

Anchoring Positively Charged Pd Single Atoms in Ordered Porous Ceria to Boost Catalytic Activity and Stability in Suzuki Coupling Reactions

Xueqin Tao, Ran Long, Di Wu, Yangguang Hu, Ganhua Qiu, Zeming Qi, Benxia Li,* Ruibin Jiang,* and Yujie Xiong*

Single-atom (SA) catalysis bridging homogeneous and heterogeneous catalysis offers new opportunities for organic synthesis, but developing SA catalysts with high activity and stability is still a great challenge. Herein, a heterogeneous catalyst of Pd SAs anchored in 3D ordered macroporous ceria (Pd-SAs/3DOM-CeO₂) is developed through a facile template-assisted pyrolysis method. The high specific surface area of 3DOM CeO₂ facilitates the heavily anchoring of Pd SAs, while the introduction of Pd atoms induces the generation of surface oxygen vacancies and prevents the grain growth of CeO₂ support. The Pd-SAs/3DOM-CeO₂ catalyst exhibits excellent activity toward Suzuki coupling reactions for a broad scope of substrates under ambient conditions, and the Pd SAs can be stabilized in CeO₂ in long-term catalytic cycles without leaching or aggregating. Theoretical calculations indicate that the CeO₂ supported Pd SAs can remarkably reduce the energy barriers of both transmetalation and reductive elimination steps for Suzuki coupling reactions. The strong metal-support interaction contributes to modulating the electronic state and maintaining the stability of Pd SA sites. This work demonstrates an effective strategy to design and synthesize stable single-atom catalysts as well as sheds new light on the origin for enhanced catalysis based on the strong metalsupport interactions.

1. Introduction

Palladium-catalyzed Suzuki coupling reactions are a class of the most straightforward and effective pathways for producing biphenyl compounds which are critical intermediates for the synthesis of pharmaceutical drugs, complex natural products and functional materials.^[1-3] The homogeneous catalysts of organometallic Pdcomplexes are traditionally used in these reactions.^[4-6] However, most of the ligands in the organometallic Pd compounds are expensive, toxic, or both. Moreover, the homogeneous catalysts face difficulty in their recovery and reusability, leading to the high cost of catalysts and the tedious procedures in product purification. In comparison, the heterogeneous catalysts of Pd clusters or nanoparticles (NPs) on solid supports may overcome these limitations and thus have been paid much attention.^[7-10] Nonetheless, these heterogeneous catalysts usually suffer from less exposed active sites and limited accessibility for reactants, compared with their

X. Tao, G. Qiu, Prof. B. Li Department of Chemistry School of Science Zhejiang Sci-Tech University Zhejiang 310018, P. R. China E-mail: libx@mail.ustc.edu.cn

Prof. R. Long, Dr. D. Wu, Y. Hu, Dr. Z. Qi, Prof. Y. Xiong Hefei National Laboratory for Physical Sciences at the Microscale iChEM (Collaborative Innovation Center of Chemistry for Energy Materials) School of Chemistry and Materials Science

and National Synchrotron Radiation Laboratory University of Science and Technology of China Hefei, Anhui 230026, P. R. China E-mail: yjxiong@ustc.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.202001782.

DOI: 10.1002/smll.202001782

Prof. R. Jiang

Key Laboratory of Applied Surface and Colloid Chemistry National Ministry of Education Shaanxi Key Laboratory for Advanced Energy Devices Shaanxi Engineering Lab for Advanced Energy Technology School of Materials Science and Engineering Shaanxi Normal University Xi'an 710119, P. R. China E-mail: rbjiang@snnu.edu.cn Prof. Y. Xiong Institute of Energy Hefei Comprehensive National Science Center 350 Shushanhu Rd., Hefei, Anhui 230031, P. R. China homogeneous counterparts. For this reason, exploring the new catalysts which have both advantages of homogeneous (high activity) and heterogeneous (high durability and easy separation) ones is of great significance for Suzuki coupling reactions.

ADVANCED SCIENCE NEWS _____

As a new frontier of heterogeneous catalysis, single-atom (SA) catalysis represents such a new opportunity to link homogeneous and heterogeneous catalysis.^[11–13] Upon isolating single metal atoms on the solid supports with high surface area, the SA catalysts exhibit great advantages in maximizing the metal atom utilization comparable to that of homogeneous catalysts.^[14–16] Although the TiO₂ nanocrystals^[17] and exfoliated graphitic carbon nitride^[18] supported Pd SAs have been demonstrated to show superior activities to homogeneous systems in Sonogashira and Suzuki C–C coupling reactions under heating conditions and protection of inert gases, respectively, the great challenges still remain in elucidating the origin for high catalytic activity and implementing the cross-coupling reactions under ambient conditions.

For the development of heterogeneous SA catalysts, support material is a non-negligible factor to be considered. The support not only determines the stability and accessibility of SA sites but also affects their activity and selectivity due to metalsupport interaction.^[19-22] Ideally, ordered porous support with a high specific surface area can expose abundant active sites and promote the diffusion of substrate molecules.^[23–25] Despite of a few recent cases for Pd SA catalysts,^[26-29] the precise integration of the support possessing 3D ordered macroporous (3DOM) structure with the in situ anchored Pd SAs has rarely been achieved. Ceria (CeO₂) is a favorable support material that can stabilize metal species even at high temperature owing to the strong metal-support interaction.^[30-32] We thus inferred that such strong metal-support interactions will endow CeO₂ with the excellent ability to stabilize Pd SAs through an adaptive coordination as well as modify the electronic structures and chemical properties of Pd atoms, playing key roles in enhancing overall catalytic performance. Furthermore, creating oxygen vacancies (OVs) on the surface of CeO2, by taking advantage of the easy shift between Ce4+ and Ce3+ ions, will offer more opportunities for reinforcing the stability as well as balancing the positive charges of Pd SA sites, thus improving the catalytic activity.^[33-35] Taken together, the parameters of oxide supports including geometric construction, electronic structure, and defective sites potentially provide additional knobs for tailoring the overall performance of SA catalysts.

Herein, the heterogeneous catalyst of Pd SAs anchored in 3DOM structural ceria (Pd-SAs/3DOM-CeO₂) has been synthesized through a facile template-assisted in situ pyrolysis method. This catalyst presents a desirable integration of atomically dispersed Pd active sites with 3DOM-structural CeO₂ support through two-way interactions. Specifically, the high specific surface area of 3DOM CeO₂ facilitates the anchoring of Pd SAs with a high loading content of 1.76 wt%, while the introduction of Pd atoms induces the generation of abundant OVs and promotes the mesoporosity of CeO₂ support. The Pd-SAs/3DOM-CeO₂ catalyst exhibits excellent activity and selectivity toward Suzuki coupling reactions under ambient conditions (298 K and air atmosphere), remarkably surpassing the homogeneous Pd(PPh₃)₄ and the supported Pd clusters or Pd NPs. The superior performance of Pd-SAs/3DOM-CeO2 is derived from the positively charged Pd SA active sites which remarkably reduce the energy barriers of transmetalation and reductive elimination steps for the Suzuki reactions. The Pd SAs can be stabilized in 3DOM CeO_2 by the strong Pd–O–Ce bonds for a long-term reaction, without leaching or aggregating.

2. Results and Discussion

The Pd-SAs/3DOM-CeO₂ catalyst is synthesized through a template-assisted in situ pyrolysis method as illustrated in Scheme 1. Specifically, polystyrene microspheres are packed to serve as colloidal crystal templates, which allows the successive impregnation of Ce and Pd precursors and their further transformation into CeO2 loaded with Pd SAs around the templates. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure 1a,b) reveal that the Pd-SAs/3DOM-CeO₂ catalyst possesses a honeycomblike structure composed of well-arranged spherical voids with diameters of ≈180 nm and honeycomb walls with thickness of ≈ 10 nm. The crystal phase in this sample is characterized as cubic CeO₂ (JCPDS No. 81-0792) by X-ray diffraction (XRD) (Figure S1, Supporting Information), without any diffraction peak of Pd species. According to the high-resolution TEM (HRTEM) images (inset of Figure 1b and Figure S2, Supporting Information), the macropore walls are constructed by CeO₂ nanocrystals with average grain size about 4.56 nm. The lattice fringes with spacing of 0.318 nm belong to the (111) plane of cubic CeO₂ nanocrystals. The granular stacking forms the randomly distributed mesopores in macropore walls, which has been further confirmed by N2 adsorption-desorption measurement indicating an average pore size of 9.59 nm (Table S1 and Figure S3, Supporting Information). The specific surface area and the cumulative pore volume of Pd-SAs/3DOM-CeO2 are determined to be 150.77 $\mathrm{m}^2~g^{-1}$ and 0.29 $\mathrm{cm}^3~g^{-1}$, respectively, which are larger than those (135.15 m² g⁻¹ and 0.26 cm³ g⁻¹) of pure 3DOM-CeO₂ support with similar honeycomb-like structures (Figure S4a,b, Supporting Information). HRTEM image (Figure S4c, Supporting Information) indicates that the CeO₂ nanocrystals in pure 3DOM-CeO₂ have a larger average grain size of 7.69 nm. The high-temperature treatment reduces a little the surface area of pure CeO₂ due to the growth of CeO₂ grains.^[36] In contrast, the introduction of Pd into CeO₂ converts the surface O-Ce species to Pd-O-Ce species, which prevents the grain growth of CeO₂ under high temperature, thus resulting in the larger surface area and pore volume of Pd-SAs/3DOM-CeO2.^[37] The large surface area and high porosity of Pd-SAs/3DOM-CeO2 are beneficial to the sufficient exposure of Pd-SA active sites and the easy diffusion of substrate molecules during catalytic reactions. Aberration-corrected high-angle annular dark-field scanning transmission electron



Scheme 1. Schematic illustration for the synthesis of Pd-SAs/3DOM-CeO_2 catalyst.



Figure 1. Electron microscopy characterizations of Pd-SAs/3DOM-CeO₂ catalyst. a) SEM, b) TEM and HRTEM (inset), and c) HAADF-STEM images, d,e) the intensity profiles taken along line 1 and line 2 in (c), f) HAADF-STEM image and EDS elemental mappings.

microscopy (AC-HAADF-STEM) provides the atomic resolution image (Figure 1c) of Pd-SAs/3DOM-CeO₂ sample, in which some dark dots related to the lower intensity of HAADF-STEM signal (Figure 1d) are most likely the isolated Pd atoms which have the smaller atomic number than that of Ce atoms.^[29,38] The elemental mappings (Figure 1f) from energy dispersive spectroscopy (EDS) confirm the uniform distribution of Ce and Pd, providing further evidence for the existence of individually dispersed Pd atoms in the material. The Pd content in Pd-SAs/3DOM-CeO₂ is determined by inductively coupled plasma mass spectrometry (ICP-MS) to be 1.76 wt%. Such a high loading of Pd SAs stabilized by oxide supports has rarely been obtained (Table S2, Supporting Information), demonstrating the advantage of 3DOM CeO₂ support.

Further insight into the local coordination structure of Pd atoms in Pd-SAs/3DOM-CeO₂ is gained by the elementselective X-ray absorption fine structure spectroscopy (XAFS). As shown in **Figure 2**a, the Fourier-transformed extended XAFS (FT-EXAFS) of Pd-SAs/3DOM-CeO₂ exhibits only one peak at 1.5 Å, corresponding to Pd–O shell in PdO reference. No Pd-Pd coordination is observed in Pd-SAs/3DOM-CeO₂, affirming that the isolated Pd atoms are anchored in 3DOM CeO₂ with Pd–O bonds. The structure parameters of Pd-SAs/3DOM-CeO₂ are further acquired by the least squares EXAFS fitting (Figure 2b,c) and summarized in Table S3 in the Supporting Information. In comparison with Pd foil and PdO references, the fitting results indicate that the Pd atoms in Pd-SAs/3DOM-CeO₂ have a coordination number of about 3 in relation with the first shell, and the average Pd–O bond length is about 2.00 Å. To look into the local environment of Pd species, we employ CO-probing diffused reflection infrared Fourier transform spectroscopy (DRIFTS) to characterize Pd-SAs/3DOM-CeO₂, by comparison with two reference samples of H₂-treated Pd-SAs/3DOM-CeO2 (Pd-SAs/3DOM-CeO2-H2) and 3DOM-CeO₂ supported Pd NPs (Pd-NPs/3DOM-CeO₂, Figure S5, Supporting Information), as shown in Figure 2d. Only one sharp peak at 2153 cm⁻¹ is observed in the DRIFT spectrum of Pd-SAs/3DOM-CeO2, which belongs to the stretching frequency of linear-adsorbed CO on Pd SAs, confirming the uniform dispersion of isolated Pd single atoms. In contrast, Pd-SAs/3DOM-CeO₂-H₂ displays another broad peak around 2098 cm⁻¹ related to the linear-adsorbed CO on Pd clusters.^[29] The multifarious adsorption sties on Pd clusters result in various vibrational frequencies of C-O bond and thus a broad peak. This suggests that the H₂ treatment of Pd-SAs/3DOM-CeO₂ at 350 °C for 1 h breaks some of Pd–O bonds and leads to the aggregation of Pd atoms into Pd clusters. Moreover, the stretching frequency peak of the linear-adsorbed CO on Pd SAs has an obvious blue-shift from that on Pd clusters, indicating that the isolated Pd SAs are more positively charged than the Pd clusters.^[39] For Pd-NPs/3DOM-CeO₂ sample, we observe the two broad bands centered at 1890 and 2090 cm⁻¹, corresponding to the threefold-hollow-adsorbed CO and minor linear-adsorbed CO on Pd NPs, respectively.^[40-42] The comparison demonstrates well that our synthetic method offers the special ability of heavily loading SA sites on oxide support. Figure S6 (Supporting Information) shows the Pd species anchored in CeO₂ without 3DOM structure (Pd/CeO₂), synthesized by the in situ 



Figure 2. Structure characterizations based on XAFS and DRIFTS. a) FT-EXAFS spectra of Pd-SAs/3DOM-CeO₂ in reference to Pd foil and PdO. b) EXAFS R space fitting curve (red line) and the experimental data (circles) of Pd-SAs/3DOM-CeO₂. c) EXAFS k space fitting curve (red line) and the experimental data (circles) of Pd-SAs/3DOM-CeO₂. c) EXAFS k space fitting curve (red line) and the experimental data (circles) of Pd-SAs/3DOM-CeO₂. d) DRIFT spectra of CO molecules absorbed on Pd-SAs/3DOM-CeO₂, Pd-SAs/3DOM-CeO₂. Pd-SAs/3DOM-CeO₂. d) DRIFT spectra of CO molecules absorbed on Pd-SAs/3DOM-CeO₂, Pd-SAs/3DOM-CeO₂. d) DRIFT spectra of CO molecules absorbed on Pd-SAs/3DOM-CeO₂, Pd-SAs/3DOM-CeO₂. respectively.

pyrolysis process without template. The Pd_{1.76}/CeO₂ sample with a higher Pd loading content about 1.76 wt% presents the multiple peaks related to the linear-adsorbed CO molecules on Pd SAs (2151 cm⁻¹) and on Pd clusters or NPs (2107 cm⁻¹) as well as the hollow-adsorbed CO on Pd NPs (1936 cm⁻¹), respectively. As the Pd loading content is reduced to about 1.0 wt%, the Pd_{1.0}/CeO₂ sample shows only one sharp peak at 2165 cm⁻¹ in its DRIFT spectrum, suggesting the formation of Pd single atoms on CeO₂. In contrast, the 3DOM CeO₂ support with large surface area can provide more sites for anchoring Pd single atoms, which is beneficial to the anchoring of Pd SAs with higher content. In addition, when SiO₂, a relatively inert and irreducible oxide, is chosen as an oxide support to synthesize the Pd/3DOM-SiO₂ catalyst (Figure S7, Supporting Information) via the same template-assisted in situ pyrolysis method, the crystalline PdO is identified to exist in this sample (Figure S7a, Supporting Information). The CO-probing DRIFT spectrum (Figure S7c, Supporting Information) shows a broad infrared (IR) band containing two peaks centered at 2027 and 2004 cm⁻¹, respectively, most likely corresponding to the bridge-adsorbed CO molecules on Pd²⁺ and Pd⁺ species.^[43] The results demonstrate that the 3DOM-CeO₂ is a desirable support to stabilize Pd SAs with a high loading content by the strong Pd-O-Ce bondings.

The valence states of Pd and Ce associated with their interaction in Pd-SAs/3DOM-CeO₂ catalyst are analyzed by X-ray photoelectron spectroscopy (XPS). The Pd $3d_{5/2}$ spectrum (**Figure 3**a) is fitted with two peaks at 338.2 and 336.5 eV, which can be assigned to high-valence Pd⁴⁺ and Pd²⁺ species, respectively.^[18,28] The metallic Pd⁰ with $3d_{5/2}$ binding energy at

≈335.0 eV is absent, consistent with the fact that Pd atoms are isolated in Pd-SAs/3DOM-CeO₂ instead of forming Pd NPs. Such a positive shift of Pd XPS signals has been found previously in the solution-combustion synthesized Pd/CeO₂, which contains Pd in the higher oxidation states being stabilized in the Ce³⁺ sites by a strong interaction of Pd–O–Ce bonding.^[44] The Ce 3d spectra of 3DOM-CeO₂ with and without Pd SAs are shown in Figure 3b. Both of the Ce 3d spectra are deconvoluted into eight peaks.^[45] The peaks at 884.8 (V') and 903.2 eV (U') correspond to the signals of Ce $3d_{3/2}$ and Ce $3d_{5/2}$ of Ce³⁺ species, and the others are assigned to the normal Ce4+ species. Interestingly, the peak area ratio of $A_{(Ce^{(3+)}/Ce^{(4+)})}$ increases after anchoring Pd SAs in 3DOM CeO2, suggesting that the introduction of Pd SAs promotes the generation of Ce3+ defects in CeO2. The structures of 3DOM-CeO2 with and without Pd SAs have also been characterized by Raman spectroscopy (Figure 3c). The sharp peak at 460 cm⁻¹ belongs to Raman active F_{2g} mode with fluorite crystal unit. This peak widens and down-shifts by 4 cm⁻¹ after incorporating Pd SAs into 3DOM-CeO₂, implying that the lattice distortions and the creation of OVs in CeO₂. The peaks at 261, 600, and 1180 cm⁻¹ related to OVs also become more obvious in the Raman spectrum of Pd-SAs/3DOM-CeO₂. Electron spin resonance (ESR) spectroscopy (Figure 3d) demonstrates a distinct signal of oxygen vacancy at the g value of 2.002, confirming the generation of abundant OVs after introducing Pd SAs into 3DOM-CeO₂. Taken together, the XPS, Raman and ESR spectroscopy characterizations indicate that electron transfer takes place from Pd to Ce4+ through Pd-O-Ce interactions and in turn generates more Ce³⁺ defect associated OVs in Pd-SAs/3DOM-CeO₂. To reveal

www.advancedsciencenews.com





Figure 3. Characterization and theoretical simulation of Pd-SAs/3DOM-CeO₂. a) Pd 3d XPS spectrum of Pd-SAs/3DOM-CeO₂. b) Ce 3d XPS spectra of 3DOM-CeO₂ and Pd-SAs/3DOM-CeO₂. and Pd-SAs/3DOM-CeO₂. c) Roman spectra of 3DOM-CeO₂ and Pd-SAs/3DOM-CeO₂. d) ESR signals of OVs in 3DOM-CeO₂ and Pd-SAs/3DOM-CeO₂. e) Energy evolution and the representative structures during the structural optimization process (Movie S1, Supporting Information) of Pd-SA/CeO₂ model.

the Pd-SA induced formation of surface OVs in CeO₂ support, we employ density functional theory (DFT) calculation to reveal the structure and energy evolution, as depicted in the video (Movie S1, Supporting Information) and Figure 3e. The calculation indicates that introducing Pd atom onto CeO₂ (111) surface causes the spontaneous reconstruction of local structure, where some oxygen atoms are extracted from CeO₂ surface, generating OVs on the surface. In the finally optimized structure (Figure S8a,b, Supporting Information), Pd atom is coordinated with three oxygen atoms to form the average Pd–O distance of 1.84 Å, consistent with the results from EXAFS measurements. The differential charge density (Figure S8c, Supporting Information) indicates clearly that the electrons are transferred from Pd atom to neighboring CeO₂, showing electron depletion at the Pd site. The Mulliken and Hirshfeld

population analyses reveal that the positive charge amount of each Pd atom is 0.60e and 0.72e, respectively. Taken together, the strong interaction between Pd atoms and CeO₂ support endows the Pd-SAs/3DOM-CeO₂ material with unique merits, i.e., atomic dispersion and high loading of positively charged Pd SAs, abundant OVs and mesoporosity in CeO₂.

Such unique features of Pd-SAs/3DOM-CeO₂ designate it as an outstanding candidate for catalyzing Suzuki coupling reactions. After optimizing the catalytic reaction conditions, including different solvents and base (Table S4, Supporting Information), the activities of various catalysts are screened by the coupling reaction of iodobenzene and phenylboronic acid in the optimal system, which is performed directly under ambient conditions (298 K, air atmosphere). The results are summarized in **Figure 4**a and Table S5 (Supporting





Figure 4. Catalytic performance toward the Suzuki reaction of iodobenzene and phenylboronic acid. a) Percent conversion of iodobenzene and selectivity for producing biphenyl over different catalysts. b) Arrhenius plots of the reaction over three different catalysts. c) Durability tests of Pd-SAs/3DOM-CeO₂ for the Suzuki reaction (4 h for each cycle). d) Pd 3d XPS spectrum of Pd-SAs/3DOM-CeO₂ after eight cycles.

Information). The reaction cannot occur in the absence of Pd, indicating the catalytic inactivity of CeO₂ support. Notably, the Pd-SAs/3DOM-CeO₂ catalyst exhibits excellent activity and selectivity (100%) toward the Suzuki coupling reaction. The iodobenzene conversion presents a turnover frequency (TOF) value of 750.99 h⁻¹ at the low conversion level (Table S7, Supporting Information) and achieves a high percent conversion of 91.50% after 4 h. In contrast, the homogeneous Pd(PPh₃)₄ catalyst shows quite poor performance under either air or N₂ atmosphere. Moreover, the activity of Pd-SAs/3DOM-CeO₂ catalyst is much higher than that of the commercial Pd/C catalyst with 5 wt% Pd loading (Figure S9, Supporting Information). These manifest the superiority of this SA catalyst to the homogeneous and traditional heterogeneous catalysts in Suzuki coupling reactions.

To demonstrate the advantages of atomically dispersing Pd active sites and the 3DOM-CeO₂ support, we also examine the catalytic performance of other as-prepared catalysts. Specifically, the Pd-SAs/3DOM-CeO₂-H₂ catalyst presents a reduced activity, compared with Pd-SAs/3DOM-CeO₂, acquiring the iodobenzene conversion of 68.28% after 4 h. Pd-NPs/3DOM-CeO₂ exhibits a further depressed iodobenzene conversion of 48.62%. The Pd_{1.76}/CeO₂ sample synthesized through the in situ pyrolysis process without template shows the iodobenzene conversion of 67.47% after 4 h, due to the non-porous structure of CeO₂ support as well as the formation of Pd clusters and NPs. Although the Pd_{1.0}/CeO₂ sample has a reduced Pd loading content, compared with the Pd_{1.76}/CeO₂ sample, it exhibits increased activity with the iodobenzene conversion of 73.34% after 4 h, which further proves the superiority

of Pd-SA active sites. Moreover, the Pd/3DOM-SiO₂ catalyst also performs a poor activity, with iodobenzene conversion of 53.26%, confirming the pivotal role of the 3DOM-CeO₂ support.

The influence of Pd content in Pd-SAs/3DOM-CeO₂ on the catalytic activity is further studied (Table S6 and Figure S10a, Supporting Information). The percent conversion of iodobenzene is boosted from 55.41% to 91.50% after the same reaction time of 4 h as the Pd content increases from 0.61 to 1.76 wt%, whereas the conversion drops down to 75.52% when the Pd content further increases to 2.36 wt%. The increased Pd content can afford more active sites in the Pd-SAs/3DOM-CeO₂ catalyst. However, too heavy Pd loading leads to the formation of Pd clusters (Figure S10b, Supporting Information) which reduces the efficient active sites.

To acquire the reaction kinetics over several different catalysts, we further take the coupling reaction between iodobenzene and phenylboronic acid in the temperature range of 293–313 K. The Suzuki coupling reactions on Pd-SAs/3DOM-GeO₂ can be accelerated substantially by slightly elevating the temperature. As a result, the iodobenzene conversion (%) versus reaction time (min) curves at different temperatures (293, 298, 303, 308, and 313 K) can be obtained (Figure S11a–c, Supporting Information). The relationship of $\ln(C_0/C_t)$ versus time turns out to match well with the first-order reaction kinetics (Figure S11d–f, Supporting Information). After calculating the corresponding reaction rate constants (*k*) by the slope of $\ln(C_0/C_t)$ -time curves, the Arrhenius plots are subsequently obtained by drawing $\ln k$ as a function of 1000/T (Figure 4b). The reaction on Pd-SAs/3DOM-CeO₂ has a lower

apparent activation energy of 0.95 eV than the ones catalyzed by Pd-SAs/3DOM-CeO₂-H₂ (1.10 eV) and Pd-NPs/3DOM-CeO₂ (1.29 eV), respectively. This suggests that the integration of Pd-SA sites with 3DOM CeO₂ support can effectively reduce the reaction activation energy and thus boost the coupling reactions.

Recyclability is another key parameter for evaluating the performance of catalysts in addition to activity and selectivity. The recycling experiments of Pd-SAs/3DOM-CeO₂ catalyst have been performed at the low conversion (1 h for each cycle, Figure S12, Supporting Information) and the high conversion (4 h for each cycle, Figure 4c), respectively. In both the cases, high activity and selectivity of Pd-SAs/3DOM-CeO2 catalyst are well maintained after eight reaction cycles. XRD, XPS, and TEM characterizations (Figure 4d and Figure S13, Supporting Information) indicate that the chemical compositions and 3DOM structure of the Pd-SAs/3DOM-CeO₂ catalyst are well maintained after eight catalytic cycles, excluding the agglomeration of Pd atoms. HAADF-STEM image with the intensity profiles and CO-probing DRIFT spectrum (Figure S14, Supporting Information) further confirm that the Pd-SAs/3DOM-CeO₂ catalyst retains the feature of Pd SAs after recycling. Moreover, it has been excluded that the possibly leached Pd species in solution has acted as a homogeneous catalyst, by monitoring the coupling reaction in the filtrate (Figure S15, Supporting Information). After a reaction cycle catalyzed by Pd-SAs/3DOM-CeO2, the catalyst particles are removed from the solution by high-speed centrifugation and filtration. Then the reactants of iodobenzene, phenylboronic acid and K₂CO₃ are added into the filtrate for reaction, where no more biphenyl can be produced even after 4 h. The Pd concentration of the filtration (10 mL) is measured to be 0.626 ppb by ICP-MS, indicating that only a negligible fraction of Pd total mass (0.012%) in the catalyst has entered into the solution. The information gleaned above proves that the Pd-SAs/3DOM-CeO₂ is a highly stable catalyst and the Pd SAs are not detached from CeO₂ support or aggregate into NPs during the long-term reaction process.

To get more insights into the high activity of Pd-SAs/3DOM-CeO₂ catalyst, the reaction pathways and corresponding energy profiles of Suzuki coupling reaction occurring on the Pd-SA/CeO2 catalyst model are simulated by DFT calculations (Figure 5). Suzuki coupling reaction proceeds generally through a three-step pathway: oxidative addition (dissociative adsorption of arylhalide), transmetalation (dissociative adsorption of alkali-activated phenylboronic acid), and reductive elimination (coupling of two phenyl groups).^[3,46] As shown in Figure 5, the oxidative addition of iodobenzene to Pd SA needs to overcome an energy barrier of 1.06 eV (TS1). However, there is only a slight barrier (0.04 eV) in the transmetalation step (TS2), indicating that this step can be easily achieved on Pd SA site. As a final step, the coupling between two phenyl groups on a Pd atom is barrier-less and highly exothermic. Therefore, the rate-determining step of this pathway is the oxidative addition step with an activation barrier of 1.06 eV, which agrees well with the experimental value (0.95 eV) from the Arrhenius plots of this reaction on Pd-SAs/3DOM-CeO2 catalyst. In sharp contrast, the Pd-cluster/CeO2 catalyst model exhibits a different rate-determining step for the Suzuki reaction (Figure S16,





Figure 5. DFT calculated reaction pathway and the corresponding energy profiles of Suzuki reaction between iodobenzene and phenylboronic acid on Pd-SA/CeO₂ catalyst model. The gray, white, purple, pink, red, yellow, and blue spheres represent carbon, hydrogen, iodine, boron, oxygen, cerium, and palladium, respectively.

Supporting Information). In addition to a barrier of 1.44 eV existing in the transmetalation step for B–C dissociation, the coupling of two phenyl groups (reductive elimination step) on Pd cluster has to overcome a higher barrier of 2.26 eV. The experimental activation energies of this Suzuki reaction on Pd-SAs/3DOM-CeO₂·H₂ (1.10 eV) and Pd-NPs/3DOM-CeO₂ (1.29 eV) are much lower than the DFT calculated barrier of the rate-determining step on Pd-cluster/CeO₂ catalyst model, most likely because the actual catalysts contain some Pd SA sites that contribute to lowering the overall activation energies. Nevertheless, the DFT calculation has unambiguously indicated that the Pd-SA/CeO₂ catalyst can remarkably reduce the barriers of transmetalation and reductive elimination steps of the Suzuki reaction.

The IR spectra of phenylboronic acid adsorbed on different catalysts (Figure S17, Supporting Information) validate experimentally that the Pd-SAs/3DOM-CeO2 catalyst is more competent to activate phenylboronic acid and promote the cleavage of B-C bond, thus greatly lowering the energy barrier of transmetalation step. The B-C stretching vibration (~1050 cm⁻¹) [47,48] of phenylboronic acid adsorbed on Pd-SAs/3DOM-CeO2 shifts (10.6 cm⁻¹) more toward low frequency region than those on Pd-SAs/3DOM-CeO2-H2 (9.7 cm⁻¹) and Pd-NPs/3DOM-CeO₂ (8.7 cm⁻¹), suggesting the more activated B-C bond on Pd-SAs/3DOM-CeO₂ catalyst. As a matter of fact, the electronic states of active centers play a key role in altering their catalytic activities toward the Suzuki coupling reaction, because the catalyst is required to serve as a charge donor in the oxidative addition step and a charge acceptor in both transmetalation and reductive elimination steps of the reaction.^[49-51] The Pd SA sites in our Pd-SAs/3DOM-CeO₂ catalyst are positively charged owing to the electron transfer from Pd atoms to the neighboring CeO₂ units, which has been verified by the aforementioned experimental and theoretical results. The high-valence Pd4+ sites in Pd-SAs/3DOM-CeO₂ catalyst can serve as a strong electron



acceptor to facilitate both the electron-withdrawing steps of transmetalation and reductive elimination. Meanwhile, the 3DOM-CeO₂ support containing abundant OVs not only affords the adaptive coordination of Pd SAs, but also modifies their electronic structures. The Ce3+ species associated with OVs may donate electrons to the high-valence Pd⁴⁺ sites and thus improve the charge-donating ability of the latter for boosting the oxidative addition step to some extent. In contrast, the Pd cluster is more apt at charge donating than electron accepting, leading to the great difficulties in implementing transmetalation and reductive elimination steps. In terms of geometric effects, the two phenyl groups bonded on a single Pd atom are very close to each other, greatly facilitating the C-C coupling to produce biphenyl via the reductive elimination step. On Pd cluster, however, the two phenyl groups have to migrate to a Pd atom for C-C coupling, which further increases the energy barrier of the reductive elimination step. In brief, the Pd SAs anchored in 3DOM-CeO₂ support can act as highly active sites for the Suzuki reactions to remarkably reduce the barriers of both transmetalation and reductive elimination steps, owing to their atomically dispersive and positively charged traits. These traits can be well maintained in long-term catalytic reactions because of the strong metal-support interaction through the unique Pd-O-Ce bonds. As a result, the Pd-SAs/3DOM-CeO₂ catalyst shows excellent activity and stability.

The universal application of the Pd-SAs/3DOM-CeO₂ catalyst is demonstrated by the Suzuki coupling reactions of various substrates. This catalyst exhibits excellent activity toward a broad scope of substrates (Table 1), far outperforming the homogeneous Pd(PPh₃)₄ catalyst. Moreover, the TOF values for bromobenzene and chlorobenzene conversion under the ambient conditions are 520.01 and 163.26 h⁻¹ (Table S7, Supporting Information), respectively, which are appealing results under such mild conditions compared with the previous reports (Table S8, Supporting Information). The percent conversions of bromobenzene and chlorobenzene can also achieve the considerable levels of 76.61% and 37.62% (Table 1, entries 2-3) after 4 h under the ambient conditions. The isolation yield of the coupling reaction between bromobenzene and phenylboronic acid over Pd-SAs/3DOM-CeO₂ catalyst is analyzed as a typical example (Figure S18, Supporting Information). After a series of purification procedure, the isolation yield is obtained to be 70.69%, which is a little lower than that determined by gas chromatography (GC) analysis due to the product loss caused by the purification process. The conversion of chlorobenzene cannot be further obviously improved, until the temperature is raised to 348 K (Figure S19, Supporting Information), possibly because the coordination of Cl⁻ ions to Pd atoms leads to the poisoning of the active sites in Pd-SAs/3DOM-CeO₂ catalyst.^[52] The arylhalides with electron-donating groups (Table 1, entries 5-9 and 18) show slightly reduced conversion rates, whereas the ones with electron-withdrawing groups (Table 1, entries 4 and 17) exhibit the increased reactivities. With the same substituent groups (entries 7-9), the conversion rate of ortho-substituted arylhalide is relatively slower than those of the para- and meta- ones due to the steric effect. The types of the substituents on phenylboronic acid have no obvious effect on the conversions of arylhalides (Table 1, entries 10-12).

The Pd-SAs/3DOM-CeO2 catalyst also exhibits excellent performance toward the cross coupling reactions involving heteroaromatics, such as 4-pyridylboronic acid, 2-iodopyridine and 2-bromopyridine (Table 1, entries 13-15). As the temperature is raised a little to 303 K, the percent conversions of bromobenzene and its derivatives can rise to around 98% (Table 1, entries 16-18) after 4 h. With further elevating the temperature to 348 K, the percent conversion of chlorobenzene increases to 64.40% after 4 h (Table 1, entry 19). As increasing the substrate concentrations at the elevated temperature of 348 K, the TOF value for bromobenzene conversion can reach up to 44 527.10 h⁻¹ (Table S7 (Supporting Information), entry 20). Overall, the performance of Pd-SAs/3DOM-CeO₂ catalyst not only far exceeds that of the homogeneous Pd(PPh₃)₄ catalyst but also much superior to those of Pd-SAs/3DOM-CeO₂-H₂, Pd-NPs/3DOM-CeO2 and commercial Pd/C with 5 wt% Pd in all the listed Suzuki coupling reactions (Figures S20 and S9, Supporting Information).

3. Conclusion

In summary, the heterogeneous single-atom catalyst of Pd-SAs/3DOM-CeO2 has been synthesized successfully by a template-assisted in situ pyrolysis method. This delicate design and convenient synthesis of material perfectly take advantage of the strong interactions between Pd SAs and 3DOM-CeO2 support, enabling a set of important characteristics in the final material. The high surface area of 3DOM-CeO₂ support facilitates the anchoring of Pd SAs with a high content of 1.76 wt%, while the presence of Pd SAs induces the generation of abundant OVs and prevents the grain growth of CeO2 under the hightemperature treatment. Benefiting from the unique structural and electronic characteristics, the Pd-SAs/3DOM-CeO₂ catalyst exhibits outstanding activity and durability toward Suzuki reactions for a broad scope of substrates under ambient conditions, far outperforming the homogeneous Pd(PPh₃)₄ catalyst and the other listed heterogeneous catalysts. The TOF values for the conversions of iodo-, bromo- and chlorobenzene under the ambient conditions are 750.99, 520.01, and 163.26 h⁻¹, respectively. Elevating the temperature to 348 K, TOF of bromobenzene conversion can reach up to 44 527.10 $h^{-1}.$ Theoretical calculations have revealed that the CeO₂ supported Pd SAs can remarkably reduce the energy barrier of transmetalation and reductive elimination steps for the Suzuki reaction, showing a lower activation energy of the cross-coupling reaction. During the long-term reaction, Pd SAs can be stabilized on CeO2 by the strong Pd-O-Ce bonds, preventing the leaching or aggregation of Pd atoms. Therefore, the 3DOM CeO₂ is a desirable support to serve as the solid-state ligand to Pd SAs as well as a charge modulator for tailoring the electronic states of Pd catalytic sites. This research not only demonstrates the facile synthesis of Pd SAs catalyst with well-designed support but also offers insights into the regulation mechanism of catalytic sites achieved by the strong metal-support interactions. Such Pd SAs catalysts possess the advantages of both homogeneous and heterogeneous catalysts in organic transformations and are expected to develop a new level for green synthesis of fine chemicals in the future.





Table 1. Catalytic activities of Pd-SAs/3DOM-CeO₂ catalyst toward some typical Suzuki reactions of different substrates, with homogeneous Pd(PPh₃)₄ catalyst for comparison. Entries 1–15: aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), K₂CO₃ (1.5 mmol), catalyst (3 mg), EtOH/ H₂O (2 mL/2 mL), 298 K and air atmosphere, 4 h. Entries 16–18: the same conditions as entries 1–15 except that the temperature is 303 K. Entry 19: the same conditions as entries 1–15 except that the temperature is 348 K.

$R' \xrightarrow{\text{catalyst}} R' \xrightarrow{\text{catalyst}} R' \xrightarrow{\text{catalyst}} R'$				
Entry	Aryl halide	Phenylboronic acid	Yield (%) ^{a)}	Yield (%) ^{b)}
1		(HO)2B	91.50	2.54 (20.87 ^{c)})
2	Br	(HO) ₂ B	76.61	1.87 (12.25 ^{c)})
3		(HO) ₂ B	37.62	1.52 (3.66 ^{c)})
4		(HO) ₂ B	94.36	3.24
5	но	(HO) ₂ B	85.17	2.43
6	Haco	(HO) ₂ B	85.74	2.35
7	H ₃ C-	(HO) ₂ B	89.37	2.41
8	H ₃ C	(HO) ₂ B	85.66	2.29
9		(HO) ₂ B	82.51	2.27
10		(HO)2B	90.33	1.83
11		(HO)2B-OCH3	93.21	1.24
12		(HO)2B CH3	91.37	2.58
13		(HO) ₂ B	90.19	2.38
14		(HO) ₂ B	92.55	3.48
15	Br Br	(HO) ₂ B	89.06	2.39
16	Br	(HO) ₂ B	98.10	8.87
17	F	(HO) ₂ B	98.68	10.78
18	H ₃ CO-Br	(HO) ₂ B	96.10	7.59
19		(HO) ₂ B	64.40	14.31

 $^{a)}$ Pd-SAs/3DOM-CeO₂; $^{b)}$ Pd(PPh₃)₄; $^{c)}$ N₂ atmosphere. All the reactions are equally (100%) selective to the desired cross-coupled product.

ADVANCED SCIENCE NEWS _____

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

X.T. and R.L. contributed equally to this work. This work was financially supported by the National Natural Science Foundation of China (21471004, 61775129, 21725102, 91961106, U1832156, 21601173), the National Key R&D Program of China (2017YFA0207301), the Natural Science Foundation of Zhejiang Province of China (No. LY19B010005), the Fundamental Research Funds of Zhejiang Sci-Tech University (2020Y003) and the Fundamental Research Funds for the Central Universities (GK201902001). The authors thank the National Synchrotron Radiation Laboratory (Hefei, China) for DRIFTS measurement (BL01B), the Shanghai Synchrotron Radiation Facility (SSRF, China) for EXAFS measurement (BL14WI), Dr. Shoujie Liu from Anhui Normal University for EXAFS data processing and Dr. Zhifeng Dai from Zhejiang Sci-Tech University for offering some help in experimental operations.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

ceria, heterogeneous catalysis, ordered porous structure, oxygen vacancies, Pd single atoms

Received: March 18, 2020 Revised: July 23, 2020 Published online:

- [1] N. Miyaura, A. Suzuki, Chem. Rev. 1995, 95, 2457.
- [2] C. C. C. J. Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, Angew. Chem., Int. Ed. 2012, 51, 5062.
- [3] A. Biffis, P. Centomo, A. Del Zotto, M. Zeccal, Chem. Rev. 2018, 118, 2249.
- [4] L. A. Labios, M. D. Millard, A. L. Rheingold, J. S. Figueroa, J. Am. Chem. Soc. 2009, 131, 11318.
- [5] J. D. Zhang, A. Bellomo, N. Trongsiriwat, T. Z. Jia, P. J. Carroll, S. D. Dreher, M. T. Tudge, H. L. Yin, J. R. Robinson, E. J. Schelter, P. J. Walsh, J. Am. Chem. Soc. 2014, 136, 6276.
- [6] S. B. Zhao, T. Gensch, B. Murray, Z. L. Niemeyer, M. S. Sigman, M. R. Biscoe, *Science* **2018**, *362*, 670.
- [7] M. Arpad, Chem. Rev. 2011, 111, 2251.
- [8] Q. Fu, Y. Meng, Z. Fang, Q. Hu, L. Xu, W. Gao, X. Huang, Q. Xue, Y. P. Sun, F. Lu, ACS Appl. Mater. Interfaces 2017, 9, 2469.
- [9] S. L. Lu, Y. M. Hu, S. Wan, R. McCaffrey, Y. H. Jin, H. W. Gu, W. Zhang, J. Am. Chem. Soc. 2017, 139, 17082.
- [10] B. F. Mohazzab, B. Jaleh, Z. Issaabadi, M. Nasrollahzadeh, R. S. Varma, Green Chem. 2019, 21, 3319.
- [11] S. Mitchell, E. Vorobyeva, J. Perez-Ramirez, Angew. Chem., Int. Ed. 2018, 57, 15316.
- [12] A. Q. Wang, J. Li, T. Zhang, Nat. Rev. Chem. 2018, 2, 65.
- [13] X. J. Cui, W. Li, P. Ryabchuk, K. Junge, M. Beller, Nat. Catal. 2018, 1, 385.
- [14] Y. J. Chen, S. F. Ji, W. M. Sun, W. X. Chen, J. C. Dong, J. F. Wen, J. Zhang, Z. Li, L. R. Zheng, C. Chen, Q. Peng, D. S. Wang, Y. D. Li, *J. Am. Chem. Soc.* **2018**, 140, 7407.

- [15] P. F. Xie, T. C. Pu, A. M. Nie, S. Hwang, S. C. Purdy, W. J. Yu, D. Su, J. T. Miller, C. Wang, ACS Catal. 2018, 8, 4044.
- [16] Y. T. Qu, B. X. Chen, Z. J. Li, X. Z. Duan, L. G. Wang, Y. Lin, T. W. Yuan, F. Y. Zhou, Y. D. Hu, Z. K. Yang, C. M. Zhao, J. Wang, C. Zhao, Y. M. Hu, G. Wu, Q. H. Zhang, Q. Xu, B. Y. Liu, P. Gao, R. You, W. X. Huang, L. R. Zheng, L. Gu, Y. Wu, Y. D. Li, *J. Am. Chem. Soc.* **2019**, *141*, 4505.
- [17] X. Y. Zhang, Z. C. Sun, B. Wang, Y. Tang, L. Nguyen, Y. T. Li, F. F. Tao, J. Am. Chem. Soc. 2018, 140, 954.
- [18] Z. P. Chen, E. Vorobyeva, S. Mitchell, E. Fako, M. A. Ortuno, N. Lopez, S. M. Collins, P. A. Midgley, S. Richard, G. Vile, J. Perez-Ramirez, *Nat. Nanotechnol.* **2018**, *13*, 702.
- [19] Y. Guo, S. Mei, K. Yuan, D. J. Wang, H. C. Liu, C. H. Yan, Y. W. Zhang, ACS Catal. 2018, 8, 6203.
- [20] J. F. Zhang, C. B. Liu, B. Zhang, Small Methods 2019, 3, 1800481.
- [21] P. P. Hu, Z. W. Huang, Z. Amghouz, M. Makkee, F. Xu, F. Kapteijn, A. Dikhtiarenko, Y. X. Chen, X. Gu, X. F. Tang, *Angew. Chem., Int. Ed.* 2014, 53, 3418.
- [22] S. F. Ji, Y. J. Chen, S. Zhao, W. X. Chen, L. J. Shi, Y. Wang, J. C. Dong, Z. Li, F. W. Li, C. Chen, Q. Peng, J. Li, D. S. Wang, Y. D. Li, Angew. Chem., Int. Ed. 2019, 58, 4271.
- [23] A. Stein, B. E. Wilson, S. G. Rudisill, Chem. Soc. Rev. 2013, 42, 2763.
- [24] X. Y. Yang, L. H. Chen, Y. Li, J. C. Rooke, C. Sanchez, B. L. Su, Chem. Soc. Rev. 2017, 46, 481.
- [25] T. T. Sun, S. Zhao, W. X. Chen, D. Zhai, J. C. Dong, Y. Wang, S. L. Zhang, A. J. Han, L. Gu, R. Yu, X. D. Wen, H. L. Ren, L. B. Xu, C. Chen, Q. Peng, D. S. Wang, Y. D. Li, *Proc. Natl. Acad. Sci. USA* **2018**, *115*, 12692.
- [26] S. Q. Zhou, L. Shang, Y. X. Zhao, R. Shi, G. I. N. Waterhouse, Y. C. Huang, L. R. Zheng, T. R. Zhang, *Adv. Mater.* **2019**, *31*, 1900509.
- [27] F. Chen, T. Li, X. Pan, Y. Guo, B. Han, F. Liu, B. Qiao, A. Wang, T. Zhang, Sci. China Mater. 2020, 63, 959.
- [28] E. Vorobyeva, Z. Chen, S. Mitchell, R. K. Leary, P. Midgley, J. M. Thomas, R. Hauert, E. Fako, N. Lopez, J. Perez-Ramirez, J. Mater. Chem. A 2017, 5, 16393.
- [29] P. Y. Xin, J. Li, Y. Xiong, X. Wu, J. C. Dong, W. X. Chen, Y. Wang, L. Gu, J. Luo, H. P. Rong, C. Chen, Q. Peng, D. S. Wang, Y. D. Li, *Angew. Chem.*, Int. Ed. 2018, 57, 4642.
- [30] J. A. Farmer, C. T. Campbell, Science 2010, 329, 933.
- [31] J. Jones, H. F. Xiong, A. T. Delariva, E. J. Peterson, H. Pham, S. R. Challa, G. S. Qi, S. Oh, M. H. Wiebenga, X. I. P. Hernandez, Y. Wang, A. K. Datye, *Science* **2016**, *353*, 150.
- [32] S. W. Li, Y. Xu, Y. F. Chen, W. Z. Li, L. L. Lin, M. Z. Li, Y. C. Deng, X. P. Wang, B. H. Ge, C. Yang, S. Y. Yao, J. L. Xie, Y. W. Li, X. Liu, D. Ma, Angew. Chem., Int. Ed. 2017, 56, 10761.
- [33] N. Acerbi, S. C. E. Tsang, G. Jones, S. Golunski, P. Collier, Angew. Chem., Int. Ed. 2013, 52, 7737.
- [34] Y. X. Chen, J. X. Chen, W. Y. Qu, C. George, M. Aouine, P. Vernoux, X. F. Tang, Chem. Commun. 2018, 54, 10140.
- [35] M. Kottwitz, Y. Y. Li, R. M. Palomino, Z. Y. Liu, G. J. Wang, Q. Wu, J. H. Huang, J. Timoshenko, S. D. Senanayake, M. Balasubramanian, D. Y. Lu, R. G. Nuzzo, A. I. Frenkel, ACS Catal. 2019, 9, 8738.
- [36] H. Jeong, J. Bae, J. W. Han, H. Lee, ACS Catal. 2017, 7, 7097.
- [37] J. Lee, Y. Ryou, X. Chan, T. J. Kim, D. H. Kim, J. Phys. Chem. C 2016, 120, 25870.
- [38] J. Resasco, L. DeRita, S. Dai, J. P. Chada, M. Xu, X. Yan, J. Finzel, S. Hanukovich, A. S. Hoffman, G. W. Graham, S. R. Bare, X. Pan, P. Christopher, J. Am. Chem. Soc. 2020, 142, 169.
- [39] L. DeRita, S. Dai, K. Lopez-Zepeda, N. Pham, G. W. Graham, X. Q. Pan, P. Christopher, J. Am. Chem. Soc. 2017, 139, 14150.
- [40] H. Unterhalt, G. Rupprechter, H.-J. Freund, J. Phys. Chem. B 2002, 106, 356.
- [41] E. Ozensoy, D. Wayne Goodman, Phys. Chem. Chem. Phys. 2004, 6, 3765.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com



- [42] Y. Q. Cao, Z. J. Sui, Y. Zhu, X. G. Zhou, D. Chen, ACS Catal. 2017, 7, 7835.
- [43] J. Szanyi, J. H. Kwak, Phys. Chem. Chem. Phys. 2014, 16, 15117.
- [44] K. R. Priolkar, P. Bera, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, N. P. Lalla, *Chem. Mater.* 2002, 14, 2120.
- [45] H. L. Jia, A. X. Du, H. Zhang, J. H. Yang, R. B. Jiang, J. F. Wang, C. Y. Zhang, J. Am. Chem. Soc. 2019, 141, 5083.
- [46] A. J. J. Lennox, G. C. Lloyd-Jones, Angew. Chem., Int. Ed. 2013, 52, 7362.
- [47] E. L. Spitler, W. R. Dichtel, Nat. Chem. 2010, 2, 672.
- [48] D. W. Aubrey, M. F. Lappert, H. Pyszora, J. Chem. Soc. 1961, 1931.
- [49] M. Perez-Rodriguez, A. A. C. Braga, M. Garcia-Melchor, M. H. Perez-Temprano, J. A. Casares, G. Ujaque, A. R. de Lera, R. Alvarez, F. Maseras, P. Espinet, J. Am. Chem. Soc. 2009, 131, 3650.
- [50] Y. Yang, A. C. Reber, S. E. Gilliland, C. E. Castano, B. F. Gupton, S. N. Khanna, J. Catal. 2018, 360, 20.
- [51] Y. Yang, A. C. Reber, E. Gilliland, C. E. Castano, B. F. Gupton, S. N. Khanna, J. Phys. Chem. C 2018, 122, 25396.
- [52] N. Yuan, V. Pascanu, Z. Huang, A. Valiente, N. Heidenreich, S. Leubner, A. K. Inge, J. Gaar, N. Stock, I. Persson, B. Martín-Matute, X. Zou, J. Am. Chem. Soc. 2018, 140, 8206.