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Highlight

Selective oxidation of C–H bonds with Fe–N–C single-atom catalyst

Xingwei Li *

Activation of C–H bonds has received considerable attention in the past decade as this provides an efficient and atom-economy strategy to access a plethora of value-added chemicals from easily available substrates [1]. Nevertheless, the high stability of C–H bonds poses significant challenge for selective functionalization. For instance, the selective oxidation of C–H bonds in hydrocarbons has proved to be high useful in synthesis of alcohol/ketone feedstocks in both areas of C1 chemistry [2] and organic synthesis [3,4]. However, given the generally high dissociation energy of C–H bonds and possible over-oxidation, it remains challenging to realize both high reactivity and selectivity.

Recently, a team led by Profs. Tao Zhang and Aiqin Wang at the Dalian Institute of Chemical Physics (DICP) has reported an interesting work on the selective oxidation of C–H bonds in aromatic and aliphatic hydrocarbons [5]. The reactions proceeded at room temperature, by using an excess or a stoichiometric amount of *tert*-butyl hydroperoxide (TBHP) as an oxidant and an atomically dispersed (single-atom catalyst) Fe–N–C as the catalyst. As given in Table 1, a wide scope of substrates, such as various aromatic hydrocarbons with an electron-donating group (–OMe) or electron-withdrawing group (–NO₂), heterocyclic substrates and an aliphatic hydrocarbon (cyclohexane) could be smoothly transformed into the corresponding ketones with >98% selectivity at high conversions. In fact, the performance of the heterogeneous Fe–N–C catalyst is well comparable to some homogeneous catalysts such as [Cu((R,R)-BPBP)]⁺ complex [6] in terms of both activity and selectivity, but it offers additional advantages such as excellent reusability and water solvent-compatibility.

A more attractive feature of this work lies in the establishment of structure-performance relationship, which is a long-standing interest in the area of heterogeneous catalysis. The authors made in-depth characterizations of the catalyst using a variety of advanced techniques including aberration-corrected HAADF-STEM, XPS, XAS, ESR, and Mössbauer spectroscopy. Thus, the coordination sphere of the Fe atom (which is actually Fe³⁺) included only nitrogen atoms so as to form Fe–N_x (*x* = 4, 5, and 6) moieties. Significantly, the catalytic activity is closely correlated to the specific structure of the

Fe–N_x. As shown in Fig. 1, the most reactive moiety for the selective C–H oxidation is ascribed to the medium-spin Fe^{III}–N₅ structure, which is at least 1 order of magnitude more reactive than the high-spin and low-spin Fe^{III}–N₆ structures and 3 times more reactive than the Fe^{II}–N₄ structure. The identification of

Table 1

Selective oxidation of hydrocarbons in water with Fe–N–C-700 as catalyst.

Entry	Substrate	Product	Conv. (%)	Selec. (%)
1			99	99
2			99	99
3			95	98
4			79	94
5			99	80
6			98	99
7			99	99
8			85	99
9			62	99 (a/ b = 1: 2.6)

Reaction conditions: 10.0 mg of catalyst, 0.5 mmol of substrates, room temperature for 7 h, 500 μ L of TBHP as a 70 wt % aqueous solution (7 equiv) diluted with 6.5 mL of H₂O.

Fig. 1. Schematic diagram of Fe-N-C single-atom catalyst for C-H bond selective oxidation.

the Fe-N₅ active site will serve to provide guidelines to design more active catalysts in this system by maximizing the number of the Fe-N₅ moiety since it only accounts for 18% of the total Fe species in this work.

The Fe-N_x-C catalyst in this work can be viewed as a single-atom catalyst (SAC) if the surrounding N_x atoms are considered as a robust multidentate ligand. Single-atom catalysis has recently become a very hot topic since it bodes well to maximize the metal utilization efficiency, offer unique selectivity, and bridge the heterogeneous and homogeneous catalysis due to the uniform active sites [7–10]. In this work, the Fe-N₅ active site is reminiscent of the structure of a hemoglobin molecule [11] which is responsible for the adsorption and activation of oxygen in living cells (Fig. 1). In this context, the Fe-N₅ structure provides a good example to bridge mononuclear enzyme catalyst and heterogeneous single-atom catalyst. However, a tiny change in the micro-environmental surrounding may greatly affect the reactivity and selectivity, as exemplified by the poor capability of the heterogeneous Fe-N₅ sites for activa-

tion of molecular oxygen. It is believed that this work will open a door of ample space for the design of robust heterogeneous single-atom catalysts to mimic the high activity and selectivity of enzymes as well as molecular catalysts.

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Received 25 December 2017

Accepted 27 December 2017

Published 5 January 2018

DOI: 10.1016/S1872-2067(17)63002-X

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Graphical Abstract

Chin. J. Catal., 2018, 39: 1–3 doi: 10.1016/S1872-2067(17)63002-X

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Fe-N-C single-atom catalyst with Fe-N₅ active sites can efficiently boost the selective oxidation of C–H bonds in hydrocarbons under room temperature.

Fe-N-C单原子催化剂的C-H键选择性氧化反应

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摘要: C-H键活化是近年来发展最为迅速的研究领域之一, 从自然界中广泛存在C-H键的简单底物为原料, 利用C-H键直接活化策略来构建高附加值的化学品是一类具有高原子经济性的化学反应. 然而, 由于C-H键的稳定性使得C-H键的选择性官能团化过程具有极大的挑战. 例如, 烃类化合物的C-H选择性氧化生成醇/酮化合物在C1化学以及有机合成反应中占据重要地位, 同时C-H键的高解离能以及氧化试剂的高活性往往使得这类反应的选择性难以调控.

近日, 中科院大连化学物理研究所张涛和王爱琴领导的团队在脂肪族、芳香族烃类化合物的C-H选择性氧化反应中取得新的研究进展. 作者使用Fe-N-C单原子催化剂, 化学计量的叔丁基过氧化氢为氧化剂, 在室温条件下实现了烃类化合物的选择性氧化反应, 一系列底物包括带有吸电子基团的硝基(-NO₂)、供电子基团的甲氧基(-OCH₃)、杂环化合物以及脂肪族化合物(环己烷)均可以高选择性(>98%)实现转化. 事实上, Fe-N-C单原子催化剂的活性与选择性可与均相催化剂([Cu((R,R)-BPBP)]⁺)相媲美, 同时该催化剂在绿色水溶剂中表现出优异的循环稳定性.

这项工作的另一个意义在于建立起多相催化领域中活性位点与反应性能之间的构效关系. 通过HAADF-STEM, XPS, XAS, ESR及穆斯堡尔谱等表征手段, 清楚地证明Fe-N-C催化剂中三价铁离子存在多种配位结构(FeN_x, $x = 4, 5, 6$), 催化活性与Fe-N_x的特定结构密切相关. C-H键选择性氧化反应的最高活性位点为中自旋FeN₅位点, 其活性高出低自旋/高自旋的FeN₆位点一个数量级, 是FeN₄位点活性的3倍之多. 而该FeN₅结构的数量在Fe-N-C-700的单原子催化剂上仅占18%, 说明Fe-N-C催化剂的活性具有很大的提升空间.

文中报道的 Fe-N_x-C 催化剂可被认为是一类新型的单原子催化剂, 其中, N_x 基团为一种强有力的配体. 由于单原子催化剂兼具均相催化剂孤立均一的活性位点及多相催化剂易于循环使用的优势, 单原子催化剂有望成为连接均相催化与非均相催化的桥梁. 目前, 单原子催化剂已成为多相催化领域一个新的研究热点与前沿. 这篇工作中的 FeN₅ 位点与血红蛋白的 Fe 中心结构类似, 从这个角度出发, FeN₅ 位点为连接酶催化剂与多相单原子催化剂提供了一个很好的案例. 然而, FeN₅ 位点周围环境的细微变化都会直接影响其反应活性以及选择性, 从而导致多相催化中的 FeN₅ 具有较差的 O₂ 活化能力. 因此, 设计更为高效的多相单原子催化剂, 实现类似于酶催化中高效高选择性地活化底物分子, 仍然具有很大的挑战与空间.

关键词: 单原子催化剂; C-H 键活化; 活性位点; 构效关系; Fe-N-C

收稿日期: 2017-12-25. 接受日期: 2017-12-27. 出版日期: 2018-01-05.

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