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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 time-scale. 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",

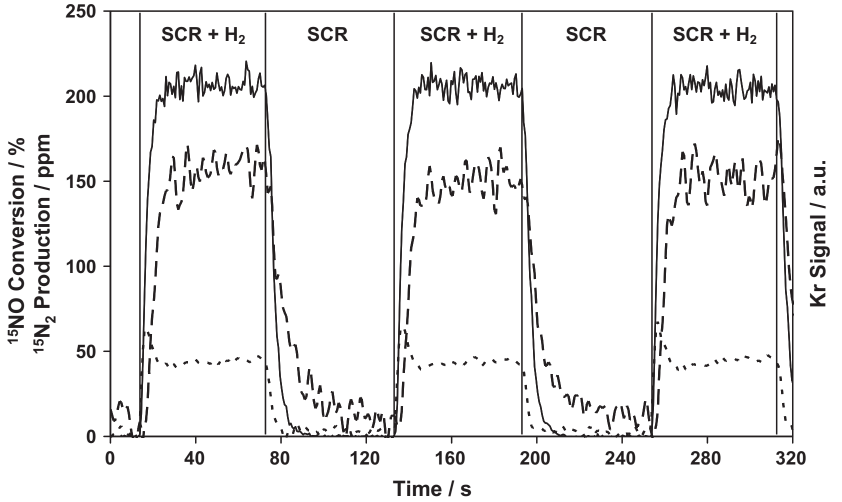


Fig. 1. Evolution of ^{15}NO conversion (- -), ^{15}N2 production (– –), Kr Signal (—) as a function of time at 245 °C on cycling the SCR feed from one containing H_2 and the Kr tracer to one in the absence of H_2 and the Kr tracer when H_2 is added to or removed from the SCR feed.

Figs. 2 and 3 compare the spectra obtained from conventional steady-state experiments with those obtained following fast periodic exposure to H_2.

Fig. 2 demonstrates that there are significant differences in the DRIFTS spectra obtained under steady-state conditions during the SCR reaction with and without H_2. The bands between 2290 and 2390 cm^{-1} can be attributed to CO_2. The bands appearing between 2886 and 3000 cm^{-1} can be associated with –CH_3 and –CH_2-stretching vibrations of hydrocarbon species [6,12]. The band at 2114 cm^{-1} observed in the absence and the presence of H_2 can be assigned to cyanide species adsorbed on Ag sites [19,20]. A number of overlapping bands are observed below 1800 cm^{-1} due to a range of adsorbed species including nitrates, nitrites, carboxylates, carbonates, formates, acetates, C=C bonds of acrylates and amines [6,12].

Most significantly for our purposes, the absorption peak at 2223 cm^{-1} is much more prominent in the presence of H_2. This band shifts to 2232 cm^{-1} when using ^{14}NO (not shown herein) and can be attributed to isocyanates adsorbed on Al_2O_3 [19,13]. From these results in isolation, it could be concluded that a surface isocyanate species is observed when the catalyst is active (i.e. when hydrogen is added) and is absent when the catalyst is inactive (i.e. when no hydrogen is added).

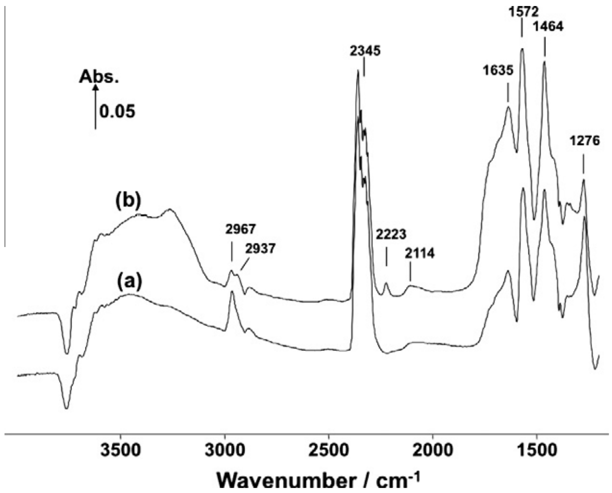


Fig. 2. A comparison of IR spectra obtained under steady-state conditions during the *n*-octane SCR reaction at 245 °C (a) without added H_2 and (b) with added H_2.

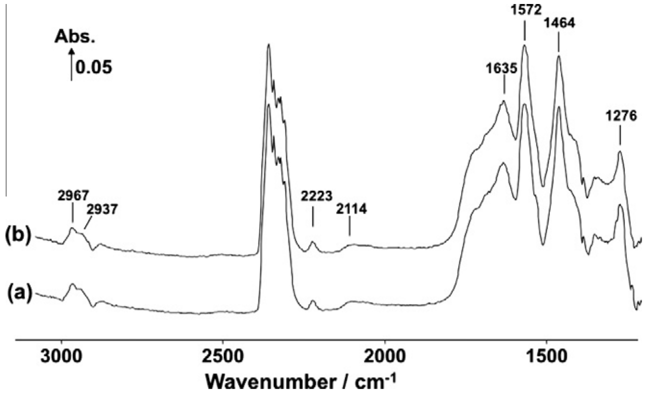


Fig. 3. DRIFTS spectra collected during cycling of H_2 in and out of the feed. A comparison of the spectra obtained (a) 2 s before (b) and 58 s after switching in H_2 to the *n*-octane-SCR feed at 245 °C. Note that the catalyst was exposed to the full SCR gas mix in the presence of 0.72% H_2 for 1 h before the H_2 on/off cycling experiments. To obtain an acceptable signal-to-noise ratio, the spectra shown here were collected for the 3-s period before the times noted above.

Fig. 3 illustrates the problem with this simple interpretation. In these experiments, the catalyst was exposed for 1 h to the SCR feed in the presence of H_2, and, thereafter, the H_2 was switched out of the feed for 60 s which initiated the periodic switching experiments which were performed. Therefore, the catalyst will be at the steady state under conditions where there is a high conversion of NOx. In Fig. 3, we compare the DRIFTS spectrum taken 2 s before switching H_2 into the feed stream with that taken only 58 s after adding H_2 to the SCR gas mix. In contrast with the DRIFTS spectra presented in Fig. 2, the spectra in Fig. 3 are very similar in all respects and yet Fig. 1 shows that the addition of hydrogen causes a dramatic increase in activity. In fact, the spectra shown in Fig. 3 show indications of the problems associated with the “conventional” steady state-type experiment (Fig. 2). Thus, the peak area for isocyanates only decreases by approximately 11% upon removal of H_2, but this is accompanied by a >90% decrease in N_2 production. This suggests that only a fraction of the observed isocyanate species are possible reaction intermediates, whereas most of the isocyanate species are relatively unreactive. Therefore, it is clear from this comparison that the vast majority of the surface species observed under steady-state conditions during the normal HC-SCR, and H_2-assisted HC-SCR reactions are not involved in the reaction and can be classified as spectator species.

These results emphasise the fact that leaving sufficient time for all the surface species on the catalyst to come to a steady state can mask the observation of potential reaction intermediates. In order to overcome this problem, fast cycling experiments were performed in which the H_2 was added or removed to “switch on” or “switch off” the NOx reduction activity for a catalyst which had already been exposed for 1 h to the full gas mixture in the presence of H_2.

Using the spectrum obtained 2 s before the addition of hydrogen as a reference allowed difference spectra to be determined. Fig. 4 shows that for the first difference spectrum obtained 3 s after switching in H_2, there is an increase in the intensity of the band at 2223 cm^{-1} (isocyanates) and a decrease in intensity of bands at 2114 cm^{-1} (cyanide). The band at 2223 cm^{-1} further increases in intensity with exposure time. Upon removal of H_2, the changes in the difference DRIFTS spectra shown in Fig. 4 are reversed (spectra not shown). The peculiar nature of the H_2 effect in NOx reduction, coupled with our fast cycling technique, has allowed us to identify surface intermediates whose concentrations change very rapidly and which, as a consequence, may be significant reaction intermediates. These surface intermediates are characterised by a band around 2223 cm^{-1} which unfortunately is the position of the band mostly associated with spectator species (Fig. 3). These changes in the spectra were observed for all the cycles performed including directly following the exposure of the catalyst to the SCR+H_2 feed for 1 h.

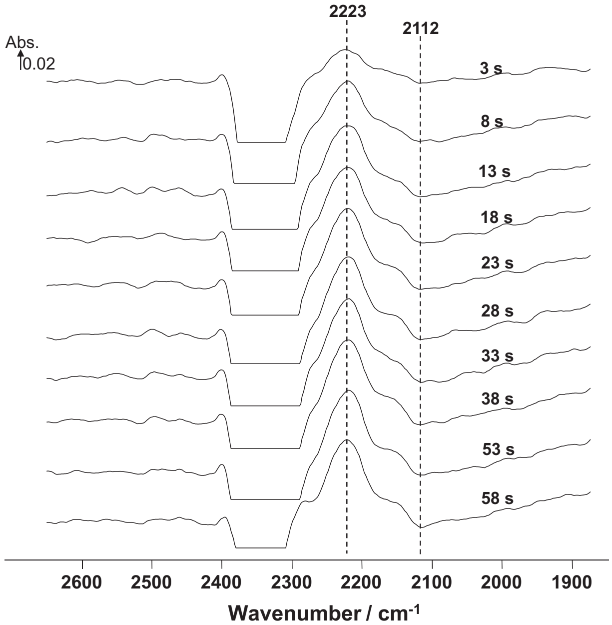


Fig. 4. Difference spectra obtained by subtracting the spectrum obtained 2 s before switching H_2 into the *n*-octane –SCR feed with those obtained at various short time intervals after switching H_2 into the feed at 245 °C. These individual spectra were obtained by summing 20 spectra from 20 separate full cycles of gas switching.

The purpose of this work is to try to identify surface species that could be reaction intermediates rather than just spectator species. Surface species that are relevant to the reaction mechanism would be expected to change concentration at a similar rate to the changes observed in the concentration of gaseous products. The comparative evolution of these species as a function of time on stream during switches of H_2 in and out of the SCR gas mixture with *n*-octane at 245 °C is depicted in Fig. 5.

Fig. 5 clearly demonstrates that the area of the peak attributed to isocyanate increases rapidly upon introduction of H_2. After an initial sharp rise in the isocyanate signal, the rate of increase slows considerably, closely matching the increasing $^{15}N_2$ signal. Upon removal of H_2, a close correlation between $^{15}N_2$ loss and the decrease in the isocyanate signal is also observed. Conversely, the peak area of the cyanide species changes in the opposite manner. The signal of cyanide initially decreases rapidly when H_2 is switched into the SCR feed and then slowly decays over a period of 60 s. When the H_2 is removed, the cyanide signal increases again over a similar period of time. Although it is not central to the present work, we note that these cyanide results may be indicative of an important role for hydrogen in “cleaning” cyanide off the silver surface which may partially at least explain the large increase in activity when hydrogen is added [4]. Note that Thibault-Starzyk et al. have recently shown by nanosecond-timescale *in situ* IR analysis that isocyanate on alumina was formed from a cyanide species adsorbed on silver [21].

The results shown in Fig. 4, and summarised in Fig. 5, refer to experiments where the catalyst was brought to a steady state under conditions where there was a high rate of conversion of NOx. The unique characteristics of the H_2-assisted HC-SCR reaction on Ag catalysts provided a means to identify reactive intermediates

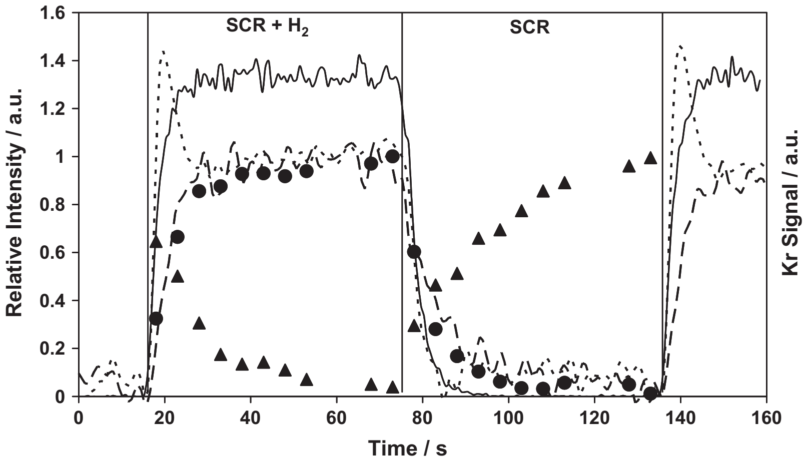


Fig. 5. Relative evolution of ^{15}NO conversion (- - -), $^{15}N_2$ production (– – –), Kr signal (—), and the intensity of bands attributed to isocyanate (●, ^{15}NCO) and cyanide (▲, C15N) surface species as a function of time at 245 °C.

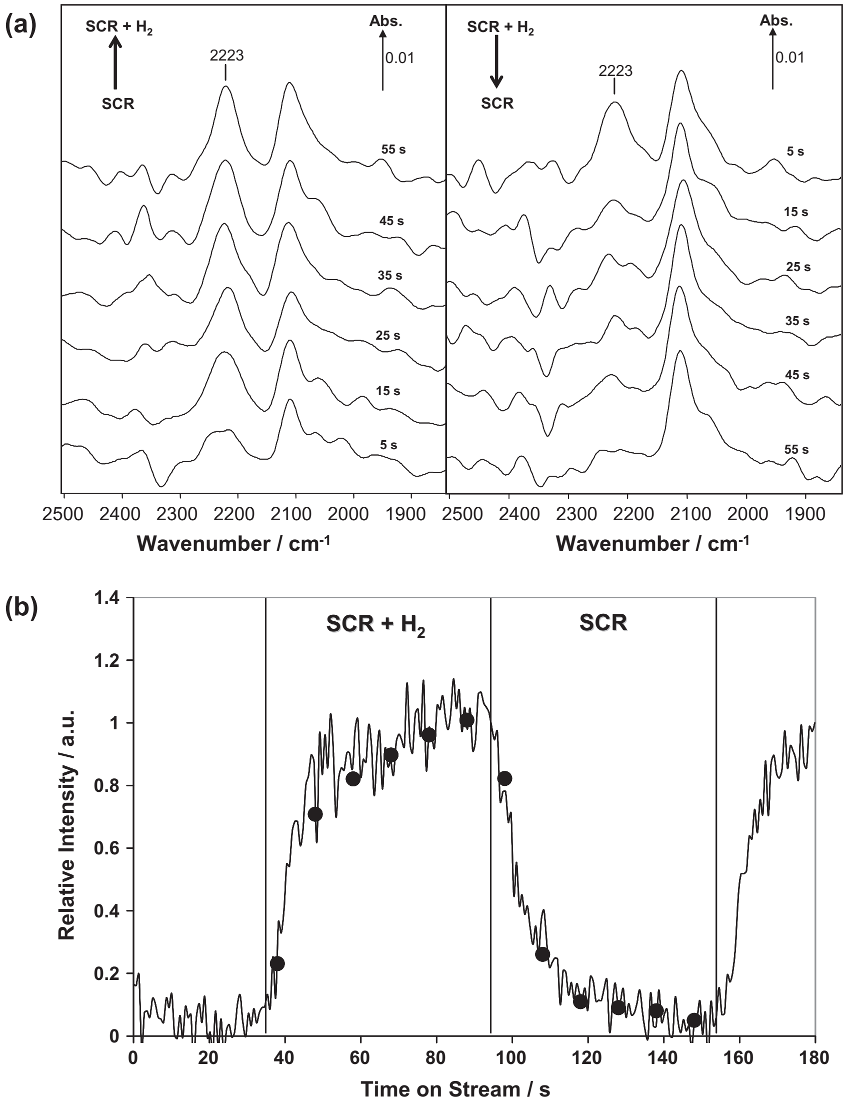


Fig. 6. Changes in the intensity of (a) *in situ* DRIFTS spectra and (b) relative evolution of $^{15}N_2$ production (—) and isocyanate (●, ^{15}NCO) surface species as a function of time at 245 °C during the second cycle switching. Note that the catalyst was exposed to the full SCR gas mix in the absence of H_2 for 90 min before cycling H_2 into and out of the SCR mix.

in the presence of a higher concentration of "spectators". However, this H_2 effect is unusual so in order to explore the feasibility of observing potential reaction intermediates in a more general way we performed the following experiments.

The catalyst was first exposed to the full SCR mix without H_2 for 90 min before cycling H_2 into and out of the SCR gas stream. The results from the second of these 60 s cycles are shown in Fig. 6. There is a very good correlation between the rate of $^{15}N_2$ production and rate of reaction of surface isocyanates compared with the data shown in Fig. 5. In contrast to Fig. 3, however, Fig. 6 shows that the area of the isocyanate peak decreased by 80% when H_2 was removed from the SCR gas mix, matching the *ca*. 90% decrease in $^{15}N_2$ production. This is consistent with the view that at these short contact times, most of the isocyanates formed (and detected by DRIFTS) are highly reactive, possibly because they are formed near active Ag sites and are consumed to produce N_2 before being transferred to alumina support as the time on stream increases.

Finally, to compare the short contact time experiments and to illustrate the problem with using a conventional SSITKA-type experiment, the results of such a SSITKA experiment are shown in Fig. 7. This clearly shows that whereas the production of nitrogen rises quickly to a constant level, the intensity of the infrared signal for the corresponding isocyanate continues to increase, i.e. long after the rate of production of nitrogen has stabilised. There can be a number of reasons why the exchange time constant value is higher for the isocyanate when compared with that of N_2. First, it is possible that all these isocyanate species are spectators and not directly involved in the production of N_2. Second, it is possible that most, but not all, of the IR signal observed is related to spectator species, for instance isocyanates located far away from the silver–alumina interface that have had time to diffuse onto the support away from the silver.

Depending on the experimental conditions, these rather inert species would create a large reservoir of isocyanate species and the corresponding infrared signal could be masking that of more reactive isocyanates located at the reaction sites (possibly the Ag–alumina interface). This effect would, in essence, be "spillover" of a possible intermediate onto a less-reactive surface and is consistent with our fast cycling experiments where the transient H_2 switching shows that isocyanates change on a timescale similar to that of the reaction.

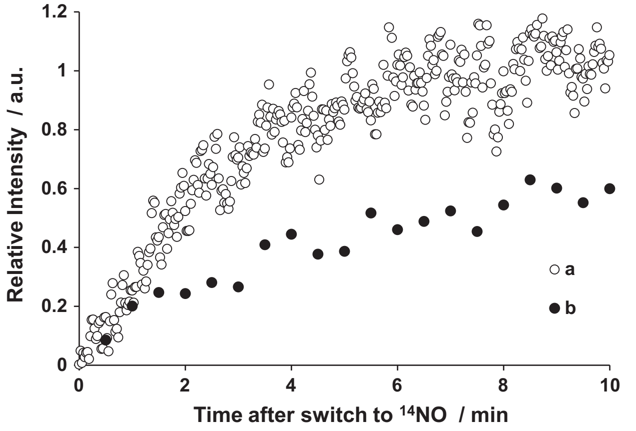
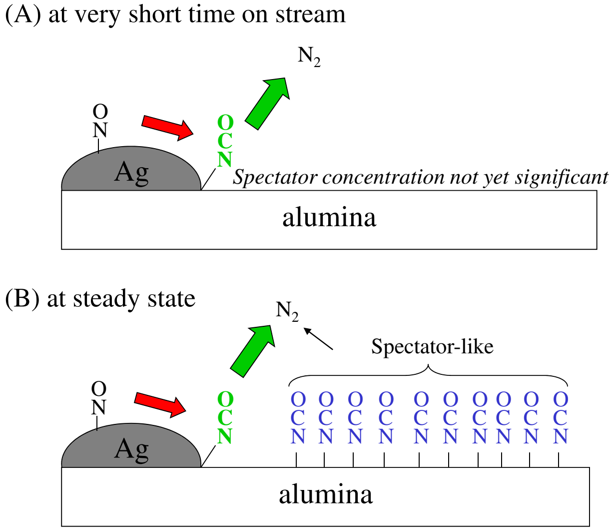


Fig. 7. Evolution of the DRIFTS intensity of ^{14}N-containing isocyanates (●) and the mass spectrometry signal for gas phase $^{14}N_2$ (○) observed during the SCR of NO reaction with *n*-octane in the presence of H_2 at 245 °C after switching to the ^{14}NO SCR feed in a typical SSITKA experiment.

These observations can be rationalised by assuming that in the case of the SSITKA experiment (Fig. 7), the IR signal observed is overwhelmingly dominated by that of the unreactive isocyanates located all over the alumina surface, which need a longer time to exchange. In contrast, in the case of the fast cycling H_2 transient-type experiments (Figs. 5 and 6), the total IR signal is dominated by the reactive isocyanate species, possibly located at the silver–alumina interface. In the latter case, the low activity species have not had time to accumulate in between the switches.

The importance of basing any mechanistic conclusions on good quality kinetic information will be clear from the results presented above. Consequently, a distinction between active species and spectator species on the surface is proposed in Scheme 1 although this should be seen as a guide to interpretation and not scientific proof of a particular effect. Note that the term "spectator" should be widely understood as describing a species which either is inert or whose rate of conversion to products is very much slower than the measured rate of product formation. True reaction intermediates should be understood to mean species that react fast enough to account for the formation of essentially all of the product. These reaction intermediates would have a very short lifetime on the surface with a correspondingly low surface coverage under reaction conditions which will make them difficult to observe.



Scheme 1. Comparison of the proposed distributions of surface isocyanate species (A) after very short exposure to reactants and (B) at steady state.

The cycling technique used here is reminiscent of that used under oscillating reaction conditions to help discriminate true reaction intermediates from spectator species as proposed by various authors for other catalytic systems [22,23].

4. Conclusions

The work presented herein highlights the issues associated with many steady-state transient kinetic investigations of catalytic reaction mechanisms. In all cases, where a reactant, a product, a by-product or an intermediate can adsorb strongly on a catalyst support and this refers to most heterogeneously catalysed reactions, there is a real danger that the easily identified surface species will not be catalytically significant. It has been demonstrated herein that it is possible that a surface species that is detected and identified using a spectroscopic technique may have the same chemical composition and structure as a true reaction intermediate. However, if the amount of the detected species, as measured by the infrared absorbance, does not change with a rate that is consistent with the rate of formation or removal of a product or a reactant, then no conclusion should be drawn about the importance or otherwise of this species in a mechanistic scheme. We recognise that this statement runs contrary to accepted practice in many publications on reaction mechanisms, but the difficulty in making measurements on a short timescale should not be allowed to disguise the fact that such measurements can be, and indeed often are, highly misleading.

Our work stresses the importance of monitoring changes in the amount of any surface species in a time frame relevant to that found for changes in the concentration of products in a transient kinetic experiment. Of those species that were observed to change during the rapid switches in and out of hydrogen, only a small fraction of the surface isocyanates changed in a timescale that matched that of the changing gas phase concentrations. Thus, it is concluded that only a fraction of all the isocyanate species that can adsorb on a Ag/Al_2O_3 catalyst, possibly those bound to aluminium sites close to the Ag, are potential intermediates in the H_2-assisted HC-SCR reaction.

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