The rise of Single-Atom Catalysts

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Abstract

In recent years, single-atom catalysts attracted lots of attention because of their high catalytic activity, selectivity, stability, maximum atom utilization, exceptional performance, and low cost. Single-atom catalyst contains isolated individual atom which are coordinated with the surface atoms of support such as a metal oxide or 2d-materials. In this review article, we present the advancement in single-atom catalysis in recent years with a focus on the various synthesis methods and their application in catalytic reactions. We also demonstrate the reaction mechanism of a single-atom catalyst for different catalytic reactions from theoretical aspects using density functional theory.

Introduction

In today’s modern society, catalysts are widely used in the industrial sectors such as petroleum refining, fuel cells, chemical intermediates, pharmaceuticals, reduction of emission, and agro-chemicals to increase the reaction rate of the desired chemical reaction\textsuperscript{1–7}. The conventional supported heterogeneous catalysts contain clusters or nanoparticles dispersed on the surfaces of appropriate support (i.e., metal oxides, 2d-materials, or porous metal-organic frameworks nanomaterials). The atom utilization and selectivity of conventional heterogeneous catalysts are very less, as only a part with a suitable size of clusters or nanoparticles participates in the catalytic reaction. Moreover, the remaining portion of clusters or nanoparticles does not participate in the catalytic reaction, and it is not useful, may be involved in unwanted reactions. The heterogeneous catalysts involved in petroleum refining, new energy application, emission reduction, and pharmaceuticals contain noble metal atoms like Pt, Pd, Ru, Rh, Ir, Ag, and Au. These noble metals are costly and low abundant in nature because of that these catalyst does not meet the current increasing demand of industries, resulting minimization of the use of such catalyst alter the catalytic activity of chemical reaction\textsuperscript{8,9}. To overcome
these issues, researchers have found the most promising way to increase the atom utilization and selectivity of catalysts by reducing the size of nanoclusters to isolated individual atoms, resulting in a catalyst containing a single atom on the surface of a support.

Single-atom catalysts (SACs) is a new class of catalyst which contain isolated individual isolated atom dispersed or coordinated with the surface atom of support. It exhibits high catalytic activity, stability, selectivity, and 100 % atom utilization because the whole surface area of a single atom is exposed to reactants in catalytic reactions\(^\text{10}\). In 2011, Zhang and co-workers\(^\text{16}\) were the first to synthesized and investigate experimentally and theoretically the catalytic activity, selectivity and stability of single-atom Pt\(_1/\text{FeO}_x\) catalyst for CO oxidation. After that, It has attracted a lot of researchers, and numerous SACs have been synthesized and developed in recent years. By combing different noble atoms with different supports such as metal oxides, 2d-materials, or porous metal-organic frameworks (MOFs) nanomaterials. The SACs fabricated on different supports such as on metal oxides, 2d-materials, MOFs are [Pt\(_1/\text{FeO}_x\)\(^\text{16}\), Rh/\(\text{ZrO}_2\)\(^\text{17}\), Pt/\(\theta-\text{Al}_2\text{O}_3\)\(^\text{18}\), Ir\(_1/\text{FeO}_x\)\(^\text{19}\), Au\(_1/\text{CeO}_2\)\(^\text{20}\), Au\(_1/\text{Co}_3\text{O}_4\)\(^\text{21}\), Au\(_1/\text{FeO}_x\)\(^\text{22}\), Pd/\(\text{FeO}_x\)\(^\text{23}\), Pd\(_1/\text{TiO}_2\)\(^\text{24}\)], [Pt/\(g-\text{C}_3\text{N}_4\)\(^\text{25}\), Pt/\(\text{MoS}_2\)\(^\text{26}\), Pt/GNS\(^\text{27}\), Pd\(_1/\text{graphene}\)\(^\text{28}\)], [Co-SAs/N-C\(^\text{29}\), Fe-SAs/N-C\(^\text{30}\), Ni-SAs/N-C\(^\text{31}\), and Ru-SAs/N-C\(^\text{32}\)], respectively. It has emerged as a new frontier in catalysis science because of its excellent performance.

In recent years, many researchers have reported that SACs shows excellent performance in various catalytic reactions, such as CO oxidation\(^\text{16,18,22,33–36}\), water–gas shift (WGS)\(^\text{19,37–42}\), water splitting, hydrogenation reaction, carbon dioxide reduction, etc. Despite the excellent performance of SACs, it has some limitations and disadvantages. The stabilization of single atoms on the surfaces of support is a very challenging process due to the agglomeration of single-atoms. It needs advanced techniques for synthesis, which we have discussed in the next section.

Remainder of the paper is organized as follows. In the next section II, we briefly discuss the advanced synthesis methods of SACs, while in section III, we describe the application of
SACs for different chemical reactions and their reaction mechanism from theoretical aspects. Finally in section IV, we summarize our review article.

**Synthesis of Single Atom Catalysis**

In this section, we present the various synthesis methods for the fabrication of single-atom catalysts. The stabilization of single atom on the surfaces of metal oxide or two-dimensional materials is a very challenging process due to the agglomeration of single-atoms and the tendency to form nanoparticles and clusters on the surfaces. The agglomeration of single atoms happens because the surface energy of nanoparticles and clusters is less than single-atom. So, advanced synthesis methods such as impregnation method, co-precipitation method, other-wet-chemical synthesis method, atomic layer deposition method, and metal-organic frameworks derived method are used for fabrication single-atom catalysts, are discussed below.

**Impregnation Method**

For the synthesis of the single-atom or supported catalyst impregnation method is the simplest and economical method. In this method, a small amount of solution containing active metal precursor is mixed with catalyst support, and using the ion-exchange and adsorption process active metals stabilized on the surface of support. Li et al. synthesized Pt/g-C$_3$N$_4$ (see Fig. 1A) by performing liquid phase reaction between graphitic carbon nitride (g-C$_3$N$_4$) and H$_2$PtCl$_6$, followed by annealing at low temperature, and this catalyst exhibit high activity for H$_2$ evolution. They prepared four samples of supported catalyst with different weight percentage (i.e. 0.075%, 0.11%, 0.16%, 0.38%) of metal loading, and found that at 0.16 wt% a bright spot center of Pt atoms are distributed on the surface on the surface of g-C$_3$N$_4$, can be seen in HAAD-STEM images. When the weight percentage is increased, up to 0.38% aggregation of small Pt atoms is observed on the surface. Yang et al. prepared Pt/TiN
catalyst (see Fig. 1 B) using wetness impregnation method, in which a small amount (0.35 wt%) of Pt atoms is loaded on the surface of acid-treated TiN support, and this catalyst is found to be active for oxygen reduction reactions, formic acid, and methanol oxidation.

Figure 1: The figure represents the HAADF-STEM images of different single atom catalysts synthesized using impregnation method: (a) Pt/g-C$_3$N$_4$, (b) Pt/TiN, (c) Pt/LSC, (d) Pt/θ−Al$_2$O$_3$. (a) reprinted/reproduce from Ref. [25] with the permission of Wiley-VCH publishing group, copyright 2016, (b) reprinted/reproduce from Ref. [43] with the permission of Wiley-VCH publishing group, copyright 2016, (c) reprinted/reproduce from Ref. [44] with the permission of Nature publishing group, copyright 2016, (d) reprinted/reproduce from Ref. [18] with the permission of American Chemical society publishing group, copyright 2013.

Yang et al. observed the formation of Pt nanoparticles on the surface of support if the weight percentage is increased above 0.35%. Recently, Choi et al. synthesized highly loaded (5 wt%) Pt/S-ZTC catalyst (see Fig. 1 C) using wet-impregnation method, in which Pt atom is atomically dispersed on the surface of sulfur-doped zeolite-templated carbon (S-ZTC). The doped sulfur and unique three-dimensional structure of ZTC stabilize the loaded Pt atoms on the support surface. They have reported Pt/S-ZTC exhibit high activity for
oxygen reduction reaction. Kwon et al.\textsuperscript{17} have studied the activation of methane for methanol production using Rh/ZrO\textsubscript{2} SACs, which were prepared by wet impregnation method.

Moses-DeBusk et al.\textsuperscript{18} have studied the CO oxidation activity of a single Pt atom supported on \(\theta\)-alumina (\(\theta\)-Al\textsubscript{2}O\textsubscript{3}). They have synthesized Pt/\(\theta\)-Al\textsubscript{2}O\textsubscript{3} SAC (see Fig. 1 D) by mixing alumina in an aqueous solution of chloroplatinic acid, heated at mild temperature for 30 hours, and placed on a rotovap for water evaporation. Resulting free flow powder is kept in an alumina crucible, and pyrolysis is done with elevated temperature 1 \(\text{deg}^\circ\text{C/min}\) to 450 \(^\circ\text{C}\) for 4 hours for obtaining Pt/\(\theta\)-Al\textsubscript{2}O\textsubscript{3} SAC. The HAADF-STEM images of single atoms catalysts Pt/g-C\textsubscript{3}N\textsubscript{4}\textsuperscript{22}, Pt/TiN\textsuperscript{43}, Pt/LSC\textsuperscript{44} and Pt/\(\theta\)-Al\textsubscript{2}O\textsubscript{3}\textsuperscript{18} with 0.16 wt\%, 0.35 wt\%, 5wt\% and 0.18 wt\%, respectively, are presented in Fig. 1.

It is challenging to produce uniformly distributed and highly loaded SACs with this method because it depends on the ability of support to adsorb the metal atoms, i.e., the loading and distribution depends on the number of anchoring sites present on the surface of support.

**Co-precipitation Method**

Co-precipitation is a convenient, cost-effective, and less time-consuming method for the synthesis of nanoparticles. This method is slightly different from the impregnation method; here, metals atom are incorporated in the interstitial sites of support, not distributed on the surface of the support. In this method, anionic and cationic solution are mixed and simultaneously nucleation, growth, coarsening, and/or agglomeration processes starts. After agglomeration, we have to followed three more steps, i.e., precipitation, filtration, and calcination, and finally, nanoparticle is obtained. Recently, Zhang’s research group have reported that they were the first one to fabricate SAC containing isolated Pt atoms uniformly dispersed on the iron oxides (FeO\textsubscript{x}) support using the co-precipitation method\textsuperscript{45,46}. Two samples of Pt\textsubscript{1}/FeO\textsubscript{x} (see Fig. 2 A) were prepared, with 0.17 wt\% and 2.5 wt\%, using an aqueous solution of chloroplatinic acid (H\textsubscript{2}PtCl\textsubscript{6},6H\textsubscript{2}O) and ferric nitrate Fe(NO\textsubscript{3})\textsubscript{3},9H\textsubscript{2}O
with precipitation agent sodium carbonate (Na$_2$CO$_3$) at 50 °C, and the PH value is maintained around 8. The resulting sample was dried at 60 °C for five hours and calcined at 400 °C for five hours. Furthermore, samples were reduced at 200 °C for half an hour with 10% H$_2$/He flow rate. They also reported that at low Pt loading 0.17 wt%, uniformly dispersed isolated Pt atom on the FeO$_x$ support can be seen HAADF images, whereas, at 2.5 wt%, mixture of Pt atoms, 2D structure of Pt atoms and cluster of Pt atoms is observed. This SAC shows excellent activity and stability for CO oxidation and NO reduction.

![Figure 2: The figure represents the HAADF-STEM images of different single atom catalyst synthesized using co-precipitation method: (a) Pt$_1$/FeO$_x$, (b) Ir$_1$/FeO$_x$, (c) Au$_1$/CeO$_2$, (d) Au$_1$/FeO$_x$. (a) reprinted/reproduce from Ref. [16] with the permission of Nature publishing group, copyright 2011, (b) reprinted/reproduce from Ref. [19] with the permission of American Chemical society publishing group, copyright 2013, (c) reprinted/reproduce from Ref. [20] with the permission of American Chemical society publishing group, copyright 2015, (d) reprinted/reproduce from Ref. [22] with the permission of Tsinghua university press and Springer publishing group, copyright 2015.](image)

In addition to that Zhang and co-workers, using co-precipitation method, have synthesized series of SACs such as Ir$_1$/FeO$_x$ (see Fig. 2 B), Au$_1$/CeO$_2$ (see Fig. 2 C),
Au/CoO<sub>3</sub><sup>21</sup>, Au/FeO<sub>x</sub><sup>22</sup> (see Fig. 2 D), and Pd/FeO<sub>x</sub><sup>22</sup>, which exhibits excellent activity and stability for water-gas shift reactions and CO oxidation.

Xing et al. have prepared single atom photo-catalyst containing isolated metal atoms (Pt, Pd, Ru and Rh) uniformly dispersed on titanium oxide (TiO<sub>2</sub>) support using co-precipitation method and studied their activity and stability for water-splitting reaction. They have synthesized 4 samples for Pt/TiO<sub>2</sub> with different metal loading percentage 0.2 wt%, 0.5 wt%, 2wt% and 1Pt/TiO<sub>2</sub>(PD) (pure photo deposited 1 wt% of Pt nanoparticles), and found that H<sub>2</sub> evolution rate for 0.2-Pt/TiO<sub>2</sub> is 169.6 µmol/h, which is 23, 57, and 136 times more than 1Pt/TiO<sub>2</sub>(PD), 0.5-Pt/TiO<sub>2</sub> and 2-Pt/TiO<sub>2</sub>, respectively. The H<sub>2</sub> evolution rate for Pd, Ru, and Rh nanoparticles supported on TiO<sub>2</sub> is 7, 7 and 13 times less than 0.2-Pt/TiO<sub>2</sub>, respectively. The HAADF-STEM images of single atoms catalysts Pt<sub>1</sub>/FeO<sub>x</sub><sup>16</sup>, Ir<sub>1</sub>/FeO<sub>x</sub><sup>19</sup>, Au<sub>1</sub>/CeO<sub>2</sub><sup>20</sup>, and Au<sub>1</sub>/FeO<sub>x</sub><sup>22</sup> with 0.17 wt%, 0.01 wt%, 0.05 wt% and 0.03 wt%, respectively, are presented in Fig. 2.

The advantages to this method are; it is a simple, rapid, easy to control the particle size and composition of the final product, energy-efficient and does not need organic solvent. Moreover, disadvantages of this method are; it does not apply to uncharged species, trace of impurities also get precipitated, reproducibility problem and does not work well if the reactants have very different precipitation rate.

Other Wet-Chemical Synthesis Method

Impregnation and Co-precipitation are the traditional wet-chemical synthesis method, but Liu et al. have used unique wet-chemical synthesis methods for the fabrication of single atom Pd<sub>1</sub>/TiO<sub>2</sub> catalyst (see Fig. 3 A) with a high metal loading up to 1.5 wt%. They dispersed a solution of H<sub>2</sub>PdCl<sub>4</sub> on the surface of TiO<sub>2</sub> support, the resulting mixture is exposed to UV rays for 10 min. After that, the irradiated sample is washed with water, and a single atom Pd<sub>1</sub>/TiO<sub>2</sub> catalyst is obtained. Form transmission electron microscopy (TEM) images and extended x-ray absorption fine structure (EXAFS) spectra, it is concluded that
the formation of Pd clusters or nanoparticles are not observed. This catalyst exhibits very high catalytic activity and stability for the hydrogenation of C=C and C=O.

Recently, Li et al. synthesized single atom Pt/MoS$_2$ catalyst (see Fig. 3 B) by injecting solution of K$_2$PtCl$_6$ using syringe pump into the mixture of MoS$_2$ nanosheets, ethanol, and water. During the chemisorption process, Mo atoms are replaced by Pt atoms in MoS$_2$ nanosheets. Pt/MoS$_2$ catalysts with different Pt loading percentages 0.2, 1.0, 5.0, 7.5 are synthesized by changing the concentration of K$_2$PtCl$_6$, and EXAFS spectra of all these catalysts confirmed that only isolated Pt is present on the surface of MoS$_2$. Researchers also investigated its catalytic activity for the conversion of CO$_2$ into methanol without the formation of formic acid. The HAADF-STEM images of single atoms catalysts Pd$_{1}$/TiO$_2$, and Pt$_{1}$/MoS$_2$ with 1.5 wt%, and 0.2 wt%, respectively, are presented in Fig. 3.

Figure 3: The figure represents the HAADF-STEM images of different single atom catalyst synthesized using other wet-chemical method: (a) Pd$_{1}$/TiO$_2$, (b) Pt$_{1}$/MoS$_2$. (a) reprinted/reproduce from Ref. [24] with the permission of Science publishing group, copyright 2016, (b) reprinted/reproduce from Ref. [26] with the permission of Macmillan Publishers Limited and part of Springer Nature publishing group, copyright 2018.
Atomic Layer Depositions Method

Atomic layer deposition (ALD) is a subclass of chemical vapor deposition, attracting many researchers because of its ability to deposit noble metal atoms and their oxides uniformly with a desirable thickness on the substrate by using sequential and self-limited surface reaction. Generally, in this method, two precursors are used, and the deposition process involves four steps: (1) Initially, precursor is inserted in the chamber and allowed to react with the substrate; (2) Purging of reaction chamber by use of carrier gas; (3) Second precursor is inserted in the reaction chamber and allowed to react with substrate containing first precursor; (4) At last, purging of reaction chamber is done, and sample is obtained. By repeating the cycles, a desired thickness of the precursor can be deposited.

Sun et al. synthesized heterogeneous catalysts consisting of isolated Pt atoms, Pt-clusters, Pt-nanoparticles dispersed on the surface graphene nanosheets (GNS) using ALD method, and also reported that these novel catalyst shows remarkable catalytic activity for methanol oxidation, almost ten times higher than the commercial carbon supported Pt (Pt/C) catalyst. For the synthesis of Pt/GNS catalyst (methylcyclopentadienyl)-trimethylplatinum (MeCpPtMe₃, 98% purity) and oxygen (99.9995%) used as precursors and nitrogen (99.9995%) use as purge and carrier gas. The HAAD-STEM images of Pt/GNS catalyst synthesized with 50, 100, and 150 ALD cycles, reveals that isolated Pt atoms and small cluster (<1 nm) are present in the 50ALD-Pt/GNS (see Fig. 4 A), whereas in the 100ALD-Pt/GNS, and 150ALD-Pt/GNS the size cluster approaches to 2 nm and 4 nm, respectively. Recently, Cheng et al. synthesized Pt/N-GNS SAC by same ALD technique discussed above, in which isolated Pt atoms are uniformly dispersed on the surface of nitrogen-doped graphene nano-sheets, and also investigated its activity for Hydrogen evolution reaction. They also reported, Pt/NGNs exhibits enhanced catalytic activity (∼37 times more than Pt/C) and high stability. The Pt loading of 2.1 and 7.6 wt% for 50 and 100 ALD cycles, respectively, was confirmed by inductively coupled plasma atomic emission spectroscopy. Similarly, as above, a bright spot of isolated Pt atoms, as well as tiny Pt cluster, are observed in 50ALD-
Pt/NGNs (see Fig. 4 B), whereas in 100ALD-Pt/NGNs, the size of Pt clusters becomes larger and formation of nanoparticles, as well as new cluster, is observed.

Lu and co-workers\textsuperscript{28} used ALD technique for preparation of single atom Pd\textsubscript{1}/graphene catalyst (see Fig. 4 D), palladium hexafluoroacetylacetate (Pd(hfac))\textsubscript{2}, Sigma Aldrich, 99\%) and formalin (Aldrich, 37\% HCHO and 15\% CH\textsubscript{3}OH in aqueous solution) used as precursors and N\textsubscript{2} (99.999\%, purity) as carrier and purge gas. Researchers explored the hydrogenation of 1,3-butadiene using Pd\textsubscript{1}/graphene SAC and observed excellent durability for catalytic deactivation and remarkable catalytic performance, i.e., 100\% butenes selectivity and 95\% conversion at 50 °C. Wang et al.\textsuperscript{36} from Lu group have synthesized single Pt\textsubscript{1}/CeO\textsubscript{2} (see Fig. 4 C) catalyst and studied its activity in water promoted CO oxidation and reported that
the contribution of water in production CO2 using Pt\textsubscript{1}/CeO\textsubscript{2} is 50\% via a water-mediated Mars-Van Krevelen (MvK) mechanism.

Piernavieja-Hermida et al.\textsuperscript{[4]} developed an exciting way to stabilized single Pd atom on the surface of Al\textsubscript{2}O\textsubscript{3} by depositing an ultra-thin layer of TiO\textsubscript{2} protective coatings. First, Pd(hfac)\textsubscript{2} precursor is allowed to chemisorbed on the surface of Al\textsubscript{2}O\textsubscript{3} using ALD; after that, TiO\textsubscript{2} is deposited on the substrate using tetrachloride and ionized water. The TiO\textsubscript{2} selectively grows on the substrate, not on the Pd(hfac)\textsubscript{2} because of the presence of remaining (hfac)\textsubscript{2}, which prevents its growth on Pd. The massive structure of (hfac)\textsubscript{2} forms a nanocavity around the Pd atoms of same size the dimension, and at last, these ligands are removed using formalin (HCHO) for obtaining the TiO\textsubscript{2} protected Pd/Al\textsubscript{2}O\textsubscript{3} catalyst. They also reported that the thermal stability of this catalyst significantly increased because of the nanocavity thin-film structure. The HAADF-STEM images of single atoms catalysts Pt/GNS\textsuperscript{[27]}, Pt/N-GNS\textsuperscript{[53]}, Pt\textsubscript{1}/CeO\textsubscript{2}\textsuperscript{[36]} and Pd/GNS\textsuperscript{[28]} with 1.52 wt\%, 2.1 wt\%, 0.22 wt\% and 0.25 wt\%, respectively, are presented in Fig. 4.

The major disadvantages of the ALD technique are; it is a time-consuming method and ALD instruments and running cost are very expensive.

**Metal-Organic Frameworks Derived Method**

Metal-organic frameworks (MOFs)\textsuperscript{[22, 55, 56]} are the porous compound in which of metal ions or clusters are attach with organic ligands to form 1-, 2- or 3- dimensional structure, and could be used as precursors or as support in the synthesis of SACs. Unique characteristics of MOFs such as high surface area, ordered pore structure with uniform sizes makes them ideal substrate for loading of single atom. In the synthesis of SACs, MOFs are emerging as a new research frontier because of the following reasons; (1) Tunable pore size enables MOFs to encapsulate metal precursors and prevent form the agglomeration. (2) The high surface area of MOFs provides a large number of anchoring sites for dispersion of metal precursors. (3) A variety of organic ligands serve as active anchoring sites for various precursors. (4) Using
the pyrolysis method, various MOFs can be easily converted into N-doped carbon materials, and act as an ideal substrate for dispersion and stabilization of metal precursors.

Figure 5: The figure represents the HAADF-STEM images of different single atom catalyst synthesized using metal-organic frameworks method: (a) Co SAs/N-C, (b) Fe SAs/N-C, (c) Ni SAs/N-C, (d) Ru SAs/N-C. (a) reprinted/reproduce from Ref. [29] with the permission of Wiley-VCH publishing group, copyright 2016, (b) reprinted/reproduce from Ref. [30] with the permission of Wiley-VCH publishing group, copyright 2017, (c) reprinted/reproduce from Ref. [31] with the permission of American Chemical society publishing group, copyright 2017, (d) reprinted/reproduce from Ref. [32] with the permission of American Chemical society publishing group, copyright 2017.

Yin et al. from Li group synthesized single atom Co/N-C catalyst (see Fig. 5 A) with high metal loading up to 4 wt%, which consists Co atom dispersed on the surface of nitrogen-doped porous carbon and investigated its activity for oxygen reduction reaction. By performing the pyrolysis of bimetallic Zn/Co metal-organic framework (BMOF) at 800 °C, the Co and Zn ions are reduced by carbonization of organic ligands and further evaporation of Zn takes place because of its low boiling point and single atom Co/N-C catalyst is obtained. Wang et al. from the same group reported that the coordination number of Co atom could
be controlled by changing the pyrolysis temperature, for example they fabricated three single atom Co-N₄, Co-N₃ and Co-N₂ catalyst by keeping the pyrolysis temperature at 800, 900 and 100 °C, respectively.

Chen et al. also from Li group synthesized isolated Fe atom supported on nitrogen-doped porous carbon (Fe SAs/N-C) catalyst (see Fig. 5B) with metal loading up to 2.16 wt% and reported its excellent activity for oxygen reduction reaction compared to Pt/C and most non-expensive-metal catalyst. They mixed Fe(acac)₃ and zeolitic imidazolate frameworks (ZIF-8) and used encapsulated-precursor pyrolysis technique for the synthesis of Fe/N-C catalyst. The molecular-scale cage structure of ZIF-8 formed by assembly of Zn²⁺ and 2-methylimidazole traps one Fe(acac)₃ molecule. After that, pyrolysis of resulting mixture at 900 °C under Ar gas converts ZIF-8 into nitrogen-doped porous carbon, and simultaneously Fe(acac)₃ was reduced by carbonized organic ligands, and Fe SAs/N-C catalyst is obtained.

Zhao et al. prepared isolated Ni atom dispersed on the nitrogen-doped porous carbon (Ni SAs/N-C) (see Fig. 5C) with metal loading up to 1.53 wt% and investigated its activity for electroreduction of CO₂. The homogeneous aqueous solution of Ni(NO₃)₂ was mixed with a solution containing ZIF-8 powder dispersed in n-hexane and actively stirred for 3 hours so that salt completely absorbed, resulting sample was centrifuged and dried at 65 °C for 6 hours. After that, pyrolysis of the sample at 1000 °C was done in the presence of Ar gas, during which the ZIF-8 is converted into nitrogen-doped porous carbon, simultaneously Zn atoms evaporate due to its low boiling point, creating nitrogen-rich sites. These sites are occupied by Ni²⁺, and act as a fence and prevent Ni atom from agglomeration; finally, Ni SAs/N-C catalyst is obtained.

Wang et al. synthesized Ru SAs/N-C catalyst (see Fig. 5D), which contains single Ru atom dispersed on the nitrogen-doped porous carbon with metal loading percentage 0.30 wt% and reported that it exhibits high catalytic and selectivity for hydrogenation of quinolines. They used amine derivative MOF UiO-66-NH₂ (Zr₆O₄(OH)₄(BDC)₆-NH₂) for synthesizing of Ru SAs/N-C catalyst, first, they mixed RuCl₃, ZrCl₄ and H₂BDC-NH₂ with an aqueous
solution of DMF and HAs. After that resulting mixture is centrifuged and washed with methanol and DMF and then heated at 700 °C for 3 hours in the presence of Ar gas, a black powder containing nitrogen-doped porous carbon (N-C) decorated with Ru and small ZrO$_2$ species is obtained. The small ZrO$_2$ species attach with N-C were etched by adding HF solution, and Ru SAs/N-C is formed.

Wei et al.$^{58}$ synthesized catalyst containing a single Pd atom supported on the nitrogen-doped porous carbon from Pd-nanoparticles by employing the top-down method, and also reported its excellent catalytic activity and selectivity for semi-hydrogenation of acetylene to ethylene. First, ZIF-8 nanocrystal was grown on the surface Pd-nanoparticles, by mixing Pd-nanoparticles in an aqueous solution Zn(NO$_3$)$_2$ and 2-methylimidazole solution. After that, the resulting mixture was heated at 900 °C in presences of inert gas for 3 hours, Pd-nanoparticles were transformed in single atoms and distributed within the substrate, and meanwhile, ZIF-8 is converted into nitrogen-doped porous carbon. Finally, single-atom Pd SAs/N-C is obtained having a thermodynamically stable Pd-N$_4$ structure. Using the same technique, they have also synthesized Pt SAs/N-C and Au SAs/N-C catalyst.

Using ZIF-8 MOF and pyrolysis method, Yang et al.$^{59}$ synthesized Ni SAs/N-C catalyst by transforming Ni nanoparticles into Ni single atom, mostly dispersed on the surface of N-doped porous carbon substrate and tested its activity and selectivity for electroreduction of CO$_2$.

Recently, Zhang et al.$^{60}$ prepared Fe$_1$-N-C SAC using porphyrinic MOF (PCN-222), the catalyst contains isolated Fe atom dispersed on the surface of nitrogen-doped porous carbon substrate, and also reported its activity for nitrogen reduction reaction is better than Co$_1$-N-C and Ni$_1$-N-C. Initially, they synthesized Fe-TPPCOOMeCl (iron (III) meso-tetra(4-methoxycarbonylphenyl) porphine chloride (Fe-TPPCOOMeCl) by dissolving TPPCOOMe and FeCl$_2$.4H$_2$O in a DMF solution and heated for 6 hours at 160 °C. Then Fe-TCPP is obtained by mixing Fe-TPPCOOMeCl THF, MeOH and KOH, and heated for 6 hours at 85 °C. After that, Fe-TCPP, ZrOCl$_2$.8H$_2$O, H$_2$-TCPP, DMF and CF$_3$COOH were mixed
and heated for 18 hours at 120 °C for the formation of PCN-222(Fe). At last pyrolysis of PCN-222(Fe) sample is done at 800 °C for 3 hours in the presence of N2 gas, and Fe1-N-C catalyst is obtained. The HAADF-STEM images of single atoms catalysts Co SAs/N-C29, Fe SAs/N-C30, Ni SAs/N-C31, and Ru SAs/N-C32 with 4 wt%, 2.16 wt%, 1.53 wt% and 0.30 wt%, respectively, are presented in Fig. 5.

Application of Single-Atom Catalysis

In recent years, researchers have reported the synthesis and catalytic behavior of many SACs. They found that these SACs show high catalytic activity, selectivity, and stability because of the maximum utilization of single atom (almost 100% utilization) during reactions and strong bonding between the single atom and the anchoring sites on the supported surfaces. Therefore, the application of many SACs in different catalytic reactions such as CO oxidation, water-gas shift reaction, water splitting reaction, oxygen reduction reaction, methanol oxidation reaction, C-H activation reactions, Hydrogen evolution reaction, carbon dioxide reduction reaction and Hydrogenation reaction, are discussed below.

CO Oxidation Reaction

In the field of catalyst science, CO oxidation is one of the most studied reaction because of its importance in protecting our environment by purifying poisonous exhaust gases coming from motor vehicles and various Industries. Moreover, CO oxidation is the most crucial step in water-gas-shift reaction and in fuel cells application for eliminating CO from reforming gas. Zhang and co-workers were the first to investigate experimentally and theoretically the catalytic activity, selectivity and stability of single-atom Pt1/FeO2 catalyst for CO oxidation, and relativistic density functional theory was used for theoretical investigation.

For computation, they used Fe- and O3- terminated Fe2O3 (011) surfaces, and after optimization found that the most likeliest position of Pt atom is 3-fold hollow sites on the
O$_3$ terminated surface, where Pt atom is linked with three oxygen atom. From HAAD images, they observed that the single Pt atom exactly replaces the single Fe atom located at 3-fold hollow sites of O$_3$-terminated surface. Before testing the catalytic performance, the Pt$_1$/FeO$_x$ catalyst was reduced by flowing H$_2$/He gas for 30 min at 200 °C. The oxidation of CO on the surface of Pt$_1$/FeO$_x$ follows Langmuir-Hinshelwood (H-L) mechanism and the step by step reaction mechanism is shown in Fig. 6. After prereduction by H$_2$, the oxygen vacancy ($O_{vac}$) near the Pt atom was created by reducing the stoichiometric hematite surfaces partially (step i), which provides an active site for adsorption of O$_2$ molecule. A Similar theoretical model was designed for computation by removing one oxygen atom, which is connected to the Pt atom, the oxygen coordination number of Pt atom reduces from 3 to 2. In step ii, O$_2$ molecule is adsorbed with adsorption energy 1.05 eV, and optimize O-O bond length signifies that it is well activated by Pt atom and $O_{vac}$ . Next, in step iii, CO molecule adsorbed on Pt$_1$ atom with binding energy 1.27 eV, and one of Oxygen atom of O$_2$ molecule comes nearer to CO molecule and form transition state (TS-1). The activation energy needed to process the reaction ($CO_{ad} + O - O_{ad} \rightarrow CO_2 + O_{ad}$) is 0.49 eV, and after releasing first CO$_2$ molecule from remaining $O_{ad}$ atom restores the Pt-loaded stoichiometric hematite surface in step iv. In step v, another CO molecule adsorbed at Pt atom and migrated to an $O_{ad}$ atom in step vi and form a second transition state (TS-2). The activation energy needed for the processing of the second reaction is 0.79 eV. After releasing the second CO$_2$ molecule, the Pt-loaded stoichiometric hematite surface reduced again to create new oxygen vacancy near Pt atom and approaches to initial step i. All of the catalytic steps are exothermic and the activation energy needed for formation of CO$_2$ molecule is small at low temperature, indicates that catalytic activity of Pt$_1$/FeO$_x$ for CO oxidation is very high.

Liang et al. and Qiao et al. investigated experimentally as well as theoretically the catalytic activity of Ir$_1$/FeO$_x$ $^{33}$, Au$_1$/FeO$_x$ $^{22}$ for CO oxidation, respectively.

Using DFT, Liang et al. explored the catalytic activity of non-noble metal single-atom catalyst (i.e., Ni$_1$/FeO$_x$ $^{34}$) and also compared the catalytic activity of Pt$_1$/FeO$_x$, Ir$_1$/FeO$_x$
and Ni$_1$/FeO$_x$ systematically. The O$_2$ molecule adsorbed on the surface of these SACs in a different manner, in the case Pt$_1$/FeO$_x$ and Ni$_1$/FeO$_x$ it adsorbed on top of Pt and Ni atoms, respectively, whereas in the case and Ir$_1$/FeO$_x$ it adsorbs dissociatively, i.e., one O atom on the top of Ir and another O atom occupy the oxygen vacancy site. The activation energy needed for the formation of CO$_2$ (TS-1) in the case of Pt$_1$/FeO$_x$, Ir$_1$/FeO$_x$ and Ni$_1$/FeO$_x$ catalysis is 0.49 eV, 0.59 eV and 0.75 eV, respectively, whereas for the formation of second CO$_2$ (TS-2) the activation barrier is 0.79 eV, 1.41 eV and 0.64 eV, respectively. The rate-determining step for Ni/FeO$_x$ (0.75 eV) catalyst is lowest compared to Pt$_1$/FeO$_x$ (0.79 eV) and Ir$_1$/FeO$_x$ (1.41 eV) catalyst, suggest that it exhibits the highest catalytic activity for CO oxidation compared to others at room temperature.

Using experimental and theoretical methods, Moses-DeBusk et al.\textsuperscript{18} examine the catalytic activity of single Pt atom dispersed on an inert substrate, $\theta$–Al$_2$O$_3$ for CO oxidation, in the presence of stoichiometric oxygen. They reported that the proposed pathway of CO oxidation
is slightly different from the conventional Langmuir-Hinshelwood mechanism because the conventional mechanism requires at least one Pt-Pt bond.

In search of non-precious and more efficient/active SACs for CO oxidation Li et al. systematically studied the catalytic activity of various single-atom catalysts M$_1$/FeO$_x$ (M= Au, Rh, Pd, Co, Cu, Ru and Ti) by employing density functional theory. They reported five SACs, especially Rh$_1$/FeO$_x$ and Pd$_1$/FeO$_x$ with oxygen vacancy, CO$_1$/FeO$_x$ and Ti$_1$/FeO$_x$ without oxygen vacancy, and Ru$_1$/FeO$_x$ with or without oxygen vacancy surface exhibits better catalytic activity compared to Pt$_1$/FeO$_x$. Furthermore, they also reported that non-precious single atom CO$_1$/FeO$_x$ and Ti$_1$/FeO$_x$ catalyst need very low activation energy for CO oxidation via L-H mechanism.

Using DFT calculation Tang et al. systematically studied the catalytic activity of single Pt atom dispersed on the CeO$_2$ (111), (110) and (100) surfaces for CO oxidation via Mars-van Krevelen mechanism. They reported that the single Pt atom loaded on the ceria surfaces are thermodynamically stable, and the oxidation state of Pt atom on (111) and (100) surfaces is +4. In contrast, the oxidation state of (110) surface is +2 due to the spontaneous formation of O$_2^{2-}$ spices, which reduces the oxidation state of Pt atom from +4 to +2, making the Pt$_1$@CeO$_2$ (110) catalyst most stable.

Water-Gas Shift Reaction

The water-gas shift (WGS) reaction was discovered in 1780 by Italian physicist Felice Fontana, but its importance in the industrial sector was realized much later. In this reaction, carbon monoxide and water vapor reacts to form carbon dioxide and hydrogen molecule ($CO + H_2O \rightleftharpoons CO_2 + H_2$). WGS is a cost-effective and more efficient method for the production of hydrogen. In industrial sectors, a large amount of hydrogen is needed for various process such as ammonia synthesis via Haber-Bosch process, synthetic liquid fuels synthesis via Fischer-Tropsch method, hydro-treating of petroleum products for removing CO contamination, in the synthesis of nitrogenous fertilizers, for preparation of ethanol, methanol,
and dimethyl ether, and hydrogenation of hazardous wastes (PCBs and dioxins)\textsuperscript{66,67}.

Apart from this, from future aspects, hydrogen is considered to be one of the cleanest and renewable energy source because it can be stored and transported efficiently and after burning, it produces only water as a byproduct\textsuperscript{68–71}.

Due to the high catalytic activity, selectivity, and efficiency of SACs, many researchers have investigated its catalytic properties for WGS reaction\textsuperscript{19,37–41,71–73}. Fu et al.\textsuperscript{72} synthesized low-content (0.2 - 0.9 wt\%) gold-cerium oxide catalyst and reported its activity and stability is high for WGS reaction. Yang et al. prepared SAC consisting of isolated Au atoms dispersed on titania support and reported that it exhibits excellent activity for WGS reaction at low temperatures. They stabilize Au atom on support by irradiating titania support by UV rays, which is suspended in ethanol solution, where the gold atom donates the separated electrons to $-\text{OH}$ groups. The Au atoms with surrounding extra surface $-\text{OH}$ groups act as active sites for the WGS reaction and also reported that its catalytic performance is better than Au/CeO$_2$\textsuperscript{72,73}. Flytzani-Stephanopoulos group members prepared single atom centric Pt (Pt(II)$-\text{O(OH)}_{x-}$) and Au (Au$-\text{O(OH)}_{x-}$) sites stabilize by sodium or potassium ion by making bond with it through $-\text{O}$ ligands on three different supports, and examine its catalytic activity for WGS reaction\textsuperscript{74,75}. They found that the reaction rate of Pt(II)$-\text{O(OH)}_{x-}$ species for WGS reaction is same for all supports (i.e., anatase (TiO$_2$), a microporous K-type L-zeolite (KTLZ) and mesoporous silica MCM-41 ([Si]MCM41) ) for Na-containing catalyst with 0.5 wt\% Pt loading\textsuperscript{74}. Similar to finding of single-site Pt(II)$-\text{O(OH)}_{x-}$ species, irrespective of the support KLTL and [Si]MCM41, TiO$_2$, CeO$_2$, and Fe$_2$O$_3$ the reaction rate of Au$-\text{O(OH)}_{x-}$ species is same with 0.25 wt\%, 0.25 wt\%, 0.12 wt\%, 0.50 wt\% and 1.16 wt\% Au loading, respectively\textsuperscript{75}.

Lin et al.\textsuperscript{19} synthesized catalyst consisting of isolated Ir atom loaded on FeO$_x$ support and found that it shows remarkable performance for WGS reaction. The catalytic activity of Ir$_1$/FeO$_x$ is higher than its cluster and nano-particle counterparts, also higher than Au- or Pt-based catalyst\textsuperscript{73}. After extensive research, they found that the single atom is responsible
for \( \approx 70\% \) catalytic activity in a single atom, clusters and nano-particles catalyst. The Ir atom helps FeO\(_x\) support in reduction for creating oxygen vacancy, which leads to enhance the catalytic activity of Ir\(_1/\)FeO\(_x\).

In literature, it has been seen that the WGS reaction mainly follows three reaction mechanisms, i.e., redox, formate, and carboxyl mechanisms. Fu et al.\(^{73}\) proposed that nanostructured gold-ceria oxide catalyst follows the redox mechanism for WGS reaction. In this reaction mechanism, CO atom adsorbed on Au atom and oxidized with the help of O atom of ceria oxide; after that, support is reoxidized by water, and hydrogen is released. Shido and Iwasawa\(^{76,77}\) were the first to propose the formate mechanism for WGS reaction, in this mechanism CO and H\(_2\)O molecule adsorbs on the surface of support, next CO molecule interact with surface OH group to form formate (HCOO) intermediate, which dissociate into CO\(_2\) molecule and H atom, and finally, two H atom recombine to form H\(_2\) molecule. Liu et al.\(^{78}\) studied the catalytic activity Au clusters-ceria oxide (Au\(_{4-6}/\)CeO\(_2\)) catalyst for WGS reaction and found that it follows the carboxyl mechanism. In this mechanism, CO\(_{ad}\) adsorbs on Au, and H\(_2\)O dissociatively (H and OH) adsorbs on Au, the adsorbed CO\(_{ad}\) interact with OH\(_{ad}\) to form carboxyl (COOH) intermediate after that COOH dissociate into CO\(_2\) molecule and H atom, and at last, two H atom recombine to form H\(_2\) molecule. Song et al.\(^{40}\) predicted the reaction mechanism of isolated and clustered Au atoms on CeO\(_2\)(110) using density functional theory for WGS reaction.

Song et al.\(^{40}\) by employing DFT methods studied reaction mechanism of isolated and clustered Au atoms on CeO\(_2\) (110) surface for WGS activity, using both pathways redox and carboxyl mechanism. The carboxyl mechanism is more favorable than redox mechanism because it requires higher energy for breaking O–H bonds, which is directly involved in the production of H\(_2\) and CO\(_2\).

Recently, Liang et al.\(^{42}\) studied the catalytic activity of Ir\(_1/\)FeO\(_x\) SAC for WGS reaction by using theoretical and experimental methods. In Fig. 7(a) and (b), a schematic diagram of Ir\(_1/\)FeO\(_x\) with oxygen vacancy, and the surface lattice oxygen atom (red) around Ir
atom blue are represented, respectively. The most favorable position of Ir atom to stabilize on the surface of FeO$_x$ is O$_3$-terminated surface, where Ir atom is bonded with three oxygen atom. The site structure of Ir$_1$/FeO$_x$ with and without oxygen vacancy is the same, and it follows two different redox reaction pathways I and II, shown in Fig. 8 for WGS reaction.

Let us considered the reaction pathways I (Fig. 8(b)), in step (i) Ir atom is bonded with two oxygen, and on the right side of the Ir atom, there is an O$_{vac}$. Next, in step (ii) H$_2$O molecule dissociate into H and OH, and adsorbed on O$_D$ atom (represented as H$_a$) and at O$_{vac}$ site (represented as O$_F$ for O atom and H$_b$ for Hydrogen), respectively. The CO (O atom of CO is represented as O$_G$) molecule is absorbed on Ir$_1$ atom in step (iii). The next step is TS1, where H$_a$ and H$_b$ directly combine to form H$_2$ and require high activation energy 3.45 $eV$, which is also a rate-determining step. Afterwards the absorbed CO atom starts moving towards the O$_F$ atom in step (iv) and gradually approaches to TS2. The energy barrier for the formation of CO$_2$ if the activation energy of 1 $eV$ is applied. The newly form bent CO$_2$ molecule with a 140.7° angle still absorbs on Ir single atom in step (v). The bent CO$_2$ can be considered as a virtual CO$^{-2}$ anion, and its absorption energy on the Ir$_1$/FeO$_x$ is 1.29 $eV$ and require another intermediate step (vi) for relaxation. The bent CO$^{-2}$ transforms
into linear CO$_2$ by losing an electron in TS3, and the activation energy of TS3 is 0.59 eV. Finally, in step (vii), the desorption of CO$_2$ from the Ir$_1$/FeO$_x$ and regeneration of O$_{vac}$ occurs on the Ir atom’s right side.

Figure 8: (a) The calculated relative energy diagram of proposed reaction pathways I and II for WGS reaction on Ir$_1$/FeO$_x$ catalyst. The reaction step and corresponding structures for (b) path I and (c) path II are shown. The rate-determining step with the energy barrier is demonstrated in a circle, and a green triangle region represents active sites in the reaction. Ir atom= blue, Oxygen atom= red, Fe atom= purple, C atom = pink and O atom of CO= dark green. (reprinted/reproduce from Ref. [42] with the permission of Wiley-VCH group, copyright 2020).

The redox reaction pathways II is presented in Fig. 8 (c), and the reaction path till step (iii) is the same as pathways I. The Next step is TS1, which needs activation energy of 1.52 eV to move the adsorbed CO molecule slowly towards the adjacent O$_a$ at the left side of Ir atom. The bent CO$_2$ (CO$^{-2}$ ) molecule is formed in step (iv). Afterward, the bent CO$_2$ requires small activation energy 0.13 eV for desorbing from the surface Ir$_1$/FeO$_x$ by
releasing an electron in TS2. The $O_{\text{vac}}$ on the left side of the Ir atom is produced after the desorption of $CO_2$ in step (v). The $H_b$ atom of $HO_F$ starts moving towards Ir atom slowly if small activation energy of 0.28 eV is applied in TS3. In the intermediate step (vi) $H_a$ and $H_b$ atoms are associated with $O_D$ and Ir atom, respectively. The $H_a$ and $H_b$ approach towards each other in TS4 for the formation $H_2 (H^*_a + H^*_b \rightarrow H^*_2)$, and energy barrier for the reaction is 1.42 eV. The obtained $H_2$ slowly migrate towards the Ir atom in step (vii). Next, $H_2$ molecule desorbs from the $Ir_1/FeO_x$ in TS5 with an energy barrier of 0.53 eV. Finally, after releasing the $H_2$ molecule, the surface of $Ir_1/FeO_x$ SAC is recovered, and $O_{\text{vac}}$ is generated on the left side of Ir atom. During the WGS reaction process on $Ir_1/FeO_x$ surface, $O_{\text{vac}}$ shifts from the right side to the left side of Ir atom.

On comparing the pathways, we found that $H_2$ is first formed before $CO_2$ in pathways I, whereas in path II, it is reversed. The most favorable pathways for WGS reaction on $Ir_1/FeO_x$ surface is path II, as the energy barrier for the rate-determining step is 1.52 eV, much lower compared to the Path I (3.45 eV). Using Bader charge analysis Liang et al.\textsuperscript{42} also reported the oxidation state of Ir and Fe atom for both pathways. In pathways I, only Ir atom changes its oxidation state, whereas, in pathways II, both Ir and Fe atom changes oxidation state. In step (i) of pathways II, the oxidation state of Ir and Fe\textsuperscript{(a)} atom are +3 and +2, respectively, whereas in the final step (viii) the oxidation of Ir atom decreases from +3 to +2 and the oxidation state of Fe atom increases from +2 to +3. We can conclude that in WGS reaction Pathways II both Ir and Fe atom changes its oxidation state.

**Summary and Conclusions**

In this review article, we presented the recent advancement in the field of single-atom catalysis with a focus on the various synthesis methods and their application in various catalytic reactions, such as CO oxidation\textsuperscript{16,18,22,33–36}, water–gas shift (WGS)\textsuperscript{19,37,42}, etc. We also discussed the reaction mechanism of a single-atom catalyst for different catalytic reactions.
from theoretical aspects using density functional theory.

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