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# Highlights of the major progress in single-atom catalysis in 2015 and 2016

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ABSTRACT

The idea that single metal atoms dispersed on a solid support can act as an efficient heterogeneous catalyst was raised in 2011 when single Pt atoms on an $FeO_x$ surface were reported to be active for CO oxidation and preferential oxidation of CO in $H_2$. The last six years have witnessed tremendous progress in the field of single-atom catalysis. Here we introduce the major achievements on this topic in 2015 and 2016. Some particular aspects of single-atom catalysis are discussed in depth, including new approaches in single-atom catalyst (SAC) synthesis, stable gold SACs for various reactions, the high selectivity of Pt and Pd SACs in hydrogenation, and the superior performance of non-noble metal SACs in electrochemistry. These accomplishments will encourage more efforts by researchers to achieve the controllable fabrication of SACs and explore their potential applications.

## 1. Introduction

Supported metal catalysts consisting of metals dispersed on high-surface-area materials are an important type of heterogeneous catalyst. Supported metal catalysts have been widely used in many industrial processes such as fine chemical production, the petrochemical industry, and automobile emission control [1]. To use metals more effectively in catalysis, they are usually finely divided into nanoparticles (NPs) with dimensions of 1–20 nm. However, even at these dimensions, the catalytic efficiency of metals is still quite low because only the surface atoms on the NPs are used to catalyze reactions. To further improve catalytic efficiency, supported catalysts with atomic dispersion are highly desired to maximize atom efficiency. However, such catalysts are extremely difficult to make.

Since the start of this century, a few studies have suggested that non-metallic metal species/cations are the real active sites, or at least much more active than their NP counterparts, in several reactions including the water–gas shift (WGS) reaction [2], selective hydrogenation [3], and selective oxidation [4]. These studies shed new light on catalysis using isolated metal atoms. However, no attempt to fabricate supported catalysts consisting of only atomically dispersed isolated atoms on a support was reported until several years ago when an iron oxide-supported Pt single-atom catalyst (SAC) [5] was developed based on the concept of "single-atom catalysis" [5,6]. This development initiated interest in the topic of single-atom catalysis, which has drawn increasing attention ever since and progressed rapidly during the last few years [7–11]. In particular, novel SACs have been developed and new applications have

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been explored in the last two years. For example, several Au SACs have been intentionally developed. Several new methods to prepare SACs with high metal loading have also been devised. In addition, more and more non-noble metal SACs are being developed and the applications of SACs are being extended to many other reactions such as fine chemical synthesis and electrocatalysis. Here we summarize the major advances in this field that occurred in 2015 and 2016 with the aim of illustrating the scientific importance and practical usage of SACs. First, we introduce some novel synthetic methods developed recently to prepare SACs. Second, the remarkable performance of Au SACs in various reactions is described. Third, the superior selectivity of single-atom Pt and Pd catalysts in hydrogenation of C–C bonds is discussed. Finally, electrochemical and photochemical conversion using SACs is considered.

## 2. Novel synthetic approaches to obtain SACs

The rational fabrication of SACs is not an easy task, because dispersed metal atoms with high surface free energy are usually unstable and tend to assemble to form larger aggregates during the synthesis and/or subsequent treatment processes. At present, most SACs prepared by wet chemistry methods that can be routinely performed in most laboratories have a very low level of metal loading to avoid aggregation. Recently, some new reliable methods to synthesize SACs with high loading have been developed.

### *2.1. Atomic layer deposition*

The atomic layer deposition (ALD) method was developed to fabricate metal oxide thin films with atomically precise control [12], and was adapted to fabricate a stable Pt SAC in 2013 [13]. ALD could be a powerful method to synthesize uniformly dispersed SACs for fundamental studies, although a few disadvantages such as limited scalability, low growth rate, and high precursor cost may make it, at least in its present format, less practical in a commercial scale [10,14–16].

In the past two years, a few supported Pd SACs prepared by ALD have shown good catalytic performance [17,18]. Lu's group [17] used the ALD technique to disperse Pd on a graphene support. Their $Pd_1$/graphene SACs catalyzed hydrogenation of 1,3-butadiene to butenes with about 100% butene selectivity at 95% conversion under mild reaction conditions. The authors suggested that the excellent selectivity was caused by the change of 1,3-butadiene adsorption mode and a favorable steric effect on the isolated Pd atoms (Fig. 1). Moreover, the $Pd_1$/graphene SAC showed high durability, resisting deactivation via metal atom aggregation or carbonaceous deposit formation during 100 h of stream reaction.

Piernavieja-Hermida et al. [18] prepared a Pd SAC by a two-step ALD process. First, a Pd precursor was adsorbed on an $Al_2O_3$ substrate. Aggregation of Pd atoms was avoided because of the presence of the large hexafluoroacetylacetonate (hfac) ligand. In the second step, $TiO_2$ was selectively grown on the $Al_2O_3$ substrate but not on $Pd(hfac)_2$, thus forming $TiO_2$ nanocavities around the $Pd(hfac)_2$ complex. After the ligands were removed, $TiO_2$ nanocavity-protected $Pd_1$ sites were formed. This Pd SAC displayed promising activity in the methanol decomposition reaction, but aggregated upon calcination or reduction at low temperature (200–300 °C). In addition, a good balance of the reaction activity and stability was needed. When the surface Pd sites were covered by more $TiO_2$ deposition cycles, the sintering of Pd atoms during heating treatment was hindered, but in the same time a lower activity was achieved.

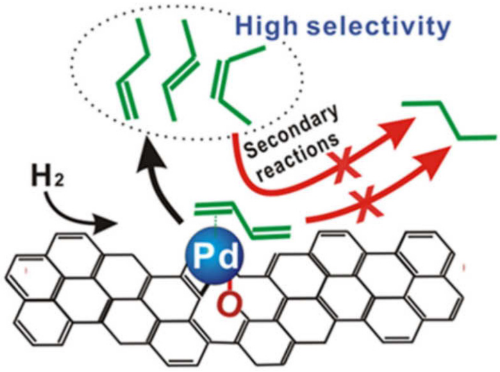

**Fig. 1.** Adsorption modes of $Pd_1$/graphene-catalyzed hydrogenative conversion of 1,3-butadiene to butenes. Reprinted with permission from Ref. [17]. Copyright 2015, American Chemical Society.

### *2.2. High-temperature vapor transport*

Datye et al. [19] reported an unexpected high-temperature vapor transport method to prepare Pt SACs by physically mixing Pt/La-$Al_2O_3$ catalyst with ceria powder under oxidizing conditions at high temperature. At 800 °C in flowing air, Pt molecules are emitted as mobile $PtO_2$ and can be trapped on a ceria surface to form stable $Pt_1/CeO_2$ SACs. Three kinds of ceria with different surface facets were investigated; ceria cubes could only slow the sintering process of Pt, while ceria rods and polyhedral ceria could effectively trap Pt species (Fig. 2). These catalysts exhibited good performance in the oxidation of CO to

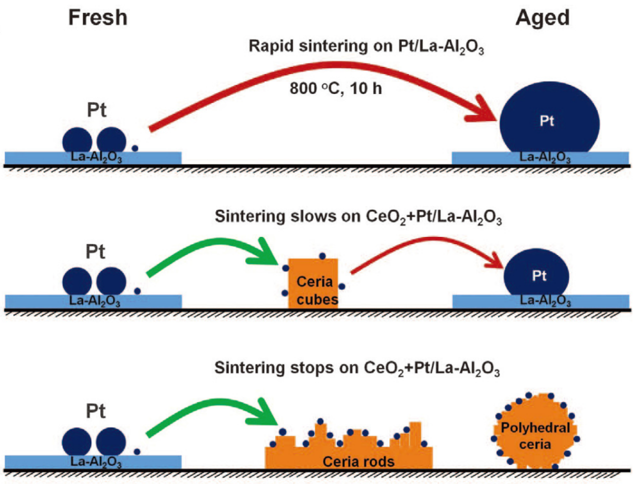

**Fig. 2.** Illustration of the sintering process of Pt nanoparticles under different conditions. Reprinted with permission from Ref. [19]. Copyright 2016, Science.