Effect of AlF₃ on the NOₓ reduction over Ag/Al₂O₃ for HC-SCR

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Introduction
The selective catalytic reduction of NOₓ by hydrocarbons (HC-SCR) is an alternative technology for removing NOₓ from automotive engine exhaust under lean condition, free from the well-known drawbacks of the commercially available deNOₓ technologies such as urea-SCR and NOₓ storage reduction (NSR) [1]. For HC-SCR, a Ag/Al₂O₃ has been regarded as one of the most promising catalysts [2]. However, its low-temperature deNOₓ activity has much room to improve for successful commercial application. NH₃ has been known to be a major byproduct when HCs are used as reductants over Ag/Al₂O₃ [3]. In this work, a new Ag-based catalyst formulation with strong Lewis acidity (for NH₃ adsorption and oxidation to N₂) has been developed. The excellent deNOₓ activity of the catalyst developed in the present study has been demonstrated by using a mixture of the simulated diesel fuel (n-dodecane + m-xylene) and ethanol (i.e., E-diesel) as the reductant.

Experimental
For preparation of Ag/Al₂O₃, the γ-Al₂O₃ (CATALOX® SBa-200, Sasol) was first impregnated with AlF₃ by using a AlF₃:3H₂O (Samchun) solution, followed by Ag impregnation with a AgNO₃ (Kojima) solution. The catalyst was oven-dried at 110 °C overnight and calcined in a muffle furnace at 550 °C for 5 h [3].

A packed-bed flow reactor system was used to evaluate the catalyst deNOₓ activity [3]. The standard feed gas stream contained 400 ppm NOₓ, 640 ppm ethanol, 320 ppm C₂H₅, equivalent simulated diesel fuel (a mixture of 17 ppm n-dodecane and 15 ppm m-xylene), 6% O₂, 2.5% H₂O, and He balance. To determine the conversion of NOₓ to N₂, an FTIR equipped with a 2m gas-cell (Nicolet 6700, Thermo Electron Co.) and a gas chromatograph (GC) equipped with a TCD (HP 6890N, Agilent) were employed. The overall reactor space velocity was maintained typically at 60,000 h⁻¹.

The Ag/Al₂O₃ catalyst was characterized by NH₃-TPD and pyridine-FTIR to determine the acidic properties such as the amount of NH₃ adsorbed and type of acidic site (Lewis / Bronsted) formed on the catalyst surface.

Results and Discussion
In order to improve the low-temperature deNOₓ efficiency of Ag/Al₂O₃ catalyst by HC-SCR technology, AlF₃ was additionally impregnated onto the surface of Al₂O₃ support, followed by Ag impregnation. When the catalyst fluorine loading increases from 0 to 2.7 wt.%, the NOₓ reduction activity gradually increases below 300 °C, while that of the catalyst containing 25 wt. % of F apparently declines. Above 2.7 wt.% of the catalyst fluorine content, NH₃ was hardly produced, probably due to the further reaction of NOₓ to N₂. Specifically, the

![Figure 1](image-url) Effect of AlF₃ loading on NOₓ reduction activity of Ag/Al₂O₃ catalysts.

When AlF₃ is added to the Ag/Al₂O₃ catalyst, NH₃ is hardly produced as shown in Figure 1. This indicates that AlF₃ increases the catalyst surface acidity, resulting in the further oxidation of NH₃ to N₂. To directly determine the amount of the surface acidity and the type of acid site included in Ag/Al₂O₃ catalyst, NH₃-TPD and pyridine-IR analysis have been conducted. The acid site densities of the Ag(3.8)/AlF₃(F: 2.7)/Al₂O₃ catalyst determined from NH₃-TPD and pyridine-IR analysis significantly increased to nearly double compared to those of the Ag(3.8)/Al₂O₃ catalyst, although the small amount of AlF₃ was added to the catalyst (Table 1). This reveals that the acid site density of the catalyst may be a criterion to develop an effective Ag-based deNOₓ catalyst by HCs.

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<th>Table 1. Acidic properties of the catalysts.</th>
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<td>Catalyst</td>
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<td>Ag(3.8)/Al₂O₃</td>
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<td>Ag(3.8)/AlF₃(F: 2.7)/Al₂O₃</td>
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[a] Amount of adsorbed NH₃ or pyridine per surface area (Ag/Al₂O₃ = 186 m²/g, Ag/AlF₃/Al₂O₃ = 155 m²/g).

Conclusion
The Ag/Al₂O₃ catalyst exhibiting an excellent deNOₓ activity and stability by the simulated E-diesel/SCR reaction has been developed in the present study. The addition of AlF₃ to Ag/Al₂O₃ strengthened the surface acidity of the catalyst, resulting in a remarkable enhancement of its deNOₓ performance, especially at low temperatures.

References