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Fundamental understanding of the Di-Air system (an alternative NO_x abatement technology). I: The difference in reductant pre-treatment of ceria

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ABSTRACT

Toyota's Di-Air $DeNO_x$ system is a promising $DeNO_x$ system to meet NO_x emission requirement during the real driving, yet, a fundamental understanding largely lacks, *e.g.* the benefit of fast frequency fuel injection. Ceria is the main ingredient in Di-Air catalyst composition. Hence, we investigated the reduction of ceria by reductants, *e.g.* CO, H_2, and hydrocarbons (C_3H_6 and C_3H_8), with Temporal Analysis of Product (TAP) technique. The results show that the reduction by CO yielded a faster catalyst reduction rate than that of H_2. However, they reached the same final degree of ceria reduction. Hydrocarbons generated almost three times deeper degree of ceria reduction than that with CO and H_2. In addition, hydrocarbons resulted in carbonaceous deposits on the ceria surface. The total amount of converted NO over the C_3H_6 reduced sample is around ten times more than that of CO. The deeper degree of reduction and the deposition of carbon by hydrocarbon explain why hydrocarbons are the most powerful reductants in Toyota's Di-Air NO_x abatement system.

1. Introduction

In the European Union (EU) the regulated NO_x emissions have decreased over the past two decades. Nevertheless, 9% of EU-28 urban live in areas in which NO_x concentrations still exceed regulated NO_x standards in 2013, according to the Air quality for EU in 2014 (source European Environmental Agency [1]). In the European Union, around 40% of the NO_x emissions are from the traffic sector [2]. Due to the limited effectiveness of currently available NO_x abatement technologies, as of September 2017, 2.1 times the current Euro 6 NO_x emission standard (as measured with the conservative, less demanding ECE & EDCE test cycle) is allowed for in the newly established real driving emission (RDE) test [3]. In the future NO_x emission will become even more stringent, which clearly indicates that currently available technologies: Three-way catalyst (TWC), Urea-SCR (Selective Catalytic Reduction), Lean NO_x Traps (NSR – NO_x Storage & Reduction), still need significant improvements. Therefore, efficient exhaust emissions after-treatment technologies are highly demanded. Recently, Bisaiji et al. (Toyota company) developed the Di-Air system (Diesel $DeNO_x$ System by Adsorbed Intermediate Reductants). Short rich and lean time intervals are created by high frequency directly injecting hydrocarbons (diesel fuel injection) into the exhaust system upstream of a typical NSR catalyst ($Pt/Rh/Ba/K/Ce/Al_2O_3$) [4,5]. The Di-Air system has shown promise to meet future NO_x emission standards under realistic driving test conditions.

In the Di-Air system, hydrocarbons are the most powerful reductants in the reduction of NO_x, as compared to other reductants, *e.g.* CO and H_2 [5]. However, the mechanism is still not clear. Before system optimisation with regard to catalyst formulation and fuel injection strategies, the principle and fundamental understanding of the Di-Air system are a prerequisite.

Ceria is an essential catalyst ingredient in the Di-Air system, as it acts as an oxygen buffer. The ceria lattice oxygen can react with hydrocarbons, CO, and H_2 under rich conditions [6]. In our research, a commercially available model Zr and La-doped ceria is used. The Zr–Ce solid solution, in which zirconium partially replaces cerium, provides a higher (hydro)thermal stability and a larger oxygen storage capacity [7], whereas lanthanum is present to increase the rate of oxygen bulk diffusion [8]. A reduced ceria can selectively convert NO into (di)nitrogen (N_2), even in the presence of an excess of oxygen [9].

In this study, we mainly focus on the investigation of the reduction behavior of the Zr and La-doped ceria catalyst, using H_2, CO, C_3H_6, and C_3H_8 as reductants. Temporal Analysis of Products (TAP) is used to ascertain the reaction between the reductants and the

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catalyst. Since high intensity of hydrocarbon reductant injections is applied in the Di-Air system, these pulses will create a locally reduced environment. Therefore, all the experiments in this study are performed in the absence of gas-phase O_2. The performed experiments will provide an illustrative model of the product evolution as a function of the catalyst-reduction degree in an attempt to obtain a fundamental understanding of the Di-Air system. To demonstrate the effect of different reductants on NO reduction, NO reduction is performed over the Zr–La doped ceria by pre-treatment of various reductants. The re-oxidation of the reduced ceria by NO is identical to the reduction of NO into N_2 over reduced ceria.

2. Experimental

The catalyst used is a commercial Zr–La doped ceria (BASF company, denoted as ceria) which serves as a core component in the Di-Air catalyst formulation. The characterisation of this Zr–La doped ceria is described in more detail elsewhere [10].

2.1. Pulses experiment in TAP

The pulse experiments were carried out in an in-house developed TAP (Temporal Analysis of Products) reactor. Small gas pulses, typically in the order of 1×10^{15} molecules, were introduced in a small volume (1 mL) upstream of the catalyst packed bed reactor. The produced pressure gradient over the catalyst packed bed thereby caused the molecules to be transported through the packed bed to the ultra-low vacuum at the opposite side of the reactor bed. Depending on the actual amount of molecules pulsed, the transport can be purely Knudsen diffusion. In other words, the molecules will only interact with the ‘walls’ (catalyst surface and reactor walls) of the system and not with each other. Upon interaction with the catalyst, the molecules can be converted into different products. The evolution of the reactant and product molecules are tracked (one mass at a time) in time with a high resolution of 10 kHz by means of a mass spectrometer. More details about TAP can be found in elsewhere [9,11].

21.2 mg ceria (100–250 μm, BET surface area 65 m^2/g) was used in the TAP reactor. In all experiments a starting pulse size of approximately 1.6×10^{15} molecules (excluding internal standard gas) was used, the pulse size gradually decreased during an experiment as the reactant was pulsed from the closed and calibrated volume of the pulse-valve line. Prior to the reduction, the ceria was firstly re-oxidised at the same temperature at which the reduction was performed, using pulses of 80 vol.% O_2 in Ar until a stable O_2/Ar signal ratio was obtained. The reduction was carried out by pulsing reductant of either 80 vol.% C_3H_6 in Ne or 80 vol.% C_3H_8 in Ne or 80 vol.% CO in Ar or 67 vol.% H_2 in Ar until a stable reactant and product to the internal standard signal ratio was achieved, indicating that the ceria was equilibrated. NO pulse experiments were performed using 80 vol.% NO in Ar.

The consumption of the oxygen species from the ceria during H_2, CO, C_3H_8, and C_3H_6 pulses experiments was calculated using the following mass balance:

$$n_{\mathrm{O,consumed}} = n_{\mathrm{H_2O,obs}} + n_{\mathrm{CO,obs}} + 2n_{\mathrm{CO_2,obs}} \quad (1)$$

where *n* is the number of molecules or atoms of the specified species observed (obs), consumed, or introduced (in).

The number of carbon species deposited on the doped ceria surface in the C_3H_6 pulse experiments was calculated using the following mass balance:

$$n_{\mathrm{C,deposited}} = 3n_{\mathrm{C_3H_6,in}} - 3n_{\mathrm{C_3H_6,obs}} - n_{\mathrm{CO,obs}} - n_{\mathrm{CO_2,obs}} \quad (2)$$

Similarly, the number of carbon species deposited on the ceria surface in the C_3H_8 pulse experiments was calculated using the following mass balance:

$$n_{\mathrm{C,deposited}} = 3n_{\mathrm{C_3H_8,in}} - 3n_{\mathrm{C_3H_8,obs}} - 3n_{\mathrm{C_3H_6,obs}} - n_{\mathrm{CO,obs}} - n_{\mathrm{CO_2,obs}} \quad (3)$$

The number of carbon species during CO pulse experiments on the ceria surface was calculated using the following material balance:

$$n_{\mathrm{C,deposited}} = n_{\mathrm{CO,in}} - n_{\mathrm{CO,obs}} - n_{\mathrm{CO_2,obs}} \quad (4)$$

The average particles size of ceria was around 5 nm, based on XRD and TEM analyses [10]. The hypothetical ceria layers concept was used in order to obtain insight in the reductant reactivity as a function of the degree of ceria reduction (surface oxidation state).

As the ceria (111) crystal plane is a stoichiometric O–Ce–O tri-layer stacked along the [111] direction, we regarded each O–Ce–O tri-layer as one hypothetical ceria layer (0.316 nm). Assuming a perfect cubic crystal structure of ceria (size 5.0 nm), the total number of hypothetical ceria layers were determined to be 16 (111) layers. Assuming that Zr is identical to Ce, a maximum of 25% of the number of O ions in each crystal layer can be reduced, the number of reducible oxygens in one hypothetical ceria layer with BET surface area of 65 m^2/g is calculated to be $5.4 \times 10^{18}/21.2\ m_{Cat}$. Details can be found in [9,10].

2.2. *In situ* Raman

In situ Raman spectra (Renishaw, 2000) were recorded using a temperature controlled *in situ* Raman cell (Linkam, THMS 600). Ten scans were collected for each spectrum in the 100–4000 cm^{-1} range using continuous grating mode with a resolution of 4 cm^{-1} and scan time of 10 s. The spectrometer was calibrated daily using a silicon standard with a strong absorption band at 520 cm^{-1}. The spectra were recorded during the flow of C_3H_6 (1000 ppm in N_2, flow rate 200 mL/min).

3. Results

3.1. Reduction of ceria by CO

Fig. 1 showed the result of CO pulses experiment at 580 °C. During the initial period (pulse number 0–2000, Fig. 1A), the CO was completely converted into CO_2. Pulse number 2000 corresponded to 0.4 hypothetical reduced ceria layers (Fig. 1B). After this initial period, the CO conversion and CO_2 production progressively decreased, but never reached a zero conversion level during the duration of the experiment. In the CO oxidation process, only oxygen from the catalyst can be consumed, as can be seen from the oxygen balance (Table 2). No carbon deposits were observed on the catalyst within experimental error.

Similar results were obtained at 400–500 °C (not shown), but CO conversion did never reach full conversion in this temperature window. At 200 °C and lower, no significant CO oxidation activity was observed (not shown). The number of hypothetical reduced ceria layers (1.2–1.0) were relatively constant in the 400–580 °C temperature window (Table 2).

3.2. Reduction by H_2

Fig. 2 shows the result of H_2 pulses experiment at 560 °C For a very short period (pulse number 0–210, Fig. 2A), hydrogen conversion was relatively high without a clear desorption of water. In contrast to the CO experiment, the H_2 conversion did not accomplish full conversion. The H_2 conversion and H_2O production decreased progressively during the remainder of the experiment

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