Influence of Ag-based Supported Catalyst via Hydrothermal Synthesis on the Catalytic Treatment Efficiency of Formaldehyde Gas

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Abstract. This study aims to explore the influencing factors of the Ag-based supported catalyst synthesized via hydrothermal synthesis method in formaldehyde catalytic oxidation treatment. CeO$_2$ nanorods (CeO$_2$-r) is prepared by hydrothermal synthesis method, and a series catalyst of Ag-K/CeO$_2$-r with different concentrations of active components are prepared by adding active components to the nanorods by maceration method. The best weight hourly space velocity (WHSV), the best concentration of formaldehyde, and the best concentration of active components are studied with the prepared catalysts. When the WHSV is between 26000cm$^3$(g h)$^{-1}$ and 42000cm$^3$(g h)$^{-1}$, the maximum conversion rate is at the WHSV of 36000cm$^3$(g h)$^{-1}$. The different formaldehyde concentrations are set, it is found that when the formaldehyde concentration is 300ppm, the conversion rate of formaldehyde through the catalyst can reach 100%. Under the condition of 300ppm, 36000cm$^3$(g h)$^{-1}$, the optimal conversion rate of 4%Ag-K/CeO$_2$-r catalyst is found to be the best at all temperatures. Moreover, the physical adsorption of the catalyst is related to whether the catalyst is loaded with auxiliary agent K. In this study, the Ag-based supported catalyst is prepared via hydrothermal synthesis method and the influencing factors of formaldehyde gas treatment are successfully investigated, which lay a solid foundation for further experiments.

Keywords. hydrothermal synthesis; CeO$_2$ nanorods; Ag; formaldehyde; catalytic oxidation.

1. Introduction

As one of the most familiar air pollutants, formaldehyde increases year by year with the increasing frequency of human activities [1]. At present, not only the indoor decoration but also the smoke exhaust ventilator, second-hand smoke, automobile, game paint, aquatic products, and even cowboy clothing will release formaldehyde gas, causing serious harm to our bodies [2, 3]. Some studies show that living in an environment full of formaldehyde for a long time can cause respiratory discomfort, eye acid, dermatitis, and psoriasis [4]. Cases of leukemia caused by prolonged exposure to formaldehyde are common, and the harm to public with low resistance to formaldehyde is greater [5]. According to the relevant investigation, when air quality is tested in the decorated residential areas in China, among which
70% of the formaldehyde emissions exceed the national standard [6]. Therefore, how to effectively remove formaldehyde in a short period of time has become a hot research topic. The common methods to solve formaldehyde pollution include ventilation, plant purification, physical adsorption, photodegradation, biological method, and catalytic oxidation. Although ventilation method and plant purification method are easy to operate and at low cost, they usually take a long time and can’t completely remove formaldehyde; while the catalytic oxidation is not only with high adsorption efficiency, easy operation, and no secondary pollution, but also with a good development prospect [7, 8]. At present, catalysts commonly used for catalytic oxidation of formaldehyde mainly are single metallic oxides, mixed metallic oxides, Au catalysts, Pt catalysts, and Ag catalysts, etc. [9]. Mixed metal oxide catalysts prepared by doping metal elements such as Ce, Sn, Cu, and Zr into single metal oxides such as CeO$_2$, MnO$_x$, and Co$_3$O$_4$ can improve the catalytic performance of single metal oxide catalysts. But by referring relevant discoveries, this kind of catalyst only carries on the formaldehyde catalytic oxidation under high temperature, while the expensive metal supported catalysts can not only achieve the same or better catalytic results as above, but also conduct catalytic oxidation at room temperature or even lower temperature.

Since Ag is relatively cheap and easy to obtain in those expensive metals, this experiment started with Ag as the active component, Ce oxide (CeO$_2$) is adopted as the carrier, Ag-based supported catalyst is synthesized by hydrothermal synthesis method, and the influencing factors of its treatment efficiency is explored.

2. Methodology

2.1. Preparation of catalyst nanorods via hydrothermal synthesis

1.96g solid Ce(NO$_3$)$_3$·6H$_2$O is precisely weighed in the electronic balance, and the solid is added to 40mL distilled water and stirred and dissolved. NaOH solution is prepared by dissolving 16.88g NaOH in 30mL distilled water. At room temperature, NaOH solution is mixed with Ce(NO$_3$)$_3$·6H$_2$O solution and stirred for 30min. The thoroughly stirred solution is poured into the polytetrafluoroethylene high-pressure reactor, and the reaction is carried out at 100°C for 24h under homogeneous conditions, then the solution is taken out for cooling. The cooling solution is filtered and washed with distilled water until it is neutral. After drying at 100°C for 12h, the cooling liquid is put into the muffle furnace and roasted at 450°C for 4h, the roasting is set to temperature rising program and the heating rate is set to 1°C/min. Then the sample CeO$_2$ catalyst nanorod is prepared, which is called CeO$_2$-r.

2.2. Preparation of nano-catalysts Ag/CeO$_2$

A certain amount of CeO$_2$ nano catalyst carrier is weighed and gently sprinkled into a 200mL beaker containing 40mL distilled water, and the carrier suspension is obtained after dispersion. A certain amount of AgNO$_3$ is weighed and added with 20mL distilled water to make AgNO$_3$ solution, and the solution slowly drooped into the suspension with the carrier. After the operation, the liquid will be sealed and kept in dark and stirred continuously for 24h. Setting the temperature to 80°C, the solution is stirred in the beaker until it becomes viscous, then it is removed and dried at 80°C for 12 hours. The solution is roasted for 4 h at 450°C in muffle furnace, the roasting is set to temperature rising program, and the heating rate is set as 5°C/min. And Ag/CeO$_2$ nanorods catalyst is prepared, which is recorded as Ag/CeO$_2$-r.

2.3. Preparation of nano-catalysts Ag-K/CeO$_2$

A certain amount of CeO$_2$ nano catalyst carrier is weighed and gently sprinkled into a 200mL beaker containing 40mL distilled water. After the carrier suspension is evenly dispersed, the carrier suspension is obtained and taken as suspension 1. A certain amount of AgNO$_3$ and KNO$_3$ is taken and dissolved together in 40mL of distilled water as solution 2. Solution 2 is slowly dropped into suspension 1, after which the solution will be sealed and kept stirring in dark for 24h. The temperature is raised to 80°C, and it is taken out after stirring and drying. It is dried at 80°C for 12h, and it is roasted at 450°C in muffle
furnace for 4 h. Then the catalyst Ag-K/CeO$_2$ nano catalyst is prepared, which is recorded as Ag-K/CeO$_2$-r. The theoretical Ag percentages of the prepared sample are 2%, 4%, 8%, and 10%. The actual contents are 2.13%, 4.23%, 8.11%, and 10.35%. The theoretical mass percentage of K remains unchanged at 1.3%; the actual percentage is 1.21%. The difference between the theoretical value and the actual value is small and the preparation is successful and doesn’t affect the following experiment.

3. Results and discussion

3.1. Effect of WHSV on catalyst performance

The 4% Ag-K/CeO$_2$-r with the best catalytic oxidation performance is selected for the test. The influence of WHSV from 26000cm$^3$(g h)$^{-1}$ to 42000cm$^3$(g h)$^{-1}$ on the catalyst performance are investigated at the same temperature (100°C), and the results are shown in figure 1.

![Figure 1](image)

**Figure 1.** Performance of 4%Ag-K/CeO$_2$-r on catalytic oxidation of formaldehyde at different WHSV.

The conversion rate of formaldehyde increases first and then decreases with the increase of WHSV. During the process of WHSV increasing, the reaction time between formaldehyde and the fixed bed is gradually shortened, so that the formaldehyde gas will leave the catalyst bed before it can fully contact and react with the catalyst, so the conversion rate of formaldehyde will inevitably decrease [10]. According to the experiment, it can be concluded that when the WHSV is at 36000cm$^3$(g h)$^{-1}$, the per unit time entering formaldehyde gas can be fully reflected in the catalyst bed, so 36000cm$^3$(g h)$^{-1}$ is selected as the reaction WHSV.
3.2. Influence of formaldehyde concentration on catalyst performance
The optimal WHSV is obtained from section 3.1, and the catalyst performance of 4% Ag-K/CeO$_2$-r is explored at this speed, as shown in figure 2.

![Figure 2. Performance of different concentrations of 4% Ag-K/CeO$_2$-r on catalytic oxidation of formaldehyde.](image)

The formaldehyde concentrations are 100ppm, 150ppm, 200ppm, 250ppm, 300ppm, 350ppm, and 400ppm, and the corresponding conversion rate of formaldehyde are 85.9%, 89.5%, 93%, 96%, 100%, 94%, and 89%. As shown in figure 2, the conversion rate of formaldehyde increases first and then decreases with the increase of formaldehyde content, and reaches the maximum conversion rate of 100% at 300ppm, the conversion rate decreases when the formaldehyde concentration increases to 350ppm, and reached 89% at 400ppm. And the optimal concentration of formaldehyde is 300ppm.

3.3. Effect of Ag content on catalyst performance
It is not difficult to find that the content of the active component Ag in the catalyst also affects the overall performance of the catalyst. The content of the active component Ag is changed by adding auxiliary agent during the preparation. Performance evaluation tests are carried out on CeO$_2$-r, 4% Ag/CeO$_2$-r, and x% Ag-K/CeO$_2$-r catalysts, and the activity of catalytic formaldehyde is shown in figure 3. The reaction conditions are obtained from section 3.1 and 3.2, the formaldehyde concentration is set to 300ppm and the WHSV is set to 36000cm$^3$(g h)$^{-1}$.

![Figure 3. Activity of formaldehyde catalyzed by different Ag contents.](image)
As shown in figure 3, the conversion rates of formaldehyde in the full temperature process from large to small are 4% Ag-K/CeO$_2$-r, 8% Ag-K/CeO$_2$-r, 2% Ag-K/CeO$_2$-r, 4% Ag/CeO$_2$-r, 10% Ag-K/CeO$_2$-r, and CeO$_2$-r, and the conversion rate of catalysts with different Ag content increase obviously with the increase of temperature. Among them, CeO$_2$-r with a content of 0 active component performs poorly at all temperatures, and the conversion rate is only 79% when the temperature is at maximum of 140°C. With the addition of auxiliary agent K and active component Ag, the catalyst conversion rates containing active component Ag of 2%, 4%, and 8% increase. The formaldehyde conversion rate of 4% Ag-K/CeO$_2$-r catalyst is optimal. At 100°C, formaldehyde can be completely decomposed into non-toxic water and carbon dioxide. However, the conversion rate will decrease when Ag content increase to 10%. For the supported catalyst, the content of active components is an important factor affecting the catalytic capacity, so it needs to be determined in repeated experiments, so as to bring out the maximum activity of catalyst [11].

3.4. Effects of auxiliaries on physical adsorption of catalysts

The results are shown in figure 4. The specific surface area of the carrier CeO$_2$-r is 103.8 m$^2$/g, and the pore diameter and pore volume are 8.1 nm and 0.41 cm$^3$/g, respectively. Base on that, the active component Ag is added for study, and it is found that the specific surface area, pore diameter, and pore volume of 4% Ag/Ag/CeO$_2$-r after loading with Ag are not much different from those without loading with active component, which indicates that the addition of Ag has little effect on the physical structure of CeO$_2$-r. After the addition of 1.3% K, the specific surface area of the catalyst at any concentration of active content decrease significantly, the pore diameter increases obviously and the pore volume decreases obviously. All these indicate that the addition of agent K has an effect on the physical structure of the catalyst itself, and also affects the physical adsorption to some extent. It is speculated that the addition of K may block the micropores on the surface of the CeO$_2$-r nano carrier, a similar phenomenon is also mentioned in the study of Lei et al. (2018) [12].

![Figure 4. Physical adsorption related data.](image)
4. Conclusion
In this study, CeO$_2$-r is prepared by hydrothermal synthesis method, and the active component Ag and auxiliary agent K are loaded by impregnation method. The optimal conditions for catalytic oxidation of formaldehyde and the concentration of the optimal active component are studied by constructing the contents of the active component Ag at different concentrations. Through relevant studies, the optimal WHSV and concentration of formaldehyde in catalytic oxidation treatment are verified, based on which the optimal active ingredient content is further explored, and the best activity of 4% Ag-1.3% K/CeO$_2$-r catalyst is finally determined, the conversion rate of formaldehyde can reach 100% at 100°C. However, the mechanism 4% Ag-1.3% K/CeO$_2$-r showing the best catalytic oxidation activity isn’t deeply studied. The results of this study provide a direction for the subsequent treatment of formaldehyde at low temperature or room temperature and lay a foundation for the home-based treatment for formaldehyde.

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