Preparing Ag/Al_2O_3 for the selective catalytic reduction of NO_x by ball-milling method

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Introduction

When encountered with a potential energy crisis, the introduction of lean-burn engines and diesel engines becomes a popular strategy to improve fuel economy. However, NO_x abatement under the oxidizing atmosphere in such engines is a major challenge [1-4]. Since the pioneering work of Iwamto et al [5] and Held et al. [6], many catalysts such as zeolite-based catalysts and supported precious metal catalysts [5, 7] have been developed for the SCR of NO_x by hydrocarbons (HC-SCR). Among them, Ag/Al_2O_3 is deemed as the most effective material for SCR of NOx in excess oxygen. However, its lack of activity in the low temperature range (< 350℃) still remains a problem.

Since the pioneering work of Burch et al. [8], the preparation of a new type of Ag/Al_2O_3 catalyst with improved low temperature performance by a solvent-free mechanochemical method has drawn widely interest. In this study, the detailed preparation conditions for this catalyst were carefully examined, including rotation speed and ball-milling time. The performance in selective reduction of NO_x with ethanol was evaluated along with monitoring of byproducts. Optimum preparation conditions were identified, with ball milling at 300 r/min for one hour giving the best results.

Materials and Methods

Ag/γ-Al_2O_3 catalysts with constant silver loading (2 wt %) were prepared by a solvent-free ball milling method. Appropriate amounts of γ-Al_2O_3 (SASOL, SBa-200) and the Ag precursor $AgNO_3$ were well mixed by hand. The resulting mixture was placed into a 125 ml sintered alumina grinding jar with several 10 mm diameter grinding balls. Milling was carried out in a Retsch PM 100 Planetary Ball Mill at several rotation speeds (150, 300, 400, 500 r/min) and for different working times (1, 3, 5, 7h). An impregnated sample was also prepared for comparison. The resulting powders were calcined at 600 ℃ for 3h. The SCR process was evaluated by an FTIR spectrometer (Nicolet Nexus is10).The concentrations of NO, NO_2, N_2O, NH_3, and CO were analyzed online simultaneously.

Results and Discussion

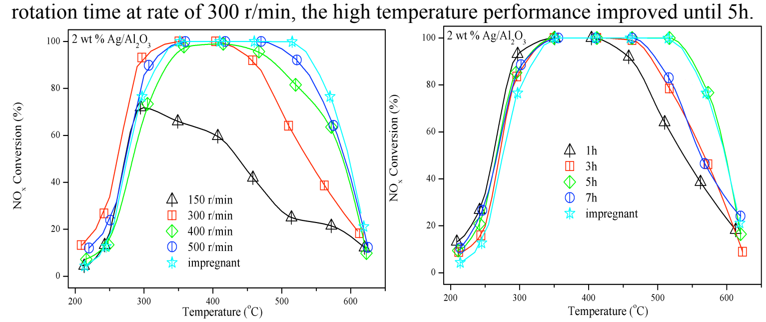
The 50% conversion temperature and max NO_x conversion are summarized and given in **Table 1** for each catalyst.

Table 1. The 50% conversion temperature and max NO_x conversion for each catalysts.

(r/min)	150 1h	300, 1h	400, 1h	500, 1h	300, 3h	300, 5h	300, 7h	impregnated catalyst
T (50%) Conv/℃	272	261	285	272	271	266	268	276
Max NO_x Conv/%, (temp/℃)	72, 295	100, 351	99, 415	100, 360	100, 350	100, 350	100, 356	100, 352

Ag/Al_2O_3 is highly active for selective reduction of NO_x in excess oxygen. Comparing different preparation methods, the solvent-free ball-milling method works as well as the traditional impregnation method in SCR process with ethanol reductant. After ball-milling at 300r/min for 1 hour, the catalyst presented the best performance in the low temperature range. The half conversion temperature (T50) was reduced by 15 ℃. Rotation speed is a crucial factor in preparing catalysts. With increasing rotation speed, the reduction performance at high temperature increased, approaching that of the impregnated sample. With increasing rotation time, the catalytic improvement in the low temperature range (<350℃) was negligible, but the activity in the high temperature range increased, with maximum activity at 5h.

Figure 1 shows the NO_x conversion as function of temperature during selective reduction of NO_x experiment. Increasing rotation speed enhanced the catalytic performance. With increased rotation time at rate of 300 r/min, the high temperature performance improved until 5h.



(A) **(B)**

Figure 1. The NO_x conversion as function of temperature in flow of NO: 800 ppm, C_2H_5OH: 1565 ppm, O_2:10%, H_2O:10%, N_2 balance, 50000h^{-1}. (A) Rotation speed, (B) Rotation time

Significance

The solvent-free ball-milling method works as well as the traditional impregnation method in the preparation of Ag/Al_2O_3 catalysts. For the ball-milled sample prepared at 300r/min for 1h, the low temperature catalytic performance was improved, reducing T50 to 261℃.

References

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