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Research

Study on the Effect of Different Preparation Methods on the Performance of $AgCl/Al_2O_3$ Catalyst Used for Diesel Exhaust Treatment

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ABSTRACT

In this study, $AgCl/Al_2O_3$ catalyst was prepared by the impregnation method to remove NO_x in diesel exhaust gas, so as to achieve the purpose of purifying exhaust gas. The $AgCl/Al_2O_3$ catalyst is a kind of hydrocarbons selective catalytic reduction (HC-SCR) catalyst. The HC-SCR catalyst uses the unsaturated hydrocarbons and the oxygen-containing derivatives of the hydrocarbons as reducing agents to convert harmful NO_x in the exhaust gas into N_2. This kind of catalyst belongs to Ag type catalyst, and because of its simple preparation conditions, low cost and good catalytic activity of this catalyst, $AgCl/Al_2O_3$ catalyst is worth studying. in this research, the catalysts were prepared under four different conditions by changing the adding order of NH_4Cl, $AgNO_3$ and γ-Al_2O_3, as well as the drying and sintering times, and through the HC-SCR test that the working environment of the catalyst in diesel exhaust gas is simulated by introducing the gas into the device equipped with the catalyst and heating, then the relationship between the NO_x conversion rate and the temperature was obtained. According to the result, it is found that the NO_x removal rate of the four catalysts is close to 100% at 350°C to 400°C. The catalyst obtained by condition C and condition D maintains a high conversion rate of NO_x in a wide temperature range. At the same time, the catalyst under condition D has good reproducibility after repeated heating and cooling experiments, therefore this catalyst is considered to have good application prospects.

Keywords: Diesel engines; NO_x purification; HC-SCR; $AgCl/Al_2O_3$ catalyst

INTRODUCTION

Research on catalytic purification of diesel exhaust contaminants is one of the most difficult and hot topics in the field of environmental catalyst all over the world [1]. With the development of social economy, diesel vehicles has become more and more popular in recent years because of low fuel consumption, high heat efficiency and other advantages. However, the emissions of diesel shoot (PM) and nitrogen oxides (NO_x) contained in diesel engine exhaust are very high, especially the emissions of diesel shoot is much higher than those of gasoline engine, and diesel shoot is harmful to the environment and human body. Therefore, nowadays, with the increasing attention of the state to environmental protection, the exhaust emission of diesel vehicles has gradually attracted people's attention. In meantime, with the development of international trade and shipping, the marine diesel engine based on petroleum products is polluting the ocean more and more serious. According to the statistics, the fuel consumption of marine diesel engine in the world is calculated by 100 million tons every year, so that NO_x is discharged into the atmosphere every year. In the developed shipping countries (such as Norway), 40% to 50% of the total NO_x emissions comes from ships. In the areas with dense ports and routes, the exhaust emissions from ships may be the main source of pollution in this

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area. Diesel exhaust emission is one of the important factors affecting global air quality.

Diesel engine has complex chemical composition, and with the change of engine working conditions, the composition of exhaust gas is also significantly different. The pollutants discharged by diesel engine include diesel shoot (PM), hydrocarbons (HC), CO and NO_x, etc. Due to the high oxygen content in the exhaust, the emission of NO_x is larger than that of gasoline engine. The emission of PM is dozens of times that of gasoline [2]. Therefore, reducing the emission of NO_x and PM is the main topic of catalytic purification of diesel engine exhaust. HC-SCR is considered to be the most promising NO_x removal technology; it uses HC compounds (such as unburned HC in the exhaust, or fuel diesel) as reducing agent to reduce NO_x into N_2 in the exhaust of diesel engine under the action of catalyst. The discovery of this new reaction breaks the concept that NH_3 is the only reductant which can selectively reduce NO_x.

Noble metal is mainly used as catalysts to remove NO_x in diesel exhaust. Noble metal catalyst such as Ag/Al_2O_3 has high SCR (Selective Catalytic Reduction) activity at low temperature, but there are some shortcomings: poor selectivity of N_2, narrow operating temperature range and high price. These problems make the noble metal catalysts can't be widely used in diesel exhaust treatment.

In this study, a novel AgCl/ Al_2O_3 catalyst was prepared. AgCl was loaded on the γ-Al_2O_3 which has high specific surface area. AgCl is used as the active component to reduce NO_x to N_2 by using hydrocarbons or oxygenated derivatives of hydrocarbons in diesel exhaust as a reducing agent, thereby reducing exhaust pollution to the environment. Unsaturated hydrocarbons show higher activity for NO_x reduction than saturated ones. It is known that oxygen-containing compounds such as acetone (CH_3COCH_3), 2-propanol ($(CH_3)_2CHOH$), and ethanol (C_2H_5OH) show higher NO_x removal performance than hydrocarbons. In the reduction reaction, the difference between oxygenated compounds and hydrocarbons is that in the case of a catalyst using hydrocarbons as a reducing agent, the removal rate of NO_x will be reduced in the presence of water vapor, while oxygenated derivatives of hydrocarbons in the same situation, Can still maintain a good NO_x removal effect, and even at low temperatures, it will maintain a high NO_x removal rate [3,4]. The purpose of this novel catalyst is to reduce the cost of catalyst preparation from the material aspect, what's more, it also has a better removal effect of NO_x, and it has the great value of popularization and use. It points out a new idea for the research of silver catalyst used in diesel exhaust treatment.

EXPERIMENTAL PROCEDURE

The experiment adopts the impregnation method, using $AgNO_3$ and NH_4Cl as raw materials. It generates AgCl as the active component of the catalyst through the reaction and was supported on γ-Al_2O_3. And γ-Al_2O_3 was used as catalyst carrier because of its large specific surface area. According to the different reaction sequence of raw materials added, drying and sintering time of the materials, the experiment was divided into four conditions for comparison.

Preparation of $AgCl/Al_2O_3$ catalyst

The following is the detailed introduction to the preparation process of catalyst (Figure 1).

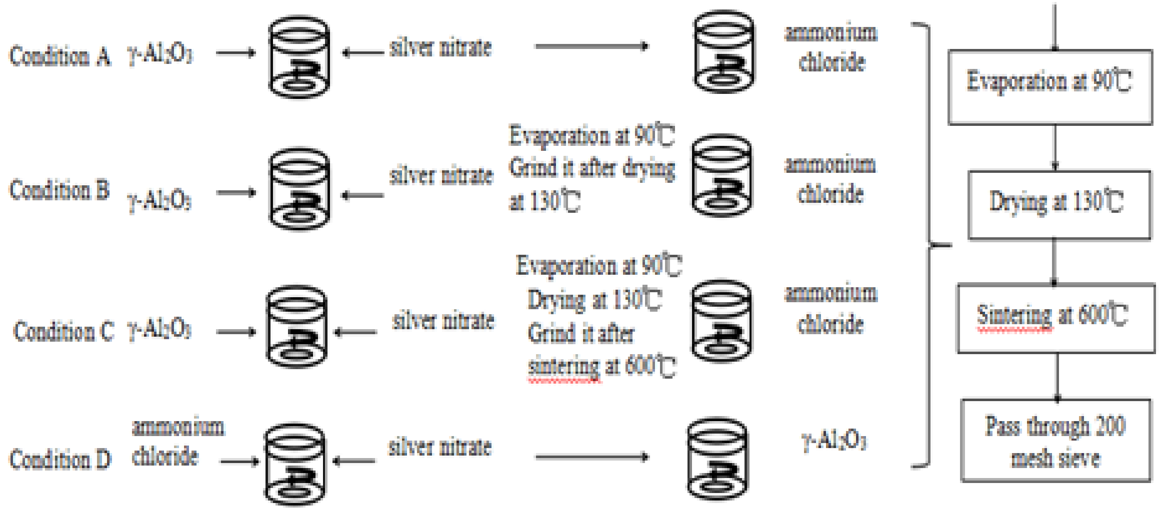

Figure 1: Flow chart of catalyst preparation under four difference conditions.

Condition A: Firstly, γ-Al_2O_3 powder (46.89 g) was added to the deionized water (100 ml), next silver nitrate (2.38 g) was added to the solution and the obtained solution was uniformly stirred to make silver nitrate fully dissolved. Then ammonium chloride (0.74 g) was added to the mixture solution, which reacted with silver nitrate to form silver chloride and attached to the carrier, as a result, a large amount of white precipitate formed in the solution, the obtained solution was ultrasonically dispersed (40 kHZ) for 30 min. The mixture solution was heated at 90°C and uniformly stirred with the 300 r/min. The obtained final mixture solutions were placed in the oven at 130°C for 5 h, and continuously treated at 600°C for 4 h. After cooling the obtained solids to the room temperature, the product was ground to 200 mesh to obtain catalyst material [5-7].

Condition B: Firstly, γ-Al_2O_3 powder (46.89 g) was added to the deionized water (100 ml), next silver nitrate (2.38 g) was added to the solution and the obtained solution was uniformly stirred. The mixture solution was heated at 90°C and stirred. The obtained mixture solutions were placed in the oven at 130°C for 5 h, next the dried material was ground and added to deionized water (100 ml), after stirred to obtain a solution. Then ammonium chloride (0.74 g) was added to the mixture solution, as a result, a large amount of white precipitate formed in the solution, the obtained solution was ultrasonically dispersed (40 kHZ) for 30 min. The mixture solution was heated at 90°C and uniformly stirred with the 300 r/min. The obtained final mixture solutions were placed in the oven at 130°C for 5 h, and continuously treated at 600°C for 4 h. After cooling the obtained solids to the room temperature, the product was ground to 200 mesh to obtain catalyst material [8].

Condition C: Firstly, γ-Al_2O_3 powder (46.89 g) was added to the deionized water (100 ml), next silver nitrate (2.38 g) was added to the solution and the obtained solution was uniformly stirred. The mixture solution was heated at 90°C and stirred. The obtained mixture solutions were placed in the oven at 130°C for 5 h, treated at 600°C for 4 h. The obtained solid was cooled to room temperature. The solid was ground and added to deionized water (100 ml) to form a solution. Then ammonium chloride (0.74 g) was added to the mixture solution, as a result, a large amount of white precipitate formed in the solution, the obtained solution was ultrasonically dispersed (40 kHZ) for 30 min. The mixture solution was heated at 90°C and uniformly stirred with the 300 r/min. The obtained final mixture solutions were placed in the oven at 130°C for 5 h, and continuously treated at 600°C for 4 h. After cooling the obtained solids to the room temperature, the product was ground to 200 mesh to obtain catalyst material.

Condition D: Firstly, ammonium chloride (0.74 g) was added to the deionized water (100 ml), next silver nitrate (2.38 g) was added to the solution and the obtained solution was uniformly stirred, as a result, a large amount of white precipitate was produced in the solution. Then γ-Al_2O_3 powder (46.89 g) was added to the mixture solution and the obtained solution was uniformly stirred. The obtained solution was ultrasonically dispersed (40 kHZ) for 30 min. The mixture solution was heated at 90°C and stirred. The obtained mixture solutions were placed in the oven at 130°C for 5 h, treated at 600°C for 4 h. After cooling the obtained solids to the room temperature, the product was ground to 200 mesh to obtain catalyst material.

RESULTS AND DISCUSSION

Evaluation of AgCl/Al_2O_3 catalyst

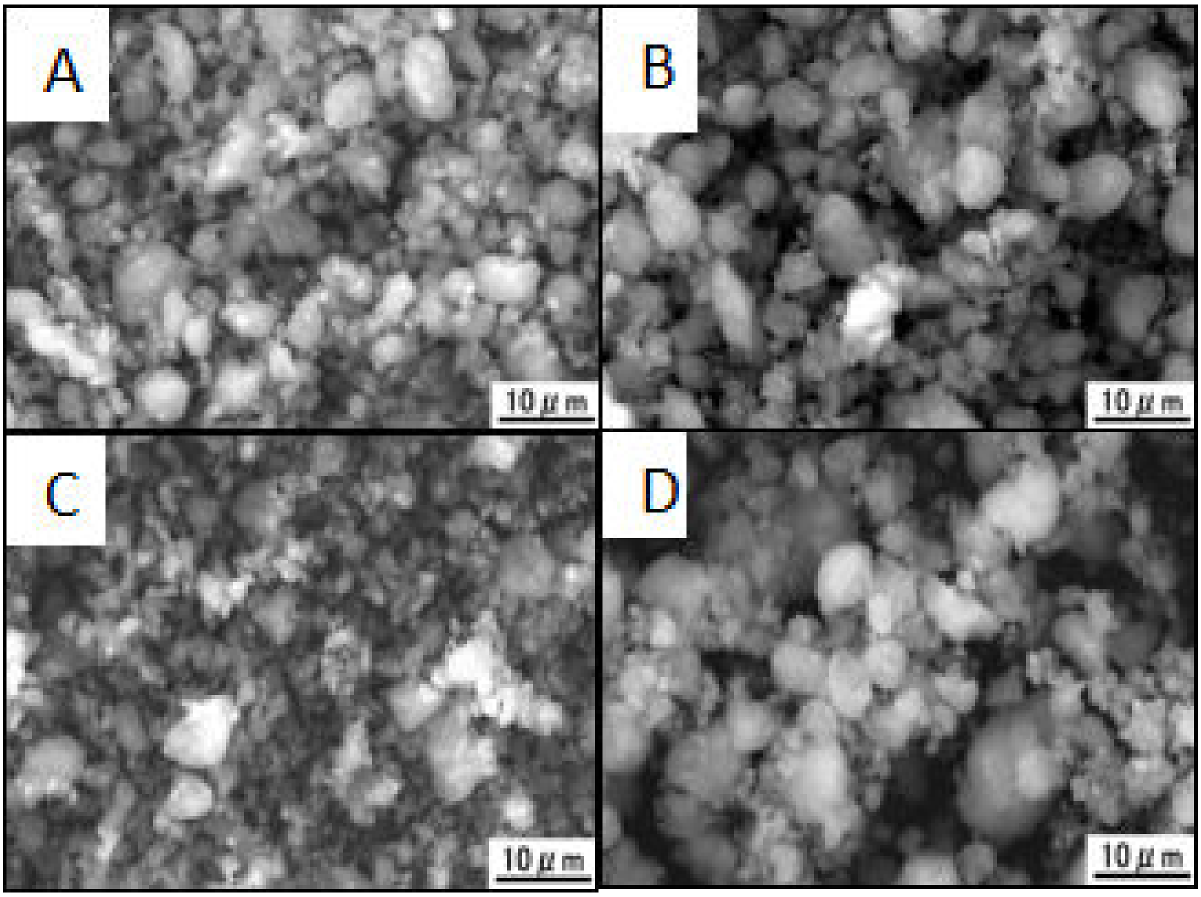

Figure 2: SEM images of the catalysts by four different conditions.

It can be observed from the Figure 2 that the catalysts prepared under the four conditions are all irregular spherical. Moreover, in the catalysts obtained under the four conditions, different degrees of agglomeration occurred between the particulate materials. This is because when the material is sintered, the solid particle spacing would be reduced when heated at high temperature.

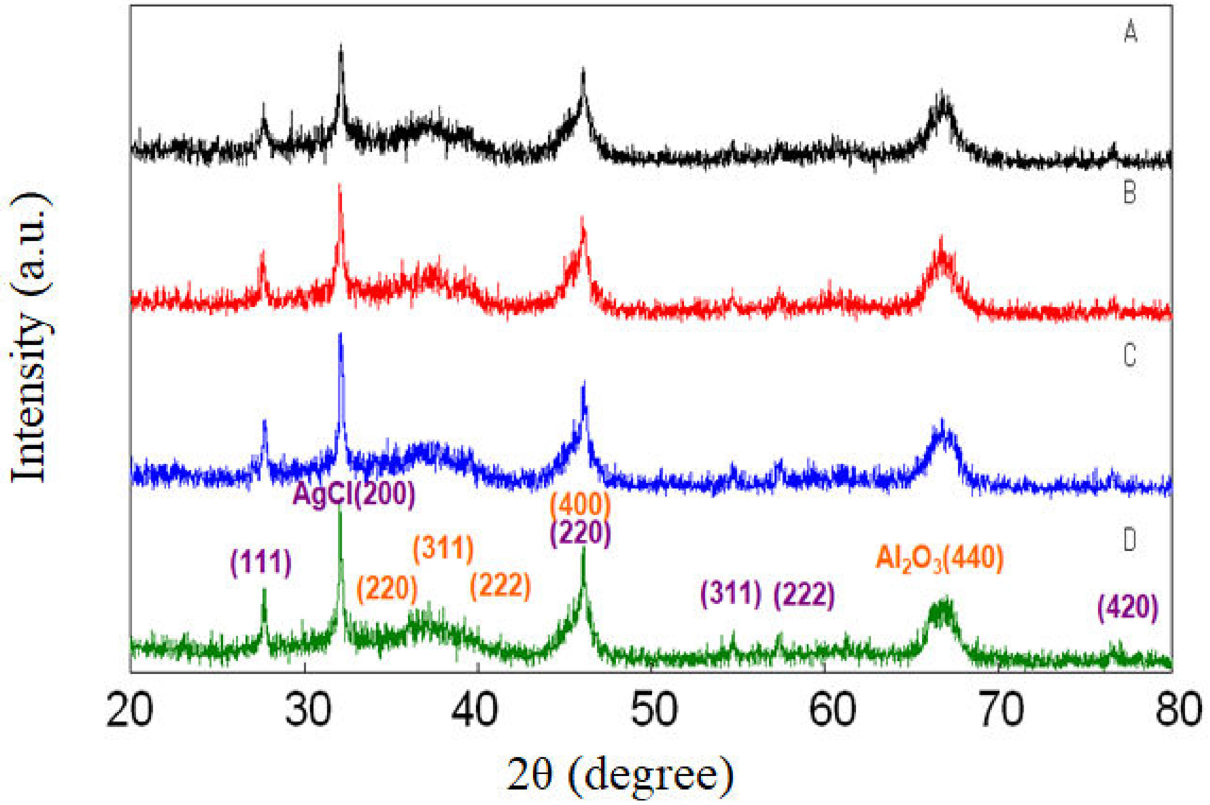

Figure 3: XRD pattern of $AgCl/Al_2O_3$ catalyst.

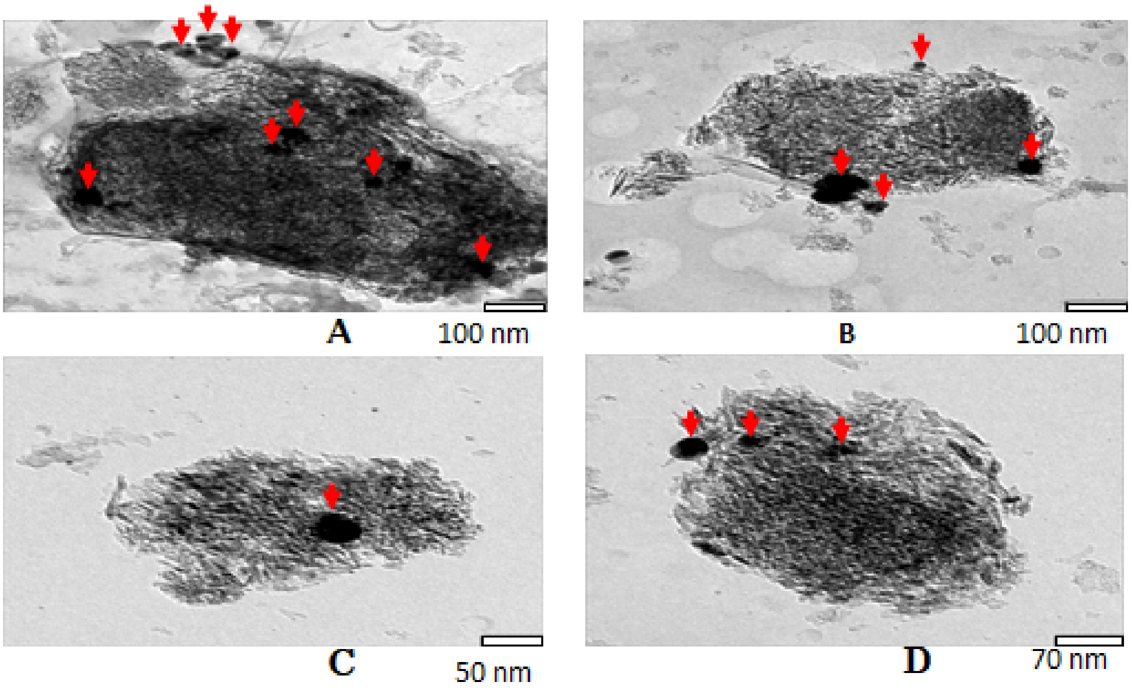

Figure 4: TEM images of the catalysts under four different conditions.

When the spacing was reduced to a certain extent, the surface force field makes the solid particles adhere, the adhesion force makes the particles deform at the contact point, increases the contact surface, then increases the adhesion force, and leads to the bonding between the particles, so the agglomeration phenomenon occurs. There are many small particles in the catalyst material obtained under condition A, the particle size is about 2 μm. There are small gaps between the materials. The gap between the catalyst particles obtained by condition B is larger than that obtained by condition A. And the materials with particle size above 5 μm are in the majority.

The particle size of the catalyst materials prepared by condition C is mostly very small, about 2 μm. And they are tightly bonded, almost no gaps. This may be the result of multiple agglomerations between the materials after multiple sintering. It can be seen from the SEM image that in the catalyst obtained under condition D, the particle size is generally large, the largest particle size is about 10 μm. There are relatively large gaps between the particles.

First of all, in accordance of the standard card as JCPDS card (Figure 3), the structures of $AgCl/Al_2O_3$ were identified accurately. The peak of the diffraction angle 2θ around 27, 32, 46, 54, 57 and 76 were coincides with the peak of AgCl. It is formed by the reaction of NH_4Cl and $AgNO_3$, and AgCl is the main active material in the catalyst. Through the action of AgCl, NO_x in diesel exhaust can be converted into N_2, so as to achieve the purpose of exhaust gas purification. The peaks around 34, 37, 39, 46 and 67 were consistent with the peaks of Al_2O_3.

In the catalyst, γ-Al_2O_3 is used as the carrier of the active component. The catalyst uses γ-Al_2O_3 as the supportbecause of its porous; it has a large specific surface area and can be used to carry more active components. At the same time, γ-Al_2O_3 has strong adsorption capacity and high temperature resistance, making it very suitable as a carrier in the catalyst.

AgCl was marked with red arrows in the TEM image (Figure 4), it was thought that AgCl particles were darker than the other parts. It could be observed from the TEM that the active component was introduced into the carrier. In the catalyst prepared under condition A, the size of AgCl was about 30 nm to50 nm. The size of AgCl particles in the catalysts obtained by condition C and D was about 50 nm. Among the four preparation conditions, the size of AgCl in the catalyst obtained under condition B was the largest, about 100 nm. The smaller the particles size of AgCl, the higher the reactivity of the catalyst.

However, when the average particle size is less than 10 nm, only the reducing agent undergoes an oxidation reaction, which suppresses the reduction of NO_x and reduces the NO_x removal rate of the catalyst. When the average particle size was more than 1000 nm, the reaction activity was decrease, and the NO_x removal rate would also reduce. Therefore, the optimal average particle size was 10-000 nm.

UV-Vis was used to study the types of Ag present in $AgCl/Al_2O_3$ catalysts. Since AgCl is light sensitive material, the $AgCl/Al_2O_3$ catalyst would changes colour when exposed to light, and it changed from white to gray as shown in Figure 5.

The gray $AgCl/Al_2O_3$ catalyst turned white again as shown in Figure 5 by heating at 500°C to 600°C.

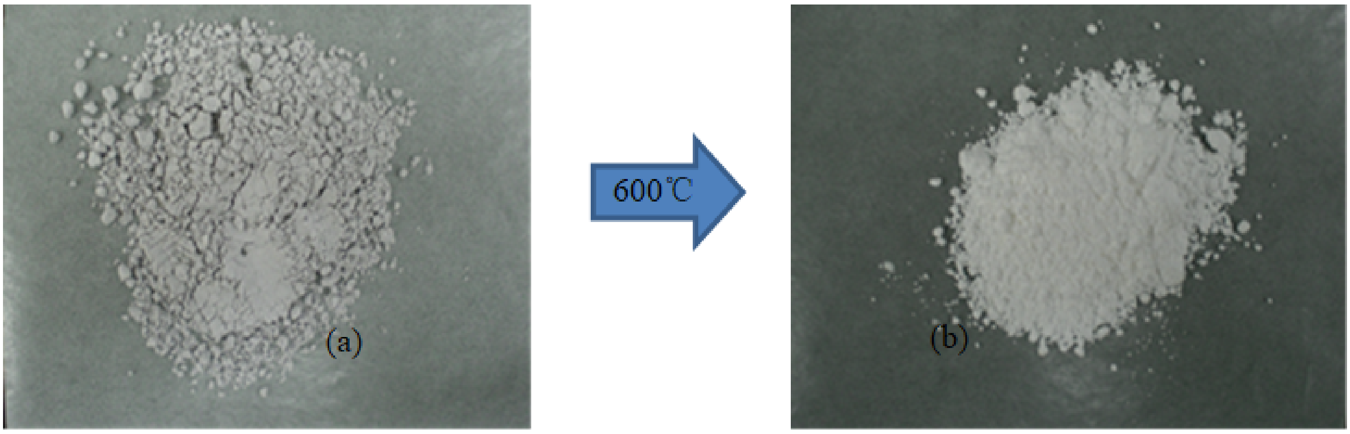

Figure 5: $AgCl/Al_2O_3$ catalysts: (a) Before heating and (b) After heating.

Figure 6 shows UV-Vis spectra before and after reaction of $AgCl/Al_2O_3$ catalyst.

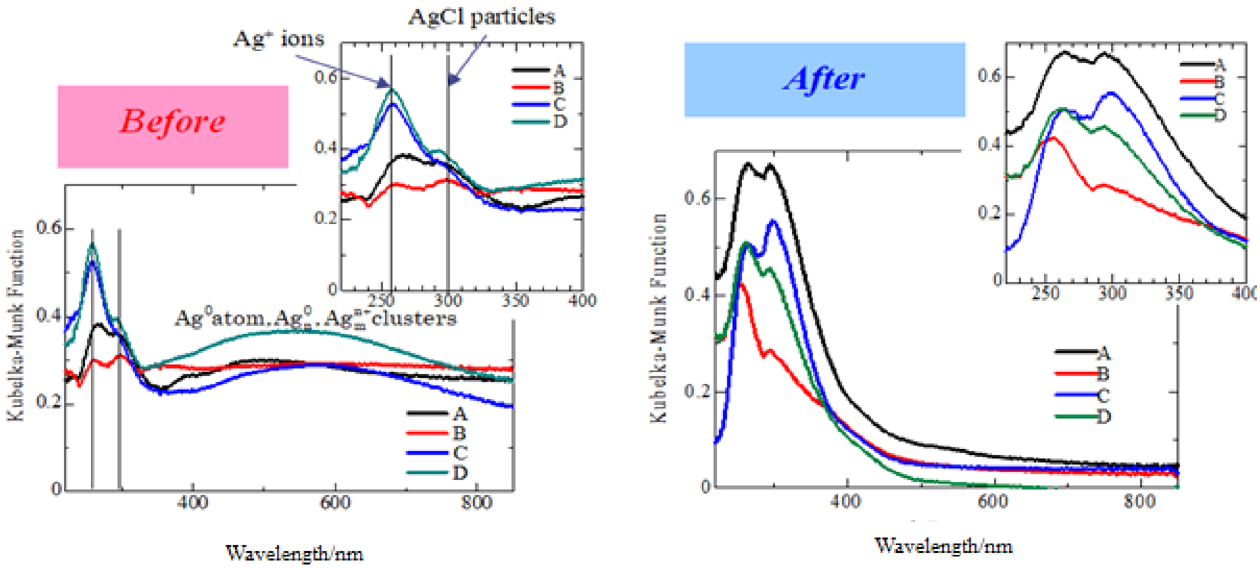

Figure 6: Diffuse reflectance UV-Vis. before reaction and after reaction.

In the sample before the reaction, peaks can be confirmed in the vicinity of 260 to 300 nm and 400 to 650 nm. In the sample after reaction, the peaks near 260 nm and 300 nm are obvious, and the peaks in the region of 400 to 650 nm disappeared. The peaks in the 400 to 650 nm region are considered to be the atoms and clusters generated by photolysis of AgCl. But these peaks disappeared after the reaction, because these atoms and atomic clusters were turned into AgCl by heating. The peaks around 260 nm and 300 nm are considered to be Ag^+ and AgCl particles. Therefore, the catalyst material decomposed when exposed to light, and silver was precipitated, making the powder gray. However, after high temperature sintering, the silver atoms in the catalyst powder were transformed into Ag^+ and exist in the form of AgCl, so the powder becomes pure white.

Performance evaluation of $AgCl/Al_2O_3$ catalyst (HC-SCR test)

Figure 7 shows the conceptual diagram of the catalytic properties evaluation test equipment. Evaluation conditions: SV (space velocity: gas flow rate / catalyst volume)=9474/h, W/F (catalyst weight/gas flow rate)=0.018 g.s.cm^{-3}, total flow rate 300 ml, NO_x:1000 ppm, ethanol+ water:bubbling (0°C), O2:10 vol %, He:balance. By introducing gas to simulate the working environment of diesel exhaust catalyst, using ethanol in the exhaust gas as a reducing agent, the relationship between temperature and NO_x conversion rate under four conditions was obtained under heating conditions.

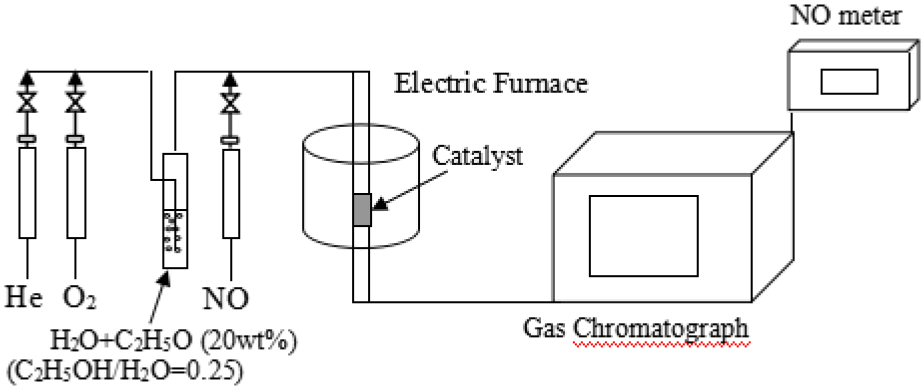

Figure 7: Schematic diagram of catalyst activity test.

Figure 8 shows the relationship between NO_x conversion rate and temperature under catalysis of $AgCl/Al_2O_3$. The four catalysts showed similar catalytic performance. The conversion rate of NO_x gradually increases with the increase of temperature. When the maximum conversion rate is reached, with the temperature continues to increase, the conversion rate shows a downward trend. The heating rate of the experiment was 5°C/ min. At 200°C, the catalyst prepared under condition B showed the highest catalytic activity, among the four catalysts. When the temperature reached to 250°C the catalysts of condition C and condition D showed the highest removal rate of NO_x. During the temperature increase from 200°C to 350°C, the catalytic performance of the catalyst by condition A was the worst among the four catalysts. Conditions B, C, D at 300°C, the catalytic performance reached the maximum, the conversion rate of NO_x was close to 100%.

When the temperature reached 350°C, the conversion rate of nitrogen oxides of all catalysts would reach the maximum. At this temperature, the catalyst could convert all the NO_x in the exhaust gas into harmless N_2. When the temperature reached 400°C, with the temperature rising, the NO_x removal capacity of catalyst prepared by condition B was decrease, NO_x conversion rate was only 65% at 500°C. Condition C and condition D have maintained the maximum NO_x conversion performance at 300°C to 450°C.

The catalyst prepared under condition B exhibited higher catalytic performance at low temperature, In contrast, the catalyst prepared under condition A maintained a higher conversion rate of NO_x at high temperature. Condition C and condition D showed good catalytic performance, they had a wide catalytic temperature range, and they could effectively remove NO_x in the exhaust gas under the action of reducing agent.

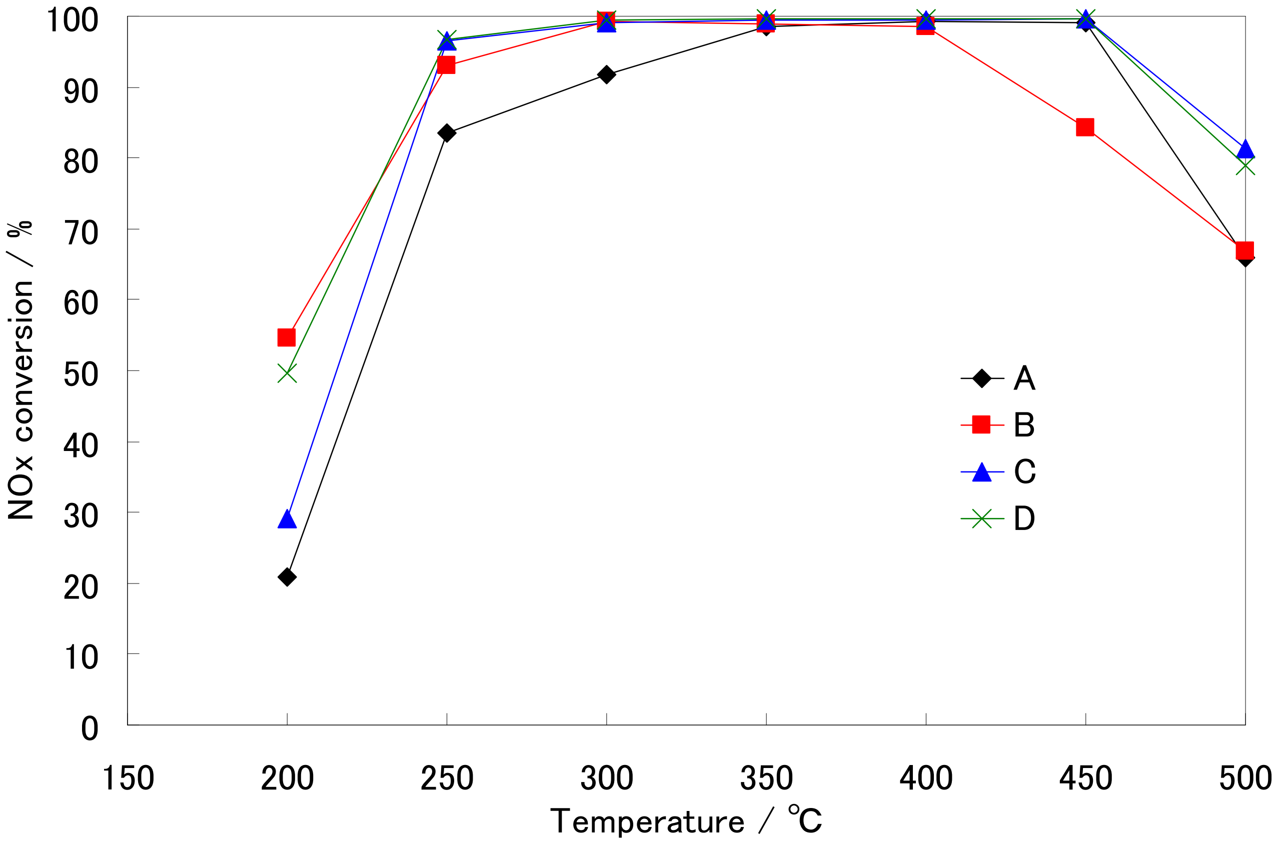

Figure 8: The catalytic activity of $AgCl/Al_2O_3$.

In order to study the reproducibility of the activity of $AgCl/Al_2O_3$ catalyst prepared by four methods, the temperature was increased from 200°C to 500°C, next decreased to 200°C, and then increased to 500°C again. The rate of temperature rise/drop was 5°C/ min. The results are shown in Figure 9.

It can be observed from the Figure 9 that for the catalysts prepared under conditions A, C, and D, when the temperature rose from 400°C to 500°C, the conversion rate of NO_x was greater than that when the temperature was reduced from 500°C to 400°C. The catalyst obtained by condition A and condition C, after the process of heating, cooling and heating again, the catalyst's ability to remove NO_x in the exhaust gas decreases.

This phenomenon indicated that these two catalysts didn't have good temperature reproducibility. Although the catalyst obtained under condition C had a wide high activity temperature range, the performance of the catalyst will decrease after repeated temperature rise. Although the catalyst obtained under condition D had a slight decrease in the catalytic performance between 200°C and 350°C, the overall performance still showed a high NO_x conversion rate and a wide temperature range. Although the catalyst obtained under condition B does not have a wide temperature range of high catalytic activity after the first temperature increase, after being cool and repeated heating, the conversion rate of NO_x increased.

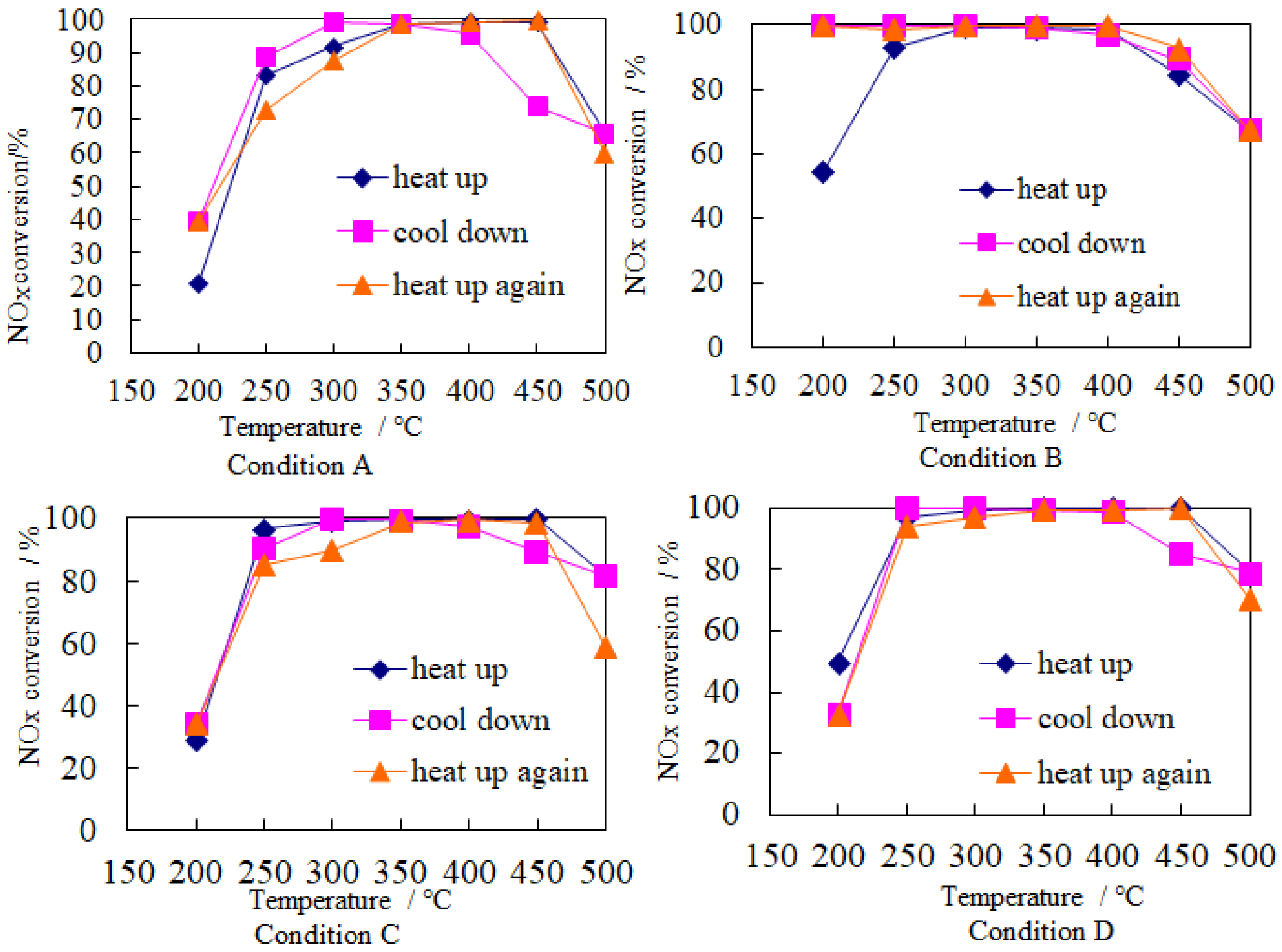

Figure 9: The catalytic activity of $AgCl/Al_2O_3$.

Reaction mechanism of $AgCl/Al_2O_3$ catalyst

In this study, the oxygen-containing hydrocarbon in diesel exhaust was used as reducing agent to convert NO_x to N_2 under the action of the catalyst. Figure 10 shows the reaction mechanism of $AgCl/Al_2O_3$ catalyst using ethanol as the reducing agent in the presence of water vapour.

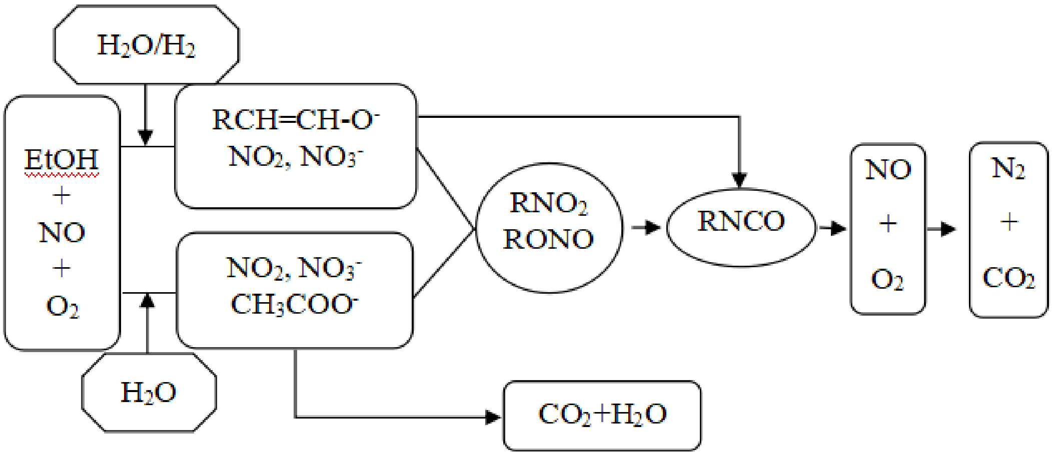

Figure 10: The mechanism of the SCR of NOx by C_2H_5OH over $AgCl/Al_2O_3$.

The key to this reaction is the formation of intermediate products such as NO_3-, $RCH=CH\text{-}O^-$, $CH_3COO^-RNO_2$, RONO, RNCOthey can promote the reaction. $RCH=CH\text{-}O^-$ and CH_3COO^- are the products obtained by ethanol oxidation; they can react with NOx to produce the RNO_2 and RONO on the carrier. RNCO was a particularly important intermediate product. It is obtained by the reaction of RNO_2 and RONO, it was able to react with NO or NO_2, converting NO_x to N_2. In addition, according to the research, it was found that the presence of water vapor can promote the reaction between RNCO and NO_x, and even can produce N_2 and CO_2 under ordinary temperature. What's more, in the actual reaction, the presence of SO_2 in the exhaust gas will affect the reaction. When the temperature was lower than 400°C, the SO_2 in the reaction gas would reduce the NO_x removal activity. The reason is that the presence of SO_2 inhibited the production of RNCO which as the intermediate of the reaction [9-12].

CONCLUSION

In this study, the experiment adopts the impregnation method, using $AgNO_3$ and NH_4Cl as raw materials, and generates AgCl as the active component of the catalyst through the reaction was supported on Al_2O_3. According to the different reaction sequence of raw materials, the drying, and sintering time of the materials, the experiment is divided into four conditions for comparison. In addition, through the characterization and simulation of diesel exhaust test, the NO_x treatment capacity of the catalyst under four different conditions was evaluated. XRD, SEM, TEM, UV-Vis were used for characterization to prove that the active substance was successfully introduced into the support after synthesis, and it had a good distribution in the support. In the experiment, through HC-SCR detection, NO, C_2H_5OH, He, O_2 and H_2O gas were introduced to simulate the tail gas environment to obtain the relationship between NO_x conversion rate and temperature. The result show that during the heating process of the catalyst prepared by the four conditions, the catalysts prepared under condition C and condition D have good catalytic activity in a wide temperature range. The catalyst produced under condition B shows good catalytic activity at low temperature; on the contrary, the catalyst prepared by condition A can convert NO_x to N_2 in the exhaust gas at high temperature. We also explored the catalytic performance of the catalysts under four different conditions after heating, cooling, and heating again. The test results show that the catalysts obtained under condition B and D have good reproducibility. After repeated use, they still have good catalytic performance.

The catalyst prepared in this study has a good activity for the conversion of NO_x in diesel exhaust, in the meantime compared with other noble metal catalysts, this method will greatly reduce the cost, and provides a new idea for the research of diesel exhaust treatment catalyst. This study has a good prospect for the future application of materials in practice.

ACKNOWLEDGMENT

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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