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Investigating the mechanism of the H_2-assisted selective catalytic reduction (SCR) of NOx with octane using fast cycling transient *in situ* DRIFTS-MS analysis

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ABSTRACT

A mechanistic study of the H_2-assisted Selective Catalytic Reduction (SCR) of NOx with octane as reductant over a Ag/Al_2O_3 catalyst was carried out using a modified DRIFTS cell coupled to a mass spectrometer. Using fast transient cycling switching of H_2, with a time resolution of a few seconds, it was possible to differentiate potential reaction intermediates from other moieties that are clearly spectator species. Using such a periodic operation mode, effects were uncovered that are normally hidden in conventional transient studies which typically consist of a single transient. In experiments based on a single transient addition of H_2 to, or removal of H_2 from, the SCR feed, it was found that the changes in the concentrations of gaseous species (products and reactants) were not matched by changes at comparable timescales of the concentration of surface species observed by IR. This observation indicates that the majority of surface species observed by DRIFTS under steady-state reaction conditions are spectators. In contrast, under fast cycling experimental conditions, it was found that a surface isocyanate species had a temporal response that matched that of $^{15}N_2$. This suggests that some of the isocyanate species observed by infrared spectroscopy could be important intermediates in the hydrogen-assisted SCR reaction although it is emphasised that this may be dependent on the way in which the infrared spectra are obtained. It is concluded that the use of fast transient cycling switching techniques may provide useful mechanistic information under certain circumstances.

1. Introduction

The potential commercial importance of silver catalysts for the Hydro Carbon Selective Catalytic Reduction (HC-SCR) of NOx in automotive applications has justified much research into the catalysts and the corresponding reaction mechanism. However, it is the case that earlier conventional mechanistic investigations using *in situ* or operand spectroscopy have suffered from not being able to differentiate between true reaction intermediates and spectator species because the latter are often the majority species. The special characteristics of silver catalysts for the NOx reduction reaction provide an opportunity to use fast transient switching techniques to identify species that could be true reaction intermediates.

Several groups have shown that the activity of Ag/Al_2O_3 catalysts in the HC-SCR reaction can be dramatically enhanced by the addition of small quantities of H_2 [1–10]. This effect is observed for a variety of aromatic and aliphatic hydrocarbons, alcohols and ketones but is apparently limited to Ag supported on Al_2O_3 and MFI zeolite. The structure of the catalyst and the reaction mechanism have been investigated extensively, and small clusters of silver atoms have been identified as the probable active form of the silver under reaction conditions. However, the rapid increase in NOx conversion upon introduction of H_2 [3] and the relatively slow rate of formation of Ag clusters [11] indicates that the mechanism of the enhancement of the SCR reaction by H_2 may be quite complicated. On the other hand, the rapid changes in activity when hydrogen is added or removed provide a unique opportunity to explore potential surface intermediates that react with a time constant that is consistent with the fast changes in activity.

In situ IR spectroscopy has been widely used to investigate the nature of reactive adsorbates under reaction conditions. Under steady-state conditions, *in situ* IR studies can identify the chemical nature and the relative coverage of adsorbates on the catalyst surface. However, there is a major problem with conventional or steady-state spectroscopy due to the fact that all the adsorbed species present on the catalyst surface contribute to the total infrared spectrum. Furthermore, as species that are closely related chemically often absorb in the same part of the infrared spectrum, it can be difficult to distinguish between different forms of chemically equivalent species. For example, it is very difficult

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to differentiate between species adsorbed on the free alumina support and similar species adsorbed at or close to an active silver cluster.

Conventional mechanistic studies of the effect of H_2 on the HC-SCR reaction using *in situ* diffuse reflectance FT-IR spectroscopy (DRIFTS) are limited by the slow collection of spectroscopic data compared with the fast changes in the formation of the products [4,12,13]. Thus, Breen et al. [3] studied the role of H_2 by using fast transient switching of isotopically labelled ^{15}NO and showed that the addition of H_2 resulted in an almost instantaneous (<1 s) increase in NO conversion. In contrast, conventional DRIFTS experiments can take several minutes to obtain good signal-to-noise ratios, and so it is normal to collect spectra on this longer timescale. As a result, much of the mechanistic information on relevant changes in the concentration of surface species is lost.

In the present study, fast switching has been used to examine how H_2 affects the HC-SCR reaction. A modified DRIFTS reactor, coupled with a mass spectrometer, was used to simultaneously measure changes in concentration of surface species and changes in reactant and product compositions in a relevant time frame [14], thus showing that some previously identified surface species are probably only side-products of the reaction and not part of the main reaction pathway leading to NO reduction.

2. Experimental

The catalyst was prepared by impregnation of γ-Al_2O_3 (LaRoche Industries Inc.). The support material was ground to a particle size of <250 μm and mixed with a solution containing 0.022 M $AgNO_3$. The catalyst was then filtered, dried at room temperature for 24 h and further dried at 100 °C for 3 h, after which the catalyst was calcined at 550 °C for 3 h. The silver content of the catalyst was determined by the Direct Current Plasma method to be approximately 2 wt.%. Ag. [15]. The specific surface area of the catalyst was 170 $m^2 g^{-1}$, and the average crystallite size of the γ-Al_2O_3 was 55 nm [16].

In situ DRIFTS measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with a liquid N_2-cooled detector. A 2.0% Ag/Al_2O_3 catalyst sample (20 mg) was placed in a ceramic crucible in an *in situ* DRIFTS cell. The exit lines were connected to a Hiden Analytical HPR20 mass spectrometer in order to monitor the gas phase species: ^{15}NO ($m/z = 31$), n-C_8H_{18} ($m/z = 57$), H_2 ($m/z = 2$) and $^{15}N_2$ ($m/z = 30$). To overcome the problem of a slow collection of infrared spectra that could allow the concentration of surface spectator species to increase and swamp the signal from reactive species, signal averaging of quickly recorded spectra over more than twenty complete cycles of the switches of H_2 into and out of the SCR feed was used and a satisfactory signal to noise ratio was thus achieved at a fast time resolution. ^{15}NO was used as a feed in order to allow the production of nitrogen to be tracked as a function of time on stream without interference from the fragmentation of CO_2 at $m/z = 28$. $^{14}N_2$ (2% N_2/Ar) was used to calibrate and quantify the signal of $^{15}N_2$ obtained by mass spectrometry. The IR data are reported as log $1/R$, where R is the sample reflectance. The function log $1/R$ (= "absorbance") gives a better linear representation of the band intensity against sample surface coverage than that given by the Kubelka–Munk function for strongly absorbing media such as those based on oxides [17].

Prior to experiments, the catalyst was pretreated by heating in 5% O_2/Ar with a total flow rate of 50 $cm^3 min^{-1}$ up to 300 °C for 1 h and then cooled down in flowing Ar to 245 °C. The IR spectrum of the Ag/Al_2O_3 catalyst at 245 °C under flowing Ar was taken as a background. The reactant gases NO (1% ^{15}NO/Ar), O_2 (100%), CO_2 (100%), H_2 (20% H_2/Ar), Kr (1% Kr/Ar) and the carrier gas Ar were fed from independent mass flow controllers. n-octane and water vapour were introduced to the system by means of separate saturators with Ar as a carrier gas. The n-C_8H_{18} saturator was placed in an ice/water bath, and the H_2O saturator temperature was controlled using a thermostatic bath. All the lines following the water saturator were heated to prevent condensation. The Kr was used a tracer for the switching experiments. The concentrations of the reactants used were 720 ppm NO, 4.3% O_2, 540 ppm n-C_8H_{18}, 4.0% H_2O, 7.2% CO_2, 0.72% H_2 (whenever added), 0.22% Kr (whenever added) and Ar balance. The total flow rate was 50 $cm^3 min^{-1}$. Gas flows were carefully equilibrated using micrometric needle valves to adjust the pressure between the gas flows on each side of the four-way valve with a high-sensitivity differential pressure detector. This avoided the production of spikes on the MS signal when switching from one mixture to another. The rate of the NOx reduction reaction was tested in the modified DRIFTS cell used in this work to allow a comparison with the rate of reaction in a conventional plug flow reactor. The results obtained were as follows: plug flow reactor, 5.0×10^{-7} mol NOx converted $g_{cat}{}^{-1} s^{-1}$; DRIFTS cell, 5.4×10^{-7} mol NOx converted $g_{cat}{}^{-1} s^{-1}$. The concentrations of the reactants used in the plug flow reactor were 720 ppm NO, 4.3% O_2, 540 ppm n-C_8H_{18}, 7.2% H_2O, 7.2% CO_2, 0.72% H_2 and Ar balance. The total flow rate was 276 $cm^3 min^{-1}$. The slightly lower H_2O concentration used in the DRIFTS cell was necessary to allow sufficiently strong IR data to be obtained. The close agreement in these two measurements shows that the DRIFTS cell can be considered to be comparable to a plug flow reactor, as previously reported [18].

Two different sets of transient H_2 switching experiments were performed. The first set of experiments was designed to obtain steady-state conditions initially at high NOx conversions. The catalyst was exposed for 60 min at 245 °C to the octane-SCR gas mix with 0.72% H_2 added before the fast cycling of H_2 into and out of the SCR feed was performed. In this case, the *in situ* DRIFTS spectra were recorded with a resolution of 4 cm^{-1} and with an accumulation of 128 scans under the initial steady-state conditions but with an accumulation of three scans (at a rate of 1 scan per second) every 5 s during the switches in and out of H_2 (40 switches were performed).

The second set of experiments was designed to achieve a steady state under H_2-free conditions, where the conversion of NOx was essentially zero. In this case, the catalyst was exposed only to the octane-SCR mix without H_2 for 90 min before the fast cycling of H_2 into and out of the SCR feed was performed. The *in situ* DRIFTS spectra were recorded with a resolution of 4 cm^{-1} and with an accumulation of 16 scans every 10 s during H_2 switching. The DRIFTS spectra were analysed by the OPUS software.

3. Results and discussion

Fig. 1 shows the change in NO conversion and N_2 production as a function of time in the presence or absence of H_2. The data illustrate the fact that the rate of change in activity for NOx reduction is very fast when H_2 is added or removed from the SCR feed. Consequently, if we are to observe any reaction intermediates, we need to have a time response of the same order of magnitude as seen in Fig. 1. In fact, the reaction is so fast that there is almost no delay between the disappearance of NO, the appearance of the N_2 signal, and the appearance of the Kr tracer. For example, the time required for Kr to attain 50% of its final concentration after switching (t_{50}) was 5 s while the ^{15}NO conversion reached its peak value of 60% conversion after 5 s before decreasing to a steady value of ~45% conversion after 10 s. (This initial peak may simply be due to the loss of some NOx by adsorption upon introduction of H_2 into the SCR feed.)

To illustrate the problem associated with conventional steady-state spectroscopy in the investigation of surface "intermediates",