Insights into the influence of the Ag loading on Al_2O_3 in the H_2-assisted C_3H_6-SCR of NO_x: a kinetic study

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Introduction

The catalytic reduction of NO_x to N_2 in a strongly oxidizing medium is not trivial. Among the catalysts evaluated in the selective catalytic reduction of NO_x by the hydrocarbons (HC-SCR), Ag/Al_2O_3 has been reported to be the most promising catalyst in the pioneering work by Miyadera [1]. Yet the use of such Ag/Al_2O_3 catalysts is limited because of the restricted operating temperature window (300 – 500 °C) within which these materials efficiently catalyze the HC-SCR reaction [1]. The discovery of a low-temperature promoting effect of H_2 on the HC-SCR of NO_x by Satokawa [2] is a major breakthrough for Ag/Al_2O_3 catalysts. To our knowledge, the influence of the Ag loading on the H_2-assisted HC-SCR of NO_x (H_2-HC-SCR) has been the subject of a very limited number of investigations [3,4], most of the works in this field reporting on Ag/Al_2O_3 samples with a nominal Ag loading close to 2 wt% which has been shown to provide optimum HC-SCR performances [5 and refs. therein].

The aim of the present work is to gain further understanding on the influence of the Ag loading of Ag/Al_2O_3 samples in the H_2-assisted C_3H_6-SCR of NO_x (H_2-C_3H_6-SCR). This study also reports on original findings in the influence of the Ag loading on the kinetics of H_2-C_3H_6-SCR correlated with the NO_x-TPD characterization of the corresponding catalysts [5]. This helps explain the observed catalytic trend in the H_2-promoted C_3H_6-SCR reaction.

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% (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 [5]). The H_2-C_3H_6-SCR performances (0.21 % H_2 - 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/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). Kinetic measurements were also performed.

Results and Discussion

In agreement with earlier investigations, the addition of H_2 drastically promoted the C_3H_6-SCR reaction for temperatures lower than 400 °C. The addition of 0.21 % H_2 in the feed shifted the NO_x to N_2 and C_3H_6 to CO_x conversions to temperatures approximately 150 °C lower than those obtained in the C_3H_6-SCR reaction for all samples. The NO_x reduction temperature window broadened to lower temperatures as the Ag surface density (Ag loading) increased. The broadening of the NO_x reduction activity to lower temperatures occurred, however, at the expense of the NO_x conversions at the higher temperatures. In contrast to C_3H_6-SCR, the present study highlights for the first time that the H_2-C_3H_6-SCR catalytic performances of Ag/Al_2O_3 samples improved as the Ag surface density (Ag loading) decreased well below 0.7 Ag/nm^2_{Al2O3} (2.2 wt% Ag, Fig. 1).

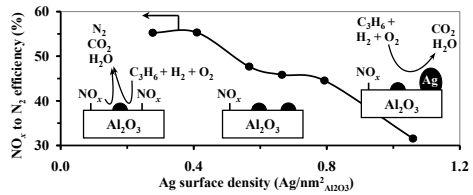

Figure 1. NO_x to N_2 efficiencies and schematic representation of the H_2-C_3H_6-SCR reaction as a function of the Ag surface density of Ag/Al_2O_3

It is remarkable that changes in the reaction orders with respect to NO, C_3H_6 and H_2 at 325 °C and in the apparent activation energy (E_a) for the reduction of NO_x to N_2 in the H_2-C_3H_6-SCR reaction occurred at the Ag surface density of ~0.7 Ag/nm^2_{Al2O3} (2.2 wt% Ag, Fig. 2), which coincides with the changes observed in the NO_x uptakes of the Al_2O_3 support of the Ag/Al_2O_3 catalysts [5]. Interpretation of the activity and kinetic data led us to conclude that the H_2-C_3H_6-SCR reaction proceeds via the activation of H_2 and C_3H_6 on Ag species and their further reaction with NO_x adspecies activated on the Al_2O_3 support (Fig. 1).

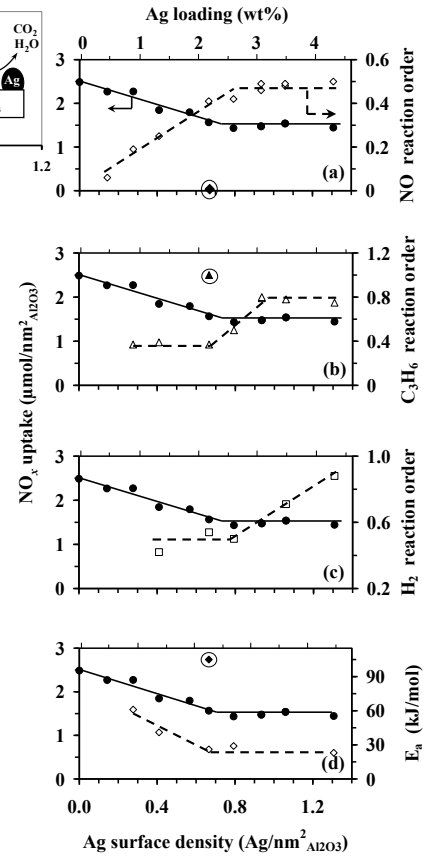

Figure 2. Influence of the Ag surface density of Ag/Al_2O_3 catalysts on the kinetic parameters of the H_2-C_3H_6-SCR reaction. (-●-) NO_x uptakes [5].

Significance

The unexpected higher catalytic performances of the Ag samples with the lower Ag surface densities was attributed to their higher concentration of Al_2O_3 sites able to chemisorb NO_x species, in agreement with the NO_x uptake data.

References

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