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# Low temperature NO adsorption over hydrothermally aged Pd/CeO<sub>2</sub> for cold start application

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## ABSTRACT

Pd/CeO<sub>2</sub> catalyst hydrothermally aged at 750 °C for 25 h was employed for NO adsorption at low temperature (80–160 °C). For comparison, Pt or Pt-Pd supported on CeO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> catalysts were also applied. Analysis of the hydrothermally aged catalysts clearly indicates that PGM (Pt and/or Pd) on CeO<sub>2</sub> is more resistant to sintering than that on Al<sub>2</sub>O<sub>3</sub> support. Reducibility test of Pd/CeO<sub>2</sub> by H<sub>2</sub>-TPR exhibits H<sub>2</sub> spillover from Pd to CeO<sub>2</sub> support, attributed to the strong interaction between Pd and CeO<sub>2</sub>. NO adsorption/desorption results demonstrate that CeO<sub>2</sub>-based catalysts exhibit superior NO adsorption ability than Al<sub>2</sub>O<sub>3</sub>-based catalysts. In addition, PGM/CeO<sub>2</sub> catalysts shows the desirable desorption temperature for cold start application. The influence of reactant in stream, NO adsorption time, and temperature on low temperature NO adsorption over Pd/CeO<sub>2</sub> is also examined to advance the understanding of NO adsorption/desorption behavior. DRIFT results of adsorbed NO<sub>x</sub> species on Pd/CeO<sub>2</sub> during NO adsorption/desorption prove that NO<sub>x</sub> desorption peaks at 250, 300, and 450 °C originate from weakly bound nitrite, nitro-nitrito species, and nitrate species, respectively. In Pd/CeO<sub>2</sub> catalyst, Pd plays a role in providing additional NO adsorption site arising from the intimate interaction between Pd and CeO<sub>2</sub> and promoting the oxidation from adsorbed nitrite to nitrate. It can be summarized that Pd/CeO<sub>2</sub> can be a good candidate as low temperature NO adsorption catalyst for cold start application.

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## 1. Introduction

Societal development has required heavy dependence on internal combustion (IC) engines, which have negative effects on the environment and human health [1,2]. In particular, automotive IC engines have emitted a large amount of pollutants into the air, and hence regulations on exhaust gas have been globally issued and enforced for several decades [3]. Recently, diesel engines, which offer advantages of high fuel efficiency and excellent durability, have received attention because of new regulations on fuel economy [4,5]. On the other hand, diesel engines release a variety of harmful pollutants including carbon monoxide (CO), hydrocarbons (HCs), particulate matter (PM), and nitrogen oxides (NO<sub>x</sub>) [6]. For the removal of NO<sub>x</sub> in the emission, selective catalytic reduction (SCR) and/or NO<sub>x</sub> storage reduction (NSR) catalysts are being implemented to remove NO<sub>x</sub> in exhaust gas. However, under the current situation where more stringent regulation on NO<sub>x</sub> is forthcoming, a novel approach to reduce NO<sub>x</sub> emission is strongly required.

A significant amount of NO<sub>x</sub> is released into air during the initial ca. 100 s of operation, in other words, the cold start period, since the SCR or NSR system is not warmed up to operate (<200 °C) [7]. Recently, in order to address the NO<sub>x</sub> emission during the initial stage of operation, cold start catalysts have been investigated in both academia and industry with the concept of adsorbing NO<sub>x</sub> at low temperature and releasing it at higher temperature, where SCR or NSR operates. Crocker et al. reported that Pt/Al<sub>2</sub>O<sub>3</sub> and Pt, Pd/CeO<sub>2</sub> catalysts have remarkable NO<sub>x</sub> adsorption ability at low temperature (80–120 °C) [8,9]. In addition, several researchers from industry have also reported about catalysts for low temperature NO adsorption. A TWC catalyst containing Pd/zeolite as a NO<sub>x</sub> trap material was reported by Honda [10]. Theis of Ford investigated various conditions influencing the low temperature NO<sub>x</sub> adsorption of Pt and Pd catalysts [11]. Chen et al. [7] reported a diesel Cold Start Concept (CSC<sup>TM</sup>) catalyst that has the ability of trapping NO<sub>x</sub> and HCs at low temperature and oxidizing CO, NO, and HCs after warming up. Moreover, Chen and coworkers reported that Pd supported on zeolites such as BEA, MFI, and CHA has the ability to store NO<sub>x</sub> at low temperature [12]. Recent patents by Johnson Matthey have claimed a cold start concept catalyst including Pt and Pd supported on Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and zeolite [13–15]. Such cold start catalysts require two important features, which are large NO<sub>x</sub>

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adsorption capacity at low temperature and proper NO<sub>x</sub> desorption temperature. In particular, the most desirable NO<sub>x</sub> desorption temperature must be located within the operating temperature of SCR or NSR.

The platinum group metal (PGM) has been used as an active phase of catalysts. Pt, a PGM, is an essential component of TWC, DOC, and NSR due to its high oxidation ability [16–18]. However, Pt is readily deactivated under a high temperature atmosphere because of sintering, and this has motivated efforts to find substitutes. Thus, Pd, which has better resistance to thermal degradation and lower price than Pt, has been intensively studied as a replacement of Pt. For example, Pt–Pd bimetallic catalysts also have been investigated to facilitate the synergistic effect of two PGMs [17,19,20]. It has been reported that both Pt and Pd metals are able to adsorb NO<sub>x</sub> molecules at low temperature [12,21–23]. Especially, it is known that the oxidation state of Pd plays a key role in NO adsorption, as evidenced by the fact that various ionic and metallic Pd species such as Pd<sup>2+</sup>, Pd<sup>+</sup>, and Pd<sup>0</sup> can adsorb NO at low temperature, although PdO cannot [24,25]. In the case of Pt, metallic Pt can adsorb NO<sub>x</sub> [21].

Due to its relatively large specific surface area and superior thermal stability, Al<sub>2</sub>O<sub>3</sub> has been applied as a support material in numerous reactions such as CO oxidation [26] and HCs oxidation [27,28]. In addition, previous literature shows that Pt/Al<sub>2</sub>O<sub>3</sub> has the ability of storing NO<sub>x</sub> at low temperature [8]. CeO<sub>2</sub>-based materials have been extensively investigated for the various application because of its excellent activity of alternating its oxidative state between Ce<sup>3+</sup> and Ce<sup>4+</sup> rather easily to store and release oxygen [29–31]. Furthermore, CeO<sub>2</sub> is well known as a low temperature NO adsorption material [32,33], and, accordingly, Ce-based materials have been widely applied to NO<sub>x</sub> reduction catalysts such as NSR and SCR [34–36].

In this work, we evaluated the intrinsic low temperature NO adsorption ability of Pd/CeO<sub>2</sub> compared with Pt, Pt–Pd supported on CeO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> catalysts after hydrothermal aging in order to use it as a NO<sub>x</sub> trap catalyst for cold start application. The NO<sub>x</sub> adsorption/desorption behavior was extensively investigated as a function of various parameters such as catalyst, adsorption time, and reactants. The combined activity and DRIFT results allow us to elucidate the role of PGMs and support, and the adsorption/desorption mechanism over the Pd/CeO<sub>2</sub> catalyst.

## 2. Experimental

### 2.1. Catalysts preparation

CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> support materials were obtained from Rhodia and Sasol, respectively. Three different combinations of Pt and Pd (2:0, 1:1 and 0:2 wt%) were loaded on these supports by the conventional incipient wetness impregnation method with aqueous solutions of Pd (NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (Sigma Aldrich) and/or Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Alfa Aesar) as a metal precursor. After impregnation, all catalysts were dried at 100 °C for 24 h and calcined at 500 °C in 15% O<sub>2</sub> balanced with N<sub>2</sub> for 2 h, which were designated as “Fresh”. Since automotive emission control catalyst requires excellent hydrothermal stability, the calcined samples were treated with 15% O<sub>2</sub> and 10% H<sub>2</sub>O in N<sub>2</sub> with a total flow rate of 200 ml/min at 750 °C for 25 h, and were denoted as hydrothermally aged (HTA) samples. We primarily investigated the HTA samples for activity measurement and characterization, if not specified.

### 2.2. Catalyst characterizations

The crystalline phase of the catalysts was analyzed by powder X-ray diffraction (XRD) using a Rigaku (mode 1 smartlab) diffrac-

tometer with Cu Kα radiation (40 kV and 30 mA). The XRD data were recorded in a range of 10–80° (2θ) with a step size of 0.02° at a rate of 2.5°/min.

N<sub>2</sub> physisorption was carried out to measure the BET surface area on a Micromeritics ASAP 2010 at –196 °C (liquid nitrogen temperature). Before measurement, the catalysts were degassed at 250 °C for 4 h under a vacuum condition.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a VG Multilab2000 spectrometer (ThermoVG Scientific) with an Al Kα (hν = 1486.6 eV). The base pressure of the spectrometer chamber was about 10<sup>–9</sup> Pa. To calibrate the shift due to the charging, the C 1s binding energy (284.8 eV) was used as a reference. The Gauss-Lorentz distribution and Shirley model were applied for peak deconvolution and background subtraction, respectively.

Cryo H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR) was carried out with a BEL-CAT-II (BEL Japan Inc.) with a thermal conductivity detector (TCD). Before measurement, 0.05 g of catalysts was pre-treated in a flow of 10% O<sub>2</sub>/N<sub>2</sub> at 300 °C for 1 h to ensure full oxidation. After cooling to –90 °C, catalysts were exposed to 10% H<sub>2</sub>/Ar and heated from –90 to 900 °C at a rate of 10 °C/min.

CO-chemisorption was conducted with the same equipment of H<sub>2</sub>-TPR. 0.05 g of sample was pretreated in 5% H<sub>2</sub>/Ar at 400 °C for 30 min and purged with He for 10 min. After pretreatment, the sample cell was cooled down to –78 °C with He gas and then 5% CO/He was introduced into reactor using pulse method. We assumed that the adsorption ratio between CO and surface PGM atoms is 1:1 for calculation [37,38].

DRIFT spectra were collected in the 4000–600 cm<sup>–1</sup> range with 128 scans at a resolution of 4 cm<sup>–1</sup> on a Nicolet 6700 (Thermo Fisher Scientific) equipped with a MCT detector using DRIFT cell (HARRIC praying mantis™). KBr background was collected at 120 °C. Prior to NO adsorption (100 ppm NO, 9.5% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub> balance, 200 ml/min), the samples were pretreated without NO (9.5% O<sub>2</sub>, 5% H<sub>2</sub>O in N<sub>2</sub> balance, 200 ml/min) at 500 °C for 30 min to remove impurities. IR spectra were collected during NO adsorption at 120 °C for 1 h and also during ramping from 120 to 500 °C under 9.5% O<sub>2</sub>, 5% H<sub>2</sub>O, and N<sub>2</sub> with an interval of 50 °C in order to investigate the change in the adsorbed NO<sub>x</sub> species on the catalyst during NO<sub>x</sub> adsorption/desorption. During the temperature ramping, each spectrum is recorded after stabilization at that temperature for at least 10 min. To extract pure nitrogenous species on catalyst, final IR spectra are obtained by subtracting those of before NO adsorption from those of after NO adsorption at the same temperature. IR spectra of before NO adsorption are collected with same method during the cool down.

### 2.3. Activity measurement for the adsorption/desorption of NO

An activity test was carried out in a continuous flow quartz reactor. The catalyst (0.1 g) was blended with inert α-Al<sub>2</sub>O<sub>3</sub> (0.1 g) to dissipate the heat generated during activity test. The catalyst powder in the reactor was sustained by quartz wool with the same height for each experiment. Before the introduction of gases to the reactor, preheated H<sub>2</sub>O (5%) was continuously injected by a syringe pump at 120 °C to the mixing line. The total flow rate of the inlet stream was 200 ml/min at a gas hourly space velocity (GHSV) of 120,000 h<sup>–1</sup>. A K-type thermocouple was located on the top of the catalyst bed to measure the temperature of the reactor.

The scheme of NO adsorption/desorption is shown in Fig. S1. To remove impurities, the catalyst was pre-treated under an oxidative condition with 5% CO<sub>2</sub> and 5% H<sub>2</sub>O at 500 °C for 30 min before the activity test. For NO adsorption, 100 ppm NO was introduced for 100 s at 80 °C with CO<sub>2</sub> (5%), H<sub>2</sub>O (5%), and O<sub>2</sub> (9.5%) in N<sub>2</sub> to simulate cold-start NO<sub>x</sub> emission. After finishing the NO adsorption procedure, the catalyst was heated with CO<sub>2</sub> (5%), H<sub>2</sub>O (5%), and O<sub>2</sub> (9.5%) in N<sub>2</sub> in a range of 80–500 °C at a rate of 10 °C/min

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