

Catalytic Decomposition of Nitrogen Oxides by Bimetallic Catalysts Synthesized by Dielectric Barrier Discharge Plasma Technology

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Abstract. Nitrous oxide (N_2O) is a common greenhouse gas and urgent need to be contained. Direct catalytic decomposition of N_2O by high activity catalyst into N_2 and O_2 is a low-cost and harmless method. Bimetallic catalysts show good catalytic activity in many classes of reactions, and plasma technologies, applied to prepare of catalyst, are considered to be a promising method. In our contribution, DBD cold plasma is applied to synthesize Rhodium and Cobalt bimetallic catalysts for catalytic N_2O decomposition. The influence of cobalt and rhodium content on N_2O decomposition activity shows that the optimal amount of metal is determined as 5wt. % cobalt and 0.5wt. % rhodium loaded on Al_2O_3 . The best working voltage is determined as 18kV. The results indicated that the Rh/ Al_2O_3 catalysts prepared by atmospheric-pressure DBD cold plasma showed smaller size and high dispersion of Rh particles, so that the metal-support interaction and the catalytic activity are enhanced. Atmospheric-pressure DBD cold plasma is proved to be an environmentally friendly and efficient method for preparing high performance Rhodium and Cobalt bimetallic catalysts for catalytic N_2O decomposition.

1 Introduction

Nitrous oxide (N_2O) is a common greenhouse gas and caused mainly by fossil fuel combustion and industrial production. This gas can lead to plenty of environmental problems like acid rain, photochemical smog and ozone-layer depletion. The concentration of N_2O has increased at an annual rate of 0.2-0.3% since the industrial revolution [1-3]. Thus, it is quite necessary to search for the way to remove N_2O .

In recent years, several ways for N_2O removal are applied such as thermal decomposition [2], selective catalytic reduction [2, 4] and direct catalytic decomposition [5, 6]. Thermal decomposition requires for excessive temperature and energy consumption. Selective catalytic reduction need consume reducing gas, resulting in the increase of treatment costs. By comparison, direct catalytic decomposition of N_2O into N_2 and O_2 is superior as this process is low-cost and harmless [7]. The catalyst for direct catalytic decomposition of N_2O mainly includes zeolite, metal oxide and noble metal catalyst. Among them, the zeolite-based catalyst is easy to be sintered, and the metal oxide catalyst has poor thermal stability and poor activity. Rh is an ideal catalyst for N_2O direct catalytic decomposition. It is very promising to improve Rh catalyst by changing catalyst morphology such as reduce the size of the loaded metal particles to improve dispersion. Studies have found that the incorporation of transition metals in Rh metal

improves catalytic N_2O direct catalytic decomposition activity.

At present, plasma technologies applied to prepare of catalyst are considered to be a promising approach. In general, three main trends in preparing catalysts using plasma technologies are attracted the attention of academia [8]: (1) ultrafine particle catalysts synthesis by plasma chemical; (2) plasma assisted deposition of catalytically active compounds on various carriers, especially plasma spraying for the preparation of supported catalysts; (3) plasma modification or plasma enhanced preparation of catalysts. Compared to conventional catalyst preparation, there are several merits of using plasmas: (1) reduced energy requirements; (2) a highly distributed active species; (3) enhanced catalyst activation, selectivity, and lifetime; (4) shortened preparation time.

Dielectric barrier discharge (DBD) is a simple and easily operated environmentally friendly approach for generating atmospheric-pressure cold plasma, and it can be used for preparing supported noble metals [9-11]. In our contribution, Rh-Co bimetallic catalyst is synthesized by means of atmospheric-pressure DBD cold plasma to catalytic decomposition of N_2O .

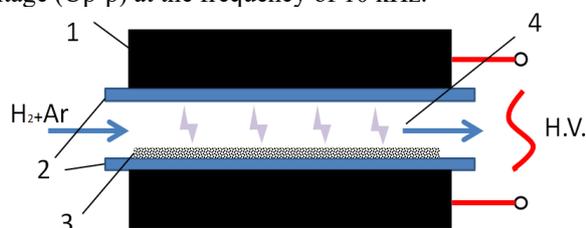
2 Experimental

2.1 Catalyst preparation

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RhCl₃ and activated aluminium oxide are purchased from Sinopharm Chemical Reagent Co., Ltd. Cobalt nitrate, ferric nitrate and nickel nitrate are purchased from Tianjin Fuchen Chemical Reagent Co., Ltd. The pretreatment of Al₂O₃ is calcined at 550°C for 4h. All of supported metal catalysts are synthesized by wetness incipient impregnation. And then the precursor is dried at 110°C for 2h and finally reduced by hydrogen at 450°C for 2h or at DBD reactor of 18kV for 6min.

The schematic DBD cold plasma device for preparing catalysts at atmospheric pressure is shown in Scheme 1. The electrodes are stainless steel plates (50 mm in diameter). A reaction cell made of quartz is placed between the electrodes. The reaction cell consisted of two parts. The upper part was a quartz plate (70 mm in diameter, 1-mm thickness), while the lower part is a tank (75 mm in diameter, 9-mm height). The discharge gap was 8 mm. The power source (CTP-2000 K, Nanjing Suman Electronic Co., Ltd) is capable of supplying a bipolar sine wave output with 0–50 kV peak-to-peak voltage (Up-p) at the frequency of 10 kHz.



Scheme 1 Schematic diagram of the atmospheric-pressure DBD cold plasma device (1–electrode, 2 – quartz glass, 3 – sample, 4 – cold plasma.)

2.2 N₂O decomposition

The decomposition of N₂O with the action of only catalysts is tested in a transparent quartz tube (6mm inner diameter) as the fixed-bed reactor. 0.3g catalyst is packed in the middle position of the tube and sealed by quartz wool both sides. A gas stream of 10% N₂O-He flowed through the tube at a rate of 30mL/min. The gas from the outlet is analyzed by a gas chromatograph (GC, Fuli 9790) that can separate He, N₂, O₂ and N₂O. The reaction begins after a one-hour gas flow process at room temperature and each reaction temperature will be kept for 30min to measure the conversion. The conversion of N₂O was calculated according to the equation (1):

$$X = \frac{[N_2O]_{\text{initial}} - [N_2O]_{\text{reaction}}}{[N_2O]_{\text{initial}}} \quad (1)$$

where X is the conversion of N₂O, [N₂O]_{initial} is the peak area of N₂O at room temperature and [N₂O]_{reaction} is the peak area of N₂O at reaction temperature.

2.3 Characterization

XRD patterns are recorded on a SHIMADZU-6100 X-Ray Diffractometer using CuK α radiation at a scanning speed of 10°C/min. TEM images are recorded on a FEI-G2F30.

3. Results and discussion

3.1 Screening of different active metals

The decomposition of N₂O reaction over the different metals supported by aluminium oxide catalysts was studied. 3wt.% Fe/Al₂O₃, 3wt.% Co/Al₂O₃, 3wt.% Ni/Al₂O₃, 0.5wt.% Rh/Al₂O₃ and 1.5wt.% Rh/Al₂O₃ catalysts were prepared by hydrogen reduction at 450°C for 2h and ready for the decomposition reaction. The experiments were performed at a constant flow of N₂O (30ml/min). The results of decomposition of N₂O reaction over five different catalysts are shown in Fig. 1, the solid lines in the figures represent the conversion of N₂O at different temperature. It can be seen that Rh/Al₂O₃ is the best catalyst and Co is another ideal active component. 0.5% Rh/Al₂O₃ and 1.5% Rh/Al₂O₃ show similar decomposition ability. There for 0.5% Rh/Al₂O₃ catalysts are the most suitable for the reaction and Co is screened as the second dipping component.

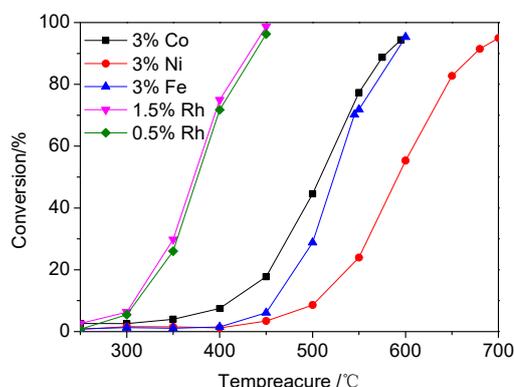


Fig. 1 Results of decomposition of N₂O reaction over four different metals supported by aluminium oxide catalysts

3.2 Bimetallic catalysts activity investigation

Catalysts with different cobalt contents were studied. 1wt.%Co-0.5wt.%Rh/Al₂O₃, 3wt.%Co-0.5wt.%Rh/Al₂O₃, 5wt.%Co-0.5wt.%Rh/Al₂O₃, catalysts were prepared by hydrogen reduction at 450°C for 2h and ready for the decomposition reaction. The results of decomposition of N₂O reaction over four different catalysts are shown in Fig. 2.

Fig. 2 shows that the incorporation of Co increases the catalytic decomposition activity of the catalyst. As the amount of Co incorporation increases, the catalytic activity increases. As a result, 5wt.% is determined the superior cobalt content.

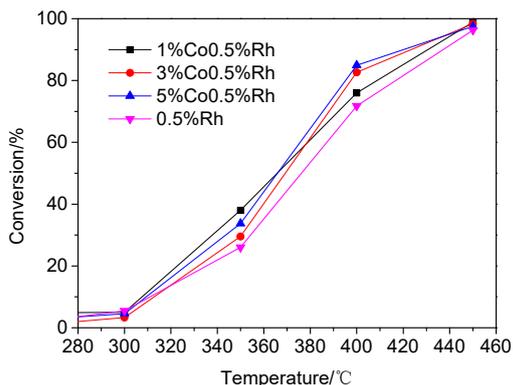


Fig. 2 Results of decomposition of N_2O reaction over bimetallic catalyst with different contents of Co

3.3 Bimetallic catalysts prepared by atmospheric-pressure DBD cold plasma activity investigation

In order to investigate the catalytic decomposition ability of the catalysts reduced by atmospheric-pressure DBD plasma at different voltage conditions, 0.5wt.%Rh/Al₂O₃ were prepared in different voltages. 9kV, 12kV, 15kV, 18kV were investigated, and the results of the N₂O decomposition conversion are shown in Fig. 3. It indicates that the higher the reduction voltage, the better catalytic activity of the N₂O decomposition. The catalyst prepared at 18kV shows the best activity, therefore, 18kV is selected as the ideal reduction condition.

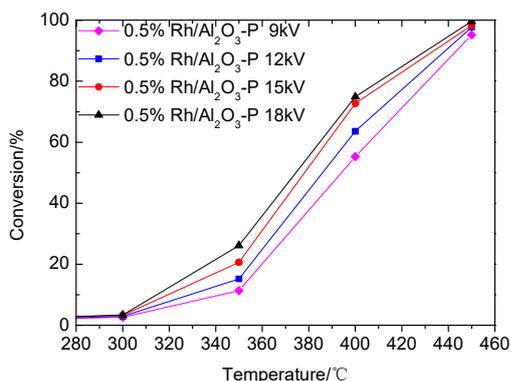


Fig. 3 N₂O decomposition conversion on the different catalysts prepared by atmospheric-pressure DBD cold plasma at 9~18kV.

In the last set of experiment two catalysts preparing methods of high-temperature hydrogen reduction and atmospheric-pressure DBD cold plasma hydrogen reduction were compared. 0.5wt.%Rh/Al₂O₃ and 5wt.%Co-0.5wt.%Rh/Al₂O₃ prepared by atmospheric-pressure DBD cold plasma hydrogen reduction at 18kV (named 0.5wt.%Rh/Al₂O₃-P and 5wt.%Co-0.5wt.%Rh/Al₂O₃-P) were compared with 0.5wt.%Rh/Al₂O₃ prepared by high-temperature

hydrogen reduction (0.5wt.%Rh/Al₂O₃-C). The result shows in Fig.4.

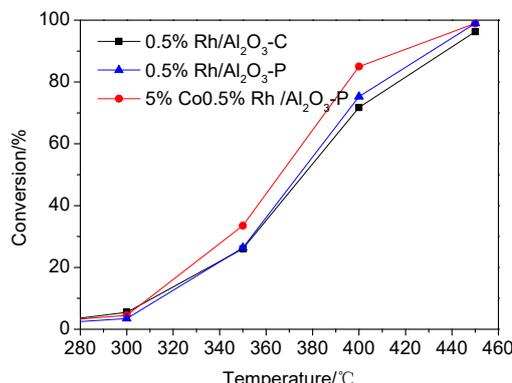


Fig. 4 N₂O decomposition conversion on the 0.5wt.%Rh/Al₂O₃-C, 0.5wt.%Rh/Al₂O₃-P and 5wt.%Co-0.5wt.%Rh/Al₂O₃.

Fig.4 shows that the order of decomposition conversion from high to low is 5wt.%Co-0.5wt.%Rh/Al₂O₃-P, 0.5wt.%Rh/Al₂O₃-P and 0.5wt.%Rh/Al₂O₃-C. It indicates that synergism of bimetal effect and atmospheric-pressure DBD cold plasma hydrogen reduction can elevate the activity of catalytic N₂O decomposition.

0.5wt.%Rh/Al₂O₃-C and 0.5wt.%Rh/Al₂O₃-P were characterized by XRD and TEM to analysis the role of atmospheric-pressure DBD cold plasma in the preparation of catalyst. The XRD diffraction pattern are shown in Fig. 5. There are no obvious differences between the patterns of 5wt.%Co-0.5wt.%Rh/Al₂O₃, 0.5wt.%Rh/Al₂O₃-P and 0.5wt.%Rh/Al₂O₃-C. It demonstrates that the nano-sized Rh metal particles of both the catalysts prepared by high-temperature hydrogen reduction and atmospheric-pressure DBD cold plasma hydrogen reduction uniform disperse on the supports.

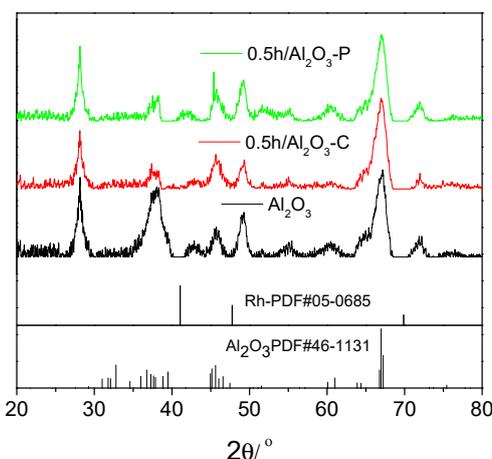


Fig. 5 XRD diffraction patterns of 0.5wt.%Rh/Al₂O₃-C, 0.5wt.%Rh/Al₂O₃-P and Al₂O₃.

TEM photos of the two class of catalysts are shown in Fig. 6.

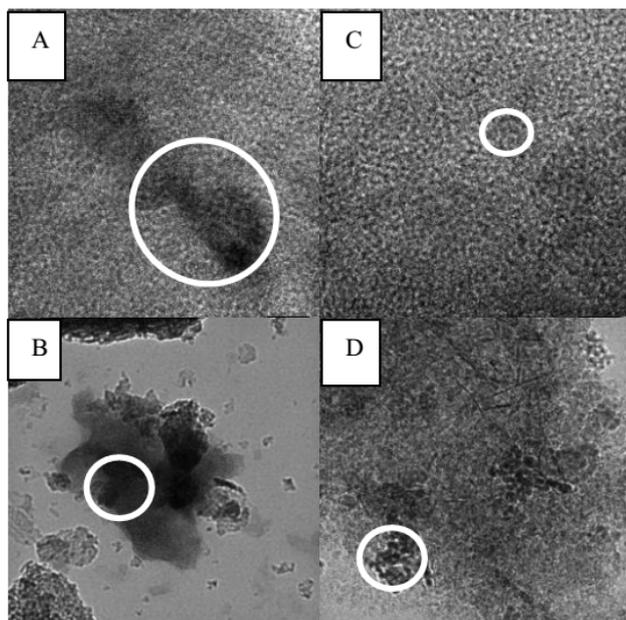


Fig. 6 The TEM photos of 0.5wt.%Rh/Al₂O₃-C (A,B), 0.5wt.%Rh/Al₂O₃-P and Al₂O₃ (C,D).

TEM images of 0.5wt.%Rh/Al₂O₃-C are shown in A and B, and 0.5wt.%Rh/Al₂O₃-P are shown in C and D. The mean particle size of Rh in 0.5wt.%Rh/Al₂O₃-P was 3-5 nm, which was much smaller than that in 0.5wt.%Rh/Al₂O₃-C (about 10 nm). This confirmed that Rh particles were better dispersion for Rh/Al₂O₃ prepared by atmospheric-pressure DBD cold plasma.

In summary, Rh-Co bimetallic catalyst can get the better catalytic activity than any other one of them, and atmospheric-pressure DBD cold plasma is proved to be an environmentally friendly and efficient method for preparing the catalysts of N₂O decomposition.

4 Conclusion

High performance Rhodium and Cobalt bimetallic catalysts were prepared by DBD cold plasma at atmospheric pressure using the mixture of H₂ and Ar as working gas to catalytic N₂O decomposition. The influence of cobalt and rhodium content on N₂O decomposition activity showed that the optimal amount of metal was 5wt.% cobalt and 0.5% rhodium loaded on Al₂O₃. The best working voltage was determined as 18kV. The results indicated that the Rh/Al₂O₃ catalysts prepared by atmospheric-pressure DBD cold plasma showed smaller size and high dispersion of Rh particles, so that the metal-support interaction and the catalytic activity were enhanced.

Atmospheric-pressure DBD cold plasma was proved to be an environmentally friendly and efficient method for preparing high performance Rhodium and Cobalt bimetallic catalysts for catalytic N₂O decomposition.

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