On the origin of the optimum loading of Ag on Al₂O₃ in the C₃H₆-SCR of NOₓ

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Introduction
An elegant alternative to the Selective Catalytic Reduction of NO by NH₃ (NH₃-SCR) from lean burn exhausts would be to use unburned hydrocarbons as reductants (HC-SCR). Miyadera first reported on the promising potential of the Ag/Al₂O₃ system for HC-SCR by various hydrocarbons [1], due to its high selectivity in N₂ compared to the platinum group metals-supported catalysts as reported by Burch [2]. Moreover, Miyadera revealed the existence of an optimum loading of silver (2 wt%) on alumina in the C₃H₆-SCR reaction [1]. Such an optimum loading of Ag has been confirmed by several groups [3-5] for Ag/Al₂O₃ samples prepared via the commonly used impregnation technique. Yet the reason for the existence of this particular optimum has not been clearly understood to date. Most studies have focused on the characterization of the Ag phases [2-5], whereas very few others have concerned the characterization of the supporting Al₂O₃ [6]. Recently, we showed that the surfaces of oxides, which is typically the case of the Ag/Al₂O₃ system, could be characterized by the adsorption of NOₓ followed by their temperature-programmed desorption (NOₓ-TPD) [7] and we reported that the introduction of Ag on Al₂O₃ led to a decrease in the amount of NOₓ stored on Al₂O₃ [8], suggesting that the NOₓ species were only chemisorbed on the Al₂O₃ sites free of Ag (available Al₂O₃ surface) and hence not on the Ag-O clusters. The aim of the present work is to gain further understanding on the origin of the existence of an optimum Ag loading for the C₃H₆-SCR of NOₓ in a series of Ag/Al₂O₃ samples prepared by impregnation, via the characterization of the available Al₂O₃ surface in Ag/Al₂O₃ catalysts by NOₓ-TPD.

Materials and Methods
Ag(Ag/nm² Al₂O₃)/Al₂O₃ samples were prepared by incipient wetness impregnation of γ-Al₂O₃ (180 m²/g) by aqueous solutions of AgNO₃ to achieve Ag loadings varying from 0.5 to 4.3 wt%, which led to Ag surface densities varying from 0.14 to 1.31 Ag/nm². After ageing at RT (6 h) and drying at 100 °C (12 h), the samples were calcined in a muffle furnace at 600 °C (3 h). The samples were characterized by N₂ sorption and NOₓ adsorption at RT (400 ppm NOₓ - 8 % O₂ - He) followed by temperature-programmed desorption from RT to 600 °C (8 % O₂/He, 3 °C/min, NOₓ-TPD method [7]). The C₃H₆-SCR performances (400 ppm C₃H₆ - 400 ppm NOₓ – 8 % O₂/He) were measured in a U-type quartz reactor on 0.38 g mechanical mixtures of the Ag(Ag/nm² Al₂O₃)/Al₂O₃ samples and Al₂O₃ so as to keep the amount of Ag in the reactor constant (30±1.2 µmol).

Results and Discussion
Fig. 1 shows the catalytic performances of the Ag(Ag/nm² Al₂O₃)/Al₂O₃ samples in the C₃H₆-SCR of NOₓ at 425 °C. As expected from earlier studies [3-5], the Ag(0.6)/Al₂O₃ and Ag(0.7)/Al₂O₃ catalysts, both corresponding to Ag loadings close to 2 wt%, showed optimum conversions of NOₓ to N₂. A decrease in NOₓ conversion is observed for Ag surface densities greater than 0.7 Ag/nm² Al₂O₃, hence for Ag loadings higher than 2.2 wt%. Below 0.6-0.7 Ag/nm² Al₂O₃, a gradual decrease in the C₃H₆-SCR performances is observed as the Ag surface density decreases, although the amount of Ag in the Ag(Ag/nm² Al₂O₃)/Al₂O₃-Al₂O₃ mechanical mixtures was kept constant.

With increasing Ag loadings, Fig. 1 also shows that the NOₓ uptake decreases linearly with a rather good correlation coefficient (R² = 0.94) and then levels off for Ag surface densities (Ag loadings) greater than 0.7 Ag/nm² Al₂O₃ (2.2 wt% Ag). These results suggest that pseudo monolayer coverage of Al₂O₃ by the AgO clusters has been reached at this particular Ag surface density (Ag loading). This means that the Al₂O₃ surface sites onto which Ag is anchored are saturated for Ag surface densities greater than or equal to 0.7 Ag/nm² Al₂O₃ (corresponding to Ag loadings close to 2 wt%) and that the dispersion of Ag decreases at higher Ag surface densities (Ag loadings).

It is remarkable that the Ag surface density for which the maximum dispersion of Ag is achieved on Al₂O₃ (0.7 Ag/nm² Al₂O₃, as determined by the NOₓ-TPD method, also corresponds to the optimum C₃H₆-SCR performances (Fig. 1). It will also be shown that the use of the concept of Ag surface density developed in the present study allows rationalizing earlier results reported in the literature [6,9].

Significance
Remarkable structure (NOₓ-TPD)-activity (C₃H₆-SCR) correlations allowed us to unravel the reason for the existence of an optimum Ag loading for Ag/Al₂O₃ catalysts in the C₃H₆-SCR of NOₓ. The so-called optimum loading of about 2 wt% Ag on Al₂O₃ corresponds to the maximum loading of Ag for which maximum dispersion of Ag can be achieved.

References