

# A combined *in situ* DRIFTS and fast transient kinetic study of the effect of H<sub>2</sub> on the Selective Catalytic Reduction of NO<sub>x</sub> with octane using isotopically labelled <sup>15</sup>NO

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## Introduction

Small quantities of hydrogen (< 1%) have a marked promotional effect on the hydrocarbon selective catalytic reduction (HC SCR) of NO<sub>x</sub> over Ag/γ-Al<sub>2</sub>O<sub>3</sub> catalysts when using a range of different reductants [1-4]. The addition of hydrogen significantly enhances the potential of these catalysts as a viable solution to the removal of NO<sub>x</sub> from automotive exhaust streams. There is general agreement about the positive effect of hydrogen on activating a variety of different reductants and on the overall rate of the HC-SCR NO<sub>x</sub> reduction reaction. However, debate continues on the mechanism by which the hydrocarbon and NO are activated. The work presented here clarifies the role of hydrogen in the reaction mechanism by using fast transient kinetics with isotopically labelled <sup>15</sup>NO during the HC SCR of NO<sub>x</sub>. The use of labelled <sup>15</sup>NO allows the evolution of N-containing products to be monitored in gas mixtures where the monitoring of products from reaction of unlabelled NO would not be possible. In addition, *in situ* DRIFTS analysis was used to correlate changes in product composition with changes in surface species.

## Materials and Methods

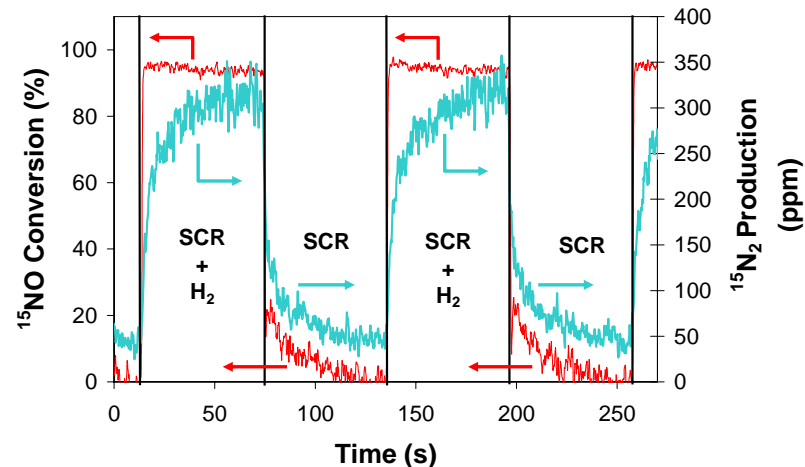
The catalyst was prepared by the impregnation of γ-Al<sub>2</sub>O<sub>3</sub> with a silver nitrate solution followed by drying and calcination to give a sample with a Ag metal loading of 2 wt%. Catalyst testing was performed in a quartz tube (3 mm i.d.) plug flow reactor into which the reactant gases (720 ppm NO, 540 ppm n-C<sub>8</sub>H<sub>18</sub>, 7.2% CO<sub>2</sub>, 7.2% H<sub>2</sub>O, 4.3% O<sub>2</sub>, 0.05 - 0.72% H<sub>2</sub> (when added), 3.7% Kr (when added), balance Ar). Kr was used as an internal standard. The analysis was carried out with 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 150 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 effect on <sup>15</sup>NO conversion and <sup>15</sup>N<sub>2</sub> production of switching 0.72% hydrogen into and out of the SCR feed stream as a function of time on stream. <sup>15</sup>NO conversion increased rapidly upon introduction of H<sub>2</sub> and then remained constant in the presence of H<sub>2</sub> over the course of 60 s. This was in contrast to the production of <sup>15</sup>N<sub>2</sub> which increased slowly over the course of 60 s. Analysis of the data showed that the N-balance varied considerably during the course of the switches even though the average nitrogen balance over a series of switches was 99±3%. The addition of hydrogen promoted the storage of nitrogen containing species on the surface of the catalyst; these stored species then reacted to form N<sub>2</sub> upon removal of H<sub>2</sub> from the gas phase. Experiments in which unlabelled NO was

used, revealed the production of small quantities (ca. 30 ppm) of NH-containing species (m/e = 15) when H<sub>2</sub> was introduced to the feed. Thus, it is proposed that one of the key roles of H<sub>2</sub> is the production of NH-containing species which can react readily with NO<sub>x</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>.

Transient *in situ* DRIFTS analysis was used to identify the species stored and released on the surface of the catalyst during the switches of H<sub>2</sub> in and out of the reaction mechanism. The combined transient kinetics and *in situ* DRIFTS analysis were used to produce a global reaction mechanism for the SCR reaction with and without H<sub>2</sub>.



**Figure 1.** Changes in <sup>15</sup>NO conversion and <sup>15</sup>N<sub>2</sub> production as a function of time during 60 s switches of 0.72% H<sub>2</sub> in and out of the SCR mix over the catalyst at 245 °C

## Significance

The addition of small quantities of H<sub>2</sub> to the HC SCR reaction results in remarkable improvement in the low temperature activity of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst making them suitable for removal of NO<sub>x</sub> from diesel exhausts which typically operate in the region of 200 °C. By using a combination of fast switching and kinetic analysis of both the gas phase and surface species, it has been possible to provide real insight into the mechanism by which H<sub>2</sub> promotes the HC SCR reaction. This information will enable catalysts to be designed to operate at lower temperatures and without the need for hydrogen to promote the reaction.

## References

1. S. Satokawa, Chem. Lett., 2000, 294.
2. R. Burch, J.P. Breen, C.J. Hill, B. Krutzsch, B. Konrad, E. Jobson, L. Cider, K. Eränen, F. Klingstedt, L-E. Lindfors, Top. Catal., 30-31 (2004) 19.
3. J.P. Breen, R. Burch, C. Hardacre, C.J. Hill, J. Phys. Chem. B, 109 (2005) 4805.
4. B. Wichterlová, P. Szama, J.P. Breen, R. Burch, C.J. Hill, L. Čapek, Z. Sobalík, J.Catal., 235 (2005) 195.