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Selective catalytic reduction of NO_x over Ag/Al_2O_3 catalyst: from reaction mechanism to diesel engine test

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Abstract

Our recent research works on the selective catalytic reduction (SCR) of diesel engine NO_x by hydrocarbons over alumina-supported silver (Ag/Al_2O_3) were reviewed. The reaction mechanism of the SCR of NO_x by C_2H_5OH over Ag/Al_2O_3 was studied using in situ DRIFTS and DFT calculations. A novel enolic species originating from the partial oxidation of C_2H_5OH and C_3H_6, was found on the surface of Ag/Al_2O_3 during the SCR of NO_x by in situ DRIFTS, which was also supported by DFT calculations. Based on this, a mechanism of the NO_x reduction was proposed, which can successfully explain the high efficiency of the NO_x reduction by C_2H_5OH over Ag/Al_2O_3. A palladium promoted Ag/Al_2O_3 catalyst (denoted $Ag–Pd/Al_2O_3$) was developed for the SCR of NO_x by C_3H_6. The $Ag–Pd/Al_2O_3$ showed a higher NO_x conversion than Ag/Al_2O_3, especially at temperatures ranging from 300 to 450 °C. The engine bench tests showed that the average NO_x conversion was greater than 80% in the diesel engine exhaust temperature range of 300–400 °C using our catalytic converter with C_2H_5OH as reductant, which represents a leap from the Euro II standard to the Euro III standard for NO_x emission control in diesel engines.

Keywords: Selective catalytic reduction (SCR) of NO_x; Alumina supported silver (Ag/Al_2O_3); Ethanol (C_2H_5OH); Diesel engine; Enolic species

1. Introduction

Due to shortages of petroleum resources, lean-burn engines have become the main option for the vehicles. The diesel engine, which is a typical lean-burn engine, has the advantage of lower consumption of fuel and lower emission of CO_2, CO and HC than stoichiometric gasoline engine. However, the exhaust from diesel engines contains a large amount of NO_x compared to stoichiometric gasoline engines equipped with three-way catalysts (TWCs). For a stoichiometric gasoline engine, a TWC provides a very high level of emission control for the removal of CO, NO_x, and unburnt hydrocarbons. However, diesel engines produce exhaust containing a large excess of oxygen. The platinum group metals based TWCs are completely ineffective for NO_x reduction under the oxygen-rich conditions. Removal of NO_x in the oxygen-rich exhausts demands a novel catalyst for a selective catalytic reduction (SCR) of NO_x. The SCR of NO_x by ammonia, or in some cases, urea, has become a fairly mature technology for stationary applications [1–4]. For mobile applications such as diesel trucks and some lean-burn gasoline cars, however, commercialization still lies somewhere in the future. Up to now, multifarious catalysts such as zeolitic oxide, base oxide/metal and noble metal catalysts have been found to be effective for NO_x reduction in the presence of excess oxygen [3,5–8]. Among them Ag/Al_2O_3 is known as one of the most effective catalysts for the SCR of NO_x by hydrocarbons [9–45]. In particular, C_2H_5OH is extremely effective for NO_x reduction over Ag/Al_2O_3 [10,11,17,36,38,41,46–51].

In this review, our recent research on the HC–SCR of NO_x over Ag/Al_2O_3 was summarized systematically on a laboratory scale and an actual diesel engine bench scale. Also, our results provided new insight into the mechanism of this NO_x reduction process.

2. Characterization and fundamental performance of Ag/Al_2O_3 in the SCR of NO_x

The supported catalysts, Ag/Al_2O_3 and Cu/Al_2O_3, were prepared by an impregnation method with an aqueous solution of silver and copper nitrate, followed by evapora-

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Table 1
BET surface area, pore volume and pore diameter of Ag/Al_2O_3 catalysts with different Ag loadings

Catalyst	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cc\ g^{-1}$)	Pore diameter (A)
2 wt.% Ag/Al_2O_3	239.8	0.7235	122.9
4 wt.% Ag/Al_2O_3	222.4	0.7107	124.9
6 wt.% Ag/Al_2O_3	211.8	0.6950	126.2
8 wt.% Ag/Al_2O_3	209.9	0.6493	130.3

tion to dryness in a rotary evaporator under pressure reduction at 60 °C. The wet sample was dried at 120 °C for 12 h, and then calcined in air at 600 °C for 3 h [39].

BET results of the catalysts are shown in Table 1. The surface area of the Ag/Al_2O_3 catalysts gradually decreased with increasing silver loading. XRD patterns of a series of Ag/Al_2O_3 catalysts are shown in Fig. 1. Only the γ-Al_2O_3 phase was detected as the silver loading increased from 2 to 6 wt.%, but the Ag and Ag_2O phases were observed at 2θ of 33.76°, 38.12°, 44.36° and 64.46° with 8 wt.% Ag loading [52,53]. TEM images of 4% Ag/Al_2O_3 catalyst are shown in Fig. 2. The Ag containing particles could be distributed evenly on the surface of Al_2O_3 with an optimum Ag loading of 4–6% and an average size of 15 nm.

Fig. 3 shows the NO_x conversions for the SCR of NO_x by C_3H_6 over Ag/Al_2O_3 catalysts with different silver loadings at various temperatures. The maximum of NO_x conversion increased significantly with an increase in silver loading from 2 to 4 wt.%, and the temperature at which the maximum NO_x conversion could be obtained (i.e. T_{max}) shifted towards a lower temperature. Further increase of the silver loading from 4 to 8 wt.% did not show any promotion of low-temperature NO_x conversion but inhibited the high temperature conversion.

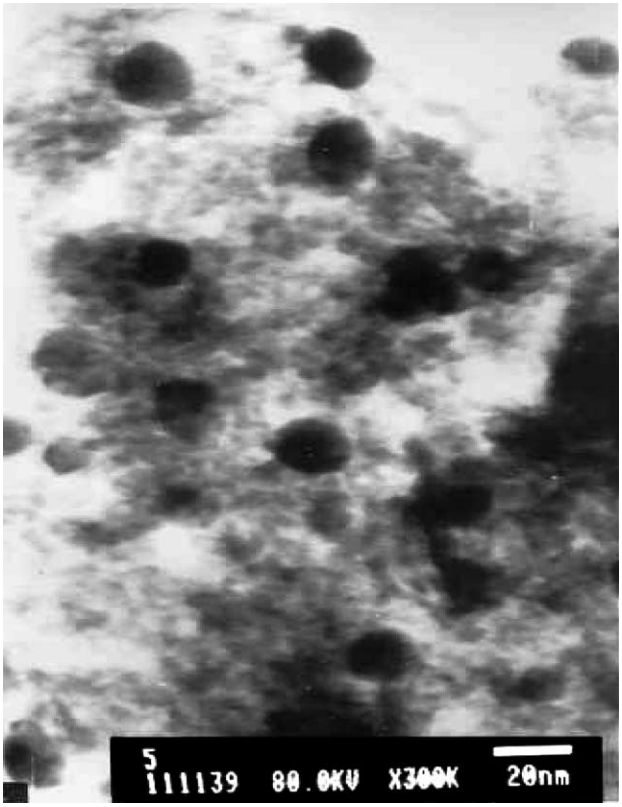

Fig. 2. TEM image of 4% Ag/Al_2O_3.

The NO_x conversions for the SCR of NO_x by C_2H_5OH over Ag/Al_2O_3 catalysts with different silver loadings are shown in Fig. 4. As same as in Fig. 3, the maximum of NO_x conversion increased significantly with an increase in silver loading from 2 to 4 wt.%, and the temperature at which the

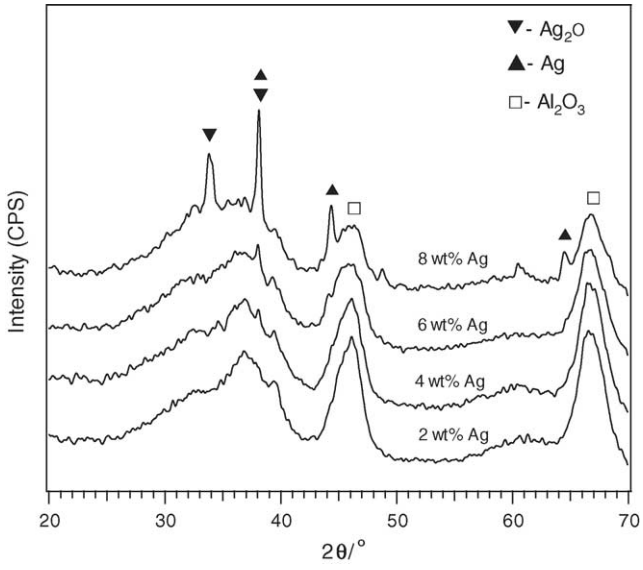

Fig. 1. XRD patterns of Ag/Al_2O_3 catalysts with different Ag loadings [39].

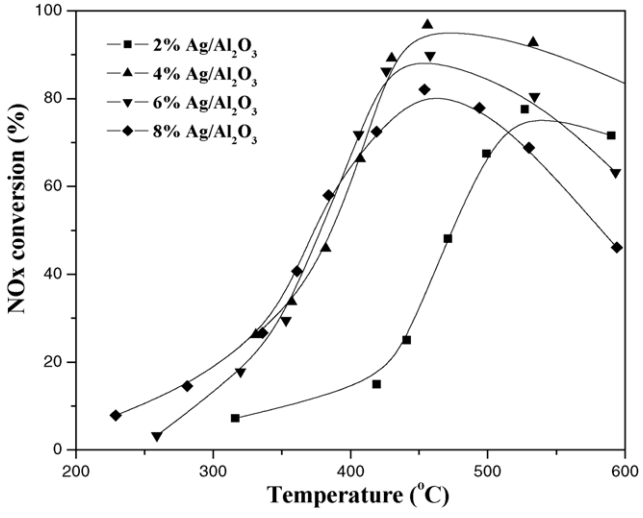

Fig. 3. NO_x conversion for the SCR of NO_x by C_3H_6 over Ag/Al_2O_3: (■) 2 wt.%, (▲) 4 wt.%, (▼) 6 wt.% and (◆) 8 wt.% at various temperatures. Conditions: 800 ppm NO, 1714 ppm C_3H_6, 10 vol.% O_2/N_2, catalyst weight = 1.2 g, W/F = 0.018 g s cm^{-3} [39].