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

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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 NOₓ 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 NOₓ reduction at low temperatures. Recently, we have discovered for the first time that methanol can enhance the HC-SCR of NOₓ 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%.

Catalytic activity tests were performed in a quartz tube plug flow reactor using 720 ppm NOₓ, 620 ppm toluene or 542 ppm C₈H₁₀, 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 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 deNOₓ performance with different hydrocarbons over 2 wt% Ag/Al₂O₃ catalyst. Although methanol on its own is not very reactive for the SCR of NOₓ reaction, it is clear that there is a remarkable improvement of NOₓ 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% NOₓ conversion ~400 °C before decreasing to 43% at 550 °C. A similar profile of NOₓ 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 NOₓ began just above 150 and 200 °C before reaching the maximum NOₓ 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 NOₓ 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 NOₓ 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 NOₓ 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 C₂D₂O₃ was used revealed the production of small quantities of D₂ (m/e=4) and ¹⁵ND₂ (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 andout of the reaction mechanism. Very similar species such isocyanate species were observed to those seen when H₂ was used to promote the HC-SCR reaction, as reported by Chansai et al. [2].

Significance
Methanol has been shown to promote the SCR of NOₓ 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