Investigating the promotional effect of methanol on the low temperature HC-SCR reaction on a Ag/Al₂O₃ catalyst

Sarayute Chansai¹, Robbie Burch¹, <u>Christopher Hardacre</u>^{*,1}, Daniel Norton², Xiaoying Bao², Larry Lewis² ¹Queen's University Belfast, Belfast, Antrim BT9 5AG, N. Ireland, U.K. ²General Electric Global Research, 1 Research Circle, Niskayuna, NY 12309, U.S.A. *corresponding author:c.hardacre@gub.ac.uk

Introduction

Hydrogen has been reported to have a significant effect on the low temperature activity of Ag/γ -Al₂O₃ catalysts for the lean burn reduction of NO_x by hydrocarbons (HC-SCR) [1,2]. However, there are difficulties with either the storage or the on-board generation of hydrogen.

Although oxygenated hydrocarbons are reported to be very active reductants for the SCR reaction, methanol is not effective for the SCR reaction over Ag catalysts [3] and no paper is reported in the literature that mixed-methanol hydrocarbons can improve the activity of NO_x reduction at low temperatures. Recently, we have discovered for the first time that methanol can enhance the HC-SCR of NO_x over Ag catalysts under lean burn conditions.

The main objective of this work is to enhance the SCR activity over Ag catalyst using simulated diesel fuels (toluene or octane) mixed with methanol and to clarify the role of methanol in the reaction mechanism by using fast transient kinetics. In addition, *in situ* DRIFTS-MS analysis was used to investigate the changes in the nature of adsorbed surface species.

Materials and Methods

The catalyst was prepared by the impregnation of γ -Al₂O₃ with a silver nitrate solution followed by drying and calcination to give a sample with an Ag metal loading of 2 wt%. Catalystic activity tests were performed in a quartz tube plug flow reactor using 720 ppm NO, 620 ppm toluene or 542 ppm C₈H₁₈, 7.2% CO₂, 7.2% H₂O, 5% O₂, 4340 ppm methanol (when added), 1% Kr (when added), and balance Ar. Kr was used as an internal standard. The analysis was carried out with a NO_x analyser and a Hiden HPR 20 mass spectrometer. Fast sampling valves allowed a global analysis time (including the switch time, the purge and the time taken for the sample to travel through the capillary to the detector) of less than 400 ms. The diffuse reflectance FT-IR (DRIFTS) measurements were carried out *in situ* in a high temperature cell fitted with ZnSe windows.

Results and Discussion

The results in **Figure 1** show the deNO_x performance with different hydrocarbons over 2 wt% Ag/Al₂O₃ catalyst. Although methanol on its own is not very reactive for the SCR of NO_x reaction, it is clear that there is a remarkable improvement of NO_x conversions with both *n*-octane and toluene in the presence of methanol. The *n*-octane-SCR activity starts at ~250 °C and reaches a broad maximum of >93% NO_x conversion ~400 °C before decreasing to 43% at 550 C. A similar profile of NO_x conversion with toluene was observed with the profile shifted to higher temperatures. However, on addition of methanol into the *n*-octane or toluene-SCR feeds, the catalytic reduction of NO_x began just above 150 and 200 °C before reaching the maximum NO_x conversions (> 93%) at 250 and 270 °C for the *n*-octane/methanol and toluene/methanol systems, respectively.

Figure 2 shows the fast-transient responses in NO_x conversions during switches of methanol in and out of the octane-SCR feed stream at three different temperatures. As the reaction temperature increased, the SCR activity increased. It was found that NO_x conversions increased rapidly upon introduction of methanol and then remained constant in the presence of methanol over the course of 60 s. However, after switching out methanol from the SCR feed, the NO_x conversions decreased slowly over 60 s and this is probably because N-containing species stored under octane/methanol-SCR conditions could react with gas phase NO.

Experiments in which labeled ¹⁵NO and CD₃OD was used revealed the production of small quantities of D₂ (m/e=4) and ¹⁵ND₃ (m/e=21) when methanol was introduced to the feed. Thus, it is proposed that one of the key roles of methanol is the production of hydrogen, which is that methanol acts as an *in situ* source of hydrogen to promote the HC- SCR reaction over Ag/Al₂O₃. Breen *et al.* [1] reported that the addition of 0.72% hydrogen improves the octane SCR reaction over Ag/Al₂O₃ catalyst and produced NH-containing species at 245 °C.

In situ DRIFTS analysis was used to identify the species stored on the surface of the catalyst during the switches of methanol in and out of the reaction mechanism. Very similar species such isocyanate species were observed to those seen when H_2 was used to promote the HC-SCR reaction, as reported by Chansai *et al.* [2].



Figure 1. NO_x conversions as a function of catalyst temperature during the HC-SCR of NO_x reaction over 2 wt% Ag/Al₂O₃ catalyst.

Figure 2. Changes in NO_x conversions as a function of time during 60 s switches of 4340 ppm methanol in and out of the octane SCR gas mix over 2 wt% Ag/Al₂O₃ catalyst.

Significance

Methanol has been shown to promote the SCR of NO_x with octane and toluene over 2 wt% Ag/Al₂O₃ catalyst for the first time. In order to understand its role in the reaction fast transient kinetic methods and *in situ* DRIFTS analysis have been used. The catalytic activity tests showed that the addition of methanol to the HC-SCR reaction results in a significant improvement in the low temperature activity of a Ag/Al₂O₃ catalyst, despite the fact that methanol on its own is not reactive for the HC-SCR reaction.

References

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