Single-Atom Catalysts: Synthesis, Performance and Applications

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Abstract. In recent years, researchers have prepared and reported many advanced monatomic electrocatalysts with good activity, selectivity, and stability through defect anchoring, space confinement, and coordination design strategies. However, due to its superior catalytic performance and potential cost advantages, people should accelerate the industrial application research of monatomic catalysis, develop preparation technologies with large-scale application prospects and promote the wide application of monatomic catalysis in various fields. This review article is about the recent advancements of single-atom catalysts for electro-catalysis under the framework of material design, performance enhancement and diverse applications. Specifically, we first classify the state-of-the-art synthesis strategies of single-atom catalysts. Then, a brief outline of their electrocatalytic properties and applications is given. We eventually find that monatomic catalysts could help improve the efficiency of reactions in many aspects and reduce their cost.

Keywords: Nanotechnology, single-atom catalyst, electro-catalysis, energy conversion, energy storage.

1. Introduction

Single-atom catalysts have the advantages of active site isolation and homogeneity of homogeneous catalysts and easy recycling of heterogeneous catalysts. Therefore, they are expected to serve as a bridge between homogeneous and heterogeneous catalysis and provide a good platform for understanding the mechanism and structure-activity relationship at the atomic scale. Therefore, combining a SAC and the metal material is expected to be a breakthrough to resolve the active site of the metal-nitrogen-carbon (M-N-C) catalyst. To determine the properties and methods to prepare catalysts, we review several methods and strategies in making SACs. At the same time, we also look into the utilization of single-atom catalysts to further their understanding.

2. Preperation Methods for SACs

2.1. Atomic Layer Deposition

The monatomic precipitation method is a method in which substances can be deposited layer by layer on the surface of the substrate in the form of a monatomic film. Originally, Finnish scientists proposed it and polycrystalline fluorescent material ZnS: Mn and amorphous AlO2 insulating film used it. Atomic layer precipitation is a method that allows the preparation of single-atom catalysts to achieve atomic-level fine control of the active site structure of the catalyst by changing the number of deposition cycles, order and types, etc.

For example, Sun's team prepared a highly stable Pt single-atom catalyst. In addition, Professor Sun Xueliang from the University of Western Ontario in Canada adjusted the number of ALD cycles to precisely control the Pt loading on graphene. For example, at 250 °C, 50 Pt ALD cycles on the N-doped graphene surface successfully prepared Pt/graphite. The preparation process of olefin single-atom catalyst is shown in Fig.1 below [1]:

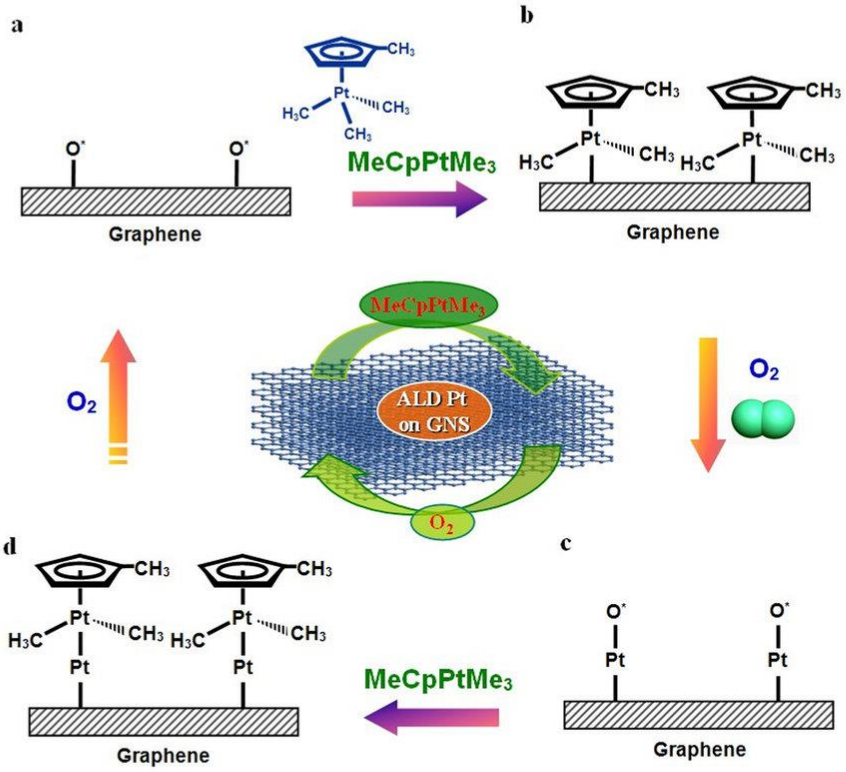

Figure 1. The process of atomic layer deposition method

Also, Lu's team controlled the type and number of oxygen-containing functional groups on graphene and performed a Pd ALD cycle (Pd(hfac)-HCHO) on the graphene surface at 150°C to synthesize atomic-level dispersed Pd single-atom catalysts [2].

At present, atomic layer deposition technology has been widely used in other places, such as thin films. However, it is also beneficial to obtain high-performance photonic crystal structures.

2.2. Co-precipitation

The co-precipitation method means two or more captions exist in the solution in a homogeneous phase, adding a precipitation agent. After the precipitation reaction, uniform precipitation of various components can be obtained. It is a preparation containing two or an important method for superfine powders of composite oxides of the above metal elements.

For example, using the co-precipitation method, prepare the Ni/A123 catalyst. Researchers add 200 ml of ionized water to the 2L beaker and stir and heat slowly to a certain temperature. Then pour the prepared solution into the beaker and co-precipitate for a while. Adjust the pH and then filter, dry, grind, and screen. And it is claimed that for another 3 hours, and hydrogen is used for the reduction reaction. After 4 hours, the temperature is reduced to isolate the air. Finally, the oil hydrogenation catalyst is obtained. A Ni/Al2O3 catalyst prepared with metallic nickel as the active component and alumina as the carrier is called the oil hydrogenation catalyst [3].

The co-precipitation method now is also helpful in the preparation process and materials.

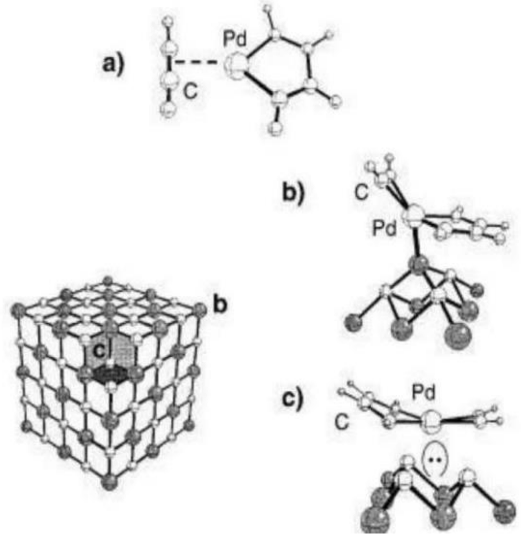

Figure 2. The cluster deposition facility at Brookhaven National Laboratory

2.3. Mass Seperation soft-landing method

In 2000, Abbet and some researchers used the mass selection-soft landing method to deposit Pdn clusters($1 \leq n \leq 30$) on MgO(100) surface for acetylene trimerization to benzene reaction. And they found that when n = 7 is the highest, and when n = 1, the catalyst can get the target product benzene at 300 K, which shows that the Pd single atom has extremely high catalytic activity [4].

3. Characteristics of Single-atom catalysis

3.1. High stability and high activity of the single-atom catalyst

Monatomic catalysts have attracted the great attention of researchers in recent years because of their high utilization of metal atoms and novel catalytic properties. However, with the increase of surface free energy brought by the reduction of size, it is easy to reduce the stability of the monatomic catalyst, easy to agglomerate, and then inactivate the catalyst.

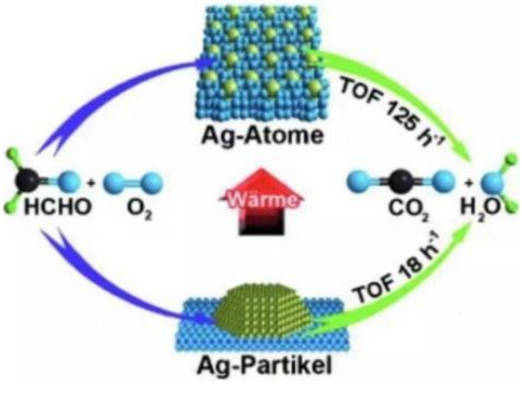

Figure 3. The process of the anti-Ostwald curing method

To solve this problem, Professor Lu Junling's research group, in cooperation with Professor Wei Shiqiang and Associate Professor Zhang Wenhua, designed a monatomic catalyst with high activity and stability by regulating the d-orbital energy level of a single metal atom by using electronic metal-support interactions (EMSIS) [8].

In this work, researchers first prepared Pt monatomic catalysts on four different supports of Co3O4, CeO2, ZrO2 and grapheme by ALD. Then, the electronic structures of the four monatomic catalysts were characterized by X-ray absorption spectroscopy (XAFS), photoelectron spectroscopy (XPS) and diffuse reflectance infrared CO absorption spectroscopy (DRIFTS). As a result, it was found that the

PT single atom in pT1 / Co2O4 had a greater degree of unoccupied 5D electronic orbital state, indicating a strong EMSIS between Pt single atom and Co3O4.

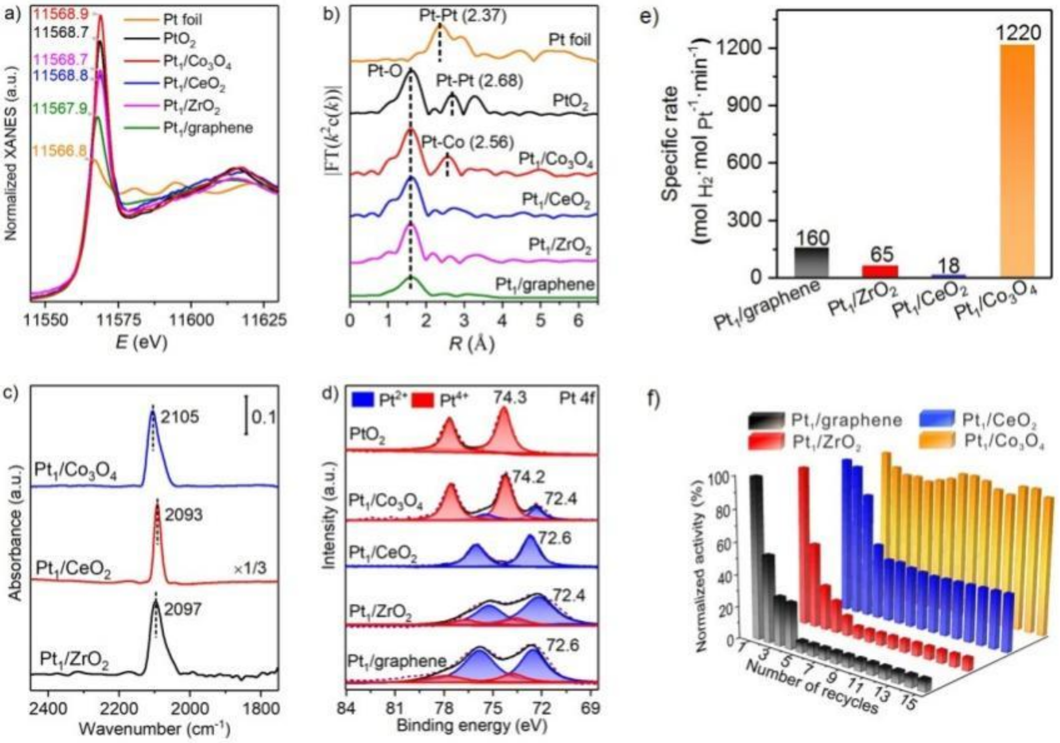

Figure 4. Monatomic structure characterization

In the hydrolysis of amino borane to hydrogen, the authors found that EMSIS had an important effect on its activity and stability. It was found that the activity and stability of pT1/Co3O4 monatomic catalyst were much higher than those of the other three Pt monatomic catalysts (Fig.4). Associate Professor Zhang Wenhua's research group analyzed the density state of Pt 5d orbital through density functional theory. It was found that the 5d electronic orbital state of Pt in pT1/Co3O4 was modulated so that the adsorption of amino borane molecule on Pt single atom was moderate, and the adsorption of hydrogen was greatly weakened, which promoted the improvement of its catalytic activity. This idea of simultaneously improving catalyst activity and stability through EMSIS can also be extended to Pd1/Co3O4 monatomic catalyst and other catalytic reactions, such as hydrogenation.

3.2. High selectivity of the single-atom catalyst

Prof. Ji Hongbing and Associate Researcher He Xiaohui from Sun Yat-sen University, in close collaboration with Prof. Martin from Peking University and Prof. Ge Binghui from the Institute of Physics, Chinese Academy of Sciences, proposed a synthetic strategy of "precursor dilution". In this strategy, specific metal porphyrins are used as the precursor of target metal. Porphyrins with very similar structures are used as diluents. The two are polymerized by the Fourier alkylation method. Then the corresponding monatomic catalyst can be obtained by carbonization at high temperature. Take platinum monatomic catalyst (Pt1/N-C) as an example, as shown in Fig.5. No metal particles were observed by transmission electron microscopy (BRIGHT/dark field). However, the spherical aberration electron microscopy (SEM) further confirmed the existence of platinum as isolated atoms, while X-ray absorption spectroscopy showed that platinum mainly existed as a PtN4 structure.

First of all, 24 kinds of metal porphyrins were synthesized under the good coordination ability of porphyrin ligands with most metal elements. Then they were polymerized and carbonized by gram alkylation. Twenty-four monatomic catalysts were prepared, including precious metals (Ru, Rh, Pd, Ag, Ir, Pt, Au). In addition, transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Mo, Cd, W, Er) and main group metals (Ga, In, Sn, Bi), as shown in Fig.6 [10].

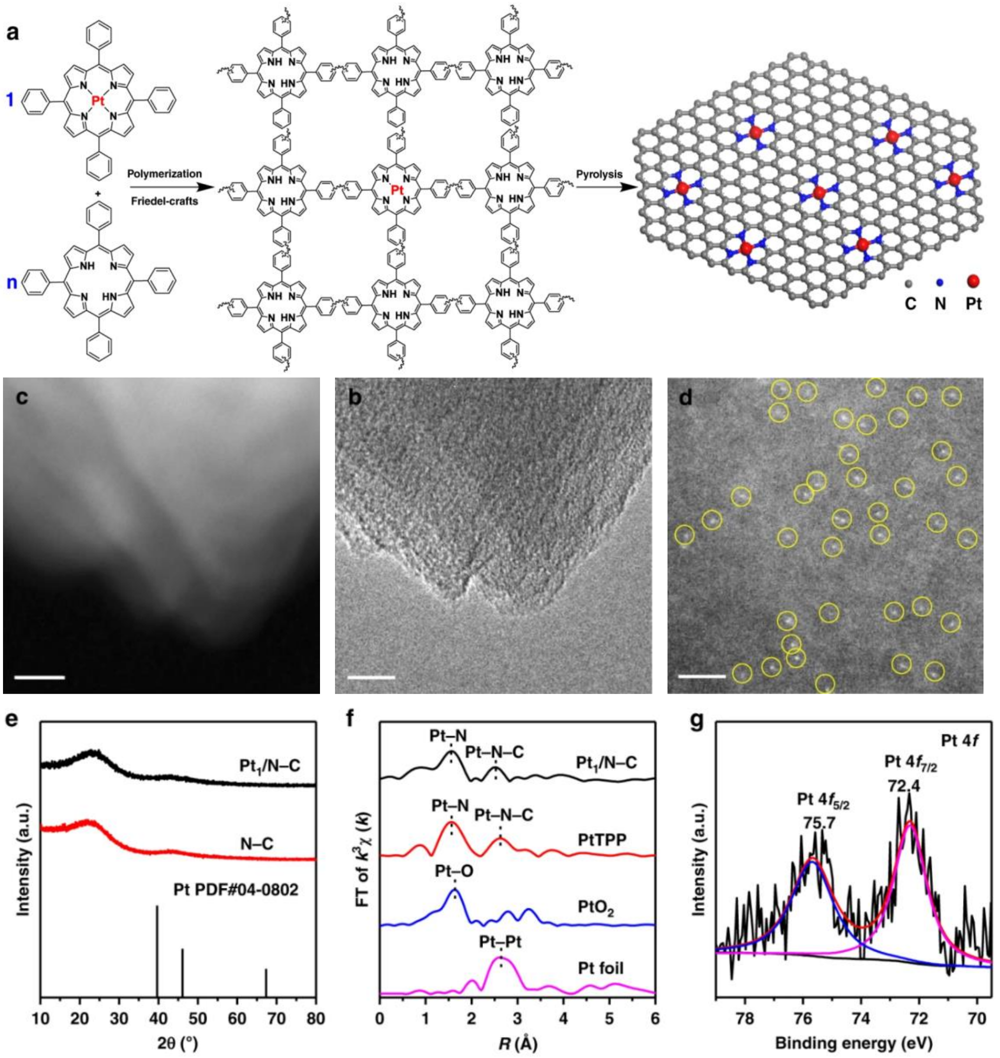

Figure 5. Preparation and structural characterization of Pt1/N-C

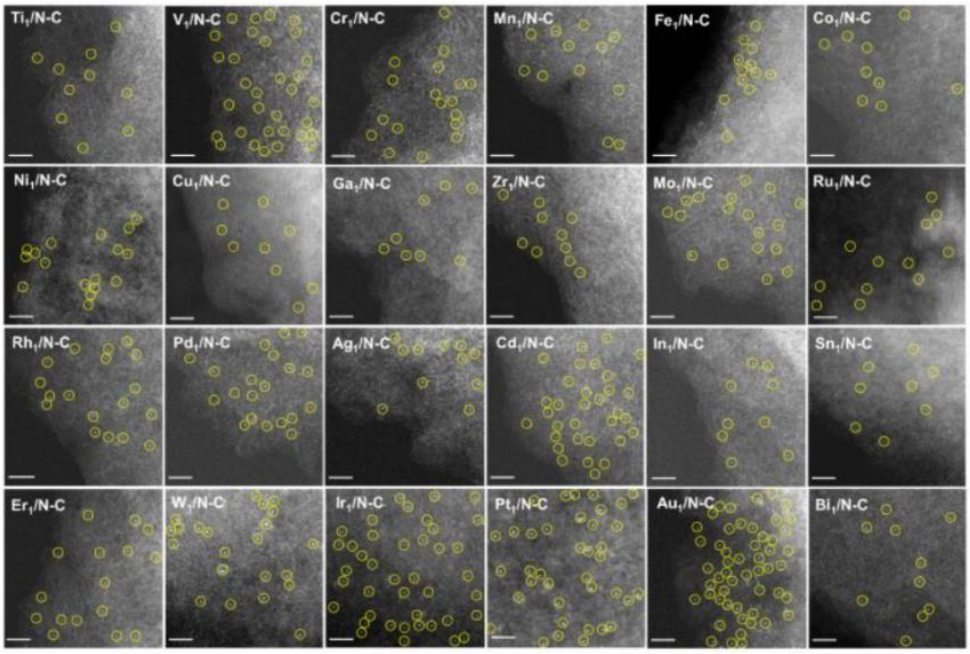

Figure 6. AC HAADF-STEM images of M1/N-C. M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, W, Ir, Pt, Au, and Bi. Yellow circles highlighted sAs. Scale bar, 2 nm.

Then, monatomic catalysts with different surface atomic densities can be obtained by adjusting the molar ratio of metallic porphyrins and their precursors. After that, bimetallic monatomic catalyst (PT1-Sn1/N-C) can be obtained by adding two kinds of metal porphyrins, such as platinum porphyrins and tin porphyrins, polymerization with the porphyrins, and then carbonization, as shown in Fig.7.

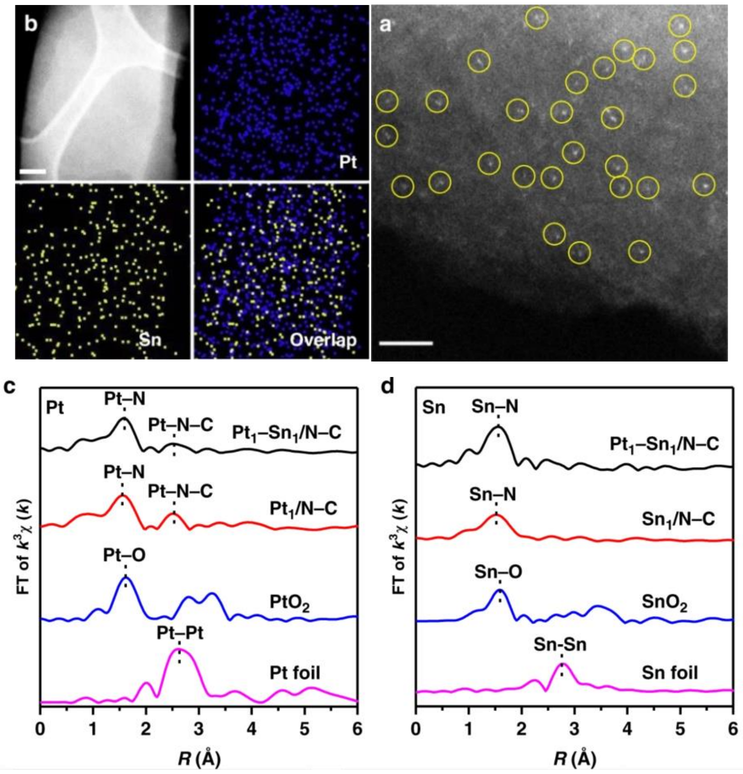

Figure 7. Structural characterization of Pt1-Sn1/N-C

Fourth, by changing the carbonization temperature (600°C, 700°C, 800°C), the aggregation state of platinum species can be transformed from a single atom to a nanocluster (1.1 nm) and then to the nanoparticle (6.9 nm), as shown in Fig.8.

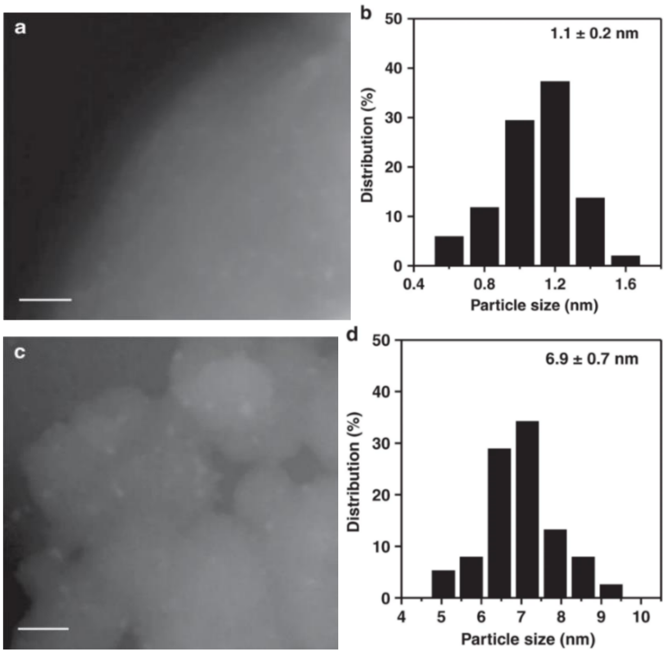

Figure 8. Structural characterization of Pt-NCs/N-C and Pt-NPs/N-C. a STEM image of Pt-NCs/N-C. Scale bar, 10 nm. b Particle size distribution of Pt-NCs/N-C. c STEM image of Pt-NPs/N-C. Scale bar, 50 nm. d Particle size distribution of Pt-NPs/N-C

Furthermore, the team applied the synthesized platinum single-atom catalyst to selective hydrogenation and found that the catalyst exhibited excellent chemical and regional selectivity. In particular, there are few reports about the regional selectivity of monatomic catalysts. We found that the platinum monatomic catalysts catalyze the semi-hydrogenation of end-alkyne groups very specifically when both end-alkyne groups and non-end-alkyne groups are present in the substrate molecules. In contrast, platinum nano-catalysts have no selectivity and simultaneously hydrogenate the two alkynyl groups, as shown in Fig.9.

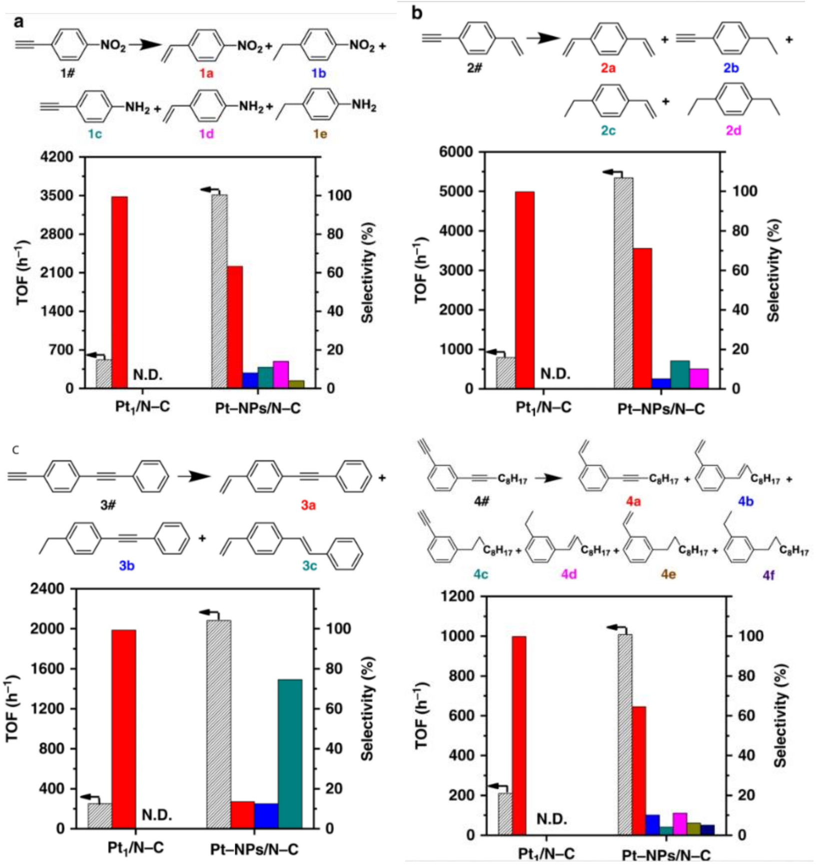

Figure 9. Catalytic performance of Pt1/N-C and Pt-NPs/N-C.

Based on the understanding of the literature, the author concluded that the reason was that the single platinum atom was very small, so the substrate could only be activated by end-position adsorption. In contrast, the platinum nanoparticles were large, and the substrate could be activated by both end-position adsorption and plane adsorption, as shown in Fig.10.

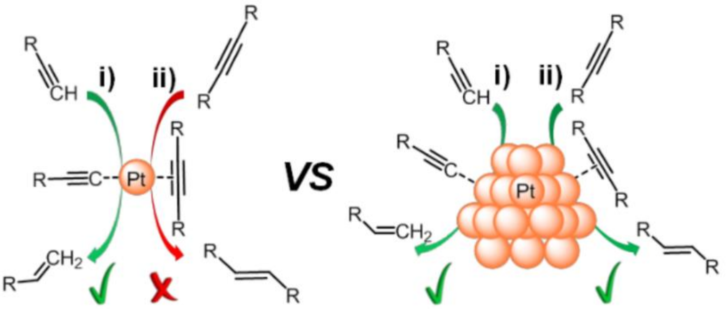

Figure 10. Schematic illustration of the hydrogenation of substrates with terminal alkyne or internal alkyne on Pt SACs and Pt NPs

To test this, the team used platinum species of different sizes (single platinum atoms, platinum nanoclusters, and platinum nanoparticles) to catalyze the hydrogenation of three non-terminal alkynes. The results were as expected, and the catalytic activity increased significantly as the size of the platinum species increased. This proves that the excellent regional selectivity of platinum monatomic catalysts is mainly due to geometric effects.

4. Conclution

Creating an active and stable metal SAC is challenging due to metal atoms' high surface free energy. However, single-atom catalyst reaches the limit of metal dispersion and maximizes atomic utilization. Monatomic catalysts have the advantages of "isolated sites" of homogeneous catalysts and stable and easy separation of heterogeneous catalysts. Thus, they closely connect heterogeneous catalysis with homogeneous catalysis and become a link between heterogeneous and homogeneous catalysis. In addition, the preparation of monatomic catalyst greatly reduces the use of precious metals, reduces the manufacturing cost, and the catalytic performance is significantly better than the traditionally supported catalyst. Therefore, single-atom catalysis technology development is significant for developing and commercial electrochemical energy conversion technology applications, and there is still a distance from industrial application, due to its superior catalytic performance and potential cost advantages, while paying attention to basic research, we are still accelerating the industrial application research of monatomic catalysis, promoting the wide application of monatomic catalysis in various fields and benefit the society as soon as possible

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