Oxidation of CO in three-way catalytic converter through single-atom catalysis

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Abstract. Automobile exhaust emissions are the main source of pollution at present, and Three-Way catalytic converter (TWC), as the main mean of automobile exhaust purification, can effectively control the negative impact posed by automobile exhaust. However, there are still some problems that can be improved in the current TWC, such as catalyst sintering and low temperature catalytic efficiency. As an advanced catalytic field, it has a good effect on CO governance in TWC. This paper mainly studies how single-atom catalysis catalyzes CO in TWC based on related literature researches and analyzes the mechanisms and experimental data from other teams. The preparation method of SAC will also be introduced. It is concluded that SAC has a good effect on CO catalysis in TWC, and it can also improve the existing problems in TWC. Different supports also have different mechanisms for CO oxidation. In the future, if SAC can be applied in TWC, all aspects will be significantly improved.

Keywords: three-way catalytic converter, single-atom catalysis, automobile exhaust treatment, Noble metals, single -atom catalyst preparation.

1. Introduction

Catalysis has important applications in industry, food, medical and other fields. Among them, catalysis includes homogeneous catalysis and heterogeneous catalysis. Homogeneous catalysis means that the catalyst and reactant have the same physical state, and homogeneous catalysis has the features of high activity and high selectivity. Heterogeneous catalysis refers to the catalysts and reactants having different physical states. Heterogeneous catalysis is generally a solid catalyst, loaded on the appropriate support of transition metal. Specifically in industrial catalysis, most of the catalysis process happens through heterogeneous way. In the research group of Zhang Tao et al., a single-atom Pt/FeOx catalyst was successfully prepared, which showed high catalytic activity and stability in CO oxidation and CO selective oxidation reactions. Meanwhile, the research group also proposed the concept of single-atom catalysis [1]. Supported noble metal catalysts are widely used in the field of industrial catalysis, and the size of metal particles in such catalytic systems is an important factor in determining the catalytic performance. It is generally believed that the nanoclusters have better catalytic activity and selectivity than the nano-scale particles. Theoretically, the ultimate state of scattered supported metal catalysts is that the metal stands in the form of a single-atom being uniformly distributed on the support. It also brings catalytic science into a smaller scale — the monoatomic catalyst [1]. With the decrease of the metal particles, more metal atoms appear on the supports surface. Strong metallic support, interaction and quantum size effects can increase the activity of these atoms in the reaction [2]. For high load metal catalysts, only in a single-atom in the process of catalytic active site connection, other ligand catalytic efficiency is highest, and the larger the metal clusters cannot play a catalytic role, so single-atom catalysis can effectively reduce the cost and maximize the use of single-atom catalytic activity.

TWC is the most important external purification device which is installed in the automobile exhaust system because it can purify three harmful gases nitrogen oxygen compounds and carbon dioxide, nitrogen and hydrogen compounds, so it is named TWC. The TWC is generally composed of shell, damping layer, support and catalyst coating. The main redox reaction occurs in the TWC. When the noble metal catalyst oxidizes or reduces the harmful gas emitted from automobile exhaust under high temperature and sufficient oxygen, it is finally released into the non-toxic and harmless atmosphere. The noble metal catalyst includes platinum, palladium, and rhodium. The noble metal is used as a catalyst coating on the honeycomb alumina support for catalysis. In today's TWC, the efficient catalytic temperature is about 200 degrees Celsius. At low temperature, the catalytic activity of the catalyst is low, and the strong adsorption of CO and HC will make the catalytic layer covered by carbon in the tail gas, and oxygen can no longer contact the catalytic layer, resulting in poisoning. In addition, the content of precious metals on the surface of the support is low, and the catalyst is sintered at a high temperature, and the surface distribution is not uniform. When the noble metal particles decrease, the monatomic catalyst can reduce the use of noble metal and improve the catalytic efficiency [3]. This article will describe how to prepare monatomic catalyst and how to use monatomic catalyst in TWC, and explain the mechanism of catalysis. Future developments and challenges in the field will also be explained.

2. Preparation for SAC

There are a variety of preparation methods for monatomic catalysts. The following four most practical methods will be introduced in this paper.

2.1. Ostwald method

In the later stage of the precipitation phase precipitated by a supersaturated solid solution, the size of the precipitated phase particles is not the same. As the smaller particles dissolve and the larger particles continue to grow, the average size of particles increases. Such a growth mechanism is called Ostwald maturation. The driving force of Ostwald maturation is interfacial energy. With the dissolving of small particles and growing of larger particles the interfacial energy for each unit way decrease, which loads to the reduction of total free energy. The Ag-HMO monatomic catalyst was prepared by the research group of Fudan University, and the single-atom Ag was utilized as the catalytically active center to realize the efficient catalytic oxidation of formaldehyde and the purpose of eliminating the formaldehyde which is harmful gas for environment. In this work, the loaded nanoparticles were automatically dispersed into single-atoms on a special support after programmed heating [4].

2.2. Impregnation

The impregnation method is to put the support into the liquid or gas containing active substances impregnation, active substances gradually would on the surface of the support, when the impregnation balance, the remaining liquid is removed, and then drying, roasting, activation and so on can be prepared catalyst. The impregnation method usually includes support pretreatment, impregnation solution preparation, removal of excess liquid, drying, roasting, activation and other processes. The impregnation method is suitable for the preparation of rare precious metal catalysts, catalysts with low content of active components, and catalysts requiring mechanical strength. The Impregnation method is due to the solid pore and liquid contact, due to the action of surface tension and capillary pressure, so that the liquid penetrated into the capillary interior; The active component diffuses in the pore and adsorbs on the surface of the support [5, 6].

2.3. Co-Precipitation

Co-precipitation is a mature and widely used method for preparing nano-scale metal catalysts. On the basis of previous research on catalysts with high dispersion, Zhang Tao's group first prepared monatomic catalyst f="">Pt/FeOx and Ir/FeOxby co-precipitation method. The specific steps are as follows: first, the metal precursor (chloroplatinic acid and chloroiridium acid) in aqueous solution and ferric nitrate solution are mixed and titrated in a certain concentration under alkaline environment with stirring. The precipitation was with processing filtering, washing, and roasting. Finally, the Pt/FeOx and Ir/FeOx monatomic catalysts are gain [1, 7].

2.4. *Atomic layer epitaxy method*

In Atomic layer deposition (ALD) method, the support material is exposed to the pulse vapor consisting of various reaction precursors and the material is deposited on the surface of supports in a self-limiting manner to form atom layer. ALD was originally proposed by Finnish scientists and was used in polycrystalline fluorescence materials ZnS: Mn and amorphous Al_2O_3. The preparation of insulating film has been successfully used in the preparation of metal monoatomic catalysts on the surface of stone dilute and other supports. The advantages of ALD lie in the precise and controllable deposition parameters, good deposition uniformity, and repeatability, which can accurately control the growth of different materials in the way of atomic layers to form complexes with different morphologies. Its disadvantage lies in the stability and cost problems. At present, this technology will not be used for the preparation of industrial monatomic catalysts [8].

3. TWC catalysis CO

3.1. *Four main catalytic mechanisms*

At present, there are mainly four catalytic mechanisms in the field of catalysis, including the Langmuir-Hinshelwood (L-H) mechanism, the Eley-Rideal (E-R) mechanism, the Mars-van Krevelen (MvK) mechanism, and the tri-molecular Eley-Rideal (TER) mechanism. When CO is oxidized, different SAC loads will choose different reaction pathways on different supports, and the content of external oxygen and the storage of active lattice in the support also play a critical role.

3.1.1. L-H mechanism. In L-H mechanism CO and oxygen are usually adsorbed together on the same active site, then CO and SAC would form covalent bonds, the same active site forms the intermediate OCOO in an oxygen rich environment, the intermediate decomposes into CO_2 molecules and atoms, O-O atoms and other remaining CO bonds, forming CO_2 molecular separation, which is repeated throughout the reaction process. The rate determining step in the reaction is usually the formation of the intermediate.

3.1.2. E-R mechanism. The E-R mechanism shows that external oxygen adsorbs to a single active site, followed by the proximity of CO molecules. CO_2 is formed by the decomposition of other ligand CO_3 intermediates, or by oxygen molecules breaking bonds with O atoms and CO molecules. The rate determining step in the reaction may be the bonding of CO with oxygen. The ER reaction mechanism and LH adaptation are in most reactions. However, both pathways have a large energy barrier [9].

3.1.3. MvK mechanism. The Mvk mechanism usually needs to be carried out in the presence of sufficient oxygen. CO reacts with lattice oxygen existing in the support to form oxygen vacancies on the surface of the support, which are supplemented by external oxygen and oxidize another CO molecule. rate determining step in the reaction is the second activation or catalysis of CO by oxygen. The reaction usually occurs on SAC supported by the CeO_2, because the CeO_2 can store a large amount of oxygen and can provide sufficient reactive oxygen species lattice during the reaction. This mechanism, due to the participation of the oxygen lattice inside the support, has a higher oxygen content and usually has a faster reaction rate than ER and LH [9].

3.1.4. TER mechanism. The TER mechanism usually refers to the oxidation of oxygen molecules with two CO molecules through the intermediate OCOOCO, which is formed by the bond breaking of the

OCO intermediate. The final step of this mechanism is usually the bond breaking of the OCOOCO intermediate to generate CO_2. Compared with the previous three reaction mechanisms, the TER mechanism has the lowest energy barrier [9].

3.2. TWC catalysis CO

The catalyst coating of TWC includes platinum, palladium, rhodium, and three precious metals, which are also the most involved in the reaction when catalyzing the conversion of harmful substances. Therefore, this section will introduce how the three noble metals SAC react, respectively.

When CO oxidizes in Pt SAC, it has high requirements on the environment around Pt and the electron density around Pt. At the same time, when CO oxidation occurs, the MVK mechanism is more likely to occur when the reaction occurs under an oxygen-rich condition. Firstly, CO is adsorbed on the surface of Pt SAC, CO is combined with the surface lattice oxygen and oxidized to CO_2. At the same time, the surface of the catalyst produces oxygen holes and is reduced. The catalyst is oxidized by the dissociated and adsorbed oxygen to fill the oxygen vacancies [3]. This mechanism assumes that when the reactant molecules react with the oxygen-rich part of the catalyst, this part can be alternately reduced and oxidized, where the oxygen in the catalyst can be either chemisorbed oxygen or lattice oxygen. This mechanism assumes that when the reactant molecules react with the oxygen-rich part of the catalyst, this part can be alternately reduced and oxidized, where the oxygen in the catalyst can be either chemisorbed oxygen or lattice oxygen [3]. The calculation shows that if the reaction is to proceed according to the MvK mechanism, it needs to overcome a higher energy barrier than that of the LH mechanism, because up to 2.76eV energy is required when the oxygen vacancy is formed. At present, there are two ways to effectively reduce the energy barrier(as shown in Figure 1). One way is to reduce the energy level required by Pt SAC by adding a compound agent. For example, the doped oxygen storage agent ceria can effectively reduce the vacancy formation energy, and the other way is to increase the surface density of the carboxyl group or oxygen lattice. Thus, a better choice of MvK path for oxidation [3].

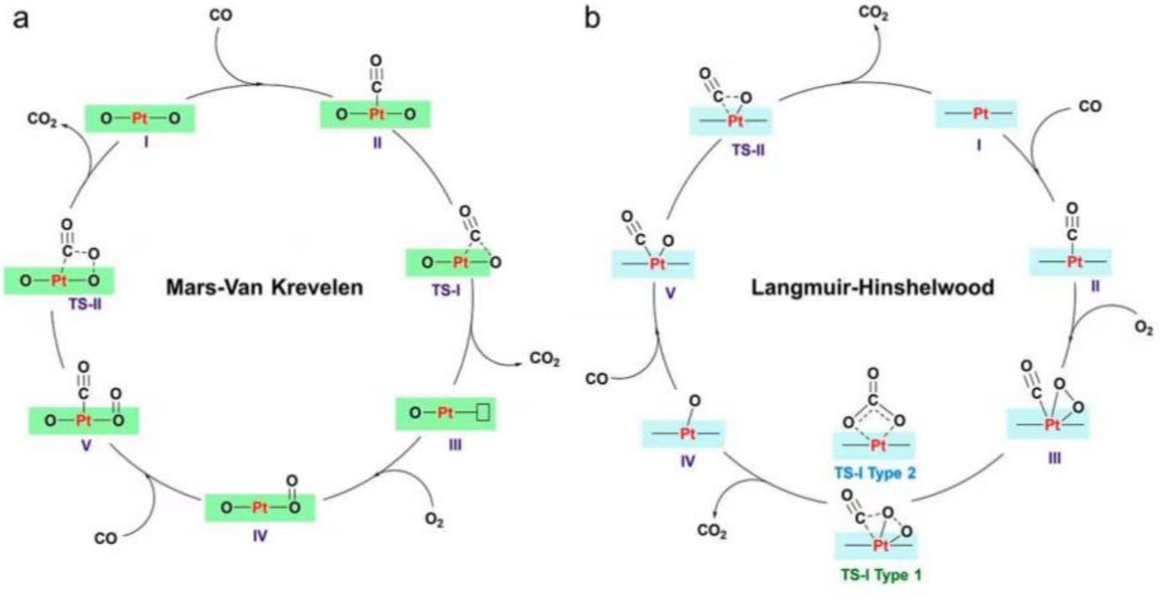

Figure 1. Typical reaction pathways of Pt SACs via the MvK (a) or the LH (b) mechanism [3].

Rhodium is also a common catalyst for CO purification. However, rhodium is highly dependent on particle size, and relatively small particles have relatively high activity, so the catalytic efficiency of CO is better. Therefore, rhodium SAC has a great improvement in the catalytic efficiency of TWC, especially at low temperature. The catalytic efficiency is up to 97%. Through calculation, the mechanism of rhodium oxidation of CO can be determined as MvK. CO reacts with lattice oxygen on the support to generate a CO_2, which also generates an O vacancy, and the O vacancy is filled by foreign oxygen. Based on Density functional theory, it can also be found that rhodium loading on aluminum oxide is more likely to cause LH oxidation, and the most important factor is CO partial pressure. At higher CO partial pressures, the reaction is initiated by the adsorption of two CO and one O_2 on an Rh single-atom. At low CO partial pressure, the reaction starts with the co-adsorption of 1 CO and 1 O_2. This indicates that the response pathway of Rh SACs is dynamic and depends on different environments [3]. (as shown in Figure 2)

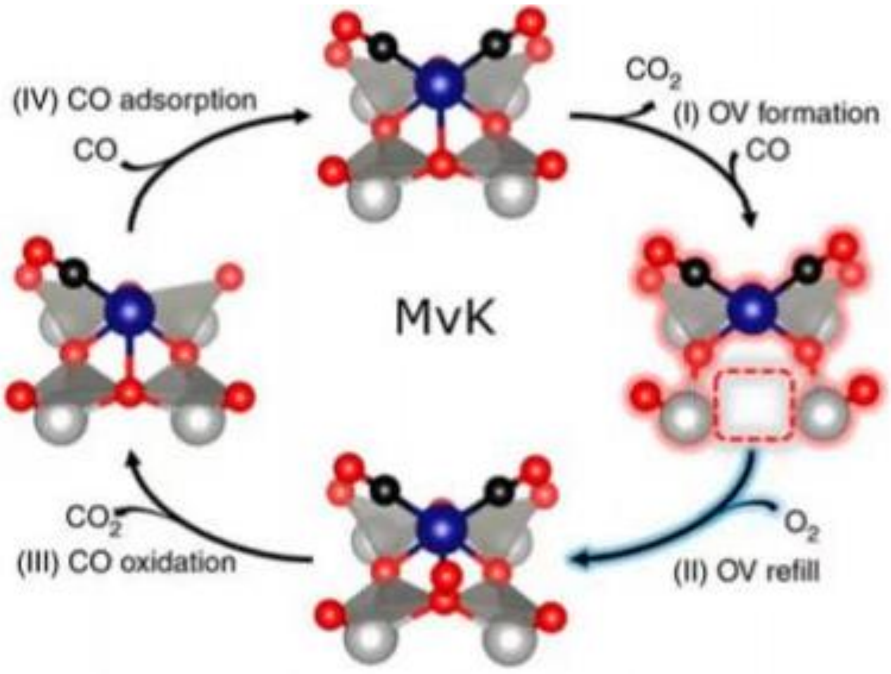

Figure 2. Rh1/NPTA. Adapted with permission from ref [10].

Palladium is also a metal in TWC. However, the current research on the oxidation of CO by palladium SAC is only in the basic stage. Most of the current research is to design Pd SAC to load on different support, and the mechanism of Pd oxidation of CO has not been determined. Different support have different effects on CO oxidation. At present, the best research effect is Pd SAC supported on TiO_2 for reaction, which has a good effect [3].

4. Conclusion

CO emissions are still a problem to solve at present. The traditional TWC is relatively perfect, but there are still some problems. For example, in the phenomenon of catalyst sintering and poisoning, low temperature catalytic efficiency is insufficient, precious metal cost is high. However, as the current leading catalytic technology, the application of single-atom catalyst in TWC can solve the existing problems to a certain extent. SAC using single-atom as the active site can greatly reduce the use of precious metal catalyst, and effectively alleviate the expensive price of precious metal and the environmental problems brought by it. Single-atom catalyst instead of traditional catalyst coating, low temperature catalysis, catalyst sintering and catalytic efficiency have been greatly improved in the experiment. At the same time, TWC support is also an important factor affecting catalysis. Titanium dioxide support is a popular choice of the support due to its high stability and non-toxic characteristics. Compared with metal oxide support, titanium dioxide has relatively weak mechanical strength, so as a dopant of metal support, titanium dioxide may be a better choice. Although the unit by catalyst in TWC has a good effect on CO oxidation and other aspects, due to its high manufacturing difficulty and preparation cost, it still needs some time in practical application. If the preparation difficulty and price of monoatomic catalyst can be reduced, it can be expected in the future. Due to the shortage of experimental equipment, most of the experimental data are from secondary literature research. Future research will be carried out to improve the existing TWC.

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