

REDUCTIVE AGGREGATION AND OXIDATIVE REDISPERSSION OF SILVER SPECIES AS A CRUCIAL STEP IN De-NO_x CATALYSIS

Nitrogen oxides (NO_x: NO and NO₂) are major air pollutants that cause photochemical smog formation and acid rain. The emission of various nitrogen oxides into our atmosphere occurs on a massive scale. Worldwide, over 30 million tons of NO_x are vented into the earth's atmosphere each year. On the other hand, the demand for diesel engines in vehicles, which is the one of the major sources of NO_x emissions, is expected to increase because of the strong efforts to reduce CO₂ emissions. However, the full worldwide expansion of such engines is hindered by the difficulties in effective NO_x and particulate removal. Three major catalytic techniques are widely proposed and used for the removal of NO_x emissions from lean-burn and diesel-operated vehicles: NO_x storage, urea-selective catalytic reduction (SCR), and HC-SCR. Among these techniques, HC-SCR is the most efficient and simplest method, because small quantities of unburnt fuel in diesel engine exhaust streams can be used to reduce the pollutant NO_x to N₂. Numerous catalysts have been tried and tested for HC-SCR. It is now well established that silver supported on alumina (Ag/Al₂O₃) is one of the most active and selective catalysts for HC-SCR. However, the temperature window for NO_x reduction is narrow and they are not sufficiently active in the low temperature region (150-300 °C), which is typical of diesel engines. Until recently, these drawbacks have prevented the commercialization of Ag/Al₂O₃ catalysts for HC-SCR. However, the recent discovery that the addition of a small amount of hydrogen to the feed of the HC-SCR can dramatically improve the

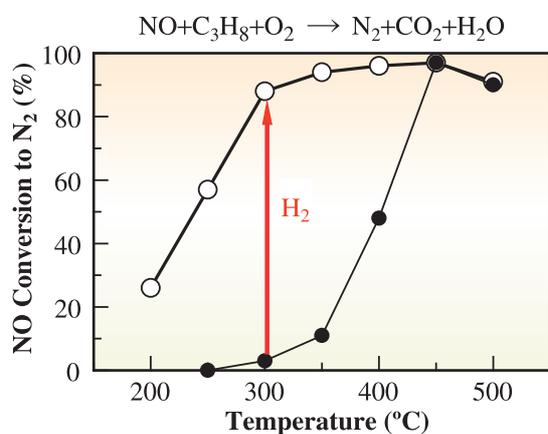


Fig. 1. Effect of H₂ addition on NO conversion in HC-SCR using Ag/Al₂O₃.

performance of Ag/Al₂O₃ catalysts has stimulated interest in HC-SCR for practical use [1]. Recent attention has been focused on the mechanistic causes of the hydrogen effect, even though a comprehensive explanation of the hydrogen effect has yet to be obtained. We performed detailed mechanistic studies, including the identification of surface intermediates and their dynamic changes [1-3].

A typical example of the H₂-promoted HC-SCR catalysis of Ag/Al₂O₃ is shown in Fig. 1. The addition of 0.5% H₂ into a NO+C₃H₈+O₂ gas mixture boosted the NO conversion rate at temperatures lower than 400 °C. Interestingly, the promotion effect of H₂ on NO conversion is reversible. The NO conversion rate decreased after the removal of H₂. This reversible change in NO conversion rate is in agreement with the time-dependence of the intensity of the band (350 nm) assignable to the Ag_n^{δ+} cluster. This finding suggests that the formation of the Ag_n^{δ+} cluster is essential for the “hydrogen effect.”

The structure of the Ag_n^{δ+} cluster was analyzed by *in situ* EXAFS at 573 K (Ag K-edge Quick XAFS

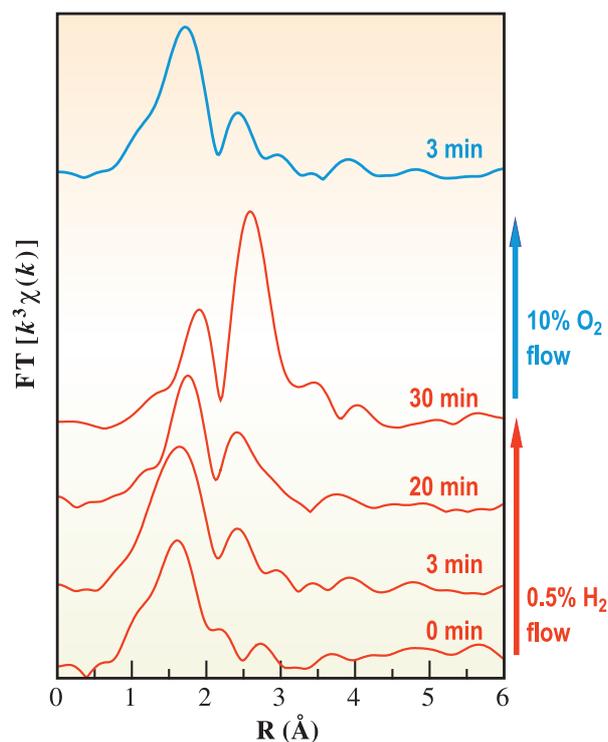


Fig. 2. Fourier transforms of Ag K-edge *in situ* EXAFS spectra measured at 573 K.

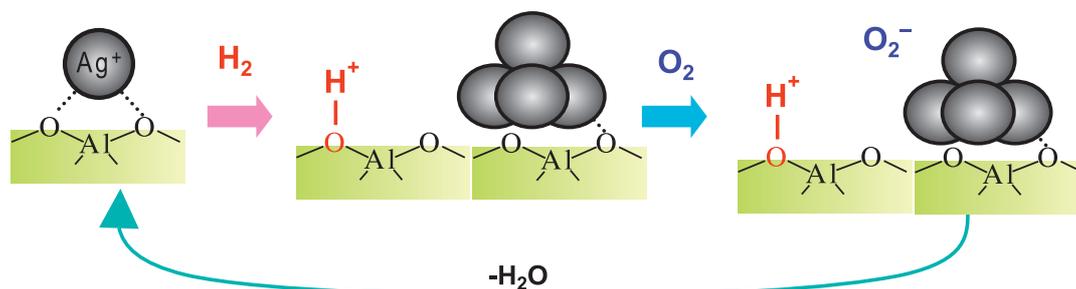


Fig. 3. Changes in structure of Ag species in Ag/Al₂O₃ upon H₂ reduction and subsequent O₂ oxidation.

measurements performed in the transmission mode at beamline **BL01B1** [2]. A wafer form of Ag/Al₂O₃ was placed in a quartz *in situ* cell [4] under a gas flow. Before the reaction, the Ag/Al₂O₃ wafer shows only a large Ag-O contribution, indicating that Ag⁺ ions are highly dispersed on the alumina surface. Results shown in Fig. 2 show that the reduction of Ag⁺ ions by 0.5% H₂ results in their aggregation to yield silver clusters. Finally, an Ag-Ag shell having a coordination number of 3.2 and a bond distance of 2.83 Å was observed. These values are smaller than those for bulk Ag metal particles (12 Ag atoms at 2.89 Å), and we assign the Ag-Ag contribution to the Ag₄²⁺ cluster. The cluster is redispersed to Ag⁺ ions upon reoxidation at 573 K. When the flowing gas was switched from H₂ to O₂, the coordination number for the Ag-Ag shell decreased, whereas that for the Ag-O shell increased. Taking into account the FTIR result that the acidic protons formed by the H₂ reduction of Ag/Al₂O₃ are consumed in the reoxidation reaction

with O₂ and the ESR result showing the formation of O₂⁻ (superoxide) radicals under a similar condition, the catalytic cycle in Fig. 3 is presented [2].

Combined with kinetic results [3], the total mechanism of the hydrogen effect is shown in Fig. 4. The reaction consists of the following steps: (1) The H₂ dissociation on the Ag site, (2) the spillover of H atoms to form protons, (3) the aggregation of isolated silver to form reduced Ag_n^{δ+}, (4) the reduction of O₂ with Ag_n^{δ+} and H⁺ to yield O₂⁻ and H₂O, (5) the partial oxidation of hydrocarbons by O₂⁻ to yield an acetate intermediate, and (6) the oxidation of NO to the NO₂ intermediate. This conclusion provides, for the first time, an explanation of H₂-promoted HC-SCR on the molecular level, which will be useful for the rational design of more efficient catalysts. The present results improve our ability to tailor the structure and catalytic behavior of silver clusters by controlling the reactant gas composition.

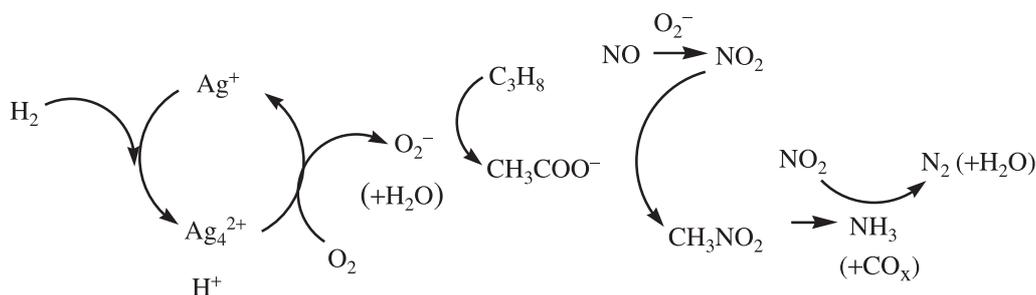


Fig. 4. Proposed mechanism of H₂ promoted HC-SCR.

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References

- [1] K. Shimizu and A. Satsuma: *Phys. Chem. Chem. Phys.* **8** (2006) 2677.
- [2] K. Shimizu, M. Tsuzuki, K. Kato, S. Yokota, K. Okumura and A. Satsuma: *J. Phys. Chem. C* **111** (2007) 950.
- [3] K. Shimizu *et al.*: *J. Catal.* **239** (2006) 402.
- [4] K. Okumura *et al.*: *J. Phys. Chem. B* **109** (2005) 12380.