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The Excellent Characteristics and Application Prospects of Single Atom Catalysts

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Abstract

Single-atom catalyst is a popular direction in the field of catalyst research at present. Due to its good dispersibility, it can ensure that every point is atomic, so it can ensure the unity of the surface properties of the catalyst, and the contact area is large, so it has It has good development and application prospects and is currently widely used in the research and development of catalysts in many fields. In this paper, the purpose of research and development of Single-atom catalysts is analyzed, and its characteristics are deeply analyzed. The advantages of Single-atom catalysts are then summarized. Through the comparison of common catalysts, the advantages of high selectivity, low dosage, low cost and large active center are reflected. And enumerate its wide application in industrial production. Through the application of Single-atom catalysts for low-temperature denitration, Single-atom catalysts for ammonia desulfurization, Single-atom catalysts for industrial conversion of VOCs, and industrial decarbonization catalysts, the good performance and development prospects of Single-atom catalysts are further reflected. Finally, the prospect of Single-atom catalyst development is prospected, and its development direction is proposed.

Keywords

Single-atom Catalyst; Active Center; Low Temperature Denitration; Desulfurization; Decarbonization; VOCs Removal.

1. Introduction

Single-atom catalysis was jointly proposed by Professor Zhang, Li and Liu in 2011. Due to its excellent catalyst properties, it has become a very popular frontier field of catalysis. Single-atom catalysts are based on the structure of supported catalysts. The metal nanoparticles on the supported catalyst are further dispersed, so that the metal is loaded on the carrier in the form of a single atom, thereby forming a Single-atom catalyst.

Single-atom catalysts do not mean that a single zero-valent metal atom is the active center, and the single atom also has coordination effects such as electron transfer with other atoms of the carrier, often showing a certain charge. The synergistic effect is also the main reason for the high activity of the catalyst. Since there are atoms on each site of the Single-atom catalyst, compared with nanoparticles of different particle sizes in the supported catalyst, this Single-atom catalyst can ensure that the surface properties of the catalyst are uniform and uniform, and the dispersibility is good. It has the advantages of large surface area and so on, so it has more excellent catalytic performance [2].

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2. Research and Development Purposes and Characteristics of Single-atom Catalysts

At present, in the field of industrial catalysis, nano-catalysts have been widely used, but due to the scarcity and high prices of precious metals such as Pt, Pd, Au, Rh, etc., the preparation cost of the catalyst is seriously increased, and the industrial production cost is seriously increased. Therefore, reducing the loading of precious metals to reduce the cost of catalysts and improve the activity, selectivity and stability of metal nanoparticles has become the research direction of catalysts.

The main performance of reducing the metal loading is to reduce the particle size, which can greatly reduce the amount of metal used as a whole. Specifically, its intrinsic behavior can be adjusted to improve the catalytic efficiency in the following aspects: surface effect , in which the metal nanoparticles Increased unsaturated coordination bonds; quantum size effects, where electron confinement leads to increased energy levels and frontier orbital gaps; metal-support interactions, where enhanced chemical bonds between metals and supports make charge transfer easier; clusters Local environment, where the number and spatial location of atoms can drastically change their physicochemical properties. Small metal nanoparticles or clusters usually show complex reaction characteristics due to size effects.

A Single-atom catalyst composed of a single metal atom and a support is characterized by the maximum atomic utilization rate and a defined active center. These Single-atom catalytic sites are anchored on the solid support in a coordinately bonded manner. The atomic utilization of isolated metal sites is close to 100%, which is a great advantage, especially for noble metal-based catalysts. In addition to the greatly improved atomic efficiency, another important feature of Single-atom catalysts is that the metal centers are spatially isolated on the support, and the support has a huge impact on the overall catalytic performance.

Single-atom catalysts have isolated metal atoms as active sites, anchored by coordination sites on the surrounding solid support. There is a strong interaction or considerable charge transfer between the Single-atom metal and the support, and a single kind of metal atom and the support cooperate to prevent the atomic diffusion of a single metal atom from agglomerating into particles, which makes the Single-atom catalyst solve the problem of nano catalysts. The cluster effect increases the catalytic reaction area, and at the same time, the catalyst has good selectivity, and the size of the metal particles will not be affected by the aggregation of metal particles, so that the catalytic products are different. For example, in the process of direct non-oxidative conversion of methane into ethylene and aromatics, Single-atom catalysts can largely inhibit the formation of coke, thereby making the product single and improving the production efficiency. At the same time, it is highly resistant to the harmful side reactions that polymetallic sites usually suffer from. The electronic structure and energy level orbits of Single-atom catalysts are different from those of traditional metal nanoparticles. Such materials can maximize the efficiency of metal dispersion and atom utilization, and are the most promising materials for rational utilization of metal resources and atomic economy [3].

Due to their unique structural properties and fully exposed active sites, Single-atom catalysts exhibit significantly enhanced catalytic activity and enhanced resistance to poisoning in various reactions compared with nano catalysts. Like homogeneous catalysts, Single-atom catalysts have highly uniform active sites and geometric configurations, which enable them to have similar electronic structures and steric interactions with substrate molecules, thereby improving catalytic selectivity while making catalytic products single, Improve productivity. Furthermore, the spatial separation of metal active sites can effectively suppress unwanted side reactions that occur on multimetallic sites. Reduce catalyst poisoning.

3. The Advantages of Single-atom Catalysts

3.1. High Selectivity

After the metal atoms are alloyed, the coordination atoms change the electronic structure of the active center atoms, both of which reduce the adsorption capacity of the metal atoms to other substances and improve the selectivity. At the same time, the Single-atom catalyst has good dispersibility, and there are atoms on each site, so that the surface structure of the catalyst is uniform, avoiding the change of the physical and chemical properties of the nano-type catalyst due to the different size and structure of the metal particles on the surface, which reduces the catalytic efficiency. The selectivity of the catalyst is greatly improved.

3.2. Less Dosage and Low Cost

It has high dispersibility on the carrier and exists in the form of a single atom. While ensuring the maximum contact area, the amount of metal used is greatly reduced, and the loading amount is extremely small. Therefore, the demand for the amount of active material is reduced, especially the amount of precious metals is greatly reduced, saving the cost of using the catalyst.

3.3. Maximize the Active Center

The study found that the contact interface between the metal atoms and the support is the active center of the catalytic reaction of the catalyst. Therefore, the close cooperation between the interface atoms and the support can greatly improve the performance of the catalyst. The Single-atom catalyst can maximize the contact surface between the metal atom and the carrier, thereby maximizing the active center, and greatly improving the catalytic effect of this catalyst.

3.4. Large Surface Free Energy

The smaller the crystal surface area, the sharply increased surface free energy. The catalyst has a strong tendency to reduce its own energy, so it is very active and has a high reaction activity, so that the Single-atom catalyst has a higher catalytic rate and better catalytic effect[4].

4. Application of Single-atom Catalysts in Industrial Flue Gas Treatment

In recent years, with the rapid development of my country's industry, environmental problems have become increasingly serious and have attracted widespread attention. To this end, China actively promotes the strategy of green, healthy and sustainable development, and accurately implements the Ten Measures for Atmosphere, Ten Measures for Water, and Ten Measures for Soil proposed in the “13th Five-Year Plan”. Toxic and harmful substances such as sulfides, nitrogen oxides and VOCs in air pollutants lead to the occurrence of environmental pollution and cause harm to the environment and human health. Therefore, the effective control of air pollutant emissions is imminent. In the process of exhaust gas treatment, the selection and use of catalysts determine the efficiency and effect of exhaust gas treatment and play a crucial role. At present, the precious metal nano-catalysts commonly used in exhaust gas treatment have problems such as small contact area, high metal usage, and increased catalyst usage cost. The research and development of Single-atom catalysts based on supported catalysts solves this problem. The following will introduce the currently developed Single-atom catalysts and their advantages from three aspects: sulfur dioxide, nitrogen oxides and VOCs.

4.1. Industrial Flue Gas Low Temperature Denitration Catalyst

NO_x is one of the important factors for the formation of haze and acid rain and photochemical smog. The sources of NO_x can be divided into fixed sources and mobile sources, and the common NO_x are mainly NO, NO_2 and nitric acid mist, among which NO_2 is the most common. As an emerging selective catalytic oxidation denitration technology (SCR), its advantages lie in higher flue gas purification efficiency and safer and more reliable performance, so it has become the main research direction of current denitration technology.

Denitrification catalyst generally refers to the catalyst used in the SCR denitration system of the power plant. In the SCR reaction, it promotes the chemical reaction between the reducing agent and the nitrogen oxides in the flue gas at a certain temperature. At present, SCR commercial catalysts basically use TiO_2 as the carrier, V_2O_5 as the main active component, and WO_3 and MoO_3 as the anti-oxidation and anti-poisoning auxiliary components. High (300-400°C) and V-based catalyst toxicity issues, and due to the use of nano-supported catalysts, metal oxides are prone to clusters on them, so that metal oxide particles of different shapes and sizes can interact with each other. After the support is combined, different physical and chemical properties are formed, and the catalyst selectivity is not single, resulting in complex reaction products, which cannot be recovered and utilized in the next step.

Aiming at the problems existing in this kind of nano metal oxide particle catalyst, a new type of Single-atom catalyst has been developed. The denitration catalyst is a Single-atom Ir denitration catalyst based on TiO mesogen, which also uses A good, supported type of Ti, the carrier of the catalyst is mesogenic TiO -MC, the active component is Single-atom Ir metal, and the noble metal Ir is dispersed into single atoms, thereby greatly reducing the amount of noble metal and reducing production costs. Due to the larger contact area and larger surface free energy of single atoms, the catalyst can complete the catalytic process at lower temperature and lower energy consumption. The catalyst exhibits good performance at 180-300 °C. Low temperature denitration activity, and the preparation method is mild, safe and environmentally friendly. Compared with the nano metal oxide catalysts used in current applications, it has lower reaction temperature, lower reaction energy consumption, higher catalytic efficiency, and in the catalytic process, the catalyst will not be SO_2 and H_2O appear poisoning, can keep high catalytic effect all the time, and are suitable for continuous use of catalyst in industrial production [5].

4.2. Industrial Flue Gas Ammonia Desulfurization Catalyst

Thermal power generation is the main force in the development of electricity in modern society. Coal is widely used in thermal power generation and plays a pivotal role in China's energy structure. However, the large amount of SO_2 emissions brought about by coal burning seriously pollutes the environment. In the context of building a harmonious society and developing a circular economy, we put more attention on environmental protection and strictly limit the sulfur content of coal. China's coal consumption structure is dominated by coal, among which electricity and industrial coal consumption dominate.

Wet flue gas desulfurization is one of the large-scale commercial desulfurization methods in the world. Due to its mature technology and stable operation, most of my country's thermal power desulfurization processes are wet flue gas desulfurization. However, with the completion of ultra-low emission transformation, the energy consumption of system operation is very high, and with the improvement of national pollutant emission standards, the requirements for desulfurization efficiency are getting higher and higher. The existing wet desulfurization technology mostly adopts the limestone gypsum method, which has a single method of resource recovery, which will lead to the rapid depletion of limestone resources , and the low-grade gypsum produced is difficult to be absorbed by the market to form new solid waste; in addition, It occupies a large area, the pipeline is easy to scale and wear, and the investment and maintenance costs are high, which is difficult to be burdened by enterprises. Therefore, the development of new flue gas desulfurization technology suitable for industrial coal-fired boilers is a major technical demand in my country. As a new type of ammonia flue gas desulfurization technology, it has strong reaction power , liquid-gas reaction, large contact area and high desulfurization efficiency; strong adaptability to flue gas conditions , which can achieve large fluctuations in gas volume and concentration ; stable source of desulfurization agent For enterprises with synthetic ammonia and coking gas production, waste can be treated with waste; desulfurization by-products have a large application market, high added value, mature technology, reliable operation, and low operating costs; no secondary pollution; low investment , no need to set up waste water and waste residue The treatment and disposal unit is used to treat the flue gas in a straight row at the top of the tower, and there is no need to set up a separate wet chimney or concrete anti-corrosion treatment . Therefore, the ammonia-based flue gas desulfurization technology has become the main research direction of the current major desulfurization technology.

However, the current homogeneous catalytic oxidation process mostly uses transition metal ions as catalysts . accelerates the oxidation process by starting a free radical chain reaction. Although it has a good catalytic effect, it is difficult to separate the ionic catalyst from the desulfurization slurry after the reaction. The secondary recovery of the catalyst is difficult, and the catalyst needs to be continuously replenished, which greatly increases the usage of the catalyst, increases the treatment cost, and causes secondary pollution of heavy metals in the by-products of desulfurization and effluent. Recycling cannot be carried out, resulting in waste of resources. These reasons lead to the high operating cost of ammonia-based flue gas desulfurization technology, which has become the bottleneck of this technology and is difficult to practically apply.

Therefore, it is currently planned to develop a series of recyclable solid-phase catalysts with high stability and high metal dispersion to achieve efficient catalytic oxidation of ammonium sulfite and recovery of ammonium sulfate resources. And in the process, the toxic elements such as selenium and arsenic in the flue gas are adsorbed to achieve synergistic removal. Therefore, in view of the shortcomings of traditional metal ion catalysts, a new type of Single-atom catalyst is being developed, which can well solve the problems of metal ion catalysts. This catalyst uses MET - 6 as a carrier and supports Co single atoms on it as an active component, reducing the size of Co metal particles, which can greatly reduce the use cost of this catalyst, and at the same time, Single-atom catalysts can make the active center better in combination with the reactants, the reaction area can be greatly increased. At the same time, the high free energy of the Single-atom catalyst makes this reaction do not require high temperature excitation, and can occur at 45 degrees Celsius, reducing the energy consumption of the reaction. In the product ammonium sulfate, since this Single-atom catalyst is a solid phase, it can be well separated to ensure the purity of ammonium sulfate, and at the same time, the catalyst can be reused many times, breaking the homogeneous catalytic oxidation technology caused by ionic catalysts. Therefore, the operating cost of ammonia desulfurization technology is greatly reduced, and it is closer to actual production.

4.3. Catalyst for Removing VOCs by Catalytic Combustion of Industrial Flue Gas

Volatile Organic Compounds (VOCs) are a class of gaseous pollutants that widely exist in the atmosphere. Most of these organic compounds are associated with odor and toxicity, and some of them are carcinogenic. As a major manufacturing country, my country's VOCs emissions are among the largest. World number one. This harmful substance not only has a direct impact on human health and ecological environment, but also generates secondary pollutants by participating in atmospheric photochemical reactions. Therefore, controlling the emission of VOCs is of great significance for the sustainable development of society. At present, the mainstream treatment method for VOCs is catalytic combustion catalyst technology, which has the advantages of low light-off temperature, high treatment efficiency, and no secondary pollution. Therefore, it has become the current research direction of VOCs treatment.

Commonly used catalysts are divided into two categories: noble metal catalysts and non-precious metal catalysts, and non-precious metal catalysts are further divided into two categories: transition metals and rare earth metal composite oxides. Supported precious metal catalysts have the characteristics of high catalytic activity, good selectivity, long service life, and excellent anti-toxicity. However, precious metals are expensive, easy to be deactivated by sintering at high temperature, and easy to be poisoned, which limits their practical use. The raw materials used by transition metal oxides are low in price, and compared with supported noble metal catalysts, they have great advantages in cost of use, and their preparation methods are relatively simple, but their catalytic activity is relatively poor, and their anti-poisoning performance is poor. The composite metal oxide has good catalytic activity and is not easy to be poisoned, and the raw materials required for preparation are rich in resources. The disadvantage is that the ignition temperature is high, the energy consumption is large, and the preparation is difficult [6].

Therefore, in response to these problems, a new type of Single-atom catalyst has been developed. The catalyst uses ferric oxide as a carrier and can support two or more precious metal single atoms including platinum. This catalyst can reduce the particle size of the supported precious metal to a single atom, which can make full use of the good catalytic effect of the precious metal, so that every atom can participate in the reaction, has good dispersibility, and significantly improves the utilization efficiency of precious metals. The contact area between the active center of the catalyst and the reactant has a better catalytic oxidation effect, which improves the catalytic performance of the supported precious metal catalyst, and greatly reduces the amount of precious metal used and reduces the cost. This kind of catalyst also reflects the good anti-toxicity of the Single-atom catalyst, which shows that the Single-atom catalyst can continuously exert the catalytic oxidation effect for a longer time than the supported catalyst, reduce the risk of catalyst poisoning, and make the catalytic oxidation effect better.

4.4. Catalyst for Catalytic Decarbonization of Industrial Flue Gas

CO_2 is an integral part of the earth's atmosphere and an essential raw material for plant photosynthesis. In the current ecological research, CO_2 has not been classified as an atmospheric pollutant, but the greenhouse effect caused by the high concentration of CO_2 has brought unprecedented challenges to human beings. Due to the thermal insulation effect of CO_2, the global temperature has risen rapidly. In the past 100 years, the global temperature has increased by 0.6 degrees Celsius on average. The increase in temperature has caused the melting of glaciers, and even raised the global sea level, threatening the life of human beings and living things on the earth. Survive. Therefore, General Secretary Xi Jinping made a solemn promise to the world in 2021 that China will achieve carbon peaking in 2030 and carbon neutrality in 2060, which reflects China's sense of responsibility as a major country.

The traditional CO_2 catalyst uses Ni nano-metal oxide material. Although this catalyst has a certain catalytic effect on CO_2, it is difficult to be put into large-scale production due to the large amount of precious metal used, which makes the catalyst cost too high. At the same time, because the catalyst adopts a nano-supported structure, the nanoparticles on it are prone to cluster phenomenon, resulting in a small contact area between the catalyst and the reactant. At the same time, due to the different size structure and exposed atoms of the cluster particles, the chemical and physical properties of the cluster particles are different. The surface properties of the catalyst are not uniform, and the non-uniform product acquisition is not conducive to the high-value resource recycling of the product.

At present, in the catalytic reduction of CO_2, a nickel Single-atom catalyst has been developed, and the low-valent Ni Single-atom was successfully anchored on the N-doped graphene substrate. The prepared catalyst has high activity and stability and is a stable and efficient electrocatalyst for CO_2 reduction. Compared with Ni nanoparticles, Ni Single-atom catalysts can selectively reduce CO_2 with excellent current density, and the Faradaic efficiency of CO generation exceeds 71.9%. This catalyst uses Ni single atoms and has good dispersibility, so the catalyst surface has a single structure and can selectively reduce CO_2. higher. At the same time, the high free energy of the Single-atom surface reduces the temperature of the catalyst reaction, which is beneficial to the selective catalytic reduction at low temperature. In addition, the Single-atom catalyst reduces the usage of precious metals and production costs, which is conducive to the production of this technology, and helps carbon peaking and carbon neutralization [7].

5. Conclusion

By comparing the Single-atom catalyst and the metal particle-supported catalyst, we can see that the single atom can have better selectivity, and the size and shape of the active components are uniform, which makes the surface properties of the catalyst single, and the product type is single, which is convenient for follow-up. processing and utilization. Compared with the large metal particles used in the supported catalyst as the active component, the Single-atom catalyst has good dispersibility, reduces the amount of metal, and greatly reduces the cost of catalyst use. At the same time, the Single-atom catalyst has a larger contact area between the carrier and the metal atom, and thus has a larger active center, thereby having a better catalytic effect and a faster catalytic rate. At the same time, due to the small crystal surface area, the free energy of the crystal surface increases sharply, so this catalyst does not require a high reaction temperature to activate the catalyst, thereby reducing the reaction energy consumption and production and processing costs. In summary, the good catalytic effect and low production cost of Single-atom catalysts make it a new trend in catalyst research and development. The catalytic effect and low cost are expected to be put into production and use in various fields. In the next stage, different kinds of Single-atom catalysts should be modified according to different production environments, adding auxiliary components, and adjusting the external conditions such as suitable pH, so that the catalytic effect can be further improved. At present, Single-atom catalysts are mainly in the laboratory research stage, the reaction conditions are relatively harsh, and the preparation amount is correspondingly small. Therefore, the realization of low-cost industrial preparation of highly active Single-atom catalysts is still the focus of breakthroughs in this field.

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