



Time resolved operando spectroscopic study of the origin of phosphorus induced chemical aging of model three-way catalysts Pd/Al₂O₃

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ABSTRACT

The origin of phosphorus (P) induced chemical aging of model three-way catalyst Pd/Al₂O₃ is studied by transient CO and NO pulses. The fresh catalyst Pd/Al/F (calcined at 500 °C for 4 h) is subjected to thermal treatment in air at 700 °C for 5 h with (7.5P/Pd/Al) and without (Pd/Al/700) P poison. The catalyst surface and reaction dynamics during CO/NO pulses at 300 °C are captured in a single shot by time resolved operando energy dispersive-extended X-ray absorption fine structure (ED-EXAFS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and mass spectrometry (MS). The results reveal the occurrence of Pd redox cycle during the temporal analysis of the catalysts by CO/NO pulses. However a secondary process, presumably PdC_x formation, is hampered under these experimental conditions on the P aged catalyst 7.5P/Pd/Al. Additionally on 7.5P/Pd/Al, reactions involving Pd redox cycle are not as efficient as on Pd/Al/700 as evident from ED-EXAFS, MS and DRIFTS data. Furthermore, DRIFTS data show a larger population of isocyanate species (reflected by bands at 2180, 2228 and 2250 cm⁻¹) on Pd/Al/700 than on 7.5P/Pd/Al that exhibits only a single band at 2260 cm⁻¹. The missing low frequency bands at 2180 and 2228 cm⁻¹ are attributed to the clogging of the surface Pd sites by P and formation of AlPO₄ species at the expense of a fraction of surface Al³⁺ sites of the support, respectively. Consequently, the production of CO₂ (and also N₂) is higher on Pd/Al/700 than on 7.5P/Pd/Al as evident by MS data confirming that the chemical aging caused by P is more detrimental than thermal aging for three-way catalytic efficiency of the model Pd/Al₂O₃ as reported in [S.K. Matam, et al., Catal. Today 184 (2012) 237].

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1. Introduction

Three-way catalytic (TWC) converters are ideal for controlling exhaust emissions from stoichiometric combustion engines. Though TWC have proven to be efficient for such applications, they tend to deactivate rapidly due to thermal and chemical aging, especially on natural gas fueled vehicles than on gasoline powered ones [1–3]. Thermal aging is due to high temperatures and chemical aging is a result of contaminants such as phosphorus (P) that is originating from engine oil additives [2–4]. In general it appears that the effect of P on noble metals is not completely understood and, there is no consensus on which aging process (thermal or chemical) causes the most damage to TWC efficiency [1–7]. For example, studies on Pd/Rh/CeZrO₂/Al₂O₃ and Pt/Rh/CeZrO₂/Al₂O₃ aged on CNG fueled vehicles conclude that chemical aging is not as

important as thermal aging and P accumulates only on the surface of the catalyst without poisoning noble metals [1,5]. In contrast, we have recently shown that the chemical aging by P can be more detrimental for catalytic efficiency than thermal aging of a model Pd/Al₂O₃ TWC [3]. Thermal aging in air at 700 °C for 5 h led to merely physical changes to the catalyst such as decreased surface area, pore volume and Pd dispersion, while chemical aging with P caused severe physical and chemical modifications to the catalyst such as clogging of support alumina pores and fouling of Pd nanoparticles, and modifying the nature of the support Al₂O₃ by formation of aluminum phosphate. The latter alters the nature of the support, chemical environment around Pd nanoparticles and the interactions between the Pd nanoparticles and support to some degree [3].

Therefore, it is of interest to investigate the influence of P on the catalyst structure and surface reaction dynamics during the reaction to gain subtle information on the structure, reaction and activity relationships at a sub millisecond range. To this end, temporal analysis of the catalysts (thermally and chemically aged model TWC Pd/Al₂O₃) by CO and NO pulses is performed by

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time resolved operando ED-EXAFS, DRIFTS and mass spectrometry, simultaneously. The time resolved spectra are subjected to phase sensitive detection (PSD) in order to extract minute details.

2. Materials and methods

2.1. Materials

Pd/Al₂O₃ catalysts (provided by Umicore AG, Germany) studied in this work are reported elsewhere [3]. Briefly, the fresh Pd/Al₂O₃ catalyst (1.6 wt% Pd; BET = 141 m² g⁻¹) was calcined in air at 500 °C for 4 h (denoted as Pd/Al/F). To study the influence of phosphorus (P) on the three-way catalytic performance, the fresh catalyst was impregnated with P (7.5 wt%) from the aqueous (NH₄)₃PO₄ solution and dried at 120 °C over-night followed by calcination in air at 700 °C for 5 h (labeled as 7.5P/Pd/Al; BET = 77 m² g⁻¹). This process is called chemical aging. For comparative purposes, the fresh catalyst was also thermally aged (without P) in air at 700 °C for 5 h (Pd/Al/700; BET = 140 m² g⁻¹). The dispersion (%) of Pd in the catalysts was determined to be 12.7, 11.5 and 3.3 for the fresh, thermally aged and chemically aged catalysts, respectively.

2.2. Methods

2.2.1. Diffuse reflectance infrared spectroscopy (DRIFTS)

Hydroxyl stretching vibrations (ν_{OH}) of the support alumina were probed using a Bruker Vector 22 instrument equipped with a diffuse reflectance accessory (Minidiff, Specac) and a liquid nitrogen cooled MCT detector. Spectra were recorded at room temperature with a resolution of 4 cm⁻¹ and an average of 100 scans.

2.2.2. Solid state ²⁷Al MAS NMR

Single pulse NMR experiments were performed (at 104.26 MHz) at room temperature on a BrukerAvance 400 NMR spectrometer using a 2.5 mm CP/MAS probe (at spinning rates of 25,000 Hz). The ²⁷Al chemical shifts were referenced to an external sample of aluminum nitrate solution (1.1 M).

2.2.3. Operando spectroscopy

The detailed description of the experimental setup and procedure used in this study was reported in ref. [8]. Briefly, time resolved energy dispersive (ED) extended X-ray absorption fine structure (EXAFS), diffuse reflectance infrared spectroscopy (DRIFTS) and mass spectrometry (MS) data were simultaneously collected at beamline ID24 at the European Synchrotron Radiation Facility (ESRF), Grenoble. ED-EXAFS spectra were obtained at the Pd K edge (24.35 keV) using a Si(3 1 1) polychromator crystal in Bragg configuration and FReLoN CCD camera. Pd metal foil was used to calibrate the ED-EXAFS. DRIFTS spectra were collected on a Bruker Optics IFS 66 equipped with a liquid nitrogen cooled MCT detector. The catalyst particles (sieve fraction of 70–90 μm) of around 100 mg were loaded in to a spectroscopic diffuse reflectance cell [9]. The cell inlet was connected to the gas feeding system (comprising of mass flow controllers, Bronkhorst) through gas actuated four port switching valves and the outlet of the cell was connected to MS (Omnistar, Pfeiffer) for online gas analysis. The mass fraction (m/z) of 2 (H₂), 4 (He), 18 (H₂O), 22 (CO₂), 28 (CO and N₂), 30 (NO), 32 (O₂) and 44 (CO₂ and N₂O) was monitored during the temporal analysis (so called concentration modulation experiments) of the catalysts by NO (5 vol.% in He) and CO (5 vol.% in He) pulses. A periodic switch between the two gas pulses of NO and CO was set for the same time of 66 s. A complete modulation period (T) is defined as the time required to conclude both NO and CO switches consecutively, which is 132 s. During this period, 504 ED-EXAFS spectra (at a time resolution of 0.26 s per spectrum) and 90 DRIFTS spectra (by co-adding 3 interferograms at 2 cm⁻¹ resolution and 0.3

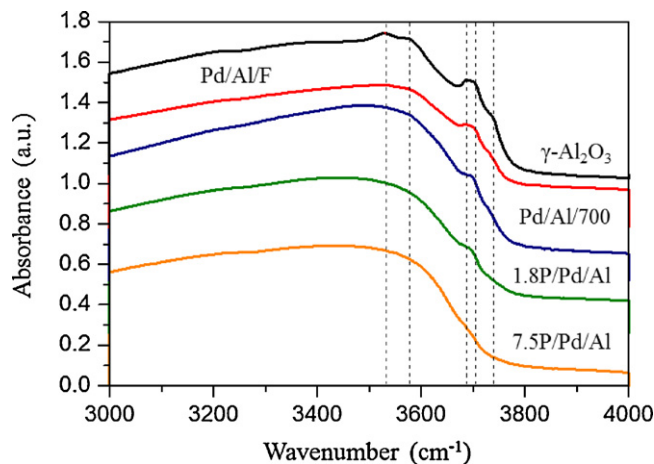


Fig. 1. Infrared spectra of the catalysts measured at room temperature. For comparative purposes, pristine alumina support and 1.8P/Pd/Al with lower P content are also included. The latter catalyst is prepared and treated in the same way as 7.5P/Pd/Al (Section 2.1).

time resolution) were collected. Each experiment consists of several modulation periods (x) yielding total number of 504 ED-EXAFS or 90 DRIFTS spectra times (x) periods. To improve the signal to noise ratio, spectra of a modulation period were averaged with the corresponding spectra of remaining periods that gives rise to a set of averaged 504 time-resolved ED-EXAFS and 90 DRIFTS spectra. The spectra were treated with a phase sensitive detection (PSD) method to remove the contribution of static signals and to extract subtle details [8]. Prior to the modulation experiment, the catalyst was pretreated in 5 vol.% H₂ in He (80 ml/min) at 300 °C for 30 min followed by flushing with He until the MS signals were stable. Then, the modulation experiment was started at this temperature by switching consecutively NO and CO for a given number of modulation periods.

3. Results and discussion

3.1. DRIFTS

The impact of P and Pd on the surface hydroxyl groups of the support alumina is studied to assess their adsorption sites on the catalyst surface [10–12]. The hydroxyl stretching bands of the pristine support alumina (Al) and slightly P poisoned catalyst 1.8P/Pd/Al are compared with the fresh, thermally aged and heavily P poisoned catalysts in Fig. 1. It can be readily seen that pristine Al exhibits bands at 3527, 3575, 3690, 3701 and 3740 cm⁻¹. Although the intensity of the bands diminishes, they are still present for the fresh Pd/Al/F and thermally aged Pd/Al/700 catalysts. The diminished intensity of the bands may suggest that Pd anchors to these hydroxyl groups. Interestingly, all these bands (except a weak band at around 3700 cm⁻¹ on 1.8P/Pd/Al) roughly completely disappear on P aged catalysts, especially on 7.5P/Pd/Al indicating that P consumes most of the surface hydroxyl groups and the catalyst surface in the form of phosphate groups, in excellent agreement with ³¹P NMR results that show formation of AlPO₄ like species in the P aged catalysts [3].

3.2. Solid state ²⁷Al NMR

Solid state ²⁷Al NMR spectra of reference samples aluminum phosphate, pristine γ -Al₂O₃ support and P aged catalyst 7.5P/Pd/Al are shown in Fig. 2. Reference aluminum phosphate (AlPO₄) exhibits a peak at 39.33 ppm which is typically assigned to AlPO₄ [3,13]. The spectrum of the reference Al support shows well

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