available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Communication

A palladium single-atom catalyst toward efficient activation of molecular oxygen for cinnamyl alcohol oxidation

Qinghao Shang^{a,b}, Nanfang Tang^{a,#}, Haifeng Qi^{a,b}, Shuai Chen^a, Guoliang Xu^a, Chuntian Wu^a, Xiaoli Pan^a, Xiaodong Wang^a, Yu Cong^{a,*}

^a CAS Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 27 February 2020

Accepted 31 March 2020

Published 5 December 2020

Keywords:

Single-atom catalysis

Palladium

Alcohol oxidation

Oxygen activation

Metal support interaction

ABSTRACT

Selective aerobic oxidation of alcohols under mild conditions is of great importance yet challenging, with the activation of molecular oxygen (O_2) as a crucial capability of the catalysts. Herein, we demonstrate that an Al_2O_3 -supported Pd single-atom catalyst leads to higher activity and selectivity compared to Pd nanoparticles for the oxidation of cinnamyl alcohol. The Al_2O_3 support used in this study is rich in coordinately unsaturated Al^{3+} sites, which are apt for binding to Pd atoms through oxygen bridges and present a distinct metal-support interaction (MSI). The suitable MSI then leads to a unique electronic characteristic of the Pd single atoms, which can be confirmed via X-ray photoelectron spectroscopy, normalized X-ray absorption near-edge structure, and diffuse reflectance Fourier transform infrared spectroscopy. Moreover, this unique electronic state is proposed to be responsible for its high catalytic activity. With the help of *in-situ* UV-vis spectra and electron spin resonance spectra, a specific alcohol oxidation route with O_2 activation mechanism is then identified. Active oxygen species behaving chemically like singlet- O_2 are generated from the interaction of O_2 with Pd_1/Al_2O_3 , and then oxidize the partially dehydrogenated intermediates produced by the adsorbed allylic alcohols and Pd atoms to the desired alkenyl aldehyde. This work provides a promising path for the design and development of high-activity catalysts for aerobic oxidation reactions.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

Selective aerobic oxidation of organic molecules (including alcohols, glucoses, hydrocarbons, and CO) under mild conditions is a great fundamental and practical issue in modern chemistry [1–3]. Because the ground state of molecular oxygen (O_2) is a triplet state, reactions between organic molecules (mainly in a singlet state) and ground-state O_2 to produce new singlet compounds are generally forbidden by the Wigners spin selection rules [4,5]. Therefore, efficiently activating O_2 under

mild reaction conditions is considered as a critical step and the greatest challenge.

In principle, organometallic catalysts, like metal alkoxides, show significant advantages in the oxidation of alcohols, owing to their defined coordination geometry, uniform active metal center, and ligands. However, their application is largely limited by their poor separation and recovery performance [6]. Since Zhang *et al.* [7] reported a Pt single-atom catalyst (SAC)

* Corresponding author. Tel: +86-411-84379676; Fax: +86-411-84685940; E-mail: ycong@dicp.ac.cn

Corresponding author. E-mail: nftang@dicp.ac.cn

This work was supported by National Natural Science Foundation of China (21802134) and National Science and Technology Major Project of China (2017-III-0005-0030).

DOI: 10.1016/S1872-2067(20)63651-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 12, December 2020

exhibiting extremely high activity for CO oxidation and proposed the concept of SACs in 2011, atomically dispersed catalysts have attracted enormous attention in the catalysis field [7–11]. Because individual metal atoms in SACs are usually stabilized by covalent coordination or ionic interactions with neighboring surface atoms like homogeneous catalysts, single-atom catalysis has been regarded as a bridge to connect homogeneous and heterogeneous catalysis [12–14]. For these reasons, currently, it has become highly desirable to develop heterogeneous SACs with reactivity and atom efficiency equivalent to those of homogeneous catalysts.

An increasing number of researchers have been studying SACs in oxidation reactions with O₂ as the oxidant. Li *et al.* [15] reported that ceria-supported Au and Pt SACs showed high activity and selectivity for benzyl alcohol oxidation owing to the restricted geometries of the active sites, which was because the lattice oxygen activated at the interfacial sites exhibited higher selectivity than the O₂ activated on the metal surfaces. Hackett *et al.* [16] reported that atomically dispersed Pd demonstrated exceptional conversion in the aerobic selective oxidation (SELOX) of allylic alcohols, and the highest activity or the maximum turnover frequency (TOF) value could be achieved on the Pd SACs according to their correlation of activity with Pd size. Although some promising results have been obtained on atomically dispersed catalysts, the activation mechanism of O₂ and the reaction route of SELOX of allylic alcohols are still ambiguous.

In this work, atomic and nano-dispersed Pd catalysts (labeled as Pd₁/Al₂O₃ and Pd/Al₂O₃) were facilely prepared with the same loading amount (0.5 wt%) of Pd anchored onto an Al₂O₃ support rich in penta-coordinate Al³⁺ (Al³⁺_{penta}) centers. The Pd₁/Al₂O₃ catalyst displayed extremely high activity for the aerobic oxidation of cinnamyl alcohol with a conversion of 92% at 80 °C after an 8-h reaction. Its TOF was 15.5 fold of that over nano Pd/Al₂O₃ and superior or comparable to other reported catalysts with similar metal loading under the same reaction

conditions. The specific O₂ activation mechanism and the alcohol oxidation route were also proposed.

The morphologies of the two catalysts were determined with aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and extended X-ray absorption fine structure (EXAFS) spectrometry. In the HAADF-STEM images in Figs. 1(a) and (b), Pd₁/Al₂O₃ clearly displays bright dots of single atoms marked with red circles. No nano Pd particles were observed in Fig. S1, and its X-ray diffraction (XRD) pattern in Fig. S2 only showed typical peaks of Al₂O₃ (JCPDS No. 10-0425). By comparison, Pd/Al₂O₃ shows nanoparticles with sizes of 3–7 nm, marked by yellow boxes in Figs. 1(c) and (d), and no Pd single atoms were observed in Fig. S3, in consistent with its XRD pattern (Fig. S2) in which a small peak of Pd (JCPDS No. 46-1043) arose. The detailed structure properties of all the samples are listed in Table S1.

In the case of EXAFS spectra, only one notable peak at 1.58 Å attributed to Pd–O coordination [17,18] was detected in Pd₁/Al₂O₃, as presented in Fig. 2, whereas no appreciable Pd–Pd coordination peak was identified, again verifying the existence of Pd single atoms. For Pd/Al₂O₃, only one main peak at 2.55 Å was detected, which was corresponding to the coordination of Pd–Pd, whereas no peak related to Pd–O bonds was measured. These results indicated the characteristics of the two catalysts, i.e., they are either entirely isolated Pd single atoms or completely Pd nanoparticles, with the same Pd loading amount on the Al₂O₃ support.

Cinnamyl alcohol was then chosen to evaluate the aerobic SELOX performance of the two catalysts. Pd₁/Al₂O₃ demonstrated extremely high activity relative to Pd/Al₂O₃. Approximately 92% conversion of cinnamyl alcohol was obtained on Pd₁/Al₂O₃ at 80 °C under 1 atm after an 8-h reaction (Fig. 3(a)), together with excellent selectivity of 91% to cinnamaldehyde. In comparison on Pd/Al₂O₃, only 29% conversion with 89% selectivity was achieved under the same reaction conditions. Lowering the Pd loading to 0.05% in weight, for which the atomically dispersed HAADF-STEM images are shown in Fig. S4, also obtained a higher cinnamyl alcohol conversion of 44% (Table S2), better than that of the nano Pd/Al₂O₃ catalyst with

Fig. 1. HAADF-STEM images of Pd₁/Al₂O₃ (a, b) and Pd/Al₂O₃ (c, d).

Fig. 2. FT-EXAFS spectra of Pd₁/Al₂O₃, Pd/Al₂O₃, and bulk palladium foil at the Pd K-edge.

Fig. 3. (a) Conversion of alcohol oxidation with different catalysts (solid line, cinnamyl alcohol; dashed line, benzyl alcohol); (b) TOF values of different catalysts in cinnamyl alcohol oxidation; (c) Conversion and selectivity for cinnamyl alcohol oxidation over the Pd₁/Al₂O₃ catalyst in the recycling tests. Reaction conditions: Catalyst 40 mg, alcohol (1 mmol) in 10 mL toluene, 80 °C, and oxidant O₂ (1 atm).

0.5 wt% loading. For the low conversion below 30%, the TOF value of Pd₁/Al₂O₃ was calculated as 775 h⁻¹ (Fig. 3(b)), which was 15.5 times higher than that of Pd/Al₂O₃ (50 h⁻¹). This performance is superior to many other catalysts with similar metal loadings reported in the literature (Table S3). High activity in SELOX of another primary alcohol, *i.e.*, benzyl alcohol, was also achieved on Pd₁/Al₂O₃, as displayed in Fig. 3(a). The apparent barrier energy (E_{app}) of Pd₁/Al₂O₃ derived from the Arrhenius plot (Fig. S5) was fairly low (34.1 ± 5.7 kJ mol⁻¹) compared to those of Pd/Al₂O₃ and similar catalysts [16,19], which reflects its high activity from another aspect. We further tested the reusability of the Pd₁/Al₂O₃ sample and observed no significant changes in either the conversion or the selectivity over five cycles (Fig. 3(c)).

To elaborate the high catalytic performance of the Pd₁/Al₂O₃ SAC, the electronic states of the Pd species were examined in detail with X-ray photoelectron spectroscopy (XPS), normalized X-ray absorption near-edge structure (XANES), and diffuse reflectance Fourier transform infrared spectroscopy (CO-DRIFT). As shown in the Pd 3d XPS spectra in Fig. 4(a), the peaks at 336.7 and 336.9 eV of the unreduced Pd/Al₂O₃ and Pd₁/Al₂O₃ could be ascribed to Pd⁰ [20–22]. After reduction at 400 °C, the Pd 3d_{5/2} peak of Pd/Al₂O₃ shifted to a lower binding

energy (BE) of 335.0 eV, which is awarded to the Pd⁰ species. In comparison, Pd₁/Al₂O₃ shifted the Pd 3d_{5/2} peak to 336.6 eV, corresponding to a partially reduced Pd^{δ+} state [21]. The normalized XANES spectra shown in Fig. 4(b) could confirm the above analysis. The white-line intensity of the Pd species of Pd₁/Al₂O₃ was much higher than those of Pd/Al₂O₃ and Pd foil, indicating that the Pd species were positively charged. The CO adsorption behavior could further attest to this. As illustrated by the CO-DRIFT in Fig. 4(c), two CO stretching vibration bands were observed at 1987 and 2079 cm⁻¹ on Pd/Al₂O₃. The former is attributed to bridge-adsorbed CO on the step sites of the Pd⁰ nanoparticles, and the latter is assigned to the linear-adsorbed CO on the Pd⁰ (111) facets [23–25]. For Pd₁/Al₂O₃, only one adsorption band at 2073 cm⁻¹ was observed, ascribed to the CO adsorbed on the Pd^{δ+} atoms in a top configuration [26,27]. In correlation with the catalytic performance, the partially reduced Pd atoms could be proposed as active sites for Pd₁/Al₂O₃, well consistent with previous reports [28,29]. On the other hand, one may notice that the peak position of the linear CO on Pd₁/Al₂O₃ was slightly red-shifted in comparison to that on Pd/Al₂O₃. This suggested that the electrons of Pd may easily transfer from the atomically dispersed samples.

Based on the above, the Pd₁/Al₂O₃ SAC possesses a unique

Fig. 4. (a) Pd 3d XPS spectra of Pd₁/Al₂O₃ and Pd/Al₂O₃ with and without reduction; (b) Normalized XANES spectra at the Pd K-edge with Pd foil as reference; (c) CO-DRIFT spectra of Pd₁/Al₂O₃ and Pd/Al₂O₃.

Fig. 5. ^{27}Al MAS NMR spectra (solid line) and their deconvolution results (short dot) of $\text{Pd}_1/\text{Al}_2\text{O}_3$, $\text{Pd}/\text{Al}_2\text{O}_3$, and Al_2O_3 .

electronic state. It has been reported that the interaction between the metal and support affects the physiochemical property and catalytic performance of a catalyst severely [30–32]. Herein, the different preparation methods may result in different metal–support interactions (MSIs) between Pd and Al_2O_3 , thereby leading to a distinct electronic state of the Pd species. To testify this, ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy was employed. Three characteristic peaks centered at 5, 35, and 65 (δ) were observed for all the samples (Fig. 5), which are attributed to Al^{3+} cations in octahedral ($\text{Al}^{3+}_{\text{octa}}$), pentahedral ($\text{Al}^{3+}_{\text{penta}}$), and tetrahedral ($\text{Al}^{3+}_{\text{tetra}}$) coordination, respectively [33]. Among them, the $\text{Al}^{3+}_{\text{penta}}$ sites are coordinately unsaturated, apt for binding to metal atoms through oxygen bridges; thus, the intensity change of $\text{Al}^{3+}_{\text{penta}}$ could reflect the interaction between Pd and Al_2O_3 . As shown in the spectra, $\text{Pd}_1/\text{Al}_2\text{O}_3$ presented a substantial drop in the $\text{Al}^{3+}_{\text{penta}}$ intensity compared to pure Al_2O_3 , indicating that strong interactions occurred between $\text{Al}^{3+}_{\text{penta}}$ and Pd atoms during calcination and reduction. In comparison for $\text{Pd}/\text{Al}_2\text{O}_3$, the number of $\text{Al}^{3+}_{\text{penta}}$ sites remained almost un-

changed under the same treatment, revealing a weak MSI. This is probably the consequence of the physical barrier of the inverse nano micelles-encapsulated Pd precursors, which are formed by surfactant P123 during the nucleation and calcination process. In addition, a strong MSI could also explain the higher BE of Pd $3d_{5/2}$ in the unreduced $\text{Pd}_1/\text{Al}_2\text{O}_3$ (336.9 eV) than that in $\text{Pd}/\text{Al}_2\text{O}_3$ (336.7 eV), as the PdO species in $\text{Pd}_1/\text{Al}_2\text{O}_3$ are mostly located on the $\text{Al}^{3+}_{\text{penta}}$ sites.

It is well known that O_2 activation is extremely critical to oxidation reactions. According to the Wigners spin selection rule, high-energy oxygen species (*e.g.*, O_2^- , $\cdot\text{OH}$, and $^1\text{O}_2$) activated from ground-state O_2 are highly desirable for the oxidation reaction. To decode the detailed activation process and reaction mechanism, *in-situ* UV-vis spectra were collected in this study. As presented in Fig. 6(a), the cinnamyl alcohol showed an absorption peak at 281.8 nm and a shoulder peak at 293.0 nm with or without $\text{Pd}/\text{Al}_2\text{O}_3$, assigned to the π – π^* transition of the conjugated bonds between the benzene ring and C=C. Contrastingly, a remarkable red shift from 281.8 to 284.2 nm occurred on contact with $\text{Pd}_1/\text{Al}_2\text{O}_3$, owing to the effective expansion of the π -conjugation induced by the charge or energy transfer between the adsorbed cinnamyl alcohol and Pd single atoms on $\text{Pd}_1/\text{Al}_2\text{O}_3$ [34]. This indicates that cinnamyl alcohol molecules adsorb over the single-atom Pd sites and form partially dehydrogenated intermediates. To detect the activated state of O_2 , 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TMP) was used as a probe molecule for electron spin resonance (ESR) examination in view of its preferable ability to trap singlet oxygen species ($^1\text{O}_2$) [35]. As shown in Fig. 6(b), no ESR signals were perceived for the Al_2O_3 support, whereas triplet ESR signals were observed for $\text{Pd}_1/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{Al}_2\text{O}_3$, suggesting that an active oxygen species behaving chemically like singlet- O_2 was formed during the O_2 activation process. Compared to $\text{Pd}/\text{Al}_2\text{O}_3$, $\text{Pd}_1/\text{Al}_2\text{O}_3$ showed an enhanced signal of the singlet O_2 species, presenting a stronger ability for O_2 activation. In addition, 5, 5-dimethyl-1-pyrroline *N*-oxide (DMPO) was employed as a probing molecule to further identify other oxygen species. No DMPO/ $\cdot\text{OH}$ (1:2:2:1 quartet signal) or DMPO/ O_2^- (1:1:1:1:1:1 6-line signal) signal was detected [4,36], suggesting that no superoxide (O_2^-) and hydroxyl radicals ($\cdot\text{OH}$) species are produced in these systems (Fig. S6).

Fig. 6. (a) UV-vis spectra of cinnamyl alcohol in toluene with and without the catalysts; (b) ESR spectra of samples formed by mixing a solution of 4-oxo-TMP with the catalysts at 60 °C.

Based on the above results, a stepwise reaction process was proposed for aerobic SELOX of allylic alcohols over the Pd₁/Al₂O₃ catalyst. First, partial dehydrogenation occurs through a charge transfer between the adsorbed allylic alcohols and the Pd atoms. Concurrently, active oxygen species behaving chemically like singlet-O₂ are generated on the interaction of O₂ with Pd₁/Al₂O₃. Then, the active oxygen species oxidize the partially dehydrogenated intermediates to the desired alkenyl aldehyde.

In summary, atomic and nano-dispersed catalysts are prepared with the same Pd loading on an Al₂O₃ support. Because of the different strengths of the MSI, the single-atom Pd₁/Al₂O₃ catalyst exhibits much higher catalytic activity than the nano Pd/Al₂O₃ catalyst for the aerobic SELOX of allylic alcohols under mild conditions. The partially positive electronic properties of the single-atom Pd sites are expected to lead to the more efficient activation of allylic alcohols and O₂. This work offers a promising path for the design and development of highly active catalysts for aerobic oxidation reactions.

Acknowledgments

We are grateful to the BL 14W beamline at the Shanghai Synchrotron Radiation Facility (SSRF).

References

- [1] R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, **1981**.
- [2] F. Su, Y. Liu, L. Wang, Y. Cao, H. He, K. Fan, *Angew. Chem. Int. Ed.*, **2008**, 47, 334–337.
- [3] S. S. Stahl, *Angew. Chem. Int. Ed.*, **2004**, 43, 3400–3420.
- [4] R. Long, H. Huang, Y. Li, L. Song, Y. Xiong, *Adv. Mater.*, **2015**, 27, 7025–7042.
- [5] D. Kovalev, M. Fujii, *Adv. Mater.*, **2005**, 17, 2531–2544.
- [6] R. A. Sheldon, I. W. C. E. Arends, G. J. Ten Brink, A. Dijkstra, *Acc. Chem. Res.*, **2002**, 35, 774–781.
- [7] B. T. Qiao, A. Q. Wang, X. F. Yang, L. F. Allard, Z. Jiang, Y. T. Cui, J. Y. Liu, J. Li, T. Zhang, *Nat. Chem.*, **2011**, 3, 634–641.
- [8] P. X. Liu, Y. Zhao, R. X. Qin, S. G. Mo, G. X. Chen, L. Gu, D. M. Chevrier, P. Zhang, Q. Guo, D. D. Zang, B. H. Wu, G. Fu, N. F. Zheng, *Science*, **2016**, 352, 797–801.
- [9] L. Nie, D. Mei, H. Xiong, B. Peng, Z. Ken, X. I. P. Hernandez, A. De-Lariva, M. Wang, M. H. Engelhard, L. Kovarik, A. K. Datye, Y. Wang, *Science*, **2017**, 358, 1419–1423.
- [10] 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, 4642–4646.
- [11] B. Han, R. Lang, B. Qiao, A. Wang, T. Zhang, *Chin. J. Catal.*, **2017**, 38, 1498–1507.
- [12] X. F. Yang, A. Q. Wang, B. T. Qiao, J. Li, J. Y. Liu, T. Zhang, *Acc. Chem. Res.*, **2013**, 46, 1740–1748.
- [13] X. J. Cui, W. Li, P. Ryabchuk, K. Junge, M. Beller, *Nat. Catal.*, **2018**, 1, 385–397.
- [14] F. Chen, X. Jiang, L. Zhang, R. Lang, B. Qiao, *Chin. J. Catal.*, **2018**, 39, 893–898.
- [15] T. Li, F. Liu, Y. Tang, L. Li, S. Miao, Y. Su, J. Zhang, J. Huang, H. Sun, M. Haruta, A. Wang, B. Qiao, J. Li, T. Zhang, *Angew. Chem. Int. Ed.*, **2018**, 57, 7795–7799.
- [16] S. E. J. Hackett, R. M. Brydson, M. H. Gass, I. Harvey, A. D. Newman, K. Wilson, A. F. Lee, *Angew. Chem. Int. Ed.*, **2007**, 46, 8593–8596.
- [17] T. Ishida, T. Honma, K. Nakada, H. Murayama, T. Mamba, K. Kume, Y. Izawa, M. Utsunomiya, M. Tokunaga, *J. Catal.*, **2019**, 374, 320–327.
- [18] T. T. Chao, X. Luo, W. X. Chen, B. Jiang, J. J. Ge, Y. Lin, G. Wu, X. Q. Wang, Y. M. Hu, Z. B. Zhuang, Y. E. Wu, X. Hong, Y. D. Li, *Angew. Chem. Int. Ed.*, **2017**, 56, 16047–16051.
- [19] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science*, **2006**, 311, 362–365.
- [20] J. F. Moulder, J. Chastain, *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification, Interpretation of XPS Data*, Physical Electronics Division, Perkin-Elmer Corporation, **1992**.
- [21] D. S. Mannel, J. King, Y. Preger, M. S. Ahmed, T. W. Root, S. S. Stahl, *ACS Catal.*, **2018**, 8, 1038–1047.
- [22] P. Mäki Arvela, A. V. Tokarev, E. V. Murzina, B. Campo, T. Heikkilä, J. M. Brozinski, D. Wolf, D. Y. Murzin, *Phys. Chem. Chem. Phys.*, **2011**, 13, 9268–9280.

Graphical Abstract

Chin. J. Catal., 2020, 41: 1812–1817 doi: 10.1016/S1872-2067(20)63651-8

A palladium single-atom catalyst toward efficient activation of molecular oxygen for cinnamyl alcohol oxidation

Qinghao Shang, Nanfang Tang*, Haifeng Qi, Shuai Chen, Guoliang Xu, Chuntian Wu, Xiaoli Pan, Xiaodong Wang, Yu Cong*
Dalian Institute of Chemical Physics, Chinese Academy of Sciences;
University of Chinese Academy of Sciences

Allylic alcohols were adsorbed on Pd atoms and produced partially dehydrogenated intermediates, whereas active oxygen species behaving chemically like singlet-O₂ were generated on the interaction of O₂ with Pd₁/Al₂O₃. Then the two active species reacted and formed the desired alkenyl aldehyde.

- [23] K. Murata, Y. Mahara, J. Ohyama, Y. Yamamoto, S. Arai, A. Satsuma, *Angew. Chem., Int. Ed.*, **2017**, 56, 15993–15997.
- [24] L. Ding, H. Yi, W. Zhang, R. You, T. Cao, J. Yang, J. Lu, W. Huang, *ACS Catal.*, **2016**, 6, 3700–3707.
- [25] M. Peter, J. M. Flores Camacho, S. Adamovski, L. K. Ono, K. H. Dostert, C. P. O'Brien, B. Roldan Cuenya, S. Schauermaier, H. J. Freund, *Angew. Chem., Int. Ed.*, **2013**, 52, 5175–5179.
- [26] P. Liu, Y. Zhao, R. Qin, S. Mo, G. Chen, L. Gu, D. M. Chevrier, P. Zhang, Q. Guo, D. Zang, B. Wu, G. Fu, N. Zheng, *Science*, **2016**, 352, 797–801.
- [27] V. V. Kaichev, I. P. Prosvirnin, V. I. Bukhtiyarov, H. Unterhalt, G. Rupprechter, H. J. Freund, *J. Phys. Chem. B*, **2003**, 107, 3522–3527.
- [28] J. D. Grunwaldt, M. Caravati, M. Ramin, A. Baiker, *Catal. Lett.*, **2003**, 90, 221–229.
- [29] T. Mallat, A. Baiker, *Chem. Rev.*, **2004**, 104, 3037–3058.
- [30] H. L. Tang, F. Liu, J. K. Wei, B. T. Qiao, K. F. Zhao, Y. Su, C. Z. Jin, L. Li, J. Y. Liu, J. H. Wang, T. Zhang, *Angew. Chem. Int. Ed.*, **2016**, 55, 10606–10611.
- [31] V. Ramalingam, P. Varadhan, H. C. Fu, H. Kim, D. L. Zhang, S. M. Chen, L. Song, D. Ma, Y. Wang, H. N. Alshareef, J. H. He, *Adv. Mater.*, **2019**, 31, 1903841.
- [32] J. J. Li, Q. Q. Guan, H. Wu, W. Liu, Y. Lin, Z. H. Sun, X. X. Ye, X. S. Zheng, H. B. Pan, J. F. Zhu, S. Chen, W. H. Zhang, S. Q. Wei, J. L. Lu, *J. Am. Chem. Soc.*, **2019**, 141, 14515–14519.
- [33] N. Tang, Y. Cong, Q. Shang, C. Wu, G. Xu, X. Wang, *ACS Catal.*, **2017**, 7, 5987–5991.
- [34] N. Tang, Y. Zhang, F. Lin, H. Lu, Z. Jiang, C. Li, *Chem. Commun.*, **2012**, 48, 11647–11649.
- [35] R. Long, K. Mao, M. Gong, S. Zhou, J. Hu, M. Zhi, Y. You, S. Bai, J. Jiang, Q. Zhang, X. Wu, Y. Xiong, *Angew. Chem. Int. Ed.*, **2014**, 53, 3205–3209.
- [36] N. Tang, Z. Jiang, C. Li, *Green Chem.*, **2015**, 17, 817–820.

单原子Pd催化剂活化分子氧用于肉桂醇氧化

商庆浩^{a,b}, 唐南方^{a,#}, 齐海峰^{a,b}, 陈 帅^a, 许国梁^a, 吴春田^a, 潘晓丽^a, 王晓东^a, 丛 昱^{a,*}

^a中国科学院大连化学物理研究所中国科学院航天催化材料重点实验室, 辽宁大连116023

^b中国科学院大学, 北京100049

摘要: 在温和条件下借助分子氧实现有机分子(包括醇类、糖类、碳氢化合物、CO等)的选择性氧化是现代化学中重要的研究课题。其中, 在温和条件下高效的活化氧气一直被视为分子氧氧化反应的关键步骤和巨大挑战。一般而言, 得益于适宜的配位结构、均一的活性金属中心和配体, 有机金属催化剂在醇氧化反应中一直有着广泛的应用, 但同时存在着难以分离和回收的问题。而与均相催化剂一样有着高原子利用率的单原子催化剂自其概念报道以来, 在催化领域吸引了越来越多的注意力。愈来愈多的研究者也开始涉足研究单原子催化剂在分子氧氧化反应中的应用。尽管已经取得一些不错的结果, 但分子氧的活化机制以及催化反应路径仍然有很多疑问有待揭示。

本文在富含不饱和五配位铝的氧化铝载体上分别负载了单原子分散和纳米颗粒的Pd, 制备了相同负载量的Pd/Al₂O₃催化剂。其中单原子Pd₁/Al₂O₃催化剂表现出非常好的肉桂醇氧化活性, 在80 °C反应8 h能达到92%肉桂醇转化率, 其TOF值是纳米颗粒Pd/Al₂O₃催化剂的15.5倍, 与类似反应条件下的其他文献报道的数值相当。我们还通过一系列表征提出了反应过程中具体的O₂的活化机理和进一步的整体反应路径。

XPS, XANES, CO-DRIFT等结果表明, Pd/Al₂O₃和Pd₁/Al₂O₃催化剂中Pd的价态迥然不同, 结合二者催化活性的显著差异, 我们推断部分还原的Pd^{δ+}正价态物种才是Pd₁/Al₂O₃催化剂中真正的活性中心。进一步结合²⁷Al NMR的表征结果发现, Pd₁/Al₂O₃催化剂中的Pd与富含不饱和五配位铝(Al³⁺_{penta})的Al₂O₃之间形成强相互作用, 从而导致其以单原子形式分散并具有独特的电子性质。为了揭示本工作中所涉及的具体的活化过程和反应机理, 我们进行了原位紫外光谱和电子顺磁共振光谱表征, 发现肉桂醇分子吸附到单原子Pd上后, 生成了部分脱氢的中间产物, 同时分子氧在单原子Pd上活化, 形成了单线态氧活性物种(¹O₂)。

综合以上结果, 我们推导出一个在Pd₁/Al₂O₃上进行的活化分子氧进行肉桂醇选择性氧化的分步反应路径。首先, 肉桂醇分子吸附到单原子Pd上, 发生电荷转移生成部分脱氢的中间产物, 同时, 分子氧也在Pd上活化, 生成单线态氧物种¹O₂, 然后和肉桂醇中间产物反应, 生成目标产物肉桂醛。

关键词: 单原子催化; 钯; 醇氧化; 氧气活化; 金属载体相互作用

收稿日期: 2020-02-27. 接受日期: 2020-03-31. 出版日期: 2020-12-05.

*通讯联系人. 电话: (0411)84379676; 传真: (0411)84685940; 电子信箱: ycong@dicp.ac.cn

#通讯联系人. 电子信箱: nftang@dicp.ac.cn

基金来源: 国家自然科学基金(21802134); 国家科技重大专项(2017-III-0005-0030).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).