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The use of short time-on-stream *in situ* spectroscopic transient kinetic isotope techniques to investigate the mechanism of hydrocarbon selective catalytic reduction (HC-SCR) of NO_x at low temperatures

Sarayute Chansai, Robbie Burch *, Christopher Hardacre, John Breen [1], Frederic Meunier [2]

CenTACat, School of Chemistry and Chemical Engineering, Queens University Belfast, Belfast BT9 5AG, Ireland

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A B S T R A C T

The problem of differentiating between active and spectator species that have similar infrared spectra has been addressed by developing short time-on-stream *in situ* spectroscopic transient isotope experimental techniques (STOS-SSITKA). The techniques have been used to investigate the reaction mechanism for the reduction of nitrogen oxides (NO_x) by hydrocarbons under lean-burn (excess oxygen) conditions on a silver catalyst. Although a nitrate-type species tracks the formation of isotopically labeled dinitrogen, the results show that this is misleading because a nitrate-type species has the same response to an isotopic switch even under conditions where no dinitrogen is produced. In the case of cyanide and isocyanate species, the results show that it is possible to differentiate between slowly reacting spectator isocyanate species, probably adsorbed on the oxide support, and reactive isocyanate species, possibly on or close to the active silver phase. The reactive isocyanate species responds to an isotope switch at a rate that matches that of the rate of formation of the main product, dinitrogen. It is concluded that these reactive isocyanates could potentially be involved in the reduction of NO_x whereas there is no evidence to support the involvement of nitrate-type species that are observable by infrared spectroscopy.

1. Introduction

The dramatic effect of H_2 in enhancing the selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) over Ag/Al_2O_3 catalysts under lean-burn (strongly oxidizing) conditions was reported several years ago [1–26]. Although it was initially proposed that the main effect of hydrogen was to modify the structure of the active form of the silver, it is now fairly well accepted that a key role of hydrogen is to modify the chemical reactions that occur in the HC-SCR reaction. Several alternative descriptions of the reaction mechanism have been made based on the use of standard experimental techniques, such as transient *in situ* DRIFTS or *in situ* DRIFTS coupled with mass spectrometry. Based on such experiments, many highly reactive species, e.g., nitrate, nitrites, isocyanates, cyanides, ammonia, amines, oximes, and organo-nitrogen compounds, have been proposed as reaction intermediates in the reduction of NO_x to N_2 [4,6,12,25–32]. However, as shown in our earlier publication [6], the use of such conventional transient techniques can provide very misleading conclusions due to the problem of differentiating between real reaction intermediates and surface spectator species. The reason is that frequently a spectator species can exhibit an IR spectrum that is indistinguishable from that of the reaction intermediate being investigated, but the spectator species may be present at much higher concentrations. This could happen if it was adsorbed on a high surface area support.

The effect of hydrogen on the rate of NO_x reduction is unique, especially in the way in which it switches on and off virtually simultaneously with the introduction or the removal of hydrogen from the normal HC-SCR reaction mixture. For this reason, we were able to monitor changes in the infrared signal from species adsorbed on a silver catalyst that was initially inactive and then became very active for NO_x reduction as soon as hydrogen was introduced [6]. In this very special case, we were then able to clearly differentiate between an isocyanate species that could potentially be an important reaction intermediate and an isocyanate species that appeared to be a spectator species. The spectator species was assumed to be adsorbed on the alumina support where it had a low activity, whereas the active isocyanate was assumed to be at, or close to, the active silver clusters that constitute the active

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* Corresponding author.
E-mail address: r.burch@qub.ac.uk (R. Burch).

[1] Present address: Merck, Sharp & Dohme, Ballydine, Clonmel, County Tipperary, Ireland.

[2] Present address: Laboratoire Catalyse et Spectrochimie, ENSICAEN-Université de Caen-CNRS, Caen, France.

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site for NO_x reduction. The reason that these two forms of isocyanate cannot be differentiated under normal transient experimental conditions is because the high steady-state concentration of the slowly reacting (spectator) isocyanate species totally dominates the infrared spectrum and so any changes in the active form of the isocyanate cannot be detected. In other words, the change in the amplitude associated with the true reaction intermediate is similar to or lower than the noise level associated with the spectator species.

The hydrogen effect appears to be unique to these specific Ag/Al_2O_3 catalysts so it is of interest to investigate whether or not for other reaction systems, true reaction intermediates could be detected and differentiated from spectator species by modifying the transient technique. In our earlier paper that corresponds to non-steady-state conditions [6], we showed that by using the hydrogen effect to rapidly change the activity of the catalyst, we had identified an isocyanate species that could be involved in the NO_x reduction reaction. In the present paper, for reactions under steady-state conditions, we first aim to demonstrate the problems that arise in identifying true reaction intermediates in HC-SCR with silver catalysts using conventional transient techniques and then to show that by carrying out the steady-state isotopic transient kinetic analysis at short time on stream (STOS-SSITKA), we can identify an isocyanate species that could be a reaction intermediate.

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 [33]. The specific surface area of the catalyst was $170\ m^2\ g^{-1}$ [3]. From earlier EXAFS measurements, we found that the average silver particle size corresponded to a cluster of about 5 silver atoms [5].

In situ DRIFTS measurements were performed with a Bruker Vertex 70 FTIR 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 to monitor the gas-phase species: $^{14}N_2/CO$ ($m/z = 28$), $^{14}NO/^{15}N_2$ ($m/z = 30$), ^{15}NO ($m/z = 31$) or $^{15}N^{18}O$ ($m/z = 33$), n-C_8H_{18} ($m/z = 57$), and Kr ($m/z = 82$).

Prior to the 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 Ag/Al_2O_3 catalyst at 245 °C under flowing Ar was taken as a background. The reactant gases, NO (1% $^{14}NO/Ar$, 1% $^{15}NO/Ar$, or 1% $^{15}N^{18}O/Ar$), O_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 vapor 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 as a tracer and internal standard for the switching experiments.

The pre-treated catalyst was introduced to the SCR mix consisting of 720 ppm NO, 4.3% O_2, 540 ppm n-C_8H_{18}, 4.0% H_2O, 0.72% H_2, 0.22% Kr (when added), and Ar balance. The total flow rate of the SCR feed was $50\ cm^3\ min^{-1}$. Kr was added to the $^{15}N^{18}O$-containing feed as a tracer and internal standard. Standard $^{14}N_2$ (2% N_2/Ar) was used to calibrate the signals of both $^{14}N_2$ and $^{14}N^{15}N$ obtained from the mass spectrometer. Before performing isotopic switches, ^{14}NO was normally used at the start under steady-state conditions for 90 min. The experiment was also repeated utilizing $^{15}N^{18}O$ instead of ^{14}NO in order to ensure that ^{14}N-containing surface species is completely replaced by ^{15}N isotopic label during the transient switches. In some cases, ^{15}NO was employed instead of $^{15}N^{18}O$ to help in the identification of some surface and gas-phase species. In addition to the SCR reaction with n-octane + H_2, the $NO + O_2 + H_2$ reaction was also performed in order to investigate the exchange rate of nitrate species even when there is no N_2 produced – the only products from the $NO + O_2 + H_2$ reaction are NO_2 and H_2O.

For the STOS-SSITKA experiments, the pre-treated Ag catalyst under Ar flow at 245 °C was first exposed to the $^{15}N^{18}O$-SCR gas mix for only 1 min. This was designed to prevent the γ-Al_2O_3 support from adsorbing large amounts of reactants, intermediates, or products. However, this is still enough time for the formation of isocyanate species to be observed and monitored. After 1 min in the $^{15}N^{18}O$ SCR feed, the SCR mix was then replaced by the ^{14}NO-SCR mix for 10 min, and changes in the isocyanate bands were investigated.

During the switches between ^{14}NO and $^{15}N^{18}O$, the DRIFTS spectra were recorded with a resolution of $4\ cm^{-1}$ and with an accumulation of 56 scans every 30 s, but with an accumulation of 128 scans during steady-state conditions. The DRIFTS spectra were analyzed by OPUS software provided by Bruker.

In order to evaluate the role of each of the possible reaction intermediates, it is necessary to determine the relative changes in the evolution of ^{14}N-containing species during isotopic switches between $^{15}N^{18}O$ and ^{14}NO in the HC-SCR feed. The IR bands of these species generally demonstrate a redshift, when the ^{14}N atom is replaced with the heavier ^{15}N isotope. Nevertheless, a complete resolution of all ^{14}N and ^{15}N IR bands is not accomplished during isotopic switches. By applying the Origin 6.0 professional program, a full deconvolution using neither Guassian nor Lorentzian curves of the IR bands provided any satisfactory outcome. However, qualitative information concerning the kinetic trends as a function of time can be obtained using an integration method [34,35] for the ^{14}N-containing species as follows:

Nitrates: $1317–1302\ cm^{-1}$ (single-point baseline at $1323\ cm^{-1}$).
Nitrates: $1538–1520\ cm^{-1}$ (single-point baseline at $1515\ cm^{-1}$).
Cyanides: $2175–2145\ cm^{-1}$ (single-point baseline at $2185\ cm^{-1}$).

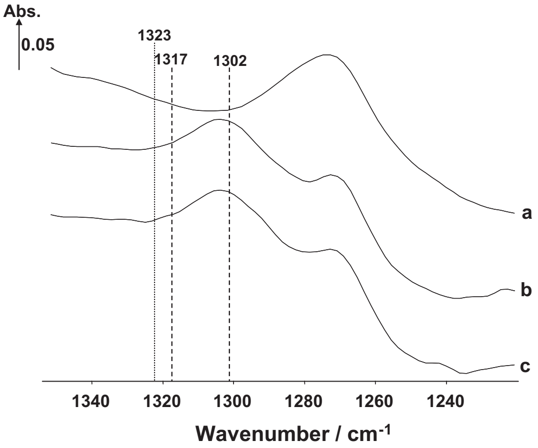

Fig. 1. Integration region (dashed lines) of the DRIFTS spectra of the surface nitrates formed over 2.0% Ag/Al_2O_3 catalyst at 245 °C at steady-state conditions with (a) the $^{15}N^{18}O$ feed, (b) after 30 min switching to ^{14}NO feed, and (c) at steady-state conditions with ^{14}NO feed. The dotted line represents the single-point baseline used for the integration.

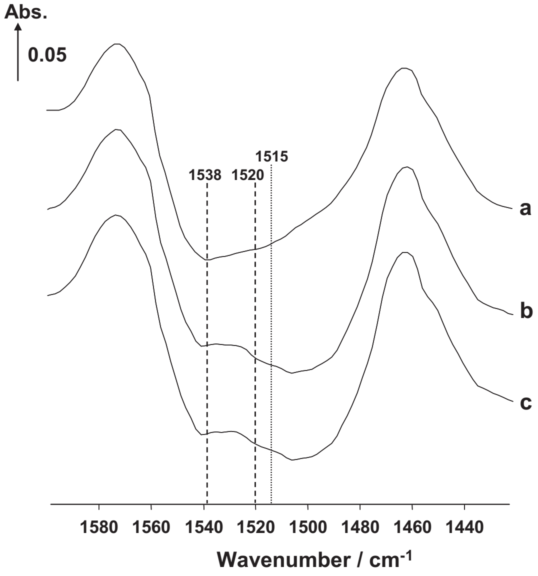

Fig. 2. Integration region (dashed lines) of the DRIFTS spectra of the surface nitrates formed over 2.0% Ag/Al_2O_3 catalyst at 245 °C at steady-state conditions (a) with the $^{15}N^{18}O$ feed, (b) after 30 min switching to ^{14}NO feed, and (c) at steady-state conditions with ^{14}NO feed. The dotted line represents the single-point baseline used for the integration.

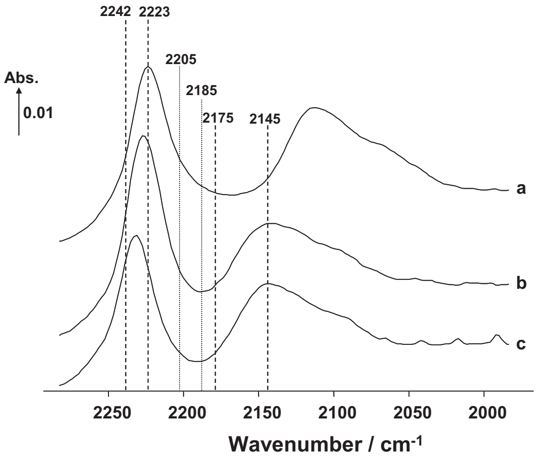

Fig. 3. Integration region (dashed lines) of the DRIFTS spectra of the surface isocyanates (left band) and cyanides (right band) formed over 2.0% Ag/Al_2O_3 catalyst at 245 °C at steady-state conditions (a) with the $^{15}N^{18}O$ feed, (b) after 30 min switching to ^{14}NO feed, and (c) at steady-state conditions with ^{14}NO feed. The dotted lines represent the single-point baseline used for the integration.

Isocyanates: 2242–2223 cm^{-1} (single-point baseline at 2205 cm^{-1}).

This single-point baseline method is a standard procedure within the OPUS software provided by Bruker whereby the integration baseline is horizontal and passing through the point selected.

The integration regions of the given bands are illustrated in Figs. 1–3.

3. Results

3.1. Assignment of the IR bands

The typical *in situ* DRIFTS spectra obtained under traditional (i.e., long time on stream) SSITKA conditions during the SCR of NO reaction with *n*-octane in the presence of H_2 at 245 °C are shown in Fig. 4. In these experiments, the catalyst is first allowed to come to steady state by a prolonged exposure to a reaction mixture containing ^{14}NO, and then a rapid isotopic switch to $^{15}N^{18}O$ is made. As will be clear later, this procedure, which we describe as the "traditional SSITKA technique," allows sufficient time for both the active component in the catalyst (silver in our case) and the support (alumina) to reach their steady equilibrium states under reaction conditions.

These DRIFTS spectra contain many overlapping bands, but a tentative assignment of the main features can be obtained by using information from the literature [7,8,10–12,17,25–32]. Fig. 4 demonstrates that there are changes in the shape and position of four types of N-containing species when we switch from ^{14}NO to $^{15}N^{18}O$. Two of these species are relatively easy to identify. In the region of 2300–2000 cm^{-1}, two IR bands appearing at 2232 and 2145 cm^{-1} are observed. The former band shifts to 2223 cm^{-1}, whereas the latter one shifts to 2112 cm^{-1}. These two bands are assigned to isocyanates adsorbed on alumina [7,36] and cyanides adsorbed on Ag sites [36,37], respectively.

The IR bands between 1800 and 1200 cm^{-1} are complicated due to the complex nature of the HC-SCR reaction that produces many different surface species. However, there are differences in the positions of the absorption bands at 1530 and 1305 cm^{-1}. The former band is difficult to assign due to the absence of any reference data and the fact that the corresponding IR bands were swamped by the spectra of other nitrogen-free species (e.g., acetates, formates, and carboxylates) located between 1800 and 1200 cm^{-1}. The peak at 1305 cm^{-1} that moves to 1272 cm^{-1} when we switch from ^{14}NO to $^{15}N^{18}O$ SCR is assigned to a nitrate species. (*Note*: this assignment is supported by the data presented in the next paragraph.)

The role of nitrates in the HC-SCR reaction has been investigated extensively by *in situ* DRIFTS measurements [7,8,10–12,17,25,26,30,31,38]. Although there appear to be contradictions in the literature on the assignment of the adsorbed nitrate species to monodentate or bidentate nitrates, most workers have assigned the IR bands between 1305 and 1295 cm^{-1} to bidentate nitrates. To avoid confusion, in this paper, we will not differentiate between monodentate and bidentate species but simply refer to these as "nitrate species".

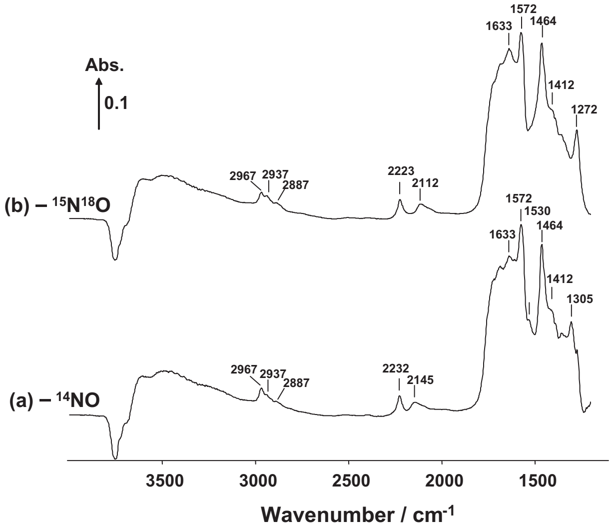

Fig. 4. A comparison of *in situ* DRIFTS spectra obtained over a 2.0% Ag/Al_2O_3 catalyst at steady-state conditions during the HC-SCR reaction with *n*-octane in the presence of H_2 at 245 °C (a) with ^{14}NO in the feed and (b) with $^{15}N^{18}O$ in the feed.

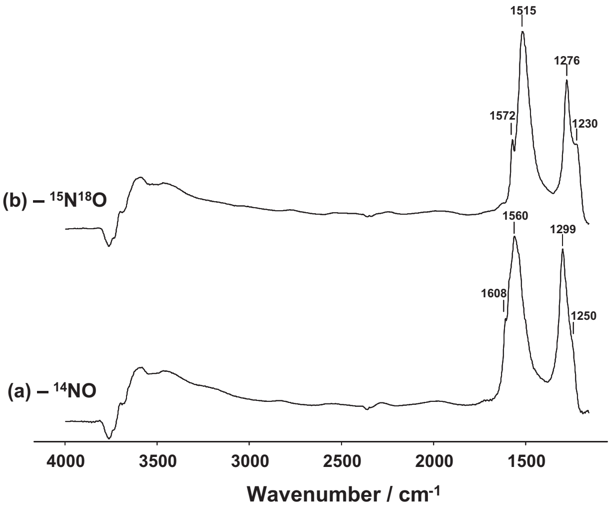

Fig. 5. A comparison of *in situ* DRIFTS spectra obtained over a 2.0% Ag/Al_2O_3 catalyst at steady-state conditions during the $NO/O_2/H_2$ reaction at 245 °C (a) with ^{14}NO in the feed and (b) with $^{15}N^{18}O$ in the feed.

As mentioned in Section 2, SSITKA experiments were also undertaken to clarify the possible role of nitrate species in the reaction mechanism. For this purpose, we performed experiments using only $NO + O_2 + H_2$ as the reaction mixture, that is, without including any hydrocarbon reductant. As indicated above, in this reaction, the only nitrogen-containing product is NO_2, i.e., dinitrogen is not observed.

Fig. 5 compares the *in situ* DRIFTS spectra taken at steady state after prolonged exposure to $^{14}NO + O_2 + H_2$ and then after switching to $^{15}N^{18}O + O_2 + H_2$. The significance of these results in relation to the possible role of nitrate species in the reaction mechanism will be discussed later, but for now, we note the shift in the nitrate bands even under conditions where no dinitrogen is produced.

3.2. Evolution with time of the DRIFTS spectra in the HC-SCR + H_2 reaction following a switch from $^{15}N^{18}O$ to ^{14}NO

3.2.1. Evolution of nitrate-type species

Figs. 6 and 7 show the evolution with time of the nitrate species after switching the labeled $^{15}N^{18}O$ HC-SCR feed to the corresponding unlabeled ^{14}NO HC-SCR feed. As we can see in Fig. 6, the intensity of the nitrate band at 1272 cm^{-1} decreases, whereas a new IR band appears at 1305 cm^{-1}. The isotopic shift (Δv) of these two bands is 33 cm^{-1}.

We note that the band at 1272 cm^{-1} does not disappear completely even 30 min after the isotopic switch. However, when we run an experiment without any source of nitrogen, that is, an octane + O_2 + H_2 experiment, we do not see a band at 1272 cm^{-1} so it seems clear that the band at 1272 cm^{-1} corresponds to a species that contains nitrogen. However, there may be more than one such species so that the overall rate of exchange of the species appears to be slower than the rate of appearance of the isotopically labeled species with a band at 1305 cm^{-1}. Thus, although the IR bands of the different species partly overlap, it can be concluded that upon switching to ^{14}NO feed, the ^{15}N-containing nitrates are replaced by the ^{14}N-containing nitrate species in about 5–10 min.

Fig. 7 shows that an unresolved band at 1492 cm^{-1}, which is attributed to nitrates, diminishes while a new IR band at 1530 cm^{-1} appears. This can be seen more clearly in the difference between DRIFTS spectra shown in Fig. 7B. The isotopic shift (Δv) of these two bands is 38 cm^{-1}.

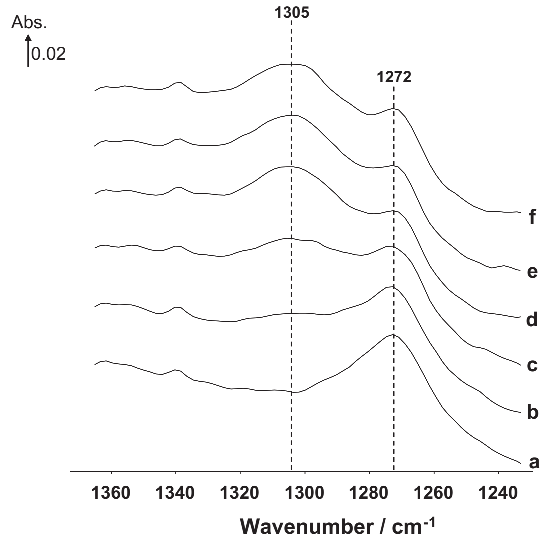

Fig. 6. *In situ* DRIFTS spectra of the surface nitrates formed over a 2.0% Ag/Al_2O_3 catalyst during the HC-SCR of NO reaction with *n*-octane in the presence of H_2 at 245 °C under (a) $^{15}N^{18}O$ HC-SCR feed and then after (b) 1 min, (c) 2 min, (d) 5 min, (e) 10 min, and (f) 30 min after switching to the ^{14}NO HC-SCR feed.

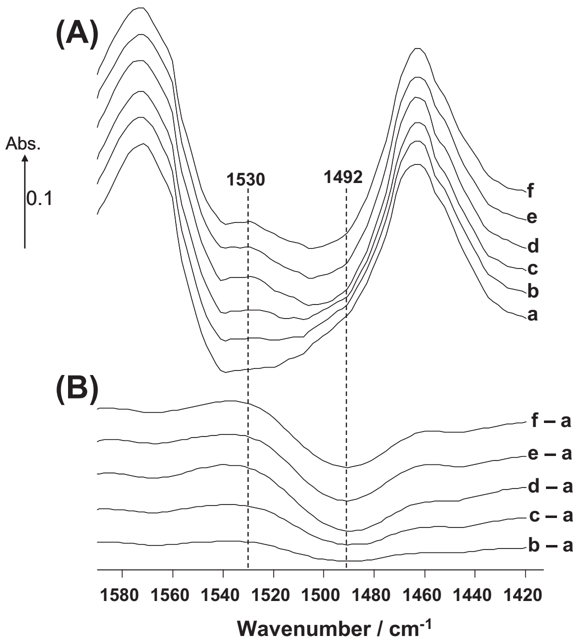

Fig. 7. (A) *In situ* DRIFTS spectra and (B) difference between DRIFTS spectra of the surface nitrates formed over a 2.0% Ag/Al_2O_3 catalyst during the HC-SCR of NO reaction with *n*-octane in the presence of H_2 at 245 °C under (a) $^{15}N^{18}O$ HC-SCR feed and then after (b) 1 min, (c) 2 min, (d) 5 min, (e) 10 min, and (f) 30 min after switching to the ^{14}NO HC-SCR feed.

3.2.2. Evolution of cyanide and isocyanate species

Fig. 8 exhibits the changes in absorbance intensity of the IR bands that are attributed to cyanide (2112–2145 cm^{-1}) and isocyanate (2223–2236 cm^{-1}) species.

On exposure to the ^{14}NO SCR feed stream, it is seen that the ^{15}N-cyanide band at 2112 cm^{-1} is slowly exchanged with the ^{14}N-containing cyanides absorbing at 2145 cm^{-1}. The isotopic shift is equal to 33 cm^{-1}. Based on the method of the reduced masses, the theoretical redshift of the cyanide band can be calculated by using the following equation:

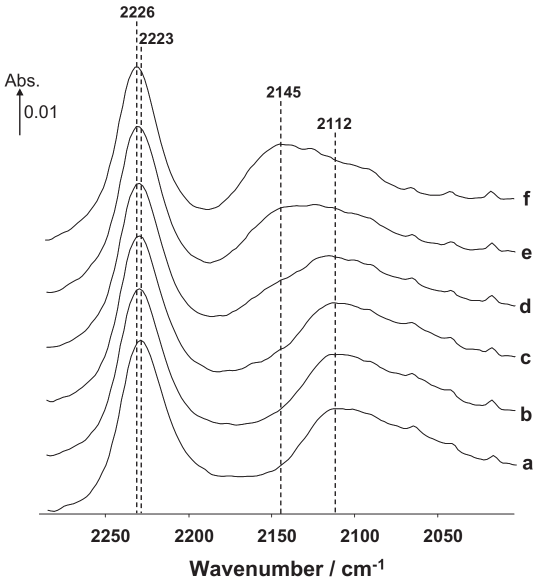

Fig. 8. *In situ* DRIFTS spectra of the surface cyanide (2112–2145 cm^{-1}) and isocyanate (2223–2236 cm^{-1}) formed over a 2.0% Ag/Al_2O_3 catalyst during the SCR of NO reaction with *n*-octane in the presence of H_2 at 245 °C under (a) $^{15}N^{18}O$ HC-SCR feed and then after (b) 1 min, (c) 2 min, (d) 5 min, (e) 10 min, and (f) 30 min after switching to the ^{14}NO HC-SCR feed.

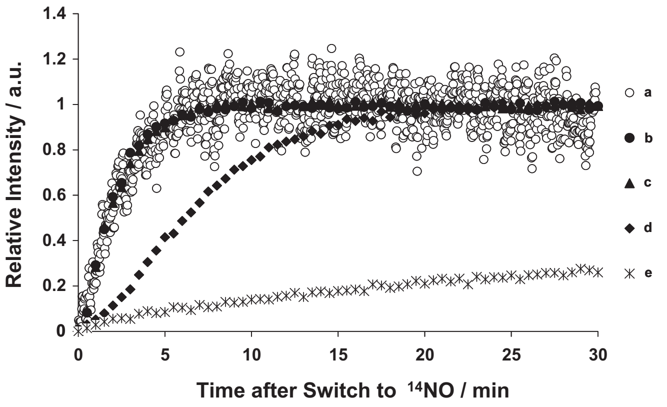

Fig. 9. Evolution with time of the relative intensities of the DRIFTS spectra of four ^{14}N-containing species and the corresponding mass spectrometry signal of gas-phase $^{14}N_2$ observed over 2.0% Ag/Al_2O_3 catalyst during the HC-SCR of NO reaction with *n*-octane in the presence of H_2 at 245 °C after switching from the $^{15}N^{18}O$ to the ^{14}NO SCR feed. (a) $^{14}N_2$ production; (b) change in the nitrate infrared signal; (c) change in the nitrate infrared signal; (d) change in the cyanide infrared signal; (e) change in the isocyanate infrared signal.

$$\text{Wavenumber}(^{15}N \equiv C) = 0.9845 \times \text{Wavenumber}(^{14}N \equiv C) \qquad (1)$$

Applying this formula, the IR bands of cyanide species observed at 2145 and 2112 cm^{-1} are in agreement with the calculated result.

Surprisingly, a much slower exchange rate of the isocyanate band is observed in comparison with the evolution of the cyanides. Fig. 8 shows that the ^{15}N-containing isocyanates gradually change to the ^{14}N-isocyanate species after switching from $^{15}N^{18}O$ to ^{14}NO. It should be noted, however, that the IR band for the $-^{15}NCO$ species shifts by only 3 cm^{-1}, which should be compared to the difference seen in the DRIFTS spectra of the isocyanates ($\Delta v = 9\ cm^{-1}$) taken under steady-state conditions when either ^{14}NO or $^{15}N^{18}O$ is used at the start of the SSITKA experiment. The smaller shift indicates that the replacement of $-^{15}NCO$ by $-^{14}NCO$ species is not complete even after 30 min.

3.2.3. The formation of nitrates, cyanides, and isocyanates during isotopic switch

As described earlier, during the HC-SCR reaction, there are four types of infrared band observed that correspond to N-containing species nitrates (two bands), cyanides, and isocyanates. The kinetic evolution of the IR bands of these species was determined by analyzing the *in situ* DRIFTS spectra shown earlier while the production of $^{14}N_2$ was followed in the SSITKA part of the experiment by using the mass spectrometer signal at $m/z = 28$.

Fig. 9 compares the evolution of the surface species and the gas-phase N_2 upon the replacement of $^{15}N^{18}O$ by ^{14}NO. It is observed that the ^{15}N-containing isocyanates gradually exchanged with the ^{14}N-containing isocyanate species, giving approximately 28% exchange to the – ^{14}NCO surface species after 30 min under the ^{14}NO SCR feed.

In contrast, the exchange of the ^{15}N-cyanide species with the ^{14}N-containing cyanides is complete in about 20 min. However, although the kinetic exchange of cyanide species is much faster than that of isocyanates, Fig. 9 still shows that the cyanide curve lags behind the curve for the formation of nitrogen. This means that we cannot claim that the cyanide species observed in such infrared experiments is really a precursor in the NO_x reduction reaction although this has been inferred by Bion et al. [36,37]. On the contrary, our observation indicates that the cyanides that are observable by IR spectroscopy are not part of the main reaction pathway to N_2.

Interestingly, as seen in Fig. 9, the curve for the evolution of nitrates is identical to that for $^{14}N_2$ production. The complete exchange of both these species is obtained in about 8 min. Based on these results, which we point out have been obtained from conventional SSITKA experiments, it would be concluded that only nitrates could be involved in the formation of N_2 whereas cyanides, and especially isocyanates, appear to exchange much too slowly to be important as reaction intermediates.

However, in a recent paper [6], we have pointed out the problems that can occur in using the conventional SSITKA methodology. In this earlier work, we have shown that under very fast switching conditions for catalysts which had not been equilibrated for long periods of time, it was possible to differentiate between isocyanate species that could be reaction intermediates and other isocyanate species that appeared to be merely spectator species. The key feature in these experiments was to prevent the gradual buildup of relatively inactive, or even inert, species on the alumina support because the infrared spectrum of these species could swamp the spectrum from active species having similar chemical compositions and structures.

In this earlier work, this was possible because in the absence of hydrogen, the rate of NO_x reduction was close to zero but as soon as hydrogen was introduced the rate increased instantaneously to a very high value. Thus, by rapidly switching the hydrogen on or off, it was possible to control the formation of potential intermediate species. At short times on stream, there is insufficient time for spectator species to develop on the support, and so it is still possible to observe the transformation of active species. However, after the much longer time on stream that is normal in conventional SSITKA experiments, perhaps many tens of minutes, the build-up of spectator-like species on the support is so large as to completely dominate the infrared spectrum and so any changes in the concentration of active intermediates are impossible to observe.

In the more general case where steady-state isotope techniques are used, rather than the non-steady-state switches in the gas composition used previously (e.g., hydrogen on or hydrogen off), we now demonstrate that by using very short times on stream, we can obtain information about potential reactive intermediates.

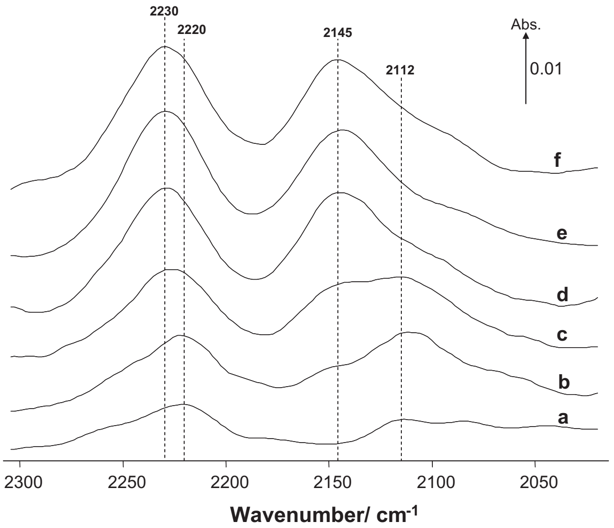

Fig. 10. Changes in intensity of DRIFTS spectra of both surface isocyanates and cyanides formed during quick-SSITKA experiment over a 2.0% Ag/Al_2O_3 catalyst under the HC-SCR of NO reaction with *n*-octane in the presence of H_2 at 245 °C under (a) $^{15}N^{18}O$ HC-SCR feed and then after (b) 1 min, (c) 2 min, (d) 5 min, (e) 8 min, and (f) 10 min after switching to the ^{14}NO HC-SCR feed.

Fig. 10 shows the results of such a STOS-SSITKA experiment. We shall discuss later the implication of these results when compared to the results obtained using the conventional SSITKA technique. However, for now we note that the point corresponding to 50% exchange from $^{15}NC^{18}O$ to ^{14}NCO occurs at a time after the isotopic switch, which is between only one minute (curve (b) in Fig. 10) and two minutes (curve (c) in Fig. 10).

4. Discussion

4.1. Evolution of nitrates

Nitrate species have been proposed as key intermediates in the SCR reaction mechanism [39–41]. Shimizu et al. [39–41] clearly showed that adsorbed nitrate species are converted to N_2 during exposure to the reductant at rates that are similar to those of the steady-state reduction of NO. Their findings suggest that nitrate species are true intermediates in the SCR reaction over Ag/Al_2O_3 catalysts. Weckhuysen and coworkers [42] have recently proposed that a nitrite species is involved as a reaction intermediate. Several other workers have reported that adsorbed nitrates could react with the activated C-containing intermediates such as acetate or other partially oxidized hydrocarbon species to yield organo-nitrogen species, subsequently leading to the formation of reactive N-containing species such as cyanides and isocyanates [4,12, 25–32,42]. Due to the complex nature of the SCR reaction, these organo-nitrogen species are not readily detectable under SCR reaction conditions, but can perhaps be observed during carefully designed experiments.

Clearly, when using conventional SSITKA techniques, our results as summarized in Fig. 9 appear to be consistent with these conclusions about the importance of nitrate-like species in the SCR reaction. However, despite the fact that the rate of evolution of nitrate species is similar to that of N_2 production, it is necessary to examine whether or not these nitrate species are really involved in the SCR reaction mechanism to form gas-phase N_2.

To address this question, further SSITKA experiments were performed using a gas mixture comprising only $NO + O_2 + H_2$. These are experimental conditions under which absolutely no N_2 is produced. The results obtained are shown in Fig. 11.

It is found that the rate of evolution of the infrared–visible nitrate species formed in $NO + O_2 + H_2$ reaction or in the full HC-SCR + H_2 reaction is identical; yet in one case, dinitrogen is formed and in the other case no dinitrogen is formed. This shows that these conventional infrared experiments cannot be used to identify nitrates as possible reaction intermediates. Of course, a nitrate species may be important, but we emphasize that this cannot be concluded from conventional SSITKA-FTIR-type experiments such as those shown here where the infrared spectra are used to support the contention that a nitrate-like species is important in the HC-SCR reaction [39–42]. However, our results, as shown in Figs. 9 and 11, suggest that such conclusions need to be treated with caution unless there is independent evidence that the change in the nitrate bands actually matches the production of nitrogen. Fig. 11 shows that this is not correct in this case. Instead, we suggest that these trends in the nitrate infrared bands are more readily explained as being due to a simple adsorption and desorption of a nitrate-like species, as shown in Eq. (2):

$$\text{Surface nitrate} \leftrightarrow (NO_2(g) \quad \text{or} \quad NO(g) + 1/2O_2(g)) + O(\text{surface}) \tag{2}$$

In other words, the rate of replacement of nitrate species at the sample surface (Fig. 11) is controlled by their desorption as NO_2 (or $NO + 1/2O_2$) from the surface and not by any hypothetical chemical conversion to N_2. Although this is a common occurrence with oxide-supported catalysts, it seems that it is often not taken into account when analyzing transient kinetic results.

The fact that the N_2 exchange was identical to that of nitrates during the H_2-promoted HC-SCR of NO (Fig. 9) therefore merely indicates that the precursor of N_2 could be any one of the following species: nitrates, NO_2(g), or NO(g), since these are all equilibrated in a pool of NO-containing species.

4.2. Evolution of cyanides and isocyanates

It has been shown in Fig. 9 for the present conventional SSITKA experiments that neither cyanides nor isocyanates have rates of isotopic exchange that are consistent with the rate of isotopic exchange of N_2. These findings obtained from the conventional SSITKA-DRIFTS-MS experiments appear to contradict the results presented in our earlier work on H_2-switching [6] and are in disagreement with previous work by other research groups [12,25,26,36,37,43].

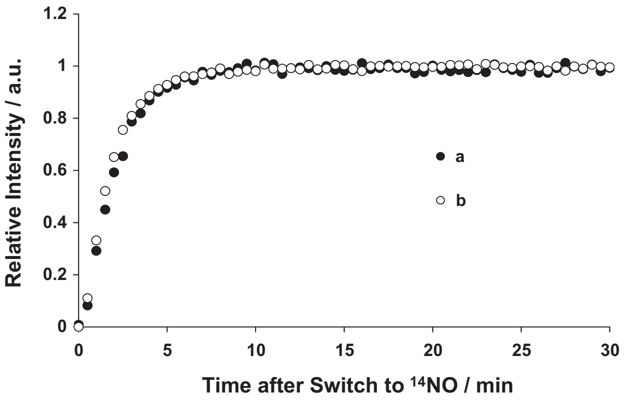

Fig. 11. Evolution of the DRIFTS intensity of ^{14}N-containing nitrate species observed over a 2.0% Ag/Al_2O_3 catalyst after switching from $^{15}N^{18}O$ to the ^{14}NO feed for (a) the HC-SCR + H_2 reaction or (b) the $NO + O_2 + H_2$ reaction. We note that the purge time for the DRIFTS system is less than 20 s so that these exchange experiments on a timescale of minutes relate to real changes on the catalyst.

However, it has been reported that gas-phase N_2 can be formed from isocyanate and cyanide species under different reaction conditions. For example, Kameoka et al. [44] studied the reactivity of surface isocyanates over a Ag/Al_2O_3 catalyst by a pulse reaction technique using NO, O_2, and NO + O_2 gas mixtures and found above 200 °C that the reaction of adsorbed isocyanate species with O_2 or NO + O_2 yielded gas-phase N_2. Bion et al. [37] also investigated the reactivity of cyanide and isocyanate species and proposed that the slow step in the SCR reaction is the transformation of cyanide to isocyanates species, which can interact with O_2 to produce N_2. Finally, it has been reported [45,46] that the reaction of cyanide species with NO_2 can lead to the production of N_2.

However, our results shown in Fig. 9, and based on the same type of conventional infrared experiments as those used in the work described above, demonstrate most clearly that no conclusions about the possible importance of cyanides or isocyanates can be drawn from these techniques because the rate of exchange of the observed species does not match the rate of exchange of the product nitrogen. One unambiguous conclusion that can be drawn is that most of these cyanides and isocyanates *seen by FTIR* are not involved in the main reaction pathway to N_2.

On the other hand, we have shown [6] that by not allowing sufficient time for spectator species to build up on the alumina support, the rate of exchange of isocyanates upon introduction of H_2 into, or the removal of hydrogen from, the HC-SCR feed matches almost perfectly the rate of exchange of gas phase N_2. This led us to conclude that in these special, non-steady-state experiments, an isocyanate species could be a potential precursor to N_2.

From Fig. 9, we can estimate that the rate of exchange of an intermediate species that matches the rate of exchange of nitrogen is such that when an isotope switch is made, there should be 50% isotopic exchange in about 2 min. In Fig. 10, we show the changes in the infrared spectra for a catalyst that has not been allowed to equilibrate for long periods of time so that essentially no time has been allowed for spectator species (especially isocyanate species) to build up a high concentration on the surface of the alumina support. It is seen that the shift in the band due to isocyanate does indeed change on this 2-min timescale.

We note, however, that these experiments are performed at the limit of sensitivity of the equipment, and so the signal-to-noise ratio is a limiting factor in terms of any detailed quantitative analysis of the spectra. The closeness of the two infrared bands for ^{14}NCO and ^{15}NCO has meant that with these data, the deconvolution of the peaks has not provided any clear trends. However, observation of the profiles in Fig. 10 shows that the double peak at 2220–2230 cm^{-1} is almost symmetrical at the 2-min point. Before this, there is less than 50% exchange; after this, there is more than 50% exchange. From an analysis of the corresponding mass spectrometer trace for $^{14}N_2$, we find that the amount of $^{14}N_2$ formed 2 min after switching from ^{15}NO to ^{14}NO is also 50%, which is at least consistent with the temporal response of the isocyanate bands and is suggestive that there is a reactive isocyanate species on the surface that could potentially be an important reaction intermediate in the HC-SCR reaction. However, under conventional SSITKA conditions, the infrared spectrum for this reactive species is swamped by the much more numerous isocyanate (spectator) species that are probably just adsorbed on the alumina support.

These conclusions echo those reported in a recent review discussing the benefits and limitations of work combining *in situ*/operando infrared spectroscopy and kinetic studies [47]. A clear caution was given that qualitative or semiquantitative analyses can easily result in unimportant surface species being mistaken for true reaction intermediates.

From the SSITKA results presented above in Fig. 9, it is possible to quantify the number of nitrogen-producing precursors. This is the most general and accurate parameter since no assumptions concerning the kinetics or the mechanism (i.e., order of the reaction, reaction pathway, etc.) have to be taken into account [48–50].

The number of intermediates can be evaluated using the area between the Kr tracer and the transient response of $^{15}N_2$ species from the start up to the steady-state condition. It can also be calculated using the decay of the unlabeled $^{14}N_2$ product upon exposure to the $^{15}N^{18}O$ SCR feed. However, due to the overlap of the signal of $m/z = 30$ (^{14}NO and $^{15}N_2$), the latter method is used to determine the quantity of adsorbed surface intermediates that lead to the production of N_2.

In our experiments, the signal of $^{14}N_2$ ($m/z = 28$) was calibrated by using N_2 and the calculation of the number of reaction intermediates (N_{N_2}) for NO to be converted to N_2 is shown below:

$$N_{N_2}(\text{mol/g}_{\text{cat}}) = \frac{A(\text{ppm min}) \times 10^{-6}(\text{ppm}^{-1}) \times \text{FR}(\text{cm}^3\ \text{min}^{-1})}{\overline{V}_{\text{NTP}}(\text{cm}^3\ \text{mol}^{-1}) \times m(\text{g})}$$

where A is the integrated area, FR is the total flow rate of the SCR feed, $\overline{V}$ is the molar volume of gas at NTP (20 °C, 1 atm), and m is the mass of 2.0% Ag/Al_2O_3 catalyst.

We calculate the number of nitrogen-producing precursors to be 36 $\mu mol\ g_{cat}^{-1}$. This may be compared with the amount of silver on the catalyst that is 185 $\mu mol\ g_{cat}^{-1}$. It is perhaps coincidence, but it is interesting to note that the ratio of nitrogen-producing surface species to silver atoms is 1:5, and we know from EXAFS studies that the structure of the active catalyst corresponds to silver clusters containing ca. 3–5 silver atoms [5,7]. These data therefore suggest that there could be one N_2-precursor per silver cluster at any one time.

5. Conclusions

The SSITKA technique is a powerful tool for investigating catalytic reaction mechanisms [50]. However, many catalysts comprise both an active component (e.g., a metal) and a support (e.g., a high surface area oxide) and adsorption on the support of species formed during the reaction can affect the ability to investigate similar species formed on the active component. The problem will be made worse when the signal-to-noise ratio is low. The types of problem that may arise when using conventional transient kinetic isotope techniques to investigate catalytic reaction mechanisms have been illustrated for the hydrocarbon selective catalytic reduction of NO_x on silver catalysts. Because the support (alumina in this specific case) can adsorb relatively large quantities of reactants, intermediates, and products, it is shown under these conventional conditions that it is often impossible to differentiate between active species and spectator species. In the case of “nitrate-type intermediates,” it has been shown that the coincidental temporal response of the nitrate infrared signals cannot be used as evidence that a nitrate-type species is a reaction intermediate for the formation of dinitrogen. The reason for this is that an identical coincidental temporal response can be generated under reaction conditions where absolutely no dinitrogen is produced.

In the case of an isocyanate species, we have shown that there are two types of isocyanate on the surface under reaction conditions, and one of these is dominant but relatively inactive. In a conventional transient kinetic isotope experiment, we propose that the surface of the alumina becomes covered with an isocyanate species. This isocyanate has an infrared spectrum that is indistinguishable from any other isocyanate species. However, after an isotopic switch from the $^{15}N^{18}O$ to the ^{14}NO SCR feed, the rate of exchange of the isocyanate formed under conventional conditions is shown to be very slow compared to the rate of exchange of nitrogen, and so this isocyanate observed by infrared spectroscopy under conventional experimental conditions cannot be a true reaction intermediate.

By developing a STOS SSITKA technique in which insufficient time is allowed for the alumina support to adsorb significant quantities of isocyanate species, we have shown that it is possible to identify a fast-reacting isocyanate species whose temporal response to a switch from $^{15}N^{18}O$ to ^{14}NO corresponds closely with the temporal response for the formation of nitrogen. It is concluded that this isocyanate species, which we speculate could be associated with the active silver clusters or the interface between the active silver clusters and the alumina support, could be an important reaction intermediate in the NO_x reduction reaction. Finally, we note that the ratio of nitrogen-producing surface species to silver atoms in the catalyst is 1:5, which may be significant given that the average size of the silver clusters is thought to contain about 3–5 silver atoms.

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