



ORIGINAL RESEARCH ARTICLE

Application of Nanotechnology in Post-treatment of Automobile Tail Gas Nitrogen Oxides

Yansheng Xie, Jianyong Tan, Miaoliang Hu

School of Environment and Municipal Engineering, Tianjin Jiaotong University, Tianjin, China

ABSTRACT

Nano-catalyst has a very high catalytic activity and has a good prospect in automobile exhaust gas purification. This paper summarizes the research status of nano-scale automobile exhaust gas purification catalytic materials in recent years, focusing on the analysis of the structure and performance of several components in the tail gas catalyst after nano-scale, and discusses its existing problems and application trends.

KEYWORDS: Nano-catalyst; catalytic activity; automobile exhaust purification; nitrogen oxides

Citation: Yansheng Xie, *et al.* Application of Nanotechnology in Post-treatment of Automobile Tail Gas Nitrogen Oxides. (2017); 1(1): 26–29.

*Correspondence to: Miaoliang Hu, School of Environment and Municipal Engineering, Tianjin Jiaotong University, Tianjin, China. humioliang@gmail.com

1. Overview

Nanometer (nm) is a length unit, one nanometer is equal to one billionth of a meter or one thousandth of a micrometer, that is, $1\text{nm} = 10^{-9}\text{m}$, the length of the nanometer is about three or four atoms in width, for macromolecules, Nano is a small unit. Internationally confirmed that when the particle size of the material below 100nm, this material can be called nano-materials. The technique of preparing and harnessing such small substances is nanotechnology.

Nano science and technology was born in the 20th century, 80 years, once the advent of nanotechnology, it quickly penetrated into various research areas. In recent years, nanotechnology has begun to be applied, the application of nanotechnology will not only lead to a revolution, promote social and economic development, and will have far-reaching impact on improving people's living standards play a positive role. Therefore, it is of great significance to study the application of nanotechnology in the purification of automobile exhaust.

In the field of catalysis, people have been looking for new and efficient catalysts, nanoparticles with its unique nature has been widely concerned. Nano-particles with high surface energy, high surface binding energy and high chemical activity, as a catalyst material can be significant, the surface area of the nanoparticles is small, the surface atoms are high and extremely unstable and are easily combined with other atoms. Improve its adsorption and catalytic performance. At present, the international nano-catalyst has been the fourth generation of catalyst for research and development.

Automobile exhaust emissions caused serious environmental pollution in today's social pollution and purification of pollution caused by the government and the public attaches great importance to the current reduction of vehicle exhaust pollution is an effective means to use three catalytic converters to promote harmful substances in the exhaust CO, HC and NO_x conversion. The three-way catalyst prepared with nano-grade components has attracted much attention in recent years because of its small particle size, uniform dispersion and high dispersibility, and can produce excellent exhaust gas purification and catalytic effect. The purpose of this paper is to summarize the research progress of nanocatalyst used in the field of automobile exhaust gas purification and to make a prospect for future research.

2. Nano-scale metal and metal oxides

2.1. Nanoscale precious metals

Precious metals Pt, Pd and Rh are often used as active ingredients in automotive tail gas catalysts. Because of the high activity of the noble metal catalyst, the good selectivity, thermal stability and mechanical strength of the catalyst, it has an absolute advantage in the catalyst market. However, the noble metal catalyst is affected by the air-fuel ratio and is prone to Pb, S, P and so on. Poisoning, high temperature performance is not ideal. And precious metals are expensive,

so it is an inevitable trend to find some or all of the alternatives to precious metals for new catalytic materials. It was found that the lower the temperature, the higher the catalytic activity, the smaller the particle size, the higher the activity, the catalytic activity and the noble metal particle size was linear. With the increase in the catalytic activity of the noble metal particles, it is important to suppress the growth of the noble metal. In order to ensure the nanoscale size of the noble metal, it is necessary to disperse it on the alumina carrier and add the rare earth and add Pt and other precious metals such as Rh, Ir, Ru and so on to enhance the stability of Al₂O₃. It is found that the noble metal particles are distributed in the alumina by means of transmission electron microscopy, and the catalyst is highly active because of the distribution of the nanoparticles in the nanoparticles. As long as the noble metal is kept at the nanometer level, the car travels 16 km after still have a higher performance.

However, the particle size of the nanoparticles should be controlled properly, otherwise the best catalytic effect is not obtained. The results show that the optimum particle size of the catalyst is about 2-3 nm in the reaction of CO catalyst. However, for some nanocatalysts, when the particle size of nanoparticles is reduced to 10 nm, the increased surface area may be offset by the large surface remixing effect, so that excessive reduction of particle size may lead to its activity decreased.

2.2. Nanometer transition metal

After a large number of experiments show that Cu, Cr, Co, Ni, Mo and Mn and other transition metals on CO, HC oxidation activity. Cu can also promote the reduction of NO to NH₃, Ni can promote the decomposition of NH₃ into N₂ and H₂, precious metal Rh in the reduction of NO_x will produce a lot of N heart, so Ni is a promising catalyst containing Rh effective additives. However, when the base metal material is used as the main catalyst, the thermal stability is poor, the ignition temperature is high, and the life is short, so it has not been widely popularized and applied. At present, how to improve the heat resistance of these catalysts is the focus of the study.

In recent years, people have found that nano-metal particles made of the catalyst for vehicle exhaust purification to achieve a good catalytic effect. In 1998, General Motors' Donald Beck study found that the ability of nanocrystalline TiO₂ to remove hydrogen sulfide from simulated vehicle exhaust gas at 500 °C after 7 hours was about five times greater than that of conventional TiO₂, and after 7 hours of exposure Nano-TiO₂ still maintains a very high desulfurization rate, while other samples have become useless. It is necessary to disperse the nano-metal particles on the carrier because the nano-metal particle catalyst has a small size, high surface energy, and is more susceptible to heat sintering in the catalytic reaction, resulting in a decrease in catalytic activity. Ueno and so on with sol-gel method to the average particle size of 3 - 13 nm nickel nanopowders evenly dispersed in the Si convex porous matrix, the catalyst on the hydrogenation of organic matter and decomposition reaction has a catalytic effect, the particle size of 30 nm of nickel So that the hydrogenation and dehydrogenation reaction speed increased by 15 times. The catalytic activity of Cu and Cr is higher than that of industrial palladium catalyst. When the copper and chromium catalyze the reaction, the nanometric residues will become oxidized things.

2.3. Nanometer metal oxide

The phase in the alumina is widely used in the vehicle exhaust gas purification catalyst because of its large surface area, wide crystal phase temperature range and strong adsorption capacity. But the actual working temperature is often as high as 1000 °C, then Al₂O₃ surface sintering and a phase change will occur, which will cause the surface area drastically reduced, and lead to catalyst activity, so improve the thermal stability of alumina has practical significance. Naoto Mlyoshi et al. Found that metal ions with a radius of 0.11 - 0.15 nm can significantly improve the thermal stability of Al₂O₃ because this ion occupies the surface space of an Al₂O₃, which can effectively prevent the surface migration of Al³⁺ and O²⁻ Lattice structure. It has been shown that the addition of La₂O₃, CeO₂, MnO_x and other metal oxides to the vehicle exhaust catalyst carrier Al₂O₃ can be reduced from 80% to less than 20% after 3 hours of treatment at 1100 °C for conversion to α -Al₂O₃ large surface area facilitates the high dispersion of the active component of the catalyst. It has been found that the aluminum oxide is made into nano-scale, which can make its surface area large, pore volume, pore distribution and surface active center, can solve the catalyst high catalytic activity, high selectivity and high reactivity, is widely used in Vehicle exhaust purification, catalytic combustion, oil refining and other aspects of the catalyst or carrier. The use of physical dry loading can be most of the active components coated in the superfine alumina carrier surface and surface pores, the precious metals and additives have a strong surface adsorption capacity, high dispersion and good dispersion state, so Which is beneficial to prevent the growth and sintering of nanoparticles. The results show that the Ni-Al₂O₃ superfine catalyst prepared by sol-gel method has uniform particle size, large specific surface area, high dispersibility and good high temperature resistance. In the study of CH₄-CO₂ the reforming reaction is shown high temperature catalytic activity, selectivity and significant resistance to carbon capacity. The results show that the catalytic efficiency of NO catalyst with alumina based aerogels as catalyst is higher than that of traditional ceramic as catalyst. This is mainly due to the sol-gel method of nano-Al₂O₃-based aerogel as a catalyst with a very large specific surface area, is the ideal carrier for the catalyst.

In addition to alumina, there are nano-cerium oxide, nano-rare earth perovskite type composite oxide used in automobile exhaust treatment technology.

3. Application of nanotechnology in improving fuel performance

Car fuel in the process of burning will produce a large number of toxic, harmful gases, causing air pollution, destruction of ecological balance, damage to human health, it must be purified vehicle exhaust to reduce harmful gas emissions. The general way to purify the car exhaust is to change the oil quality to reduce fuel consumption and keep the fuel as complete as possible in the cylinder. By adding a small amount of chemical additives to change and improve the overall performance of the fuel is one of its methods. Common fuel additives are octane number enhancers, gasoline cleaners, metal deactivators, lubricating improvers, combustion fuels and the like.

The traditional liquid fuel combustion process is fuel through the nozzle after high pressure atomization, the fuel droplets in the combustion zone and the air mixed with the evaporation, and then fuel combustion products, heat work into mechanical energy. During the early stages of combustion, liquid nuclei are present, and the evaporation process and the combustion process occur simultaneously. During the combustion process, as the fuel evaporates, the droplets continue to shrink until they disappear, and the rate of combustion depends on the rate of diffusion of the fuel vapor. The nano-fuel additive is an additive that makes the diameter of the additive smaller. The use of nanotechnology to disperse the nanoparticles into the fuel, can form a stable suspension, so that water and other additives into the cylinder before the emulsion into tiny droplets. After adding the additive fuel through the nozzle into the combustion chamber, when the water droplets in the water droplets temperature is higher than the boiling point, it will quickly disguise, in the moment of one millionth of a second, the volume increased by 3 orders of magnitude, that Steam explosion (micro-explosion), so that the mist droplets second atomization, split into tiny or even nano-scale oil and gas particles, so that combustion more complete. When the micro-explosion in the coke layer of the surface and the gap occurred, you can eliminate coke, so that the combustion chamber to restore clean. This will not only improve the thermal efficiency, protect the equipment, but also reduce the maintenance costs. Gasoline added to the nano-fuel additives, due to the 'micro-explosion' effect greatly improve the fuel atomization and the uniformity of the mixture and the ignition effect, but also inhibit the phenomenon of automatic fire, reduce or eliminate the 'fast burning' and 'burning' The phenomenon of frequent occurrence, thereby reducing the exhaust emissions of pollution. Nano-emulsified fuel to solve the ordinary long-term placement of emulsified oil will appear stratification of this serious flaw.

4. Nano-technology on the car exhaust outside the machine purification

External purification refers to the process of converting CO, HC and nitrogen oxides into a harmless gas prior to exhausting the cylinder into the atmosphere using an engine outside purification reaction unit. The main methods used in the purification of the machine are the purification method, the catalytic combustion method and the three-way catalytic method. Among them, the three-way catalytic conversion technology is the most effective and the most widely used catalyst. The three-way catalyst is a catalyst that simultaneously catalyzes and controls CO, HC and NO_x in the exhaust gas. Automotive exhaust gas in the three-way catalytic converter on the chemical reaction can be divided into the following categories:

CO, HC oxidation: $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$

$\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$

$\text{HC} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

NO reaction: $\text{CO} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2$

$\text{HC} + \text{NO} \rightarrow \text{CO}_2 + \text{N}_2$

$\text{H} + \text{NO} \rightarrow \text{H}_2\text{O} + \text{N}_2$

Water vapor reforming reaction: $\text{HC} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$

Water gas conversion reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

At present, the world's automobile exhaust catalyst market is mainly a precious metal catalyst, which CO, HC and NO_x at the same time have a high catalytic conversion efficiency. Catalysts containing noble metals such as Pt, Pd and Rh as active ingredients have not only suitable hydrocarbon adsorption sites but also large amounts of oxygen adsorption sites. As the surface reaction progresses, oxygen activation and hydrocarbon adsorption can occur quickly. Nano-materials as a vehicle exhaust catalytic converter to reduce the amount of precious metals. Using nano-metal ultrafine particle load on the activated alumina molding, sintering as a vehicle exhaust purification catalyst. In the role of the catalyst, the first reaction of oxygen and nitric oxide to produce nitrogen oxide, and then nitrogen and hydrocarbons or carbon monoxide reaction, reduced to nitrogen. Due to the current lack of precious metals resources. The use of

cheap catalytic materials to replace precious metals for exhaust gas purification is of great importance. Nano-sized rare earth compounds instead of precious metals as a catalyst, nano-powder has a strong redox capacity, its application can completely solve the vehicle exhaust gas carbon monoxide and nitrogen oxides pollution problems. Nano-rare earth compounds with special catalytic properties. Rare earth element atomic structure is special, the inner layer 4f end of the end of the multi-pair of electrons, high atomic magnetic moment, the electronic energy level is extremely rich, than all the other elements of the periodic table electronic energy level transition number of 1-3 orders of magnitude; , Almost all elements can be used to play, easy to lose electrons to form a variety of valence, multi-coordination number (from 3 to 12) of the compound, which has a unique catalytic and nature, adding it to the catalytic component, will greatly improve Precious metal catalyst anti-toxic properties, high temperature stability, while reducing the amount of precious metals. Therefore, rare earth is an ideal vehicle after the gas purification catalyst or auxiliaries. And because the material made of nano-particles with surface and small size and other effects, so that material properties of mutations, resulting in other more excellent hope, so the rare earth materials made of nano-materials used in motor vehicle exhaust treatment will have other Material cannot match the effect.

5. Conclusions

The application of nanotechnology in the reduction of automobile exhaust pollution is mainly to change the performance of the engine, improve the nature of the fuel, the use of reasonable and effective catalyst in the post-treatment of tail gas. The application of nanotechnology can reduce the fuel consumption of the automobile and reduce the vehicle exhaust Environmental pollution, is conducive to protecting the green environment, the treatment of automobile exhaust and environmental protection made no small contribution.

The nano-scale exhaust gas purification catalyst and carrier made by nano-preparation technology, in essence, is a kind of material with special function, and great progress has been made in applied research. However, the preparation and design of nanomaterials have not yet matured. At present, the stability control technology of nano-catalyst has not yet been grasped, and the separation of nano-particles is difficult, which brings the practical application of nano-catalytic materials obstacle. Therefore, to strengthen the life of nano-materials, performance stability control and anti-agglomeration technology research, to further improve the industrial production of nano-catalyst equipment.

Because nano-alumina, nano-rare earth, nano-transition metals and nano-precious metals are the existence of nano-materials in the catalytic superiority, there is a lack of complementarity between them, so these components can be mixed in a certain proportion, and appropriate to add a small amount of other additives made of automotive exhaust gas purification catalyst. Systematically research and development of this nano-level vehicle exhaust gas purification catalyst has far-reaching significance. The emergence of a new catalyst and catalytic industry is often based on the research and development of new catalytic materials, and more nanomaterials will be used in the field of automobile exhaust treatment.

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