Tracking Phase Transitions on Palladium Catalytic Bed Using *In Situ* Full-Field Hyperspectral XAS Imaging

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Resumo/Abstract

RESUMO – Catalisadores compostos por nanopartículas exibem transformações altamente dinâmicas durante a operação. No entanto, estudos sob condições reais de trabalho, em escala de reator, ainda são limitados. O imageamento hiperespectral por espectroscopia de absorção de raios X em campo total está surgindo como uma técnica promissora para esse tipo de análise. Neste estudo, aplicamos essa abordagem para monitorar as transições de fase em catalisadores de Pd durante o tratamento sob diferentes concentrações de H_2, com o objetivo de entender a influência espacial do suporte na dinâmica das transformações.
Palavras-chave: Espectroscopia operando, Interação metal-suporte, Leito catalítico.

ABSTRACT – Catalysts composed of nanoparticles exhibit highly dynamic transformations during operation. However, studies under working conditions at the reactor scale remain limited. Full-field hyperspectral X-ray absorption spectroscopy (XAS) imaging is a promising technique for this type of analysis. In this study, we applied it to monitor phase transitions in Pd catalysts during treatment under varying H_2 concentrations, aiming to understand the spatial influence of the support on the transformation dynamics.
Keywords: hyperspectral XAS imaging, Metal-support interaction, Catalytic bed.

Introduction

Catalysts can undergo spatial changes under working conditions, which may impact their performance by inducing reactant gradients, pressure variations, and phase transitions (1). To better understand such modifications at the reactor scale under *in situ/operando* conditions, full-field hyperspectral X-ray absorption spectroscopy (XAS) imaging has emerged as a promising synchrotron technique, enabling the real-time monitoring of dynamic transformations in the catalytic bed with high spatial and temporal resolution (2, 3).

Palladium nanoparticles (PdNP) are widely recognized as highly active catalysts for hydrogenation reactions and hydrogen storage, owing to their remarkable hydrogen absorption capacity (4). In this work, we investigate the impacts of the support composition (titania and alumina) on the spatial transformations of PdNP during atmospheric gas changes under varying hydrogen concentrations.

Experimental

The catalysts 5 wt% Pd/TiO_2 (Pd/Ti) and 5 wt% Pd/Al_2O_3 (Pd/Al) were synthesized using the wetness impregnation method (5). Full-field hyperspectral XAS imaging measurements at the Pd K-edge were carried out on the ROCK beamline at the synchrotron SOLEIL (6), following gas changes from air to pure He, and then to varying concentrations of H_2 in He, ranging from 0.04% to 5%. These measurements resulted in hyperspectral cubes, each composed of 580 energy points stacked into a single image acquired every ~11s, where every pixel contains a full XAS spectrum. Data processing was performed using a Jupyter Notebook tool provided by the beamline. The data analysis, by multivariate curve resolution with alternating least squares (MCR-ALS) minimization was conducted in MATLAB using the MCR_Toolbox 2 (7). The results were used to generate speciation maps derived from MCR-ALS fitting of the hyperspectral images of the entire catalytic bed, where each pixel corresponds to an individual XAS spectrum.

Results and discussions

The initial state of the pristine catalyst was identified as PdO, based on a resonance peak in the rising edge region at 24 365 eV, which is characteristic of this phase (Figure 1A). The speciation maps of both samples (Figure 1B,C) indicated a high degree of homogeneity in this initial state.

Interestingly, after introducing a low concentration of H_2 (0.08%) in He, we were able to track two resonance peaks at 24 385 and 24 425 eV in the XANES spectra (Figure 1D), characteristic of metallic Pd species (8). The Pd/Ti sample exhibited a rapid transition from the oxidized to the metallic state, starting at the cube 19 and reaching 90% of the metallic species after approximately 35 hyperspectral cubes at 0.08% H_2. In contrast, the Pd/Al sample (Figure 1E), we

observed a slower conversion compared to the titania sample, which started at the hyperspectral cube 30 and only reached 75% of metallic species after 70 hyperspectral cubes at 0.08% H_2.

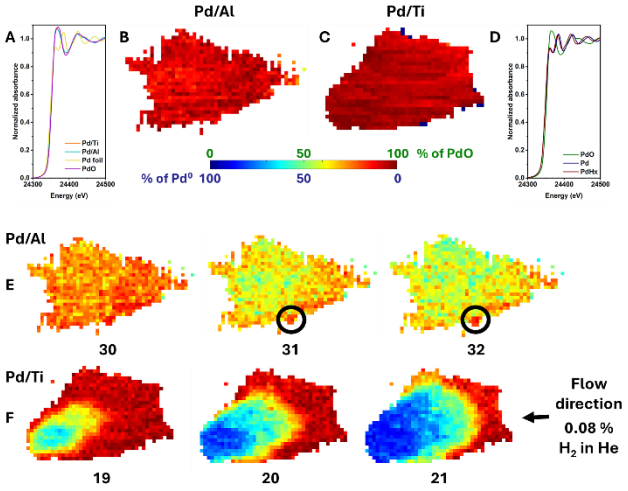

Figure 1. (A) XANES spectra obtained from the average of all pixels in the hyperspectral XAS image for the pristine catalyst and references. (B, C) Speciation maps derived from MCR-ALS minimization of the hyperspectral XAS dataset collected during exposure to He atmosphere for the Pd/Al and Pd/Ti samples, respectively. (D) XANES spectra of the pure species extracted through MCR-ALS of the hyperspectral XAS imaging for the complete dataset. (E, F) Speciation maps derived from MCR-ALS minimization of the hyperspectral XAS imaging dataset of the catalytic bed during exposure to 0.08% H_2 in He, for the Pd/Al and Pd/Ti samples, respectively. The black arrow indicates the gas flow direction, and the black circles highlight regions of heterogeneity. The color gradients represent the spatial distribution of the identified phases, and the numbers indicate the percentage of each phase, as shown in the scale bar.

The speciation maps highlight the spatial dynamics during the phase transition. For the Pd/Ti sample, we observed the process beginning with a homogeneous wavefront propagating from the outlet toward the inlet of the gas flow (Figure 1F). However, the region near the gas inlet remained in a highly oxidic state for approximately 14 additional cubes before it was fully reduced to metallic Pd. Remarkably, the speciation maps of the Pd/Al sample revealed completely different spatial behavior. During the transition from the oxidic to the metallic state, the entire catalytic bed of this sample underwent a homogeneous transformation, without the formation of a wavefront as observed in the Pd/Ti sample (Figure 1E).

Despite the initial homogeneity of the sample, localized heterogeneities were identified in the Pd/Al sample (black circles in Figure 1E) through hyperspectral XAS imaging analysis. A few pixels exhibited greater stability, with PdO remaining at high concentration throughout the entire exposure to 0.08% H_2. Upon increasing the H_2 concentration in He from 0.17% to 0.83%, we identified the formation of Pd hydrides (PdH_x). This transformation was evidenced by a shift to lower energies in the XANES spectra, with the resonance peaks moving to 24 380 and 24 420 eV (Figure 1D).

Conclusions

Full-field hyperspectral XAS imaging clearly revealed the spatial dynamics of phase transformations in Pd catalysts during changes in H_2 concentration, demonstrating the significant advantage of this technique for reactor-scale analysis under working conditions.

This study provided valuable insights into the influence of the support on the kinetics of phase transitions, the resulting variations in spatial dynamics across the catalytic bed, and the presence of localized heterogeneities.

Acknowledgments

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