Close coupling of atmospheric pressure nonthermal plasma with a Ag/Al_2O_3 catalyst for the selective catalytic reduction of NO_x at low temperature

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Introduction

Hybrid heterogeneous catalyst-plasma systems represent an important advance in catalytic reaction engineering as they combine the advantages of having fast and low temperature reactions from atmospheric nonthermal plasma (NTP) and high product selectivity from the catalyst. They have been successfully applied in a large number of reactions, from VOC oxidations and automotive catalysis to reforming and hydrogenation reactions. However, the effect of plasma on the catalytic reaction mechanism is most of the times not well understood, therefore, optimisation of the catalyst and/or the plasma specifications is hard to be achieved.

In the present work, we report evidence of a NTP-assisted hydrocarbon selective catalytic reduction (HC-SCR) deNOx reaction over a silver-based catalyst.[1] A newly designed diffuse *in situ* reflectance infra-red (DRIFTS) system coupled with the plasma was designed to investigate the reaction mechanism.

Materials and Methods

A 2 wt% Ag/Al_2O_3 catalyst was prepared by the impregnation of γ-Al_2O_3 support with a silver nitrate solution followed by drying and calcination at 550°C. Catalytic activity tests were performed at 250 °C and ambient temperatures with 720 ppm NO, 620 ppm toluene or 542 ppm C_8H_{18}, 7.2% CO_2, 7.2% H_2O, 5% O_2, and with the balance He. The experiments were designed to obtain information on the activity of the SCR catalyst when the atmospheric pressure helium-NTP was in direct contact with the catalyst bed. Two different electrode configurations were used to generate the plasma. For the catalytic activity tests, the dielectric barrier discharge was generated between two external circular copper electrodes and the 2% Ag/Al_2O_3 catalyst sample was placed in the centre of a fixed-bed flow system with T-shape quartz tube reactor. The DRIFTS-MS measurements were carried out at ambient temperature *in situ* in a high temperature cell fitted with ZnSe windows. A quartz covered tungsten wire with a pencil-shaped tapered end was inserted into a quartz tube to act as a powered electrode. The capillary tube, with a 50 cm^3 min^{-1} helium flow, was one arm of a T-shape quartz tube.

A high voltage probe (Tektronix, P6015) and a calibrated Rogowski coil (Pearson) connected to a digital oscilloscope (LeCroy WavePro 7300A) were used to measure the variable, time-dependent applied voltage and current. The powered electrode was driven at peak voltages from 6 to 7 kV and modulated from 16 to 23 kHz.

Results and Discussion

When the plasma was combined with an Ag/Al_2O_3 catalyst a strong enhancement in activity was observed when compared with conventional thermal activation with high conversions of both NO_x and hydrocarbons obtained at temperature ≤250 °C, where the silver catalyst is normally inactive. As shown in **Figure 1**, the conversion of NO_x with octane and toluene was significantly improved at 250 °C and was found to be 25 and 74%, respectively, when the NTP was on. Furthermore, the conversion of both octane and toluene was almost complete (> 99%) in the presence of NTP. A remarkable SCR activity of the Ag-catalyst was also observed in the absence of an external heat source with NTP.[1] NO_x conversions of ~52% in the case of *n*-octane and ~42% in the case of toluene were obtained, with hydrocarbon conversions of ~99% and ~89%, respectively.

Figure 2 shows the substantial differences of *in situ* DRIFTS spectra of surface species adsorbed on the Ag/Al_2O_3 catalyst during the octane-SCR reaction with plasma at ambient temperature. It is evident that switching on NTP has resulted in changes in the intensity of surface species in which adsorbed octane was decreased together with the formation of other adsorbed species such as nitrates, acetates, carboxylates and so on. It is interesting to note that similar species such isocyanates (2260 cm^{-1}) and cyanides (2165 cm^{-1}) were observed to those seen when H_2 was used to promote the HC-SCR reaction, as reported by Chansai et al.[2] This indicates that the plasma could help to activate both NO and hydrocarbon.

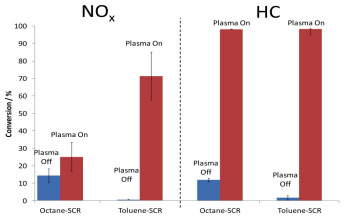

Figure 1. NO_x and hydrocarbon conversions during the HC-SCR of NO_x reaction over 2 wt% Ag/Al_2O_3. Feed composition: 720 ppm NO, 4340 ppm (as C1) HC, 4.3% O_2, 7.2% CO_2, 7.2% H_2O and He balance. The total flow rate and space velocity was 276 cm^3 min^{-1} and 165600 cm^3 g^{-1} h^{-1}, respectively.

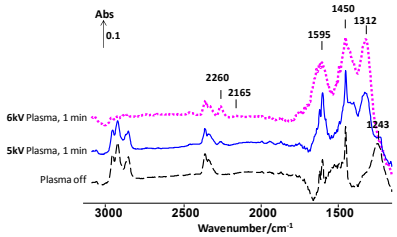

Figure 2. Changes in surface species observe during the octane-SCR of NOx reaction on Ag/Al_2O_3 with and without plasma. Feed composition: 720 ppm NO, 4340 ppm (as C1) C_8H_{18}, 5% O_2, 4% H_2O and He balance. The total flow rate was 100 cm^3 min^{-1}.

Significance

An atmospheric pressure non-thermal plasma system was developed to assist the low temperature SCR activity of an Ag/Al_2O_3 catalyst with octane and toluene. It has been shown that NOx reduction is remarkably enhanced at very low temperatures. The *in situ* DRIFTS measurement indicated that the NTP could help to activate both NO and hydrocarbon, proving a real insight into the mechanism by which plasma can promote this reaction at 25 °C. This low temperature activity provides the basis for increased exhaust gas treatment during cold start conditions which remains an important issue for mobile and stationary applications.

References

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2. Chansai, S.; Burch, R.; Hardacre, C.; Breen, J.; Meunier, F. *J. Catal.* **2011**, 281, 98.