

A fast transient kinetic study of the effect of H₂ on the selective catalytic reduction of NO_x with octane using isotopically labelled ¹⁵NO

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Abstract

The H₂-assisted hydrocarbon selective catalytic reduction (HC-SCR) of NO_x was investigated using fast transient kinetic analysis coupled with isotopically labelled ¹⁵NO. This allowed monitoring of the evolution of products and reactants during switches of H₂ in and out of the SCR reaction mix. The results obtained with a time resolution of less than 1 s showed that the effect on the reaction of the removal or addition of H₂ was essentially instantaneous. This is consistent with the view that H₂ has a direct chemical effect on the reaction mechanism rather than a secondary one through the formation of “active” Ag clusters. The effect of H₂ partial pressure was investigated at 245 °C, it was found that increasing partial pressure of H₂ resulted in increasing conversion of NO and octane. It was also found that the addition of H₂ at 245 °C had different effects on the product distribution depending on its partial pressure. The change of the nitrogen balance over time during switches in and out of hydrogen showed that significant quantities of N-containing species were stored when hydrogen was introduced to the system. The positive nitrogen balance on removal of H₂ from the gas phase showed that these stored species continued to react after removal of hydrogen to form N₂.

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1. Introduction

Since the pioneering work of Iwamoto et al. [1] and Held et al. [2], many papers have been published on the hydrocarbon selective catalytic reduction (HC-SCR) of NO_x to N₂. Numerous catalyst formulations have been tried and tested under various different reaction conditions. A small number of catalyst combinations have shown promise; of these, a low-loading Ag/Al₂O₃ catalyst appears to be the most promising [3]. These catalysts are active and selective for N₂ production using various hydrocarbon feeds. However, the temperature window for NO_x reduction is narrow, and these catalysts are not sufficiently active in the low-temperature region (150–300 °C) typical of some lean-burn engine exhausts (especially diesel engines).

The discovery that adding small amounts of hydrogen could dramatically improve the performance of Ag/Al₂O₃ catalysts in the HC-SCR reaction has resulted in renewed interest in these

systems [4,5]. Since then, several authors have investigated the factors influencing the “hydrogen effect” over these catalysts, including the nature of the active site and the effect of hydrogen on the reaction mechanism [6–25].

Hydrogen promotes NO_x reduction over Ag/γ-Al₂O₃ catalysts when using a range of lower alkanes and alkenes [6] and higher alkanes [16,19] as reductants. The “hydrogen effect” appears to be limited to Ag-based catalysts but depends greatly on the support used; the activities of Ag supported on TiO₂, ZrO₂, SiO₂, or Ga₂O₃ are not enhanced by the addition of hydrogen [6]. However, Ag/γ-Al₂O₃ and Ag/MFI catalysts [9,10,26] show markedly improved performance after the addition of hydrogen to the feed. The effect of hydrogen is reversible, and removal of hydrogen results in decreased NO_x conversion, but the activity can be rapidly recovered by reintroducing the hydrogen [16]. These cycles can be repeated without any loss of catalyst performance.

There is general agreement about the positive effect of hydrogen on activating various different reductants and on the overall rate of the HC-SCR NO_x reduction reaction. However, debate continues on the mechanism by which the hydrocarbon

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and NO are activated. Several authors have proposed that hydrogen promotes the reaction by removing a poison that inhibits the reaction. Based on spectroscopic evidence, Burch and co-workers [16,21] and Sazama et al. [19] have proposed that the key role of hydrogen is to remove Ag^+CN , which blocks the active site during the SCR reaction. Bion et al. [27] proposed that the slow step in the SCR reaction is the transformation of Ag^+CN species to $\text{Al}_{\text{tetra}}^{3+}\text{NCO}$ species. Therefore, it is reasonable to propose that one role of hydrogen could be to speed up this slow step in the reaction. Isocyanate is readily hydrolysed to form ammonia, which can subsequently react with NO to form N_2 . However, it is clear from the literature that the SCR reaction is very complex and that the rate-determining step(s) can change depending on the temperature of the reaction and the composition of the feed. For example, silver cyanide species were not observed at low temperatures ($<250^\circ\text{C}$), and so under these conditions, it was speculated that the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst might be poisoned by strongly bound nitrates and that hydrogen could promote the reaction by removing these species [17]. Brosius et al. [15] have shown that in the absence of a hydrocarbon, hydrogen can promote the removal of nitrates from Ag and the formation of nitrates on the Al_2O_3 support. They speculated that the reduced Ag may then promote the partial oxidation of the hydrocarbon. More recent work by Shimizu et al. [28] also suggests that adding H_2 can retard nitrate poisoning, although they emphasised that the essential role of H_2 is in the reductive activation of molecular oxygen into reactive oxygen species involved in the oxidative activation of the hydrocarbon. On a similar theme, Bentrup et al. [14] found that the type of adsorbed NO_x species formed on the surface is important. Nitrate and acetate species found during the SCR reaction are relatively unreactive. H_2 promotes the formation of nitrite and nitro species, which are much more reactive than nitrate species and more readily able to activate the hydrocarbon.

Shibata et al. [11] carried out a detailed study of the mechanistic cause of enhancement of C_3H_8 -SCR activity by adding H_2 over $\text{Ag}/\text{Al}_2\text{O}_3$ using in situ FTIR spectroscopy. They proposed that adding H_2 results in the promotion of the partial oxidation of C_3H_8 to mainly surface acetates, which they suggest is the rate-determining step of C_3H_8 -SCR in the absence of H_2 .

Eränen et al. found that gas-phase species also need to be taken into account when discussing the SCR reaction [29]. They showed that HC-SCR over $\text{Ag}/\text{Al}_2\text{O}_3$ does not occur exclusively on the surface of the catalyst, but that significant reactions occur between reactive gas-phase species, leading to the production of N_2 . More recently, these authors investigated the effect of hydrogen on the production of gas-phase species during the SCR reaction [20]. Hydrogen was shown to have two main functions: (1) contributing to improved oxidation of a wide variety of different surface species, resulting in faster production of key intermediates, and (2) aiding in the formation of activated NO_x species for the gas-phase reactions.

Based on experiments in which hydrogen peroxide and hydrogen were used to promote the SCR reaction, Sazama et al. [30] invoked highly reactive hydroxyl and hydroperoxy radicals in their reaction mechanism. Fricke et al. [13] specu-

lated that highly active O surface species are important in the H_2 -assisted SCR mechanism. In their recent review of the SCR reaction over $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts, Shimizu and Satsuma [23] invoked the formation of a hydride species on silver clusters that then reacts with oxygen to form a reactive oxidant such as hydroperoxy radicals, peroxide or superoxide ions as the key steps in the promotional effect of hydrogen.

In summary, all of the previous studies clearly show that hydrogen promotes the number and quantity of surface species during the SCR reaction. The large number of surface species produced and complex nature of the SCR reaction make identifying the main role of hydrogen in the reaction mechanism difficult. To increase the rate of NO_x conversion, the hydrogen must accelerate the rates(s) of the slow step(s) in the reaction. The slow step(s) are likely to vary depending on the reaction temperature and feed conditions.

In this study, transient kinetic analysis coupled with isotopically labelled ^{15}NO is used to gain insight into the reaction mechanism, especially with respect to the effect of H_2 concentration.

2. Experimental

The catalyst, provided by Johnson Matthey, was prepared by impregnating $\gamma\text{-Al}_2\text{O}_3$ 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 using a bench flow reactor consisting of a quartz tube (3 mm i.d.) enclosed in an electric furnace. The catalyst sample (0.1 g, with particle size 250–425 μm) was held in place between two plugs of quartz wool, and a thermocouple was placed just after the catalyst bed. The reactant gases NO (1% $^{15}\text{NO}/\text{Ar}$ or $^{14}\text{NO}/\text{Ar}$), CO_2 (100%), H_2 (5% H_2/Ar), O_2 (100%), and Kr (1% Kr/Ar) and the carrier gas Ar were fed from independent mass flow controllers, while *n*-octane was fed using a Razel syringe pump and H_2O was supplied using a Bronkhorst controlled evaporator mixer. All reactor lines were heated to prevent condensation. The concentrations of the reactants used were 720 ppm of NO, 540 ppm of *n*- C_8H_{18} , 7.2% of CO_2 , 7.2% of H_2O , 4.3% of O_2 , 0.72% of H_2 (when added), and 3.7% of Kr (when added). In some experiments, lower concentrations of H_2 were used. The total flow rate was 276 ml min^{-1} .

A fast switching experimental apparatus was used, using helium-actuated high-speed switching VICI valves. The four-way valves allow rapid switching between two gas mixtures in <20 ms. Furthermore, great care was taken to limit as much as possible any dead volume. Considering the inner diameter and length of the tubing, the reactor and the gas flow, the purge time was estimated to be <20 ms. The analysis was done using a Hitachi HPR 20 mass spectrometer with a short capillary connected as close as possible to the exit of the catalyst bed. The global analysis time (including switch time, purge time, and the time for the sample to travel through the capillary to the detector) was <150 ms.

Gas flows were carefully equilibrated, and micrometric needle valves were strategically positioned to equilibrate the pressure between the gas flows on each side of the four-way

valves with a high-sensitivity differential pressure detector. This avoided the production of spikes on the MS signal when switching from one mixture to another.

For most of the experiments, isotopically labelled ^{15}NO was used. This allowed monitoring of the potential products $^{15}\text{N}_2$, $^{15}\text{N}_2\text{O}$, and $^{15}\text{NO}_2$ without interference from the signals from CO and CO_2 which overlap with $^{14}\text{N}_2$ and $^{14}\text{N}_2\text{O}$, respectively. Kr was added to the H_2 -containing feed to trace the quality of the switches and also as an internal standard. Quantification was carried out with reference to the Kr signal. For most of the experiments, the following mass-to-charge (m/e) ratios were monitored as a function of time: 2 (H_2), 31 (^{15}NO), 30 ($^{15}\text{N}_2$), 46 ($^{15}\text{N}_2\text{O}$), 47 ($^{15}\text{NO}_2$), 57 ($n\text{-C}_8\text{H}_{18}$), and 82 (Kr). For the experiments with ^{14}NO , a m/e ratio of 30 (^{14}NO) was monitored. For both the ^{14}NO and ^{15}NO experiments, various other m/e ratios were also logged to pick up traces of some of the other gases, such as NH_3 , CH_3CN , and HCN , that also can be formed under SCR conditions [31]. With quantification of ^{15}N -containing species, it was possible to monitor the ^{15}N balance as a function of time during the switching experiments. The ^{15}N balance was calculated as

$$^{15}\text{N balance} = 2 \times ^{15}\text{N}_2 \text{ produced} / ^{15}\text{NO consumed}.$$

At 400°C (result not shown here), the only product detected was $^{15}\text{N}_2$; the average ^{15}N balance (over a series of switches of H_2 into and out of the feed) at this temperature was $99 \pm 3\%$. At 245°C , the ^{15}N balance ranged from 98 ± 3 to $101 \pm 3\%$ (Table 1) depending on the partial pressure of H_2 .

Fig. 1 shows the results of a typical experiment in which H_2 was switched into and out of the SCR mix. Here 3.7% Kr was added to the H_2 -containing feed as a tracer. The response of the Kr signal during the switches clearly shows that the system gives very good resolution for the switches, the typical time for the Kr signal to decrease to $<3\%$ of its initial value when

switched out of the gas stream was <1 s; the time for the Kr signal to attain its steady-state value when it was switched into the gas stream was also typically 1 s. In addition, the response of ^{15}NO to the introduction of H_2 is essentially instantaneous and reaches its steady-state value in 1 s.

3. Results

The results in Fig. 2 show the effect on the reactant and product concentrations of switching 0.72% hydrogen into and out of the SCR feed stream as a function of time on stream. $^{15}\text{N}_2$ was the main product detected; there was no evidence of $^{15}\text{N}_2\text{O}$ or $^{15}\text{NO}_2$ formation. There was some evidence of the formation of

Table 1

Average conversions of reactants and ^{15}N balance during the octane SCR reaction with and without H_2 as a function of H_2 concentration during transient conditions (60 s switches) at 245°C

	Feed	H_2 concentration (%)		
		0.05	0.10	0.72
NO conversion (%)	Average	12	19	50
	H_2	26	38	92
	No H_2	-2	-1	7
N balance (%)	Average	101	98	99
	H_2	90	84	84
	No H_2	112	113	113
C_8H_{16} conversion (%)	Average	13	26	28
	H_2	24	41	47
	No H_2	2	11	7
H_2 conversion (%)	H_2	46	43	38

Note. ' H_2 ' and 'no H_2 ' refer to the average values over the course of 60 s in which H_2 is present and absent, respectively. The average of these two values is also given.

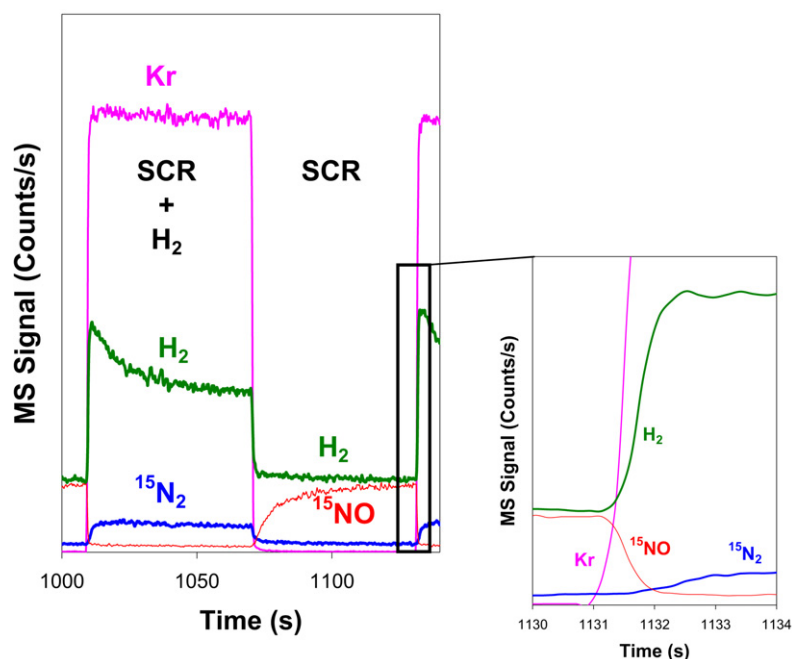


Fig. 1. Mass spectrometer response for $^{15}\text{N}_2$, ^{15}NO , H_2 , and Kr when switching 0.72% H_2 in and out of a SCR feed stream over the catalyst at 300°C .

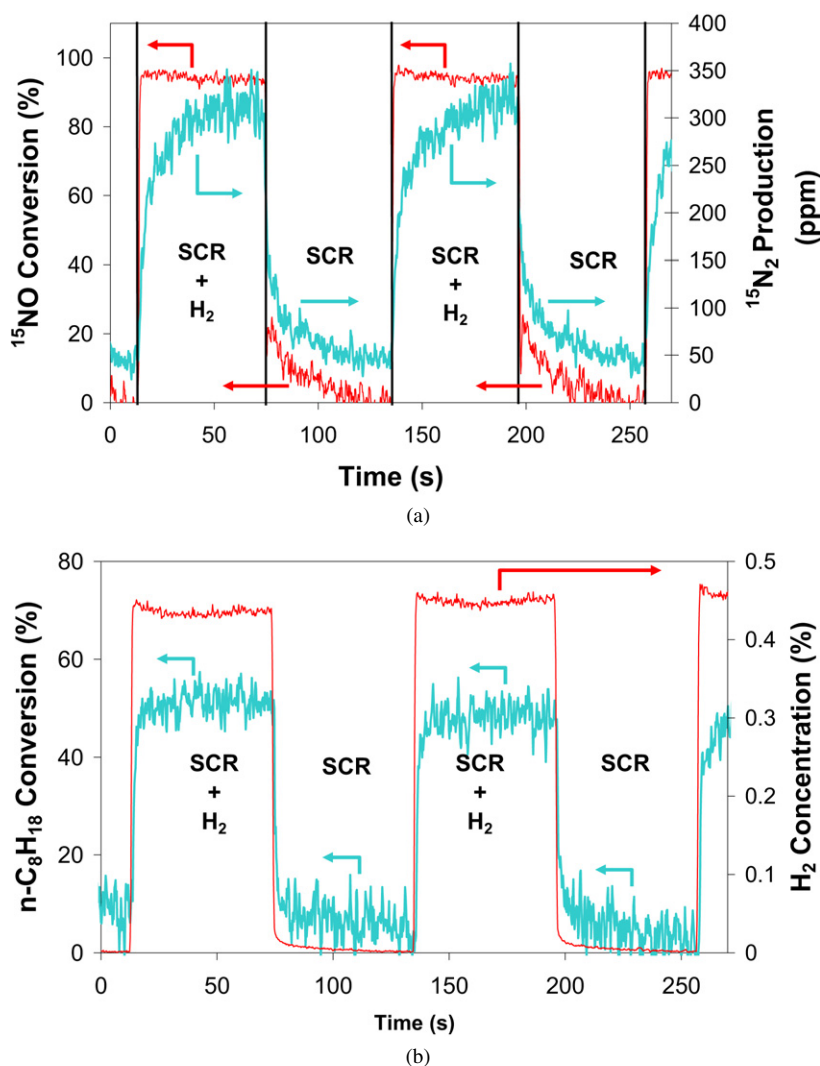


Fig. 2. Changes in (a) ^{15}NO conversion and $^{15}\text{N}_2$ production and (b) *n*-C₈H₁₈ conversion and H₂ concentration as a function of time during 60 s switches of 0.72% H₂ in and out of the SCR mix over the catalyst at 245 °C.

small amounts of an NH-type species at 245 °C; we discuss this in more detail later.

Fig. 2 shows some interesting features in the transient responses of the products and reactants. As expected, adding hydrogen promotes the conversion of NO and *n*-C₈H₁₈ at 245 °C [16]. Fig. 2a shows that ^{15}NO conversion increased rapidly on introduction of H₂ and then remained constant in the presence of H₂ over 60 s. The average conversion of ^{15}NO was 92% (Table 1). After H₂ was removed from the feed, there was a significant time lag in the decreased conversion of ^{15}NO . The conversion decreased sharply from 92 to 25% in 1 s, then decreased slowly to 0% over the remaining 59 s. An average conversion of 7% was obtained during the 60 s after the switch out of H₂. This should be compared with the situation under normal steady-state conditions, in which no conversion of ^{15}NO occurred at 245 °C. This means that H₂ has a residual effect on ^{15}NO conversion on removal of H₂ from the gas phase. If there were no residual effect, then ^{15}NO conversion would be expected to decrease rapidly after removal of H₂ from the gas stream. Conversions of ^{15}NO were similar when H₂ was

present either during steady state (93%) or under transient conditions (92%).

The $^{15}\text{N}_2$ trace (Fig. 2a) varied considerably over time at 245 °C. In contrast to ^{15}NO conversion, the $^{15}\text{N}_2$ signal increased slowly when H₂ was present in the SCR mix. There was an initial sharp decrease in $^{15}\text{N}_2$ production when H₂ was switched out of the mix, followed by a slow decrease in the signal over the remaining 60 s of the period without H₂. These trends were repeated on reintroduction of H₂.

Interestingly, under our realistic experimental conditions, the concentration of hydrogen exiting the catalyst bed was 0.45%, showing that only 38% of the H₂ was converted. Thus hydrogen can have a promotional effect along the full length of the catalyst bed (Fig. 2b). Adding H₂ also promoted conversion of *n*-C₈H₁₈, with an increase from 7 to 47% on addition of H₂ before a rapid decrease on removal of H₂ from the feed stream.

The effect of hydrogen was further investigated by studying the transient kinetics of switching in and out hydrogen at lower concentrations. Fig. 3 shows that decreasing the hydrogen concentration resulted in lower conversions of ^{15}NO during

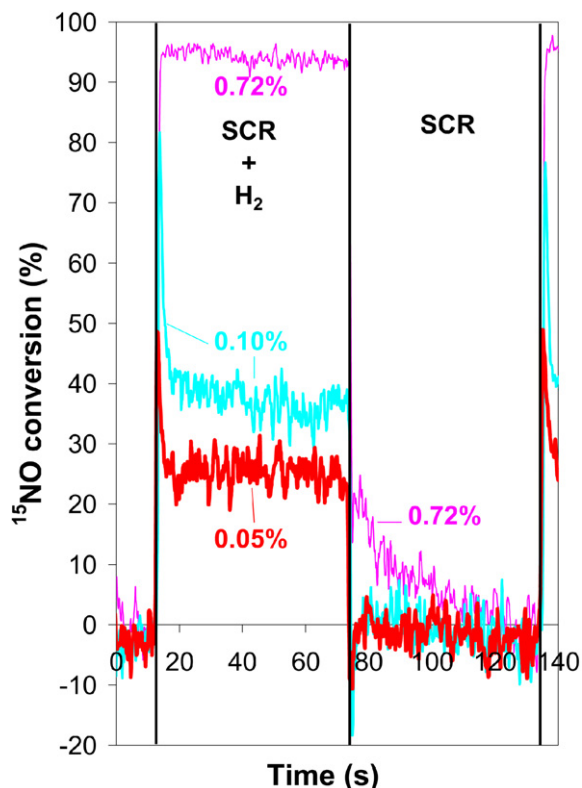


Fig. 3. Changes in ^{15}NO conversion over time during 60 s switches of H_2 in and out of the SCR mix over the catalyst as a function of H_2 concentration at 245°C .

the SCR reaction. This is in agreement with Satokawa et al. [6], who showed that even at low levels of H_2 (227 ppm), the NO_x SCR reaction can be promoted with propane. However, the decreased conversion of ^{15}NO is not linear with decreasing H_2 concentration. The average conversions of ^{15}NO are 26%, 38%, and 92% for the addition of 0.05%, 0.10%, and 0.72% H_2 , respectively. The changes in the conversion of ^{15}NO on removal of H_2 differs for the lower concentrations, with a much sharper decrease in ^{15}NO conversion on removal of 0.05 and 0.10% H_2 compared with removal of 0.72% H_2 .

Fig. 4 shows $^{15}\text{N}_2$ production as a function of time for different H_2 concentrations during the switches. A similar trend is apparent, with $^{15}\text{N}_2$ production increasing with introduction of H_2 . $^{15}\text{N}_2$ production also increased with increasing H_2 concentration, which is consistent with increasing ^{15}NO conversion. Nitrogen production decreased slowly when H_2 was removed, providing evidence of catalyst activity after removal of hydrogen from the gas stream.

It is evident from the data in Figs. 2–4 that steady-state conditions (especially with respect to N_2 production) were not attained within 60 s of a switch in feed at 245°C . The varied evolution of ^{15}NO and $^{15}\text{N}_2$ concentrations over the course of the cycles leads to a complex ^{15}N balance (Fig. 5), which varies significantly with time. The trends are the same for hydrogen concentrations ranging from 0.05 to 0.72%. Clearly, transient ^{15}N balances significantly above and below 100% were obtained. A ^{15}N balance $>100\%$ implies that ^{15}N is released from the catalyst, whereas a balance $<100\%$ suggests that ^{15}N

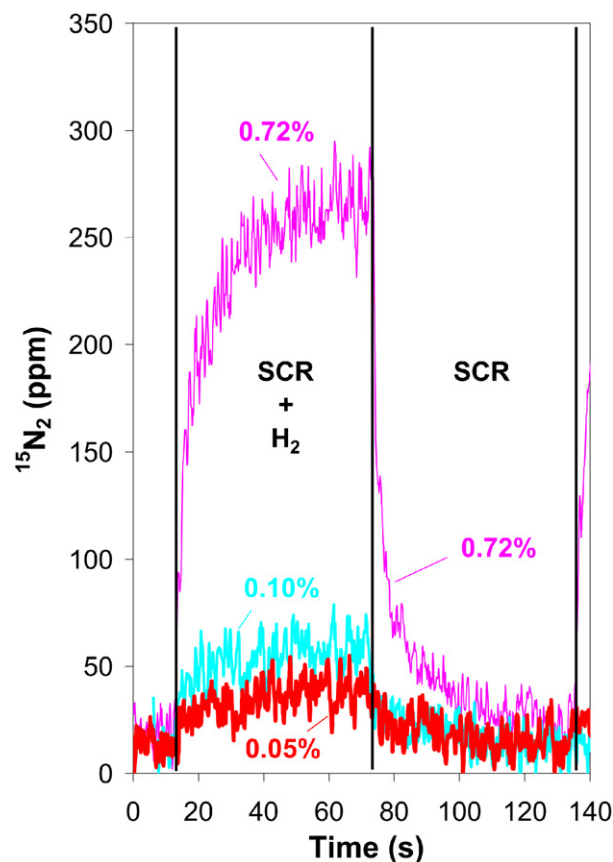


Fig. 4. Changes in $^{15}\text{N}_2$ production over time during 60 s switches of H_2 in and out of the SCR mix over the catalyst as a function of H_2 concentration at 245°C .

is stored on the catalyst. Table 1 shows that despite the large swings in the ^{15}N balance over a series of cycles, the overall balance was 100% (within experimental error).

There was an initial sharp loss of nitrogen balance when H_2 was introduced into the SCR feed stream (Fig. 5), which recovered slowly to a value approaching 100% after 60 s. For example, the average nitrogen balance over the course of 60 s when 0.72% H_2 was present was 84% (Table 1). This suggests that ^{15}N was initially stored when H_2 was introduced. The reverse was true when H_2 was removed; in this case there was an upward spike in the balance, followed by a slow decrease toward 100% over time, giving an average balance of 113%, indicating that ^{15}N is released when H_2 is removed. The sums of the balances with and without H_2 were 101%, 98%, and 99% for 0.05%, 0.10%, and 0.72% H_2 , respectively.

An important observation from the data in Figs. 1–5 is that they clearly show that hydrogen has an effect on the SCR reaction after it has been removed from the gas stream. The effect differs depending on the concentration of hydrogen added to the feed. This is most evident for ^{15}NO conversion, which decreases slowly for 0.72% H_2 but instantaneously for 0.05 and 0.10% H_2 . The data in Fig. 6 showing the evolution of H_2 as a function of time during the cycles may offer an explanation for the ^{15}NO conversion data. This shows that the hydrogen concentration decreased much more slowly on removal of 0.72% H_2 from the stream than 0.10 or 0.05% H_2 . This slow de-

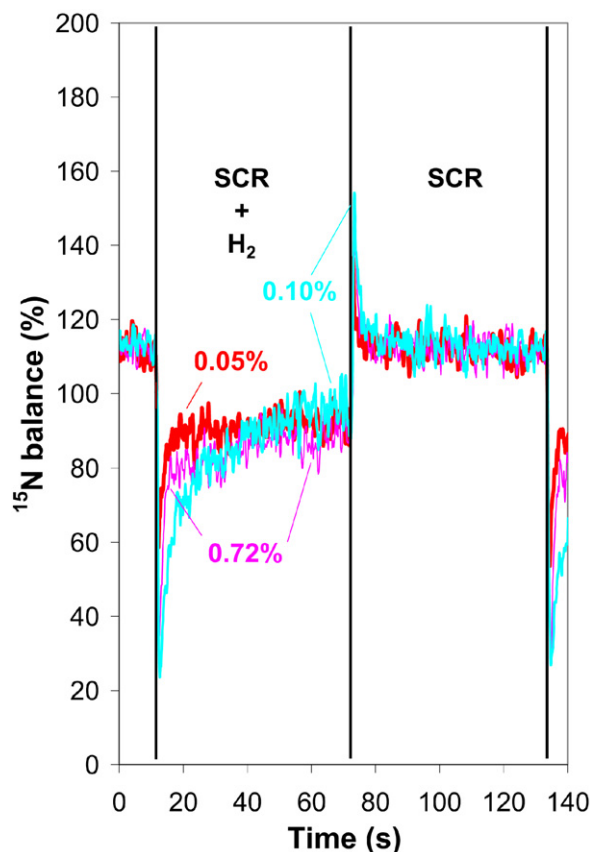


Fig. 5. Changes in ^{15}N balance as a function of time on stream during 60 s switches of 0.72, 0.10, and 0.05% hydrogen in and out of the SCR feed at 245 °C.

crease in H_2 cannot be attributed to a delay in flushing the system of residual gas phase H_2 , because the H_2 concentration decreased to zero through a blank reactor in <3 s after the switch out, and remained at this level until the H_2 was switched back in again. It is unlikely that the hydrogen release is due to release of stored H on the surface of the catalyst. Although Baba et al. [32] have shown that hydrogen dissociates over Ag_3^+ sites to generate an acidic proton and $\text{Ag}_3\text{-H}$, it is unlikely that the H would desorb from the surface as H_2 in an oxygen-rich atmosphere. The slower decrease in H_2 concentration at 245 °C probably has another explanation. For example, Eränen et al. [20] speculated that H_2 could be produced by partial oxidation of a hydrocarbon. Regardless of the H_2 source, the promotional effect of residual H_2 can explain the slow decrease in ^{15}NO conversion after switching out 0.72% H_2 from the feed.

Fig. 6 shows that the hydrogen concentration decreased sharply on removal of 0.05 and 0.10% H_2 from the feed. The trace for the lower concentrations is similar to that in a blank reactor. Thus, the presence of residual hydrogen cannot explain the nitrogen production in the 60 s after removal of 0.10 and 0.05% H_2 from the feed.

Analysis of the data also revealed the formation of $^{15}\text{NO}_2$ (Fig. 7) when H_2 was introduced to the feed at low concentrations (0.05 and 0.10%). The $^{15}\text{NO}_2$ signal returned to baseline when H_2 was removed, indicating no formation of NO_2 in the

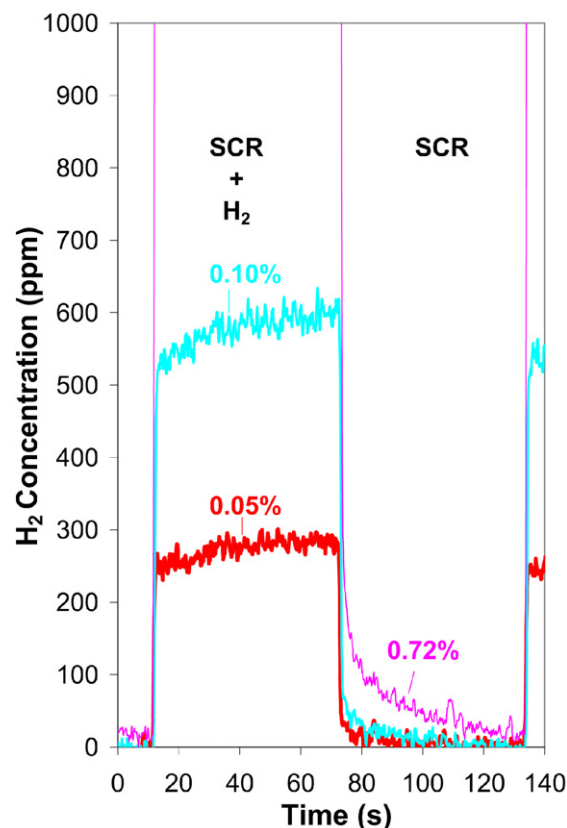


Fig. 6. Changes in H_2 concentration over time during 60 s switches of H_2 in and out of the SCR mix over the catalyst as a function of H_2 concentration at 245 °C.

absence of H_2 . Most interestingly, NO_2 was not formed at high H_2 concentration (0.72%). It was not possible to accurately quantify the NO_2 concentration. However, based on an error of $\pm 3\%$ in the mass balances, the average concentration of $^{15}\text{NO}_2$ formed is of the order of 30 ppm.

No other species was identified during experiments with ^{15}NO . Therefore, experiments were also carried out using ^{14}NO to aid identification of species that may have overlapped with other fragments during the ^{15}NO experiments. Fig. 8 shows that during the experiments in which ^{14}NO was used instead of ^{15}NO , a change in the signal associated with $m/e = 15$ was observed when 0.72% H_2 was present in the feed but not at the lower H_2 concentrations. At the lower concentrations, the signal remained at background levels for $m/e = 15$ when no reaction was occurring. The signal at $m/e = 15$ can be attributed to a $^{14}\text{NH}^+$ ion, probably formed from gas-phase NH_3 or an amine-type species. The other ions of ammonia (NH_2^+ and NH_3^+) could not be investigated due to overlap with ions from water ($m/e = 18, 17,$ and 16) present in large excess. Overlaps with fragments of water would explain why the NH^+ fragment was not observed when using ^{15}NO . With 0.72% H_2 in the feed, the signal increased when H_2 was introduced and then decreased back to baseline levels when H_2 was removed. This suggests that NH -containing species were formed when high concentrations of hydrogen were present in the gas mix but not when hydrogen was removed. The low intensity of the peak at $m/e = 15$ prevented accurate quantification of

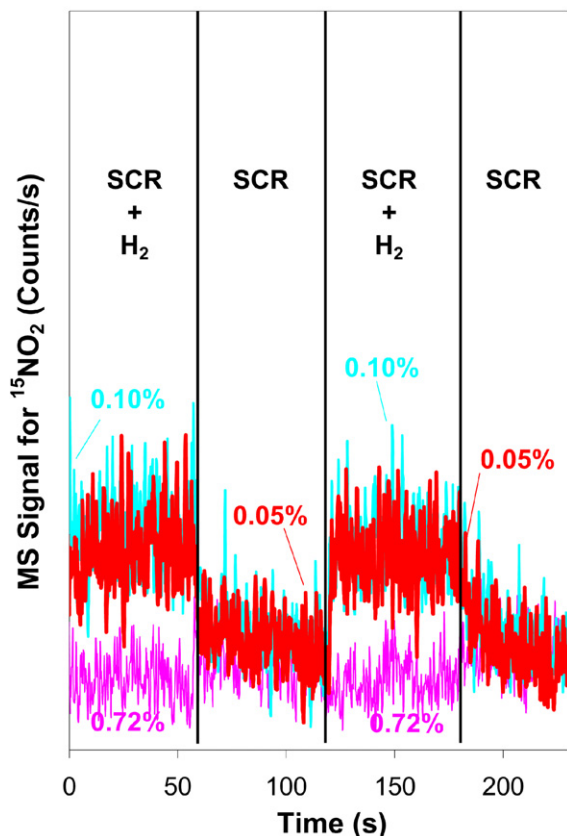


Fig. 7. Changes in $^{15}\text{NO}_2$ production over time during 60 s switches of H_2 in and out of the SCR mix over the catalyst as a function of H_2 concentration at 245°C .

the species. However, an average nitrogen balance of $99 \pm 3\%$ during the course of the cycles suggests that the average concentration of the NH-containing species did not exceed 30 ppm. Shimizu et al. [28] reported NH_3 formation in the gas phase during the reaction of $\text{NO} + \text{H}_2$ over $\text{Ag}/\text{Al}_2\text{O}_3$ but not in the presence of O_2 . The results presented here show that NH_3 or NH-type species can be produced in the gas phase in the presence of O_2 provided that the concentration of H_2 is sufficiently high.

4. Discussion

The results obtained using isotopically labelled compounds show that adding H_2 had a direct effect on the reaction mechanism. The evolution of the ^{15}N balance in Fig. 5 and data in Table 1 show that ^{15}N -containing species were stored and released during the pulsing of H_2 . For example, at 245°C , 16% of ^{15}N passing through the catalyst was stored over the course of 60 s when 0.72% H_2 was present in the feed and released when H_2 was removed. The NO_x storage/release values were similar for 0.05 and 0.10% H_2 .

This is consistent with the findings of several researchers, including Wichterlová et al. [21], who found a significantly increased intensity of adsorbed species using DRIFTS analysis to study the effect of adding H_2 to the decane SCR reaction. Among the species that demonstrated an increase in intensity

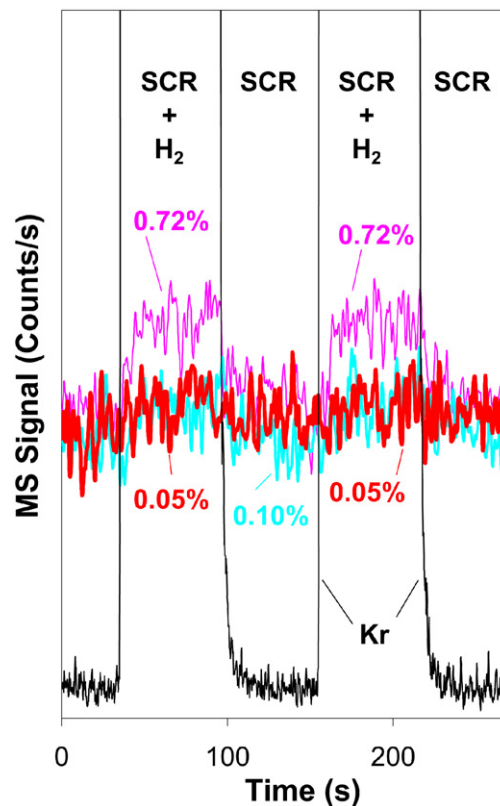


Fig. 8. Changes in mass spectrometer signal for $m/e = 15$ as a function of time during switches of different concentrations of H_2 in and out of the ^{14}NO SCR reaction.

were nitrates, isocyanates, and oxygenated hydrocarbons. The work of Shimizu et al. [28] provides evidence that NO can react with H_2 (in the absence of O_2) over a $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst to produce gas-phase NH_3 , NH_3 coordinatively bound to the surface, and surface NH^{4+} species. In our case, NH-type species were observed in the gas phase (in the presence of O_2) at high concentrations of H_2 (0.72%), suggesting that NH-type species were also formed and stored on the catalyst surface.

Regardless of whether the species released from the surface when H_2 was removed from the gas phase were NH_3 , amine species, or H_2 , the availability of these highly reactive reductants promoted the SCR reaction after H_2 was removed from the gas phase, as evidenced by continued production of $^{15}\text{N}_2$. The positive nitrogen balance in the absence of gas phase H_2 suggests that N_2 was produced from reaction of stored species or alternatively by reaction of NO with released NH-type species in the gas phase. Eränen et al. [20] showed that NH_3 can react with NO in the gas phase to produce N_2 . Moreover, Richter et al. [12] reported that $\text{Ag}/\text{Al}_2\text{O}_3$ is an active catalyst for the NH_3 -SCR reaction and that adding H_2 also has a promotional effect on this reaction. In a recent TAP study of the NH_3 -SCR reaction, Kondratenko et al. [33] found that NH^+ fragments play key roles as reaction intermediates in a coupling reaction between NO and NH_3 to produce N_2 .

It should be noted that the presence of gas-phase NH-type species is not a necessary requirement for enhanced activity when H_2 is present. The data in Fig. 3 show that H_2 can enhance

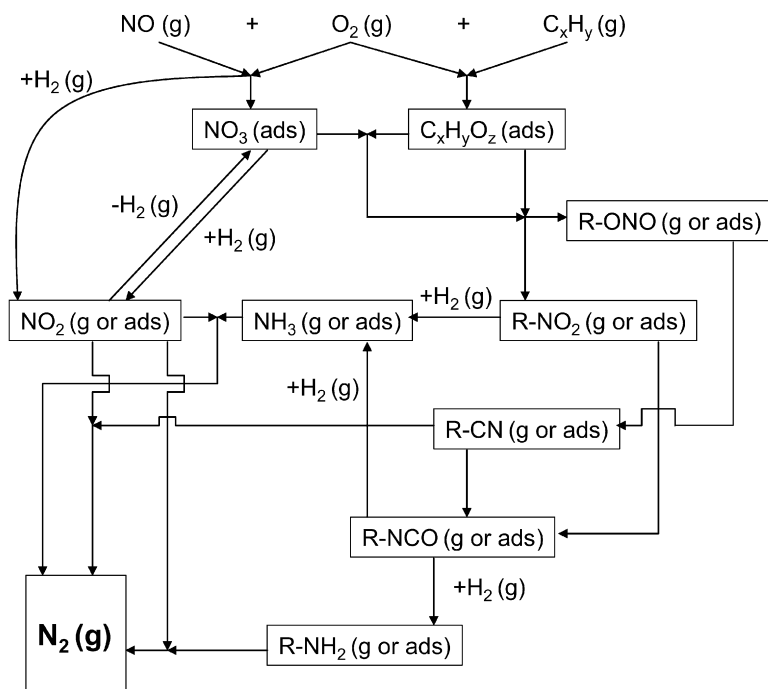


Fig. 9. Schematic diagram of the H_2 assisted SCR reaction over $\text{Ag}/\text{Al}_2\text{O}_3$, adapted from Refs. [20,34].

the activity of the SCR reaction at much lower concentrations of H_2 (0.05 and 0.1%) with no production of gas-phase NH -containing species. The conversion of ^{15}NO was not as high as that observed for 0.72% H_2 addition, and the decrease in ^{15}NO conversion was much faster. In addition, gas-phase NO_2 was produced when low concentrations of H_2 were used but not when 0.72% H_2 was used.

These results could be rationalised by reference to a slightly modified version of a reaction mechanism (Fig. 9) originally proposed by Meunier et al. [34] but more recently modified and updated to include gas-phase reactions by Eränen et al. [20]. In the absence of H_2 , the reaction can proceed by the mechanism proposed in Fig. 9; however, at low temperatures, the reaction is slow, due primarily to poisoning of the catalyst by strongly bound nitrates and/or Ag^+CN [16,17]. On introduction of H_2 , nitrates are readily reduced to nitrites [15,17,28]. These nitrites could then desorb as gas-phase NO_2 or react on the surface with a number of different reduced N-containing adsorbed species to produce N_2 . The removal of strongly bound nitrates from Ag sites is likely to allow a significant increase in both oxidation of NO to NO_2 and partial oxidation of the hydrocarbon. The reduction of nitrate to nitrite and subsequent release of $\text{NO}_2(\text{g})$ is a fast reaction, as evidenced by the rapid appearance of gas-phase NO_2 on addition of low concentrations of H_2 (Fig. 7). At low H_2 partial pressure, virtually all of the H_2 will be utilised in this initial step of the reaction, and there will be insufficient partial pressure of H_2 to promote subsequent steps in the mechanism. It should be noted that H_2 conversion was <50% at all hydrogen concentrations, indicating the presence of gas-phase H_2 throughout the catalyst bed. However, for low feed concentrations of H_2 , the partial pressure may not have been high enough to allow H_2 to compete effectively with other strongly adsorbed molecules, thereby resulting in lower surface

coverage of H atoms. This low surface coverage may have prevented H_2 from having a promotional effect on other steps of the reaction (e.g., NH_x formation), which can require high surface coverage of H atoms.

However, if the H_2 concentration is higher, as in the case of the experiments with 0.72% H_2 , then there is the potential for further improving the rate of reaction by promoting other slow steps in the reaction. The transient kinetic results show that at higher H_2 concentrations, gas-phase NH -containing species were formed, and gas-phase NO_2 was no longer produced. This indicates that the residual H_2 not consumed in the reduction of nitrates to nitrites was free to promote the NH_x -forming reactions. The reaction schematic suggests that the hydrogen can promote any number of the steps, for example, nitro \rightarrow oxime \rightarrow nitrile N oxide \rightarrow isocyanate \rightarrow amine, leading to ammonia formation [34].

Another possibility proposed by Sazama and Wichterlova [30] and Satsuma et al. [26] is that the combination of hydrogen and oxygen on the silver surface can result in the formation of hydroperoxy radicals (HO_2), peroxide (O_2^{2-}), or superoxide ions (O_2^-). Perhaps low concentrations of H_2 are sufficient to promote the formation of these active oxygen species, which can readily react with NO to form $\text{NO}_2(\text{g or ads})$ and in turn activate the hydrocarbon and thus promote the SCR reaction. At higher H_2 concentrations, the AgO_x surface may become more reduced, allowing dissociation of NO on the surface and formation of a greater quantity of reduced NH -containing species (e.g., NH_3 and amine-type species). These reduced NH -containing species were very reactive for NO_x reduction to N_2 . Kondratenko et al. [33] found that for the NH_3 SCR reaction, a reduced Ag surface is much more active than an oxidised surface. They related this to the ability of reduced Ag to dissociate NO and O_2 .

5. Conclusion

Based on our findings, we can draw the following conclusions:

1. Increasing hydrogen partial pressure results in increased NO and hydrocarbon conversion.
2. The change in nitrogen balance as a function of time on stream during switches of hydrogen in and out of the reaction mix demonstrates that nitrogen-containing species are stored on the surface of the catalyst in the presence of hydrogen and released as N₂ on removal of hydrogen from the feed stream.
3. At 245 °C, the introduction of 0.72% H₂ promotes formation of gas-phase NH-type species, whereas at lower H₂ concentrations (0.05 and 0.10%), gas-phase NO₂ is produced instead of NH₃. It is proposed that the hydrogen promotes the reaction in two different ways depending on the partial pressure of H₂. At low concentrations, it promotes the formation of NO₂ (g and/or ads), which can directly activate the hydrocarbon. In addition, the release of NO₂ may be an indication that H₂ promotes the decomposition of strongly bound nitrates that may be poisoning the reaction. Sufficiently high hydrogen partial pressure can result in the formation of reduced NH-containing species, which can readily react with NO_x (g and/or ads) to form N₂.

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