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NOx storage during H_2 assisted selective catalytic reduction of NOx reaction over a Ag/Al_2O_3 catalyst

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ABSTRACT

The effect of temperature and transient addition of H_2 on the NOx–SCR reaction was investigated over a 2-wt.% Ag/Al_2O_3 catalyst using isotopically labelled ^{15}NO. The addition and removal of hydrogen had a marked effect on the nitrogen balance at temperatures ranging from 245 to 400 °C. At a low temperature (245 °C), the addition of hydrogen resulted in the storage of NOx, whereas, the reverse was true at 400 °C, where NOx was stored upon removal of hydrogen from the feed. The transient NOx storage effect could be harnessed to allow continuous high NOx conversion with intermittent hydrogen addition. In particular, an average NOx conversion of 79% could be achieved during transient experiments in which H_2 was switched in and out of the feed in 6-s intervals at 300 °C.

1. Introduction

The activity of Ag/Al_2O_3 catalysts for the selective catalytic reduction of NOx with hydrocarbons can be dramatically enhanced by the addition of small quantities of H_2 [1–10]. The effect is apparent for a variety of different aromatic and aliphatic hydrocarbons, alcohols and ketones but is limited to Ag supported on Al_2O_3 and MFI. Structural studies have identified small silver clusters in active catalysts. However, the rapid increase in NOx conversion upon introduction of H_2 [3] compared with the relatively slow rate of formation of Ag clusters [11] indicates that the enhancement of the SCR reaction by H_2 must also be dependent on the chemical action of hydrogen.

There is some debate concerning the nature of the chemical action of hydrogen. It has been proposed that hydrogen promotes the reaction through the removal of a poison which inhibits the reaction. Silver cyanide ($Ag^{+}CN$) has been proposed as a poison [4,6,12], and more recently, Houel et al. [13] have suggested that carbon-rich surfaces poison the SCR reaction and that H_2 promotes the formation of NO_2 which is effective in oxidising carbon deposits at low temperatures. Strongly bound nitrate species have also been proposed as a potential poison which hydrogen can remove [14]. Brosius et al. [15] have shown in the absence of a hydrocarbon that hydrogen can promote the removal of nitrates from Ag and promote the formation of nitrates on the Al_2O_3 support. Shimizu et al. [16] have also suggested that addition of H_2 can inhibit nitrate poisoning. Bentrup et al. [7] found that H_2 promotes the formation of nitrite and nitro species which are much more reactive than nitrato species and are more readily able to activate the hydrocarbon.

Sazama et al. [17] have suggested that hydrogen promotes the formation of highly reactive hydroxyl and hydroperoxy radicals. Fricke and co-workers [18] have also speculated that highly active O surface species are important in the H_2-assisted SCR mechanism. Shimizu and Satsuma [19] have recently confirmed the *in situ* generation of superoxide ions during the H_2-assisted C_3H_8–SCR reaction.

In an earlier study [3], we explored the transient kinetics of the H_2-assisted SCR reaction as a function of hydrogen concentration at 245 °C using isotopically labelled ^{15}NO. 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 upon removal of H_2 from the gas phase showed that these stored species continued to react after removal of hydrogen to form N_2, thus stressing the importance of stored N-containing species in the SCR reaction. The work presented here continues this study by investigating the storage effect at different temperatures. It is interesting to know whether the results at lower temperatures can be extrapolated to higher reaction temperatures. The results at 245 °C are included for the sake of comparison.

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2. Experimental

The 2-wt.% Ag/Al_2O_3 catalyst was provided by Johnson Matthey Plc. It was prepared by the impregnation of γ-Al_2O_3 with a silver nitrate solution followed by drying and calcination. Catalyst testing was performed using a micro-reactor which consisted of a quartz tube (3 mm i.d.) enclosed in furnace. The 0.1-g catalyst sample (particle size of 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% $^{15}NO/Ar$ or $^{14}NO/Ar$), CO_2 (100%), H_2 (5% H_2/Ar), O_2 (100%), 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 controlled evaporator mixer from Bronkhorst. The total flow rate was 276 ml min^{-1}. The concentration of reactants used was 720 ppm NO, 540 ppm n-C_8H_{18}, 7.2% CO_2, 7.2% H_2O, 4.3% O_2, 0.72% H_2 (when added) and 3.7% Kr (when added). Details of the full experimental procedure and apparatus used to carry out the transient switches of hydrogen in and out of the feed are given in a previous publication [3].

3. Results and discussion

The results in Fig. 1 show the effect on reactant and product concentration of switching hydrogen in and out of the SCR feed stream as a function of catalyst bed temperature. $^{15}N_2$ was the main product detected at each of the temperatures; there was no evidence for the formation of $^{15}N_2O$ or $^{15}NO_2$. Although there was some evidence for the formation of small amounts of a $^{15}NH_3$-type species at 245 °C [3], there was none detected at 300 or 400 °C.

Fig. 1 shows that the transient responses of the products and reactants are very dependent on the reaction temperature and shows some interesting features. Before discussing these, it is worth noting some overall trends. Firstly, the addition of hydrogen

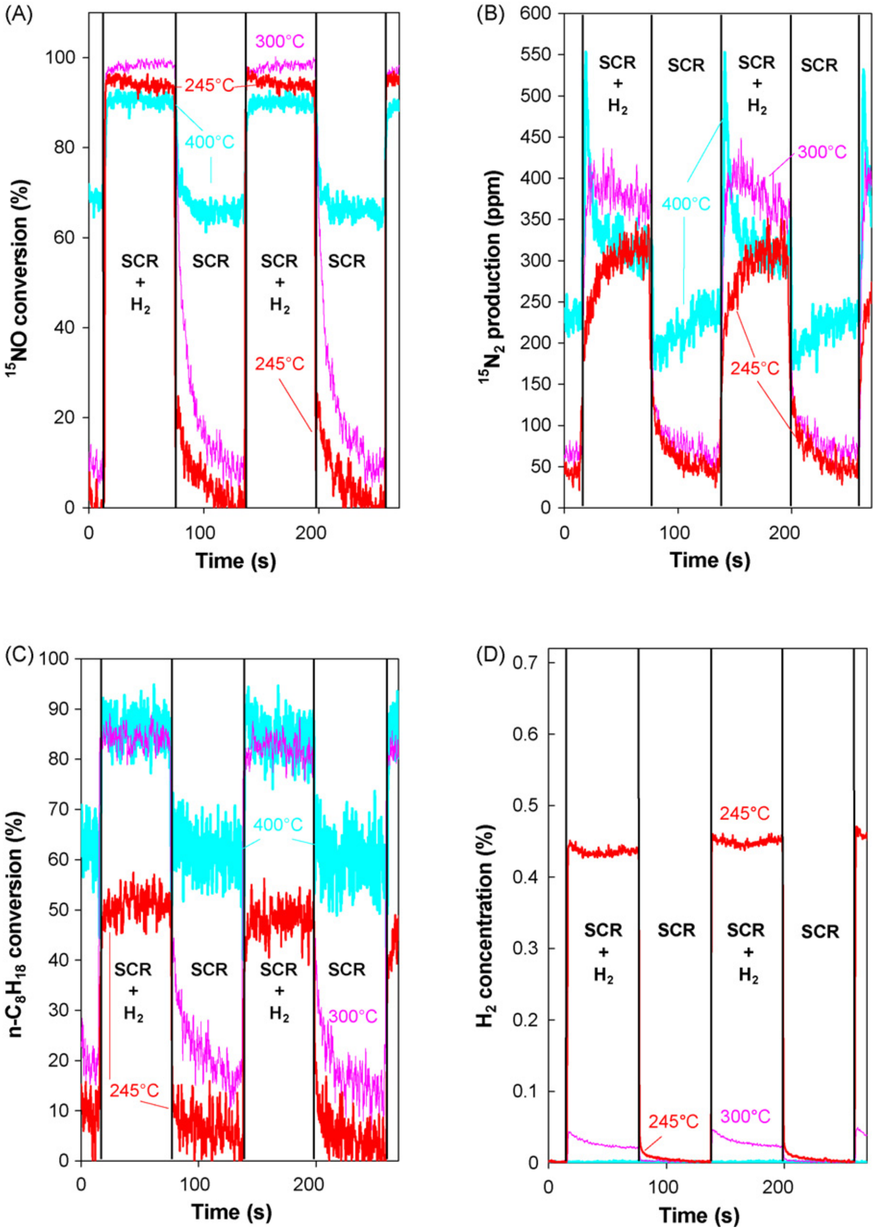

Fig. 1. Evolution of ^{15}NO conversion (A), $^{15}N_2$ production (B), n-C_8H_{18} conversion (C), and H_2 concentration (D) as a function of time during 60-s switches of 0.72% H_2 in and out of the SCR mix over the catalyst at different temperatures.

promotes the conversion of NO and n-C_8H_{18} at each temperature (Fig. 1A and C). This is in agreement with an earlier steady state kinetic study [4]. Secondly, hydrogen conversion increases with increasing temperature. Interestingly, conversion of hydrogen only reaches 100% at 400 °C; at lower temperatures there is hydrogen present in the product stream, indicating that hydrogen can have a promotional effect along the full length of the catalyst bed at 245 and 300 °C.

The key feature of the responses is the large time lags in the response of reactants and products to changing feed conditions. It is evident that steady state conditions (especially with respect to N_2 production) were not attained within 60 s of a switch in feed at any of the three temperatures. The evolution of conversion of both ^{15}NO and n-C_8H_{18} over time was similar and both increased rapidly upon introduction of H_2 and then remained constant in the presence of H_2 over the course of 60 s. Upon removal of H_2 from the feed, there was a significant time lag in the decrease in conversions; this was most apparent at 245 and 300 °C. This cannot be due to significant residual H_2 being present during the switch of H_2 out of the stream, as blank switches (in the absence of catalyst using an SCR feed at 245 and 300 °C) have shown that the hydrogen concentration decreases from 0.72% to less than 0.01% in less than 1.5 s.

The ^{15}NO and n-C_8H_{18} conversions show similar trends for each of the temperatures but the evolution of the $^{15}N_2$ traces vary considerably over time for each of the temperatures. At 245 °C, the $^{15}N_2$ signal increases slowly when H_2 is present in the SCR mix. There is an initial sharp decrease in $^{15}N_2$ production when H_2 is switched out of the mix followed by a slow decrease in the signal over the remaining 60 s of the period without H_2. This trend is repeated again upon re-introduction of H_2. At 300 °C, there is much faster increase in $^{15}N_2$ production which reaches a maximum before decreasing slowly. $^{15}N_2$ production then decreases rapidly when H_2 is removed before entering a period of slowly declining N_2 production similar to that observed at 245 °C. At 400 °C, there is an initial sharp spike of $^{15}N_2$ production when hydrogen is introduced followed by a steady decrease. Production of $^{15}N_2$ initially decreases sharply when H_2 is removed but then, in contrast to the trends at 245 and 300 °C, the signal starts to rise.

The varied evolution of ^{15}NO and $^{15}N_2$ concentrations over the course of the cycles at each temperature leads to a complex ^{15}N balance (Fig. 2) which varies significantly with temperature. Clearly, transient ^{15}N balances significantly above and below 100% are obtained over time. A ^{15}N balance > 100% implies that ^{15}N is released from the catalyst, whereas a balance < 100% suggests that ^{15}N is stored on the catalyst. Table 1 shows that despite the large swings, the ^{15}N balance over a series of cycles is 100% within experimental error. At 245 °C, there is an initial sharp loss of nitrogen balance when H_2 is introduced into the SCR feed stream, which recovers slowly to a value approaching 100% after 60 s. The average nitrogen balance over the course of 60 s when H_2 is present is 84% (Table 1). This suggests that ^{15}N is initially stored when H_2 is introduced. The reverse is true when H_2 is removed; in this case, there is an upward spike in the balance which then decreases slowly towards 100% over time (giving an average balance of 113%), indicating that ^{15}N is released when H_2 is removed. The evolution of ^{15}N at 400 °C is almost a mirror image of that at 245 °C. The data in this case suggests that ^{15}N is released from the surface of the catalyst when H_2 is introduced (average balance of 104%) and stored when H_2 is removed (average balance of 94%). This could tentatively be explained by a mechanism in which the hydrogen reacts with strongly bound nitrate species to release gaseous NOx, thus decreasing the surface coverage of N-containing species. This is in contrast to the effect that hydrogen has at 245 °C, where it aids storage. In this case, hydrogen acts to activate the hydrocarbon and promote NO oxidation to NO_2, leading to species that are more readily stored at lower temperature. At 300 °C, the trace is similar to that at 400 °C in the absence of H_2 and has features of the traces at 245 and 400 °C when hydrogen is present.

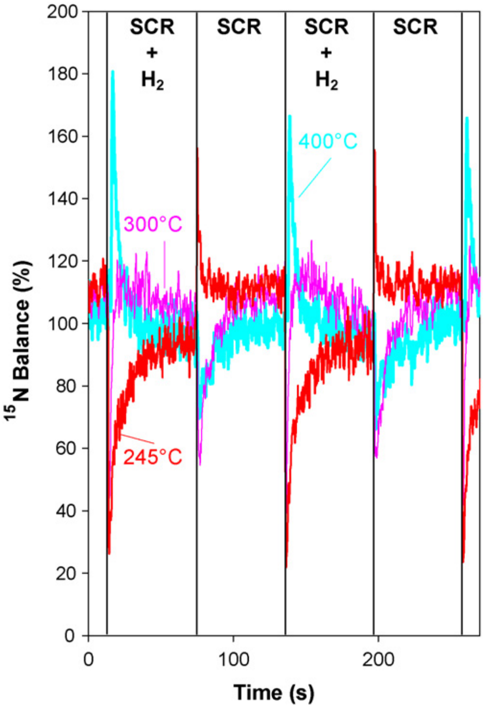

Fig. 2. Evolution of ^{15}N balance as a function of time on stream and temperature during 60-s switches of 0.72% hydrogen in and out of the SCR feed.

There are some other interesting features of the data in Fig. 1 which are summarised in Table 1, which gives values for the average conversions of reactants, production of $^{15}N_2$ and ^{15}N balance at different temperatures during the 60-s periods with and without H_2. The combined averages over the course of three cycles are given. The findings from the data can be summarised as follows:

(a) At 245 and 300 °C, the average conversion of ^{15}NO is higher over the course of 60 s during transient switches when H_2 *is not* present than under steady state conditions in the absence of

Table 1
Average conversions of reactants and ^{15}N balance during the SCR reaction with and without H_2 as a function of temperature

	Reaction	Feed	Temperature (°C)		
			245	300	400
NO conversion (%)	Transient	Average	50	59	78
		H_2	92	96	89
		No H_2	7	24	67
	Steady state	Average	47	51	77
		H_2	93	99	88
		No H_2	0	4	66
N_2 balance (%)	Transient	Average	99	103	99
		H_2	84	106	104
		No H_2	113	100	94
C_8H_{16} conversion (%)	Transient	Average	28	52	72
		H_2	47	81	83
		No H_2	7	21	61
H_2 conversion (%)	Transient	H_2	38	96	100

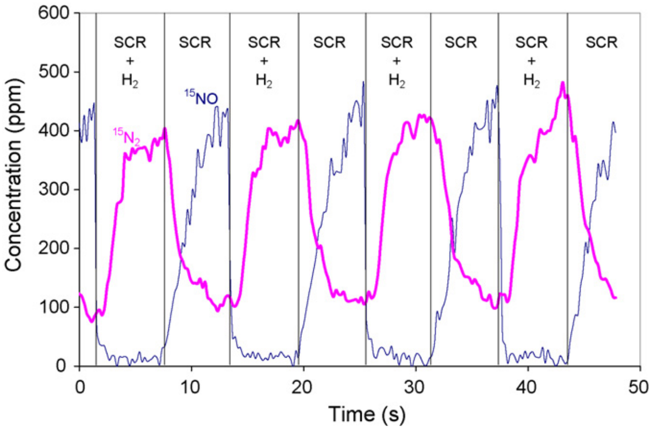

Fig. 3. Evolution of ^{15}NO and $^{15}N_2$ concentrations as a function of time during 6-s switches of 0.72% H_2 in and out of the SCR feed at 300 °C.

hydrogen. This is especially striking at 300 °C, where there is 20% more conversion under transient conditions than under steady state conditions even though the feed composition is the same.

(b) Conversions of ^{15}NO during steady state and under transient conditions when H_2 *is* present are similar.

(c) The implication of the observations in (a) and (b) is that the average conversion of ^{15}NO (particularly at 245 and 300 °C) is greater under transient conditions than the average of an equal exposure to a steady state mixture with and without H_2.

The slow decrease in ^{15}NO conversion (and $^{15}N_2$ production) after switching out H_2 observed in Fig. 1 suggests that even greater improvements in average ^{15}NO conversion could be achieved (especially at 300 °C) by using even shorter transient pulses than 60 s. The data in Fig. 3 shows the evolution of ^{15}NO and $^{15}N_2$ concentration as a function of time during 6-s switches of H_2 in and out of the SCR feed at 300 °C. The average ^{15}NO conversion during the 6-s switches was 79% compared to an average conversion of 59% observed during the 60-s switches. The difference is even higher if this is compared to the average value (with and without hydrogen) of nitric oxide conversion obtained under steady state conditions (51%) (Table 1). Thus, at 300 °C (and to a lesser extent at 245 °C), there is clearly a storage effect in which species produced when hydrogen is present can react with and produce nitrogen after H_2 is removed.

4. Conclusions

At 245, 300 and 400 °C, the addition of hydrogen to the SCR of NOx reaction mixture resulted in an improvement in NOx conversion over a 2-wt.% Ag/Al_2O_3 catalyst. Removal of hydrogen from the feed mixture at 245 and 300 °C resulted in residual NOx conversion and N_2 production extending for more than a minute after removal of hydrogen. This residual activity can most likely be attributed to the promotion of the formation of active surface species by hydrogen. Upon removal of hydrogen from the feed, these stored species could then either decompose or react with incoming NOx to produce nitrogen. This storage effect was utilised by operating the reactor under transient conditions in which hydrogen was switched in and out in at 6-s intervals. Under these conditions, it was possible to obtain higher average NOx conversion (79%) compared to that obtained by taking the average steady state NOx conversion with and without H_2. This was especially apparent at 300 °C.

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