Structural changes of Ag/y-Al₂O₃ during H₂-assisted C₃H₈-SCR of NOx

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Introduction

H₂-assisted HC-SCR using Ag/γ-Al₂O₃ is an interesting alternative for reduction of NOx at low temperature (<200°C) in lean effluents, such as those from Diesel and other lean burn engines [1, 2]. It is now generally accepted that H₂ increases the NOx reduction activity over Ag/Al₂O₃ catalyst, regardless of the type of HC reductant [3]. The reasons for the low temperature activity are not yet understood, although the variations in Ag species may play a role. There are reports about the coexistence of Ag⁺ ions and Ag⁵⁺ clusters at 300°C on 1-3 wt % Ag/γ-Al₂O₃ during H₂-C₃H₈-SCR [4]. In this work we report what are the structural changes of silver caused by the addition of H₂ during H₂-C₃H₈-SCR. We show for the first time that Ag_n cluster species appear to be responsible for the low temperature lean SCR activity (<200°C) and that silver nanoparticles might be the active species at high temperature (>250°C).

Materials and Methods

An Ag/ γ -Al₂O₃ catalyst containing ~2 wt% Ag was prepared by impregnation. The catalyst was dried at 110°C for 12 h and then calcined at 600°C for 3 h. The catalytic activity was measured in a quartz tubular flow reactor. The feed gas mixture contained 200 ppm NO, 1750 ppm C₃H₈, 0-1% H₂, 3% O₂, and 6% H₂O diluted in nitrogen. The space velocity was varied between 60,000 and 240,000 h⁻¹. The reactor temperature was raised from 25°C to 500°C at 4°C/min. The compositions of the feed and product streams were determined by GC (Shimadzu GC-12A), on line with an FTIR (Bruker Tensor 27) and a chemiluminescence NO-NOx analyzer (Eco Physics CLD 70 S). The surface area was similar for Ag/ γ -Al₂O₃ (173 m²/g) and for γ -Al₂O₃ (179 m²/g). For the fresh catalyst, only the XRD signature of γ -Al₂O₃ was observed. UV-vis diffuse reflectance (Cary 5000, Agilent) was used to determine the silver species and structural changes suffered during reaction.

Results and Discussion

Ex-situ UV-vis spectra of fresh Ag/γ - Al_2O_3 showed absorption bands at 240, 260 and 290-350 nm, corresponding to the $4d^{10} \rightarrow 4d^9s^1$ transition of highly dispersed Ag^+ ions, Ag_n^{5+} and Ag_n clusters, respectively [5]. The same species were identified after C_3H_8 -SCR (Figure 1), and the addition of 500 and 1000 ppm of H_2 to the feed did not cause significant changes either. However, when 1% of H_2 was present in the feed we observed a new broad band between 400-800 nm, a signature for silver nanoparticles [6].

The in-situ UV-vis analysis while heating $H_2-C_3H_8$ -SCR shows appreciable structural changes as the temperature rises, which were not detected ex-situ. In the 80-120°C range, Ag_n clusters form and then disappear above 160°C. At about 300°C the surface plasmon of silver nanoparticles is apparent, centered about 550 nm. These structural changes track the variations in activity. Figure 2a shows that in the absence of hydrogen Ag/ γ -Al₂O₃ lights off above 400°C. The addition of a small amount of hydrogen shifts down the NO reduction light off, to nearly 100°C. We also observed that during heating the SCR occurs in two stages, presumably as a result of the changes in Ag moieties. However, this effect was not observed during cooling (Figure 2b), probably because silver nanoparticles do not restructure fast enough.



Figure 1. a) Ex-situ UV-vis spectra of Ag/γ - Al_2O_3 fresh and after reaction. b) In-situ UV-vis under reaction: 200 ppm NO, 1750 ppm C₃H₈, 1% H₂, 3% O₂, 6% H₂O in N₂; 120,000 h⁻¹.



Figure 2. NO conversion over Ag/γ -Al₂O₃ during C₃H₈-SCR and H₂-C₃H₈-SCR: a) heating, b) heating vs. cooling using 1% H₂ in the feed. Reaction condition similar to those in Fig. 1.

Significance

In-situ studies during H_2 -HC-SCR of NOx show that the presence of H_2 favors the appearance of Ag_n clusters, apparently responsible for low temperature activity. At higher temperatures Ag rearranges into Ag nanoparticles, presumably the catalytic species above 300°C.

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