Study on Adsorption Reduction of NO\textsubscript{X} Emission in Lean Burn Gasoline Engine

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ABSTRACT: In order to solve the question that the emissions of NO\textsubscript{X} is so high which is leaded by lean burning, the traditional way of burning are introduced: three-way catalytic converter technology on gasoline engine, direct catalytic decomposition of NO\textsubscript{X} technology on industry and selective catalytic reduction of NO\textsubscript{X} technology on diesel engine. The problem is analyzed when they are used on the rarefied burning. On this basis, the technology of absorption reduction catalysis is discussed according to the basic mechanism of the catalysis. The active component, strong component and carrier of the agent of the adsorption reducing are improved and an efficient technological schemes to clean up the NO\textsubscript{X} is designed.

1 INTRODUCTION

The rarefied burning of the gasoline engine is the effective measure in order to reduce automobile exhaust pollution. Fuel can be saved 15% to 20% by using the engine. The content of CO, HC and CO\textsubscript{2} in the tail gas can be reduced substantially. Because of the existence of excessive oxygen, the reduction reaction of NO\textsubscript{X} is restrained which leads to the emission of the NO\textsubscript{X} increased relatively\cite{1,2}. This solution is one of the hot topics in current research on energy saving and emission reduction.

It is a very difficult researching work that exploit the equipment of the exhaust after treatment. The catalyst is poisoned easily, mainly because of highly oxygen, the temperature is low, plenty of SO\textsubscript{X} and particulates is in lean burning. The adsorption reduction catalytic technology whose purification effect is better than other was studied deeply when some after the treatment technology of NO\textsubscript{X} emission of lean burn gasoline engine is compared.

2 THE TRADITIONAL NO\textsubscript{X} AFTER TREATMENT TECHNOLOGY

The three way catalyst technology of gasoline engine, the direct catalytic decomposition of NO\textsubscript{X} technology in nitric acid industry and the selective catalytic reduction technology of NO\textsubscript{X} used in diesel engine are commonly used purification technology of NO\textsubscript{X}\cite{3}.

The excellent purification effect of three way catalytic converter technology can be realized only in theoretical air fuel ratio of gasoline engine. Because of the CO and HC should be the reducing agent during the reduction reaction of NO\textsubscript{X} in three way catalyst. The CO and HC react with O\textsubscript{2} firstly, which lead the reduction reaction of NO\textsubscript{X} can’t react effectively in the condition of lean burning. The emission of NO\textsubscript{X} reach the maximum\cite{4,5}, when the excess air coefficients is 1.1-1.2. So only use the three way catalyst technology to reduce the emissions of emissions of NO\textsubscript{X} of the gasoline engine who is in lean burning.

NO\textsubscript{X} is resolved into N\textsubscript{2} and O\textsubscript{2} in the direct catalytic decomposition of NO\textsubscript{X} technology. It has some benefits: without secondary pollution, don’t need reducing agent, economical, the process is simple and it can be implemented in thermodynamics. While the high activation energy is needed in this reaction, so the catalyst is used to reduce activation energy that is needed which is also the simplest purification program, in order to promote the reaction. Precious metal Pt or Pd is used as catalytic\cite{6,7} in the direct catalytic decomposition technique of NO\textsubscript{X}. NO\textsubscript{X} is adsorbed in the active site on the surface of precious metal then it is resolved into N and O firstly. Then it desorbs in the form of oxygen atom and nitrogen atom which makes the active site regenerate. But in practical, the oxygen is adsorbed on the surface of the catalyst easily that makes the catalyst loses its activity in the process of decomposition, which is the phenomenon of “oxygen inhibition”. The activity of Cu-ZSM-5 is the highest and the conversion rate of NO can be 90 percent. The direct decomposition catalyst is influenced by O\textsubscript{2}. The use of SO\textsubscript{2} and H\textsubscript{2}O in practice is hard to be found. The process of decomposition reaction is restrained for the...
desorption of oxygen atom is hard and the effect of catalytic decomposition is weakened. It’s hard to use the direct catalytic decomposition technique of NOX which is used on the engine.

The selective catalytic reduction technology of NOX is a method that N2 is produced by reducing agent react with NO firstly when the oxygen is surplus. The reducing agent such as HC, urea and ammonia which are injected into tail gas of engine, react with NOX firstly in oxygen-rich condition and N2 is produced, in this way NOX is purified[8]. Ammonia is used as reducing agent in general. The reaction process of NH3 and NOX is (1)-(3)

\[
\begin{align*}
4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \\
4NH_3 + 2NO + O_2 \rightarrow 3N_2 + 6H_2O \\
4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O
\end{align*}
\]

The conversion of in the direct catalytic decomposition technology is high, the fuel economy of the engine is well; it is obtained by spraying solution of urea into the exhaust and the engine is controlled easily. While the using of selective catalytic reduction technology in the gasoline engine is limited because of the thermal stability in high temperature, the resistance of water is poor and the temperature of gasoline engine exhaust is high and unstable. Also it is expensive and will result the second pollution.

3 THE ADSORPTION REDUCTION CATALYTIC TECHNOLOGY OF NOX IN LEAN BURN GASOLINE ENGINE

The post processing techniques of NOX in lean burn gasoline engine which are referred in front can’t be used in practically, because of the defects which is insurmountable. The adsorption reduction catalytic technology of NOX is the further development of the direct catalytic decomposition technique[9,10], the purification effect of NOX is improved by delaying the purification reduction reaction until it is reacted in exhaust gas which is in the reduction atmosphere, and the storage component of the catalyst can be stored in NOX adsorption storage. The NOX adsorption reduction catalytic converter which is functioned in lean burn engine should be worked between the dense and lean burn periodically. The change of torque which is exported should be small and the driving performance of the car is improved. The throttle and ignition advance angle size of engine can be controlled dynamically by using high speed development of electronic control technology, when the mixing ratio is changing in thick and thin. In this way the torque which is exported of the engine should be constantly.

3.1 The basic mechanism of adsorption reduction catalytic (ARC) technology of NOX

Adsorption reduction catalyst is constituted by active component which is oxidizing and storage component which is alkaline and the surface of carrier is bigger. Active component is the catalyst in this reaction which is consisted of Pt and other auxiliary agent; storage component is consisted of alkaline earth metal compound, alkali metal compound or their complex substance; the carrier is always oxide or composite oxide of magnesium, aluminum, cerium, titanium and silicon.

The purification mechanism of ARC to NOX is shown in the Figure.1 and Figure.2:

3.1.1 Adsorption process

The engine is in the working condition of dilute mixed gas during the adsorption process, the main NOX is NO in the tail gas, the adsorption process of NO is divided into two steps: NO2 is generated by NO and O2 which is catalysed by platinum firstly when the oxygen is rich. The reaction is as (4):

\[
2NO + O_2 \rightarrow 2NO_2
\]

Then the nitrate is produced by NO2 and alkali metal oxide or alkaline earth metal oxides which the platinum is added into. It is adsorbed on the surface of alkaline earth metal oxides in the forms of nitrate. For example, the Ba (NO3)2 is produced by BaO and NO2 when the oxygen is excessive. The reaction is as (5):

\[
NO + O_2 + BaO \rightarrow BaNO_3
\]

3.1.2 The process of reduction

With the increasing of NOX which is absorbed in the catalytic converter of LNT, the adsorption efficiency will decline. The catalytic converter of LNT should be revived when the adsorption NOX is in a certain
extent. The dense mixed gas needs to be added in order to thicken the HC and CO which has not burned in the tail gas. The adsorption vacancy of LNT is recovered when the NO₂ and NO is released because of the thermodynamic properties of Ba(NO₃)₂, it becomes unstable when it is in tail gas who has stronger reducing agent.

The chemical reaction equation is as (6)-(8):
\[
\begin{align*}
\text{Ba(NO}_3\text{)}_2 + \text{CO} & \rightarrow \text{BaO} + \text{NO}_2 (\text{or NO}) + \text{CO}_2 \quad (6) \\
\text{Ba(NO}_3\text{)}_2 + \text{HC} & \rightarrow \text{BaO} + \text{NO}_2 (\text{or NO}) + \text{CO}_2 + \text{H}_2\text{O} \quad (7) \\
\text{Ba(NO}_3\text{)}_2 + \text{H}_2 & \rightarrow \text{BaO} + \text{NO}_2 (\text{or NO}) + \text{H}_2\text{O} \quad (8)
\end{align*}
\]

The NO and NO₂ is reduced to N₂, whose reduction mechanism is the same as three way catalyst. The chemical reactions is as (9):

\[
\text{NO}_2 \text{ (or NO)} + \text{CO(HorH}_2\text{)} \rightarrow \text{N}_2 + \text{CO}_2 (\text{or} + \text{H}_2\text{O})
\]

From the chemical reaction above the harmful emissions which is discharged by lean burn engine is purified.

3.1.3 The reaction in the process of adsorption reduction

(1) The oxidation of NO₂

The NOₓ in the exhaust of an engine exists in the form of NO, NO is oxidized into NO₂ by the catalytic action of noble metal, because NO₂ is easier to be adsorbed than NO. The properties of noble metals play a key role in the oxidation of NO. Pt has a better oxidation ability of NO than PD and Rh.

(2) The adsorption of NOₓ

The main idea is that NOₓ is adsorbed on the two active sites in the forms of nitrate, despite there is a dispute about storage mechanism of catalyst surface of NOₓ, NOₓ is stored in Ba which is next to Pt in the early stage of adsorption. The nitrate is produced by the disproportion reaction in Ba which is far from Pt, in order to ensure the balance of nitrogen in the late stage of adsorption. BaO, Ba(OH)₂ and BaCO₃ are all existed on the surface of catalyst in the adsorption process of NOₓ, but the adsorption capacity is that BaO > Ba(OH)₂ > BaCO₃, so the storage capacity of catalyst is influenced by the form where the Ba is existing.

(3) The change of reaction atmosphere

The catalyst should be regenerated periodically and N₂ should be reduced from NOₓ which has been stored so the reaction atmosphere should be changed from oxidizing atmosphere to reduce atmosphere, the reducing agent which is added in has three kinds of function: ①The oxidizing atmosphere is changed to reducing atmosphere by consuming the O₂ which is redundant. ②React with oxygen or oxide which is on the surface of catalytic. ③NOₓ is reduced to N₂. Therefore the reducing agent which is added must be sufficient.

H₂ which is the most effective reducing agent can promote the regeneration of catalyst is equal to CO or propylene when the temperature relatively high. The fuel should be treated periodically or continuously in order to obtain the reducing agent which is ideal, the H₂, CO or hydrocarbon which is small is produced after it is reformed or oxidized partially but the require is complex. Lean-burn engine burns in the concentrated oxygen intermittent when the time scale is 10:1, the reducing agent is produced intermittently in the conditions of oxygen enriched.

(4) The desorption of NOₓ

The desorption of NOₓ is not only the reduction transformation of NOₓ, but also the regeneration of noble metal catalysts. The desorption of NOₓ is leded by adding plant of reducing agent which leaded the reducing agent in the atmosphere of reduction, reduced the stability of nitrate, leaded the resolution of nitrate. Meanwhile it is reduced by reduction which is adsorbed on the surface of catalytic, plenty of heat is generated, temperature is risen and the stability of nitrate is further reduced which has been stored. The desorption of NOₓ is the same as it’s adsorbent, it is limited by temperature, gas composition, noble metal catalyst, stronger component and the category of carrier.

(5) The reduction of NOₓ

Plant of NOₓ should be reduced by catalytic, in order to reduce the by-product, higher selectivity is required, the reduction process is similar to TWC and the reaction is more faster. The reduction of NOₓ can be accelerated by the existence of K which is alkali metal relatives to Pt/Al₂O₃. The reduction process of NOₓ which is in reducing gas phase is different from which is stored on the surface of catalyst. The NOₓ can be reduced even though there are plenty of reducing agent, the catalyst is still in the process of lean burning when it is switching from lean burning to fuel burning.

3.2 The technical scheme about catalytic conversion method of adsorption reduction of NOₓ

3.2.1 The optimization of active component

The noble metal is the active center of ARC redox, NO is oxidized to NO₂ which is easy to store in the storage process. The NOₓ which has been desorbed is translated into N₂ in the process of reduction. It is thought that Pt has the best ability of capture and oxidation generally. As it is shown in studying the ability of storage and reduction is relatively weak when Pt, Ba and Al₂O₃ is in a lower temperature (250 ~ 350 °C). The noble metal is easily to be sintered seriously, the duct of carrier is blocked, the specific surface area is dropped and the deactivation of catalyst is leaded. NOₓ is hardly to be purified in practice by the catalytic whose type or component is single because of tail gas temperature range is relatively wide, water and SO₂ are contained in it. Two or more active component are combined by its characteristics which produces a good result for the
selective reduction of NO\textsubscript{X}. So some transition metals are added in the active component in order to achieve the effect that the metals catalyze cooperatively.

The Co has two valences which is a transition metal: Co\textsuperscript{2+} and Co\textsuperscript{3+}, they can translate to each other so it is conducive to the conversion of NO\textsubscript{2} to NO. The optimum calcination temperature is raised to 800\degree C by adding Co, which the activity of noble metal in high temperature tail gas is ensured when it is burning in sparse oxygen. The interaction of Ba and Al\textsubscript{2}O\textsubscript{3} can be reduced in high temperature. The CoAl\textsubscript{2}O\textsubscript{4} which is dispersed seriously makes the grain of alumina smaller which has a better storage capacity of NO\textsubscript{X}, the interaction of atomic cluster of Pt and carrier is restrained, meanwhile the adsorption, oxidation and storage on the catalytic of NO is promoted. There for the active component should be composed of Pt and Co.

3.2.2 The optimization of storage components
The storage component of adsorption reduction catalyst is alkali metal or alkaline earth metal, the storage capacity and sulfur tolerance of alkali metal is better than alkaline earth metal while the NO\textsubscript{X} is hard to be released in the process of full burning, because the alkaline of alkaline metal is stronger. The alkaline metal is easy dissolves in water that is agglomerated in the tail gas, the collapse of catalyst structure could be leaded when the car is started in cold.

There are two kinds of precursors: Ba(NO\textsubscript{3})\textsubscript{2} and Ba(CO\textsubscript{3})\textsubscript{2}, when Ba is used as a storage component. The water solubility of Ba(CO\textsubscript{3})\textsubscript{2} is better than Ba(NO\textsubscript{3})\textsubscript{2} and it is easier to load and control load, so Ba(CO\textsubscript{3})\textsubscript{2} is used as the mainly storage activity center commonly. The storage capacity of Ba is weaker than K when the temperature is higher than 350\degree C. The existence of Ba and K is a good choice, not only the storage capacity of the catalytic is improved in high temperature, but also the sulfur resistance of the storage capacity is improved in a certain extent.

3.2.3 The optimization of carrier
The carrier which is the skeleton of the whole catalyst should have a high specific surface area and stability, which includes not only thermal stability, but also chemical stability and resistance to sulfur poisoning. The carrier who has a bigger surface, also has some adsorption capacity of NO\textsubscript{X}. The phase transition is happened easily in high temperature or the BaAl\textsubscript{2}O\textsubscript{4} which is a spinel structure which is produced by the carrier and Ba that is the adsorption component of NO\textsubscript{X}, the loss of storage active site of NO\textsubscript{X} is leaded by that and its sulfur resistance needs to be improved.

Therefore, some assistant should be added in order to improve the thermal stability and sulfur resistance of the catalyst. The acid oxide such as CeO\textsubscript{2}, TiO\textsubscript{2} and ZrO\textsubscript{2} is added in the study of carrier modification. The deposition of the sulfur on the surface of catalytic is reduced by adding TiO\textsubscript{2}, the desorption of surface is improved.

When the composite oxide of TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} is used as the carrier of adsorption reduction catalyzator the catalytic performance is better than the traditional catalytic whose carrier is Al\textsubscript{2}O\textsubscript{3}.

It is a good choice when the composite oxide support which is consisted of TiO\textsubscript{2} is added in for the carrier; the ability of storage and anti sulfur has been raised when Ba and K exists at the same time for the storage group. When the transition metal Co and its oxide additives is added in the active component the activity of precious metals is ensured in high temperature, the ability of adsorption, oxidation and storage for the nitrogen oxides is increased.

4 CONCLUSION
The technology of NO\textsubscript{X} emission purification is explored for future, since the lean burning technology has become a hot technology in the practical application of gasoline engine, which is based on the value of engine energy saving. Because the traditional technology of gasoline engine exhaust gas purification can’t reach the environmental protection requirement. In the revelation in technology of industrial denitrification and the technology of purification of NO\textsubscript{X} in diesel engine NO\textsubscript{X}, the method that adsorption reduction catalytic efficiency of NO\textsubscript{X} can be improved has been studied, based on the technology theory of catalytic conversion. The bimetallic catalyst which is composed by precious metals and transition metals can improve the efficiency of catalytic reaction in the exhaust gas whose temperature is high. The K\textsubscript{2}O is added in the storage component in order to improve the storage capacity of the purification equipment. This basic research provide theoretical basis and technical support for a further practical of lean burn technology of gasoline engine that the purpose of conserve energy and reduce emissions can be achieved.

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