On the origin of the optimum loading of Ag on Al_2O_3 in the C_3H_6-SCR of NO_x

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Introduction

An elegant alternative to the Selective Catalytic Reduction of NO_x by NH_3 (NH_3-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/Al_2O_3 system for HC-SCR by various hydrocarbons [1], due to its high selectivity in N_2 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 C_3H_6-SCR reaction [1]. Such an optimum loading of Ag has been confirmed by several groups [3-5] for Ag/Al_2O_3 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 Al_2O_3 [6]. Recently, we showed that the surfaces of oxides, which is typically the case of the Ag/Al_2O_3 system, could be characterized by the adsorption of NO_x followed by their temperature-programmed desorption (NO_x-TPD [7]) and we reported that the introduction of Ag on Al_2O_3 led to a decrease in the amount of NO_x stored on Al_2O_3 [8], suggesting that the NO_x species were only chemisorbed on the Al_2O_3 sites free of Ag (available Al_2O_3 surface) and hence not on the Ag_2O 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 C_3H_6-SCR of NO_x in a series of Ag/Al_2O_3 samples prepared by impregnation, via the characterization of the available Al_2O_3 surface in Ag/Al_2O_3 catalysts by NO_x-TPD.

Materials and Methods

$Ag(Ag/nm^2_{Al2O3})/Al_2O_3$ samples were prepared by incipient wetness impregnation of γ-Al_2O_3 (180 m^2/g) by aqueous solutions of $AgNO_3$ 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/nm^2_{Al2O3}. 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 N_2 sorption and NO_x adsorption at RT (400 ppm NO_x - 8 % O_2 - He) followed by temperature-programmed desorption from RT to 600 °C (8 % O_2/He, 3 °C/min, NO_x-TPD method [7]). The C_3H_6-SCR performances (400 ppm C_3H_6 - 400 ppm NO_x – 8 % O_2/He) were measured in a U-type quartz reactor on 0.38 g mechanical mixtures of the $Ag(Ag/nm^2_{Al2O3})/Al_2O_3$ samples and Al_2O_3 so as to keep the amount of Ag in the reactor constant (30.9±1.2 µmol).

Results and Discussion

Fig. 1 shows the catalytic performances of the $Ag(Ag/nm^2_{Al2O3})/Al_2O_3$ samples in the C_3H_6-SCR of NO_x at 425 °C. As expected from earlier studies [3-5], the $Ag(0.6)/Al_2O_3$ and $Ag(0.7)/Al_2O_3$ catalysts, both corresponding to Ag loadings close to 2 wt%, showed optimum conversions of NO_x to N_2. A decrease in NO_x conversion is observed for Ag surface densities greater than 0.7 Ag/nm^2_{Al2O3}, hence for Ag loadings higher than 2.2 wt%. Below 0.6-0.7 Ag/nm^2_{Al2O3}, a gradual decrease in the C_3H_6-SCR performances is observed as the Ag surface density decreases, although the amount of Ag in the $Ag(Ag/nm^2_{Al2O3})/Al_2O_3$-$Al_2O_3$ mechanical mixtures was kept constant.

With increasing Ag loadings, Fig. 1 also shows that the NO_x uptake decreases linearly with a rather good correlation coefficient (R^2 = 0.94) and then levels off for Ag surface densities (Ag loadings) greater than 0.7 Ag/nm^2_{Al2O3} (2.2 wt% Ag). These results suggest that pseudo monolayer coverage of Al_2O_3 by the Ag_2O clusters has been reached at this particular Ag surface density (Ag loading). This means that the Al_2O_3 surface sites onto which Ag is anchored are saturated for Ag surface densities greater than or equal to 0.7 Ag/nm^2_{Al2O3} (corresponding to Ag loadings close to 2 wt%) and that the dispersion of Ag decreases at higher Ag surface densities (Ag loadings).

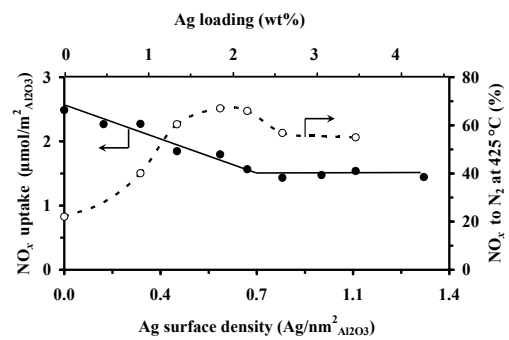

Figure 1. NO_x uptakes (●) and NO_x conversion to N_2 at 425 °C (○) as a function of Ag surface density (Ag loading) of Ag/Al_2O_3 catalysts.

It is remarkable that the Ag surface density for which the maximum dispersion of Ag is achieved on Al_2O_3 (0.7 Ag/nm^2_{Al2O3}), as determined by the NO_x-TPD method, also corresponds to the optimum C_3H_6-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 (NO_x-TPD)-activity (C_3H_6-SCR) correlations allowed us to unravel the reason for the existence of an optimum Ag loading for Ag/Al_2O_3 catalysts in the C_3H_6-SCR of NO_x. The so-called optimum loading of about 2 wt% Ag on Al_2O_3 corresponds to the maximum loading of Ag for which maximum dispersion of Ag can be achieved.

References

1. Miyadera, T. *Appl. Catal. B* **1993**, *2*, 199.
2. Burch, R. *Catal. Rev. Sci. Eng.* **2004**, *46*, 271.
3. Shimizu, K.-I.; Shibata, J.; Satsuma, A.; Hattori, T. *Appl. Catal. B* **2001**, *30*, 151.
4. Arve, K.; Čapek, L.; Klingstedt, F.; Eränen, K.; Lindfors, L.-E.; Murzin, D. Y.; Dědeček, J.; Sobalik, Z.; Wichterlová, B. *Topics Catal.* **2004**, *30/31*, 91.
5. Zhang, R.; Kaliaguine, S. *Appl. Catal. B* **2008**, *78*, 275.
6. Jen, H.-W. *Catal. Today* **1998**, *42*, 37.
7. Law, H-Y.; Blanchard, J.; Carrier, X.; Thomas, C. *J. Phys. Chem. C* **2010**, *114*, 9731.
8. Blanchard, J.; Doherty, R.P.; Law, H-Y.; Thomas, C. *Topics Catal.* **2013**, *56*, 134.
9. Meunier, F. C.; Ukropec, R.; Stapelton, C.; Ross, J. R. H. *Appl. Catal. B* **2001**, *30*, 163.