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Highlight

Single Co atom catalyst stabilized in C/N containing matrix

Can Li *

Single-atom-catalyst (SAC), which was defined as the active metal site in a catalyst exist as isolated single atoms stabilized by a support or in an alloy by the second coordinate round atoms, is emerging as a new class of heterogeneous catalysts [1,2]. Compared with nano- and subnano-catalysts, SACs could achieve the atom utilization efficiency up to 100%, offer the opportunities for achieving high activity/selectivity in reactions, and bridge the gap between homogeneous and heterogeneous catalysts. Therefore, SACs may provide a good platform to understand the structure-reactivity relationship at atomic scale.

The highly dispersed metal catalysts (extremely up to 100%) have been a long standing interest in heterogeneous catalysis field. In 2011, Zhang and co-workers reported the first Pt_1/FeO_x catalyst with single Pt atom dispersion [2]. The catalysts were prepared by a co-precipitation method and demonstrated the catalytic activity in CO oxidation and selective preferential oxidation (PROX) reaction with a turnover frequency (TOF) of 3-fold higher than the nano-counterpart. In the following years, they developed different noble metal SACs, such as Ir/FeO_x [3], Pd/ZnO [4], Au/CeO_2 [5] and $\text{Ag-Pd}/\text{SiO}_2$ [6]. These catalysts showed high activity in water-gas-shift reaction and high selectivity in hydrogenation reactions of acetylene and functionalized nitroarenes [7]. In particular for the chemoselective hydrogenation of functionalized nitroarenes, the Pt_1/FeO_x SAC afforded a TOF of $\sim 1500 \text{ h}^{-1}$, 20-fold higher than the best result reported in Ref. [8], and a selectivity to 3-aminostyrene close to 99%, the best ever achieved over platinum group metals. Motivated by these work, some other researchers also made progress [9–13]. However, owing to the high surface energy of single atoms, the ever prepared SACs only have low metal loading ($< 0.5 \text{ wt\%}$), and moreover, the transition metal SACs, have rarely been developed.

Recently, this group has made further progress in preparing transition metal single-atom catalyst, Co-N-C, with relatively high metal loading [14]. The Co(Fe)-N-C catalysts have been widely investigated and demonstrated excellent catalytic performance in electro-chemical reactions, such as oxygen reduction reaction (ORR), hydrogen evolution reaction (HER) as well as CO_2 reduction reaction, and have been regarded as one of the most promising substitutes of Pt/C [15–18]. Despite intensive

research, great debate still exists on the exact structure of the active sites because of the heterogeneity in composition. Usually, this type of catalysts are prepared by pyrolysis of a specific precursor containing Co(Fe), N, and C elements supported on activated carbon at high temperatures ($600\text{--}900^\circ\text{C}$), which often leads to complex species, such as the mixture of Co(0) , CoO_x and CoN_x with size of tens of nanometers, as well as the Co (Fe) single atoms only visible under atomic-resolution scanning electron microscope (STEM). Zhang and his colleagues employed Mg(OH)_2 instead of carbon as the sacrificial support and prepared the single-atom Co-N-C catalyst where cobalt exists exclusively as single atoms (Fig. 1(a)). By using a combination of subångström-resolution high angle annular dark field (HAADF)-STEM, X-ray absorption fine structure, and density functional theory calculations, the exact structure of the Co-N-C catalyst was identified as $\text{CoN}_4\text{C}_8\text{-1-2O}_2$, where Co center atom is coordinated with four pyridinic N atoms in the graphitic layer while two oxygen molecules are weakly adsorbed on Co atoms in perpendicular to the Co-N_4 plane (Fig. 1(b)). Different from the noble metal SACs reported earlier, the Co loadings in the Co-N-C SAC could be as high as 3.6 wt%.

Notably, the Co-N-C SAC exhibited catalytic activity and selectivity comparable to noble metal catalysts in the chemoselective hydrogenation of functionalized nitroarenes to produce azo compounds. By using Co-N-C SACs as the catalysts, direct synthesis of azo compounds from nitroarenes through the green hydrogenation strategy could be achieved under mild conditions. The catalyst was also effective for a broad scope of substrates with different functional groups, such as $-\text{C}=\text{C}$, $-\text{I}$, $-\text{Br}$, etc.

It is of particular merit that the unrivalled uniformity of Co species in the atomically dispersed Co-N-C catalyst provides a good entry to the identification of active sites without much ambiguity. In this respect, revisiting other earlier reported Co-N-C catalysts containing mixed Co species will be helpful to elucidating the nature of genuine active sites [19–21].

The Co complex as a molecular catalyst has been widely used in homogeneous catalysis. However, in this work, Co site is fixed in a C, N containing matrix which is analogous to the molecular catalyst in nature, while a truly heterogeneous catalyst with highly dispersed single atom site. Here it could be

Fig. 1. (a) HAADF-STEM images of Co-N-C catalyst. The white dots are Co single atoms. (b) Comparison between the K-edge XANES experimental spectrum of Co-N-C (solid red line) and the theoretical spectrum (black dotted line) calculated with the inset structure.

anticipated that, in more general way, many other transition metal complex could be also possibly transformed into solid catalysts with single active sites following the strategy reported in this work.

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Received 1 August 2016
Accepted 4 August 2016
Published 5 September 2016
DOI: 10.1016/S1872-2067(16)62520-2

References

- [1] X. F. Yang, A. Q. Wang, B. T. Qiao, J. Li, J. Y. Liu, T. Zhang, *Acc. Chem. Res.*, **2013**, 46, 1740–1748.
- [2] 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.
- [3] J. Lin, A. Q. Wang, B. T. Qiao, X. Y. Liu, X. F. Yang, X. D. Wang, J. X. Liang, J. Li, J. Y. Liu, T. Zhang, *J. Am. Chem. Soc.*, **2013**, 135, 15314–15317.
- [4] H. R. Zhou, X. F. Yang, L. Li, X. Y. Liu, Y. Q. Huang, X. L. Pan, A. Q. Wang, J. Li, T. Zhang, *ACS Catal.*, **2016**, 6, 1054–1061.
- [5] B. T. Qiao, J. Liu, Y. G. Wang, Q. Q. Lin, X. Y. Liu, A. Q. Wang, J. Li, T. Zhang, J. Liu, *ACS Catal.*, **2015**, 5, 6249–6254.
- [6] G. X. Pei, X. Y. Liu, A. Q. Wang, A. F. Lee, M. A. Isaacs, L. Li, X. L. Pan, X. F. Yang, X. D. Wang, Z. J. Tai, K. Wilson, T. Zhang, *ACS Catal.*, **2015**, 5, 3717–3725.
- [7] H. S. Wei, X. Y. Liu, A. Q. Wang, L. L. Zhang, B. T. Qiao, X. F. Yang, Y. Q. Huang, S. Miao, J. Y. Liu, T. Zhang, *Nat. Commun.*, **2014**, 5, 5634.
- [8] P. Serna, P. Concepción, A. Corma, *J. Catal.*, **2009**, 265, 19–25.
- [9] 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.
- [10] 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. Pereira Hernandez, Y. Wang, A. K. Datye, **2016**, *Science*, 353, 150–154.
- [11] X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng, M. Wei, D. Tan, R. Si, S. Zhang, J. Li, L. Sun, Z. Tang, X. Pan, X. Bao, *Science*, **2014**, 344, 616–619.
- [12] G. Kyriakou, M. B. Boucher, A. D. Jewell, E. A. Lewis, T. J. Lawton, A. E. Baber, H. L. Tierney, M. Flytzani-Stephanopoulos, E. C. H. Sykes, *Science*, **2012**, 335, 1209–1212.
- [13] J. D. Kistler, N. Chotigkrai, P. Xu, B. Enderle, P. Praserthdam, C. Y. Chen, N. D. Browning, B. C. Gates, *Angew. Chem. Int. Ed.*, **2014**, 53, 8904–8907.
- [14] W. Liu, L. Zhang, W. Yan, X. Liu, X. Yang, S. Miao, W. Wang, A. Wang, T. Zhang, *Chem. Sci.*, **2016**, 7, 5758–5764.
- [15] M. Lefevre, E. Proietti, F. Jaouen, J. P. Dodelet, *Science*, **2009**, 324, 71–74.
- [16] G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science*, **2011**, 332,

Graphical Abstract

Chin. J. Catal., 2016, 37: 1443–1445 doi: 10.1016/S1872-2067(16)62520-2

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The single-atom Co-N-C catalyst recently published on *Chemical Sciences* (**2016**, 7, 5758–5764) has been highlighted in terms of correlation between homogeneous and heterogeneous catalysis.

- 443–447.
- [17] R. Bashyam, P. Zelenay, *Nature*, **2006**, 443, 63–66.
- [18] A. Zitolo, V. Goellner, V. Armel, M. T. Sougrati, T. Mineva, L. Stievano, E. Fonda, F. Jaouen, *Nat. Mater.*, **2015**, 14, 937–942.
- [19] F. A. Westerhaus, R. V. Jagadeesh, G. Wienhofer, M. M. Pohl, J. Radnik, A. E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Bruckner, M. Beller, *Nat. Chem.*, **2013**, 5, 537–543.
- [20] H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang, Y. Wang, *J. Am. Chem. Soc.*, **2015**, 137, 2688–2694.
- [21] D. Singh, I. I. Soykal, J. Tian, D. von Deak, J. King, J. T. Miller, U. S. Ozkan, *J. Catal.*, **2013**, 304, 100–111.

N/C稳定的单原子Co催化剂

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单原子催化剂(SAC)是多相催化领域一个新兴的研究热点,是指催化剂中活性组分完全以孤立的单个原子的形式存在,并通过与载体作用或与第二种金属形成合金得以稳定。相比于纳米/亚纳米催化剂,单原子催化剂具有诸多优势:(1)活性组分达到最大程度分散(100%),可有效提高金属(特别是贵金属)原子利用率;(2)活性位点的组成和结构单一,可避免因活性组分组成和结构不均匀导致的副反应,从而显著提高目标产物的选择性;(3)单原子催化剂兼具高活性、高选择性和可循环使用的优点,有望成为连接均相催化与非均相催化的桥梁。因此,单原子催化剂为在原子尺度上理解催化机理和构效关系提供了一个很好的平台。

2011年,中国科学院大连化学物理研究所张涛院士团队首次合成了单原子铂催化剂Pt₁/FeO_x。该催化剂通过共沉淀法制备,在CO氧化以及PROX反应中展示出优异的催化性能,其TOF值为相应的纳米催化剂3倍之高。在此基础上,该团队随后发展了一系列贵金属单原子催化剂,例如Ir/FeO_x, Pd/ZnO, Au/CeO₂和Ag-Pd/SiO₂。这些催化剂在水气变换反应、乙炔选择性加氢反应、芳香硝基化合物选择加氢等反应中表现出了优异的催化活性及选择性。尤其是在3-硝基苯乙烯选择性加氢反应中,单原子催化剂Pt₁/FeO_x的TOF值高达1500 h⁻¹,是文献报道最优催化剂的20倍;产物3-氨基苯乙烯的选择性高达99%。在单原子催化剂概念提出的短短几年,它已经成为目前多相催化领域的研究热点,并且发展出许多新的单原子催化剂制备方法。然而,由于单个原子具有较高的表面能,因此目前制备的单原子催化剂负载量往往较低(<0.5 wt%)。另一方面,目前单原子催化剂的研究对象主要为贵金属,而非贵金属单原子催化剂却鲜有报道。

近日,张涛团队在非贵金属单原子催化剂领域取得新的进展。他们成功制备出了负载量高达3.6 wt%的Co-N-C单原子催化剂,并结合密度泛函理论(DFT)和X-射线吸收精细结构(XAFS)技术首次解析出Co-N-C催化位点的精确结构。Co(Fe)-N-C是一类在电催化领域受到广泛关注的材料,在氧还原反应,析氢反应以及CO₂电还原反应中均有良好的催化性能,被认为是一种最有希望取代商业Pt/C电极的非贵金属催化剂。然而,由于其组成较为复杂,人们对其活性中心的认识存在诸多争议。Co(Fe)-N-C催化剂通常采用高温焙烧法制备,即将金属前驱体,含N,C配体以及碳载体在600–900 °C高温下焙烧,这往往导致催化剂中同时含有不同尺寸的Co(0), CoO_x以及CoN_x,也含有常规表征手段难以发现的Co(Fe)单原子。张涛团队利用Mg(OH)₂作为牺牲载体,制备出了完全单原子分散的Co-N-C催化剂(图1(a))。作者通过原子分辨的高角环形暗场-扫描透射电镜(HAADF-STEM), XAFS和DFT计算,首次证明Co-N-C催化活性中心的结构为CoN₄C₈-1-2O₂。在这种模型中,Co中心在径向方向与4个N配位,轴向有2个弱吸附的氧气分子吸附在Co原子上(图1(b))。与之前报道的贵金属催化剂显著不同的是,在Co-N-C单原子催化剂中,Co含量高达3.6%。

值得称道的是,这种Co-N-C单原子催化剂在芳香硝基化合物选择加氢制备偶氮化合物的反应中的催化活性和选择性可媲美贵金属催化剂。使用Co-N-C催化剂,在温和条件下即可实现从芳香硝基化合物一锅法绿色合成偶氮化合物,并且该催化剂具有优异的底物普适性,即使底物含有–C=C, –I, –Br等基团时,也可高效生成相应的偶氮苯。

这项工作的另外一个意义在于获得了非常均一的Co-N-C活性位组成和结构,这为利用多种表征手段精确解析结构提供了一个很好的切入点。某种意义上讲,之前文献中报道的含有多种Co物种的Co-N-C催化剂,其活性中心的认定需要重新审视。

事实上,Co的配合物作为分子催化剂已经广泛应用于均相催化中;而这项工作中的Co单原子通过与N,C配位而稳定,活性中心类似于均相催化剂中的Co配合物,但却形成了真正的多相催化剂。因此我们可以预测,许多过渡金属均相催化剂有可能通过该工作中的单原子制备策略转化为多相催化剂,从而使单原子催化剂真正成为均相催化和多相催化的桥梁。

关键词: 单原子催化; Co-N-C; 结构鉴定; 活性位点; 选择加氢

收稿日期: 2016-08-01. 接受日期: 2016-08-04. 出版日期: 2016-09-05.

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