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Regeneration mechanism of a Lean NO_x Trap (LNT) catalyst in the presence of NO investigated using isotope labelling techniques

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ABSTRACT

The presence of NO during the regeneration period of a Pt–Ba/Al_2O_3 Lean NO_x Trap (LNT) catalyst modifies significantly the evolution of products formed from the reduction of stored nitrates, particularly nitrogen and ammonia. The use of isotope labelling techniques, feeding ^{14}NO during the storage period and ^{15}NO during regeneration allows us to propose three different routes for nitrogen formation based on the different masses detected during regeneration, i.e. $^{14}N_2$ (m/e = 28), $^{14}N^{15}N$ (m/e = 29) and $^{15}N_2$ (m/e = 30). It is proposed that the formation of nitrogen via Route 1 involves the reaction between hydrogen and $^{14}NO_x$ released from the storage component to form $^{14}NH_3$ mainly. Then, ammonia further reacts with $^{14}NO_x$ located downstream to form $^{14}N_2$. In Route 2, it is postulated that the incoming ^{15}NO reacts with hydrogen to form $^{15}NH_3$ in the reactor zone where the trap has been already regenerated. This isotopically labelled ammonia travels through the catalyst bed until it reaches the regeneration front where it participates in the reduction of stored nitrates ($^{14}NO_x$) to form $^{14}N^{15}N$. The formation of $^{15}N_2$ via Route 3 is believed to occur by the reaction between incoming ^{15}NO and H_2. The modification of the hydrogen concentration fed during regeneration affects the relative importance of H_2 or $^{15}NH_3$ as reductants and thus the production of $^{14}N_2$ via Route 1 and $^{14}N^{15}N$ via Route 2.

1. Introduction

The reduction in NO_x emission from lean-burn engines has been the subject of several studies during the last decade. NO_x storage and reduction (NSR), also known as Lean NO_x Trap (LNT) catalysts, is considered to be one of the most promising technologies to solve the problem. However, most published work on LNT regeneration has been performed *in the absence of NO*. In the present work, we find that the inclusion of NO during the regeneration phase, as would occur in a real system, has a significant effect on the distribution of products.

The NSR technique was introduced by Toyota in the mid-1990s for automotive emission control [1]. A typical NSR catalyst consists of a noble metal coupled with an alkaline or alkaline-earth compound, for example Pt–BaO/Al_2O_3. The basis of this technology is to trap NO_x under lean conditions on the alkaline-earth compound (BaO) and then for the NO_x to be released and reduced to N_2 during a short rich period on the noble metal (Pt).

First studies established that the first step of the NO_x storage process is the oxidation of NO to NO_2 over platinum sites [2–6] and that NO_2 is subsequently stored on the barium component. Nova et al. [7,8] described the mechanism of NO_x storage by two routes that operate simultaneously: the "nitrite route" and the "nitrate route". The nitrite route involves the direct uptake of NO in the presence of O_2 on the barium component to form adsorbed nitrite species, which are then oxidized to nitrates. Simultaneously, the nitrate route considers the NO oxidation to NO_2, and the NO_2 formed can then adsorb on barium in the form of nitrates via a disproportionation reaction.

The regeneration step is not so well understood as the storage step. Several studies have been published on the chemistry and mechanisms that rule the reduction in NO_x ad species by H_2. The nitrate decomposition can be driven by either the heat generated from the reducing switch [9,10] or the decrease in oxygen concentration that lowers the equilibrium stability of nitrates [11,12]. However, under near isothermal conditions, it was found that the reduction process is not initiated by the thermal decomposition of the stored nitrates, but rather by a catalytic pathway involving Pt [13].

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More recent studies better describe both the very high selectivity to N_2 and the temporal sequence of products, with ammonia detection following that of nitrogen, in the reduction of stored NO_x by H_2 [9,14–18]. The proposed mechanism consists of a sequential two-step pathway for nitrogen formation involving the fast formation of ammonia on reaction of nitrates with H_2, followed by the slower reaction of the ammonia thus formed with the stored nitrates leading to the selective formation of N_2. For these studies, NO_x was adsorbed on the catalyst surface from a NO/O_2 stream, and then, the regeneration of the catalyst was simulated with only H_2 or NH_3 in the injected rich stream. However, in real automobile operation, NO will also be present in the gas phase during the regeneration period and this could modify the reaction network for NO_x reduction to N_2 and NH_3. The behaviour of a Pt–BaO/Al_2O_3 monolith catalyst during NO_x storage and reduction when NO is also fed together with H_2 in the regeneration period has been studied by Pereda-Ayo et al. [19,20]. This study provided information on the $N_2/N_2O/NH_3$ distribution at the exit of the trap at different temperatures and with different hydrogen concentrations. In order to obtain further insights into the complete reaction pathway governing the reduction in both stored NO_x and that fed during the regeneration period, the use of isotopically labelled NO_x has been utilized in the present study.

The use of labelled species has allowed a detailed analysis of the products and reactants involved in the regeneration of a NSR catalyst. Breen et al. [21] used isotopic labelling (^{15}NO) coupled with fast transient kinetic switching during NSR. They used ^{15}NO instead of ^{14}NO to differentiate $^{15}N_2$ from CO and $^{15}N_2O$ from CO_2 in the mass spectrometry analysis. This technique can be used to differentiate NO fed during the lean and rich periods if one of them is isotopically labelled as ^{15}NO. Kumar et al. [22] carried out isotopically labelled storage and reduction over Pt–BaO/Al_2O_3 in a TAP reactor system to elucidate the role of spillover processes and the Pt–BaO interphase during NO_x storage and reduction. The sequential pre-nitration of Pt–BaO/Al_2O_3 using NO and ^{15}NO followed by reduction with H_2 resulted in the preferential evolution of ^{15}N-containing species during the initial H_2 pulses. The evolution shifted towards unlabelled N-containing species in later H_2 pulses.

In the present study, isotopically labelled ^{15}NO is fed together with the reductant H_2 during the rich (regeneration) period while unlabelled NO is used during the lean (storage) period. The use of isotopic species helps to elucidate the different routes by which nitrogen can be formed as three different species, namely $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$, can be detected as products.

2. Experimental

2.1. Catalyst preparation

The γ-Al_2O_3 (SA6173) used in this study was supplied by Saint Gobain as 3-mm-diameter pellets. The as-received alumina was crushed, sieved to 0.3–0.5 mm and calcined in air at 700 °C for 4 h, resulting in a BET surface area of 190 $m^2\,g^{-1}$. The incorporation of the active phases to obtain the nominal 1.2 wt% Pt/15 wt% Ba/Al_2O_3 catalyst was carried out by adsorption from solution and wet impregnation for the platinum and barium components, respectively. The incorporation order was Pt and then Ba. First, 0.8 g of Al_2O_3 was immersed in an aqueous solution containing 650 ppm Pt with a total volume of 50 ml. The precursor used for platinum was tetraamine platinum (II) nitrate supplied by Alpha Aesar. In order to facilitate the platinum incorporation, the pH of the solution was modified by adding ammonia (25% as NH_3, Panreac) until optimum pH for platinum adsorption was obtained, i.e. a pH = 11.6 [23]. The alumina was maintained in contact with the solution for 24 h and under continuous stirring to assure that the adsorption equilibrium was obtained. Afterwards, the alumina was filtered and finally calcined in air at 500 °C for 4 h. Before incorporation of barium, the Pt/Al_2O_3 catalyst was reduced in a 5% H_2/N_2 stream at 450 °C for 2 h. The precursor used for barium incorporation was barium acetate supplied by Aldrich. After Ba incorporation via wet impregnation, the catalyst was calcined at 500 °C for 4 h.

2.2. Experimental set-up

The catalyst was evaluated using a fast transient kinetic apparatus described in more detail elsewhere [24]. Briefly, the fast switching experimental set-up was assembled using helium actuated high-speed VICI four-way valves, permitting fast feedstream changes between lean and rich cycles. The bench flow reactor consisted of a Pyrex tube enclosed in an electric furnace, and the gas mixtures used to simulate the exhaust were introduced using Aera mass flow controllers. The temperature of the catalyst bed was continuously recorded using a thermocouple located at the exit of the catalyst bed. Gas analysis was performed using a Hiden HPR 20 quadrupole mass spectrometer, the sampling inlet being positioned immediately after the catalyst bed.

2.3. NO_x storage and reduction experiments

2.3.1. Long-term NO_x storage and reduction experiments

54.9 mg of Pt–Ba/Al_2O_3 catalyst was packed in a 4-mm-internal diameter Pyrex tube. In order to follow accurately the formation of different species during catalyst regeneration, long-term NO_x storage and reduction cycles were carried out at 190 and 340 °C. The lean period was extended until the catalyst surface was saturated with NO_x, and the regeneration period was extended until complete regeneration was obtained, i.e. when N_2 and H_2O signals (main products of the regeneration) decreased to the baseline. Since the storage capacity and the regeneration pattern are dependent on the reaction temperature, the duration of lean and rich periods was 15 min and 5 min, respectively, when the temperature was set at 190 °C. When the temperature was increased to 340 °C, the duration of lean and rich periods was extended to 20 min and 7 min, respectively.

First, the influence of the presence or absence of ^{14}NO during the regeneration period was studied. When ^{14}NO was present, the regeneration feedstream consisted of 800 ppm ^{14}NO, 0.46% H_2, 5.6% Kr and balance to Ar. Kr was used as an internal standard as well as an internal marker to differentiate between lean and rich gas mixtures. In the absence of ^{14}NO during the rich period, the feedstream was composed of 0.46% H_2, 13.6% Kr and balance to Ar, maintaining the total flow rate at 130.4 ml min^{-1}, equivalent to a space velocity of 124,500 h^{-1}.

The following masses were continuously monitored to have a clear picture of the regeneration process: (m/e = 30) for ^{14}NO, (m/e = 18) for H_2O, (m/e = 28) for $^{14}N_2$, (m/e = 32) for O_2, (m/e = 46) for NO_2, (m/e = 44) for N_2O, (m/e = 2) for H_2 and (m/e = 15) for ^{14}NH, which can be attributed to the ^{14}NH fragment of $^{14}NH_3$, avoiding the overlapping of H_2O when the monitoring of ammonia is being done with the mass (m/e = 17) $^{14}NH_3$ or (m/e = 16) $^{14}NH_2$.

When ^{15}NO was admitted during regeneration instead of ^{14}NO, the composition of the feedstream was not altered: 800 ppm of ^{15}NO, 0.46% H_2, 5.6% Kr and balance to Ar. In this case, apart from the masses already reported, the following masses were also continuously monitored: (m/e = 29) for $^{14}N^{15}N$, (m/e = 30) for $^{15}N_2$ or ^{14}NO and (m/e = 31) for ^{15}NO.