The origin of phosphorus induced chemical aging of model three-way catalyst Pd/Al₂O₃ studied by operando XAS/IR/MS

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Introduction

Although three-way catalysts (TWC) are efficient to control exhaust emissions from stoichiometric engines, they tend to be deactivated due to thermal (high temperature excursions) and chemical aging (namely by phosphorus (P) originating from engine oil additives) [1,2]. Especially, new fuel concepts like compressed natural gas (CNG) consisting of mainly methane and new EURO VI legislations post greater challenges and impart more significance to the issue than ever before. However, the precise nature of deactivation mechanism is not completely understood and is highly controversial [1-4]. Our initial studies indicate that the chemical aging caused by P is more detrimental than thermal aging for TWC efficiency [2]. However, it was not clear how P decreases the TWC efficiency. Therefore, the objective of this work is to understand the origin of P induced deactivation mechanism by following the catalyst bulk structure and surface reaction dynamics during the reaction between CO and NO at sub-millisecond range by XAS/IR/MS.

Materials and Methods

Model three-way catalyst powder (1.6 wt%) Pd/Al₂O₃ was provided by Umicore. The catalyst was calcined in air at 500°C for 5 h (Pd/Al/F). The fresh catalyst was impregnated with P (1.8 or 7.5 wt%) and then dried at 110°C for 4 h followed by calcination at 700°C for 5 h, referred to as chemical aging (Pd/Al/C). For comparative purposes, the fresh catalyst (without P) was also subjected to calcination at 700°C for 5 h to study the effect of temperature on the catalytic properties, denoted as thermal aging (Pd/Al/T).

Operando XAS/IR/mass spectroscopy data were collected at beam line ID24 of ESRF. Temporal analysis of catalysts was conducted by switching between NO and CO at 300°C over a pre-reduced catalyst surface. Spectra were obtained at the Pd K edge (24.35 keV).

Results and Discussion

The physisorption data show that both the surface area and pore volume decrease considerably for P aged catalysts as compared to the fresh and thermally aged catalysts, indicating the presence of P on the surface and within the pores of the support. Solid state Al²⁷ and P³¹ MAS NMR spectra suggest the formation (even at 1.8 wt% P) of AlPO₄ like species in the Pd/Al/C [2]. CO-chemisorption data show that dispersion of Pd in the catalysts decreases from the fresh catalyst to the thermally and chemically aged catalysts. It appears that with increasing P content from 1.8 to 7.5 wt%, Pd dispersion further decreases. However, the dispersion data should be treated with caution because P can foul the Pd particle surface which in turn reduces the number of surface Pd sites for CO adsorption, and hence decreases Pd dispersion.

The P species mitigate the oxidation and reduction efficiency of the catalysts as evident from the activity data obtained under simulated λ = 1 conditions [2]. The operando XAS/IR/MS results reveal the occurrence of Pd redox cycle during the temporal analysis of the catalysts by CO/NO pulses. Besides this, XAS results suggest PdCx formation on the catalysts, however this is hampered under these experimental conditions on Pd/Al/C. These observations are reflected on the surface reaction dynamics which were followed by DRIFTS (Fig. 1).

Figure 1. Selected (from 90 spectra) time resolved DRIFTS spectra obtained during the temporal analysis of the catalysts.

DRIFTS data show a larger population of isocyanate species (reflected by bands at 2180, 2228 and 2250 cm⁻¹) on Pd/Al/T than on Pd/Al/C that exhibits only a single band at 2260 cm⁻¹ (Fig. 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⁺ oxide sites of the support, respectively. Consequently, the production of CO₂ (and also N₂) is higher on Pd/Al/T than on Pd/Al/C as evident by MS data confirming that the chemical aging caused by P is more detrimental than thermal aging as reported in [2].

Significance

The origin of phosphorous induced chemical aging of TWC is discovered.

References