

Investigation of NO_x Reduction over Pd-Based FCC Additives Using *In-situ* FTIR

Sundaram Krishnamoorthy,^{*1} Michael S. Ziebarth,¹ George Yaluris,¹ Terry G. Roberie,¹
Oleg S. Alexeev,² and Michael D. Amiridis²

¹ W.R. Grace & Co.- Conn., 7500 Grace Drive, Columbia, MD, 21044 (USA)

² Department of Chemical Engineering,
University of South Carolina, Columbia, SC 29208(USA)

^{*}Sundaram.Krishnamoorthy@grace.com

Introduction

The Fluid Catalytic Cracking (FCC) process, which is the primary hydrocarbon conversion/molecular reduction unit in the modern petroleum refinery, is also responsible for approximately 50% of the refinery NO_x emissions. Extensive pilot plant experiments using the Davison Circulating Riser have shown that about 35-45% of the nitrogen in the gas oil feed ends up in the coke formed during the cracking process and about 10% of this nitrogen exits the FCC regenerator in the form of NO_x [1]. Pt-based catalysts, commonly used as combustion promoters in FCC regenerators to oxidize CO to CO₂, also significantly contribute to NO_x formation. Among several approaches currently being investigated by the industry for the reduction of NO_x in FCC units, the *in-situ* additive approach, which is based on the use of non-Pt noble metal-based catalysts and/or transition metal-based catalysts, has proven to be the most efficient and cost-effective. Previous work carried out at W.R. Grace has indicated that one of the key catalytic pathways for NO_x reduction in the FCC regenerator, by noble metal additives, is the reduction of NO with species such as CO and hydrocarbons that are present in the FCC regenerator (at least during the initial stages of coke combustion) [2]. The number of other literature reports outlining the NO_x reduction chemistry under the FCC regenerator conditions is very limited [3]. In this work, we present our efforts to understand the chemistry of NO_x reduction by CO and C₃H₆ over a commercial Pd⁰/Ce^{III}/Na⁺/?-Al₂O₃ catalyst using *in-situ* FTIR spectroscopy, under conditions approaching those existing in FCC units, with the desire to better understand the role of each catalyst component in the NO_x reduction process. EXAFS was used to characterize the form of the Pd in the catalyst.

Materials and Methods

Ce^{III}/Na⁺/?-Al₂O₃ was prepared as a slurry containing proprietary quantities of each component and then spray dried. Milling of the slurry was carried out in a 4L media mill. The spray-dried material was calcined for 2 hours at 538°C. The palladium containing samples were prepared by incipient wetness impregnation of the respective support with an aqueous solution of palladium nitrate. The amount of the palladium precursor was chosen to yield samples containing approximately 0.11 wt% of Pd. The samples were then dried in air at 110°C for 24 h and calcined for 2 hours at 538°C. FTIR spectra were collected with a Nicolet Nexus 470 spectrometer equipped with a MCT-B detector, cooled by liquid nitrogen. EXAFS spectra were collected at beamline 2-3 at SSRL.

Results and Discussion

EXAFS characterization of the Pd⁰/Ce^{III}/Na⁺/?-Al₂O₃ catalyst revealed that in freshly prepared samples Pd is present in the form of highly dispersed PdO species. Reduction

with H₂ at 500°C leads to the formation of small Pd clusters incorporating only a few metal atoms, as evidenced by the presence of only the first-shell Pd⁰/Pd contributions with an average coordination number of 4.9 at a bonding distance of 2.76 Å.

The FTIR data shows that all components of the Pd⁰/Ce^{III}/Na⁺/?-Al₂O₃ material (i.e., Pd⁰, Ce^{III}, and Na⁺) interact with NO at elevated temperatures and promote the formation of nitrate/nitrite species to various degrees, essentially "trapping" NO_x species on the catalyst surface. The Na⁺ species show the most pronounced effect among all supported components due to the formation of sodium nitrates with a characteristic IR band at approximately 1372 cm⁻¹. The formation of nitrates is accelerated in the presence of oxygen and Pd. Hydroxyls from the support also actively participate in the formation of HNO_x type compounds with characteristic stretching vibrations in the 3500-3572 cm⁻¹ region.

All components of the Pd⁰/Ce^{III}/Na⁺/?-Al₂O₃ catalyst are capable of interacting with CO in the 400-600 °C temperature range. Such interactions led to the formation of carboxylates and carbonates, the concentration of which was higher in samples containing Pd, indicating that palladium catalyzes their formation. The Pd⁰ cations initially present in these samples undergo partial reduction to form metallic Pd in the presence of CO even at room temperature. More complete reduction of Pd along with some aggregation was observed after exposure to CO at elevated temperatures.

Exposure of the sample to the NO/CO mixture in the 400-600 °C temperature range led to the formation of an isocyanate (NCO) species. Both Na⁺ and Ce^{III} are capable of promoting the formation of such NCO species. However, surface isocyanate species were formed with substantially higher rates in the presence of palladium. The formation of isocyanates strongly correlates with changes observed in the ν_{OH} region, indicating that hydroxyls actively participate in the reaction and are capable of protonating the NCO species, which are stabilized on the support in such a form. When the Pd⁰/Ce^{III}/Na⁺/?-Al₂O₃ material was reduced prior to exposure to the NO/CO mixture, the NCO species were also formed but at a lower rate. Similarly, when the NO/C₃H₆ mixture was used, the isocyanates were also formed at a lower rate. It appears that the reaction between NO and C₃H₆ takes place through the initial oxidation of C₃H₆ to CO on the catalyst surface, which is followed by the reaction of NO with CO. The kinetic data show that when substoichiometric amounts of oxygen were present in the feed, NH₃ can also be formed. The FTIR and kinetic data indicate that regardless of their origin, the isocyanate species formed on the surface of the Pd⁰/Ce^{III}/Na⁺/?-Al₂O₃ catalyst react readily with either O₂ or NO to form CO₂ and N₂ and are likely surface intermediates in the CO+NO reaction over these catalysts.

This work has led to a working understanding of the mechanism of NO_x reduction over commercial additives in FCC regenerators. Such an understanding can assist in the further improvement of the catalysts used commercially, with substantial benefits to this industrial sector and the environment.

References

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