atom catalyst can transfer different aryl iodides to corresponding products. The catalyst can be easily recovered and reused four times without significant loss of reactivity.

Keywords: single-atom catalyst, alkoxycarbonylation, Pd₁/CeO₂, heterogenization, base-free

INTRODUCTION

Homogeneous catalysis still plays an important role in today's industrial processes. It was estimated that homogeneous transition metal catalysis had 10%–15% share in the catalytic processes and was applied in almost all areas of the chemical industry [1]. Besides designing new ligand motifs to enrich the homogeneous catalysts, studies on the heterogenization of homogeneous catalysts have long been kept for solving the sustainability issues,

and the general method is to immobilize the metallic compounds or clusters on insoluble solid supports such as silica, alumina or polymers. However, the catalysts' leaching problem, reduced accessibility and restricted structural flexibility limit their application [2,3].

Single-atom catalysts (SACs), with the advantages of both heterogeneous catalysts (stable and easy separation) and homogeneous catalysts (uniform active sites and high activity and selectivity), have been predicted to be able to bridge the gap between homo- and heterogeneous catalysis since it was first proposed in 2011 [4,5]. But until 2016, when Zhang's group [6] reported that Rh₁/ZnO SAC showed similar activity comparable to the homogeneous RhCl(PPh₃)₃ in the hydroformylation reaction, has the prediction been experimentally demonstrated. Since then, utilizing SACs in homogeneous catalyzed reaction has become a hot research topic. For example, Pt/Al₂O₃ [7] and Pt/TiO₂ [8] SACs were successfully used in hydrosilylation reaction. The porous organic polymer supported Ir-SAC [9] performed a quasi-homogeneous hydrogenation transformation of CO₂ to formate. Exfoliated graphitic carbon nitride loaded Pd SAC [10] showed higher activity than the homogeneous systems in Suzuki couplings reaction. And Fe-N-C SAC [11] exhibited high activity and excellent reusability for the selective oxidation of the C–H bond. Therefore, SACs provided a new way to realize the heterogenization of the homogeneous catalyzed reaction.

Palladium-catalyzed carbonylation of aryl halides occupies a special place in organic synthesis. With CO and

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appropriate nucleophile, aryl halides can be conveniently transformed into various carbonyl compounds such as acids, amides, esters, ketones and aldehydes which are useful intermediates to produce pharmaceuticals, agrochemicals, dyes and other industrial chemicals [12]. Homogeneous Pd complexes such as $\text{Pd}(\text{OAc})_2$ or $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ with N/P-containing ligands as stabilizer and organic/inorganic base as promoter were commonly used for these reactions. Despite their high activity, selectivity and low amount of catalyst usage, the reuse of the homogeneous palladium catalysts remains a challenging issue. Lots of traditional heterogeneous Pd-based catalysts have been investigated to solve the recovery and recycling problem (like Pd/C [13,14], Pd/MOF [15,16], Pd/POC [17], etc.), and significant progress has been achieved. However, phosphine ligands and/or base were usually needed to improve their activity. Notably, in 2016, Zicarelli *et al.* [18] reported that in the absence of base and ligand palladium supported on N-doped carbon (Pd/PdO@NGr-C) catalyst showed good performance on the alkoxycarbonylation of aryl iodides. At 393 K and 20 bar CO (1 bar = 10^5 Pa), different aryl iodides can be completely transformed, but the reusability of the catalyst is not very good.

In this work, we firstly reported that, without any external ligands or base, Pd_1/CeO_2 SAC showed high activity and very good stability in the alkoxycarbonylation of aryl iodides reaction. With 0.03% Pd_1/CeO_2 SAC as catalyst, the turnover number (TON) of iodobenzene can reach about 6300, and no activity decrease was observed over four cycles.

EXPERIMENTAL SECTION

Reagents

Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and sodium carbonate (Na_2CO_3) were purchased from Sigma-Aldrich. PdCl_2 was purchased from Tianjin Fengchuan. Polyvinyl alcohol (PVA 97%, molecular mass 1750 ± 50) was bought from Tianjin Damao. Iodobenzene, 1-iodonaphthalene, 4-iodoanisole and octane were commercially provided by Aladdin. Ethanol and hydrochloric acid were purchased from Tianjin Kemiou. Deionized water was obtained from a Millipore Autopure system. All reagents were used without further purification.

Catalysts preparation

Preparation of CeO_2 support

CeO_2 support was synthesized by a co-precipitation

method as reported in our previous work [19,20]. Specifically, 1 mol L^{-1} $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ aqueous solution was dropped into an aqueous solution of Na_2CO_3 (1 mol L^{-1}) under stirring at 323 K, with the pH of the final solution being controlled at approximately 8. After being continuously stirred and aged for 3 h, respectively, the resulting precipitate was filtered, and washed with distilled water several times. The recovered solid was dried at 333 K overnight and then calcined at 673 K for 5 h.

Preparation of Pd_1/CeO_2

Homemade CeO_2 powder (1 g) was dispersed in deionized water with rigorous stirring. Appropriate amount of H_2PdCl_4 solution, which was prepared by dissolving PdCl_2 in hydrochloric acid with the mole ratio of Pd and HCl maintaining at 10, was added dropwise into the CeO_2 solution under stirring. After the solution was dried at 368 K, the obtained powder was calcined at 673 K for 5 h.

Preparation of NP-Pd/ CeO_2

For comparison, Pd/ CeO_2 catalyst containing Pd nanoparticles (NPs) of 2–6 nm in size was prepared by the same method with Pd_1/CeO_2 except depositing colloidal Pd NPs onto the CeO_2 surface instead of H_2PdCl_4 . The final catalyst was denoted as NP-Pd/ CeO_2 .

Colloidal Pd NPs were prepared similarly to the previously reported procedure [21]. 0.6 mmol of PdCl_2 , 6.0 mL of 0.2 mol L^{-1} HCl, and 294 mL of H_2O were mixed to prepare H_2PdCl_4 solution (2.0 mmol L^{-1}). Then 15 mL of the H_2PdCl_4 solution, 21 mL of H_2O , 14 mL of ethanol (40 vol%), and 0.0333 g of PVA were mixed and stirred for 3 h at room temperature. The prepared solution had a dark brown color. The obtained Pd nanocluster solution was very stable and ready for deposition on CeO_2 support.

Catalyst characterization

Power X-ray diffraction (XRD) patterns were acquired on a X'Pert PRO (PANalytical) diffractometer equipped with a Cu K α radiation source operated at 40 kV and 40 mA. The XRD patterns of samples were collected in the 2θ range from 20° to 80° .

Scanning transmission electron microscopy (STEM) combined with energy disperse X-ray spectroscopy (EDS) microanalysis system were implemented on a JEOL JEM-2100F microscope operated at 200 kV. The aberration-corrected high-angle annual dark-field STEM (AC-HAADF-STEM) images were obtained on the JEOL JEM-ARM200F with a guaranteed resolution of 0.08 nm. Prior to the measurements, the samples were dispersed ultra-

sonically in ethanol and then a few droplets of each sample were deposited on a carbon coated Cu grid.

Inductively coupled plasma optical emission spectrometer (ICP-OES) was performed on PerkinElmer ICP-OES 7300DV instrument. Inductively coupled plasma mass spectroscopy (ICP-MS) measurements were performed on a NexION 300D (PerkinElmer) instrument.

Activity test

Alkoxy carbonylation of aryl iodides reaction was conducted in an autoclave equipped with a magnetic bar. Typically, 50 mg catalyst, 150 μL iodobenzene and 8 mL methanol were added into the autoclave which was then purged with CO for six times and charged successively with 2 MPa CO. After reacting at 393 K for a certain time, the reactor was quenched to room temperature by cool water. 100 μL octane was added into the reaction mixture as inner standard and the product was analyzed by Agilent 7890B gas chromatography (GC) with a HP-5 capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 mm) and a flame ionization detector.

For the recycling test, after each run, the catalysts were separated by centrifugation, washed thoroughly with methanol, and dried overnight at 353 K before being used in the next run under same conditions.

RESULTS

The XRD patterns of the synthesized catalysts were shown in Fig. S1. Only diffraction peaks of CeO_2 were observed. No Pd or PdO diffraction peaks were found on the spectrum which should be due to the extremely low Pd loading. Representative STEM images (Fig. S2) and EDS measurement (Fig. S3a) of Pd_1/CeO_2 show that no distinct Pd NPs were observed. To confirm the atomic dispersion of Pd, AC-HAADF-STEM examination was conducted. As shown in Fig. 1, because of the low Z-contrast of Pd and Ce, it is difficult to distinctly observe the single Pd atoms on CeO_2 support. However, according to our previous work and considering the fact that both high- and low-magnification images did not reveal any Pd NPs and nanoclusters, we can reasonably conclude that Pd was atomically dispersed on the CeO_2 . The loading of Pd is 0.03 wt% based on the ICP-OES analysis. For comparison, NP-Pd/ CeO_2 catalyst with the same Pd loading to Pd_1/CeO_2 was synthesized and the size of colloidal Pd NPs was 2–6 nm (shown in Fig. S4).

The carbonylation reaction was performed at 393 K with iodobenzene as substrate and methanol as nucleophile. The results are presented in Table 1. A blank experiment without any catalyst reveals no **1A** product was

Figure 1 Representative AC-HAADF-STEM images of Pd_1/CeO_2 .

Table 1 The performance of different catalysts on alkoxy carbonylation of iodobenzene^a

Entry	Catalyst	Conversion (%)	Yield of 1A (%)
1	None	3.9	n.d. ^b
2	CeO_2	8.4	5.8
3	Pd_1/CeO_2	46	41
4	NP-Pd/ CeO_2	28	26

a) Reaction conditions: 50 mg catalyst, 150 μL iodobenzene, 8 mL methanol, 2 MPa CO, 393 K, 8 h; b) n.d.: not detected.

obtained. Considering the fact that no other products were detected either on the GC, the negligible conversion of iodobenzene should be due to the analysis error. The control experiment shows that CeO_2 had a little activity in this reaction (~8% conversion). However, when 0.03 wt% Pd atoms were loaded, the conversion of iodobenzene increased significantly to 46%, indicating a very high activity of the Pd atoms or the entity of Pd_1/CeO_2 . The turnover frequency (TOF) can reach up to 465 h^{-1} . For comparison, NP-Pd/ CeO_2 catalyst was also tested. As shown in Table 1, the conversion of iodobenzene and yield of **1A** were 28% and 26%, respectively. Therefore, Pd_1/CeO_2 SAC demonstrated higher activity than the NPs catalyst.

To eliminate the possibility that the high activity of

SAC may originate from a homogenous catalysis process by the leached Pd species, we have performed the filtration experiment. After the reaction was conducted for 4 h, the catalyst was filtered and the residual solution was subjected to another 4-h reaction. As shown in Table S1, only additional 3% conversion of iodobenzene was tested which means that the Pd atoms left in the solution are negligible. The reusability of Pd₁/CeO₂ SAC was also examined. As shown in Fig. 2, no significant loss of activity was observed over four cycles. The used Pd₁/CeO₂ SAC was analyzed by ICP-MS and no Pd loss was detected. The EDS mapping of the used catalyst also showed that no obvious Pd NP was detected (Fig. S3b). So Pd atoms strongly bonded to the CeO₂ support and the synthesized Pd₁/CeO₂ SAC was stable under working conditions without obvious leaching or aggregation.

The above results show clearly Pd₁/CeO₂ SAC has high activity and good stability in alkoxycarbonylation of aryl iodides reaction. The higher activity compared with NP-Pd/CeO₂ is not related to the chemical state of Pd as the XPS measurements show that in both catalysts Pd exists as same oxidative state (Fig. S5). The rate-determining step in alkoxycarbonylation of aryl iodides reaction is usually the dissociation of the nucleophile which is mainly facilitated by the inorganic or organic alkali. Typically, in this work, the interfacial site of Pd/CeO₂ played an important role in dissociation of methanol [22]. Therefore, we believe the higher activity of Pd₁/CeO₂ SAC than NP-Pd/CeO₂ should be owing to the maximized atom utilization efficiency and the maximized interfacial sites of SAC [20,23–25].

At last, substrate scope was explored. Different aryl iodides and nucleophiles were tested. The results are lis-

Figure 2 Recycle performance of Pd₁/CeO₂ catalyst in alkoxycarbonylation of iodobenzene reaction. Reaction conditions: 50 mg catalyst, 150 μ L iodobenzene, 8 mL methanol, 2 MPa CO, 393 K, 8 h.

Table 2 Substrate scope for the alkoxycarbonylation of aryl iodides catalyzed by Pd₁/CeO₂^a

Substrate	TON	Product	Yield (%)
6343		73
+ MeOH
6004		71
+ EtOH
6596		99
+ MeOH
5527		91
+ MeOH			

a) Reaction conditions: 50 mg 0.03% Pd₁/CeO₂, 8 mL nucleophile, 2 MPa CO, 393 K, 24 h, 150 μ L aryl iodides or 1 mmol 4-iodoanisole.

ted in Table 2. For the iodobenzene and methanol as substrate, when increasing the reaction time to 24 h, the TON of iodobenzene can reach up to 6343 and the yield of **1A** is 73%. Ethanol as nucleophile, shows the similar results. For other iodides, the catalyst Pd₁/CeO₂ SAC also exhibits high activity. What is more, we have also tested Pd₁/CeO₂ SAC in the aminocarbonylation of aryl iodides with aniline as nucleophile. The conversion of iodobenzene and the yield of *N*-phenyl benzamide are 71% and 50%, respectively, which means that Pd₁/CeO₂ SAC can be expanded to catalyze the aminocarbonylation of aryl iodides reaction (shown in Table S2).

CONCLUSIONS

We have synthesized Pd₁/CeO₂ SAC and used it in the alkoxycarbonylation of iodobenzene reaction which was commonly catalyzed by homogeneous Pd-based catalyst. Without the addition of external base and ligand, satisfactory performance in the alkoxycarbonylation of aryl iodides reaction could be obtained with excellent stability and substrate universality, which makes Pd₁/CeO₂ SAC a promising candidate for synthesis of useful chemicals. This work further demonstrates that SAC provides a new path to realize the heterogenization of homogeneous catalysis.

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- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Supporting data are available in the online version of the paper.

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单原子Pd₁/CeO₂催化剂催化芳香族碘化物烷氧基羰基化反应

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摘要 均相反应多相化是一个由来已久的研究课题. 作为多相催化研究的新前沿, 单原子催化剂兼具均相催化剂孤立活性位点和多相催化剂简单易分离的优势, 自提出以来便被认为有望成为联系均相催化与多相催化的桥梁, 而且近几年来已从实验上得到了证实. 因此单原子催化剂为均相催化反应多相化提供了新途径. 卤代芳烃烷氧基羰基化反应被广泛用于合成芳香族醛、酮、酸及其衍生物, 但该反应目前主要采用均相Pd基催化剂, 而且还需添加配体或有机/无机碱. 本文中, 我们首次报道了将单原子催化剂Pd₁/CeO₂用于芳香族碘化物烷氧基羰基化反应中, 在无配体和无外加碱辅助下, 催化剂表现出优异的活性、良好的循环稳定性以及底物普适性.