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Shedding Light on the Deactivation Pathways of a CrO_x/Al_2O_3 Dehydrogenation Catalyst with Emission Spectroscopy

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Introduction

Time on stream (TOS) performance is the primary measure of deactivation in catalyst systems and there are various phenomena that give rise to activity loss, including structural, chemical, thermal and mechanical mechanisms. One of the primary routes for deactivation in the commercial Catofin process, used for paraffin dehydrogenation, is attributed to interfacial CrO_x/Al_2O_3 transformation into the solid solution of α-(Al, Cr)$_2$O$_3$.[1] Commonly available spectroscopic techniques such as diffuse reflectance Raman and UV-Vis indicate deactivation based on the loss of specific Cr_2O_3 spectral features. Alternatively, photoluminescence (emission) spectroscopy is less widely encountered and typically requires specialized equipment. Herein, we describe a customized emission spectroscopy experiment with exceptional signal-to-noise detection and demonstrate how this niche method can be used to detect well-defined spectral signatures of deactivation *onset and acceleration*, specifically the direct measurement of Cr^{3+} diffusion from the chromia metal oxide into the alumina support.

Materials and Methods

Model CrO_x/Al_2O_3 catalysts with different TOS were prepared by Clariant Corporation as described previously.[1,2] The TOS performance, or loss in PDH activity relative to the fresh catalyst, was also determined through artificial aging tests. UV-VIS diffuse reflectance spectroscopy was collected with a commercial fiberoptic system on the powdered catalysts. Both the Raman and emission experiments use a customized spectroscopy probe designed for 532 nm laser excitation. The Raman signals are recorded with a spectrograph/CCD camera allowing for simultaneous acquisition of all Raman signals while emission experiments are collected on a monochromator/PMT for high signal amplification and access to a wide range of wavelengths.

Results and Discussion

Raman spectroscopy collected on CrO_x/Al_2O_3 at early TOS (Figure 1 left column) reveals one prominent Raman mode at 548 cm^{-1} resulting from the crystalline α-Cr_2O_3 A_{g1} metal-oxygen vibration. As the catalyst spends more TOS and becomes deactivated the α-Cr_2O_3 A_{g1} mode loses intensity. By >80% TOS the vibration is no longer observed; the concentration of α-Cr_2O_3 in the catalyst is below the detection limit of the Raman experiment.

UV-VIS diffuse reflectance spectroscopy (Figure 1 middle column) provides insight into the α-Cr_2O_3 loss phenomena. Four different electronic transitions are observed at all TOS. Bands at 270 and 360 nm result from ligand-to-metal charge transfer from oxygen to Cr^{6+} ions present in the chromia catalyst. The bands at 455 and 595 nm are d-to-d transitions of Cr^{3+} ions sitting in an octahedral field of oxygen (e.g., in the case of α-Cr_2O_3). The Cr^{3+} transitions blue shift and lose intensity with TOS. However, there is still significant amplitude in these transitions at >80% TOS even though the Raman results indicate the majority of α-Cr_2O_3 has been lost. The reflection spectrum of ruby, Al_2O_3 where some of the octahedral Al sites have been replaced by Cr^{3+}, is provided as the gray trace. As the CrO_x/Al_2O_3 catalyst spends increasing TOS the center wavelength of the Cr^{3+} transitions shift from that of chromia to that of ruby, evidence that the chromium ions are diffusing from the catalyst into the support.

The emission spectra of CrO_x/Al_2O_3 at early TOS (Figure 1 right column) show a broad signal centered at 785 nm resulting from α-Cr_2O_3 emission. By 7% TOS, a spectral feature appears in the emission at 694 nm, resulting from the $^2E \rightarrow {}^4A_2$ transition of octahedral Cr^{3+} sitting in Al_2O_3, and is well defined by 19% TOS. Increasing TOS results in loss of the 785 nm α-Cr_2O_3 emission and further growth of the 694 nm ruby emission as Cr^{3+} diffuses from the chromia into the support. By >80% TOS the $^2E \rightarrow {}^4A_2$ emission feature is resolved into a doublet, an exemplary feature of ruby emission.

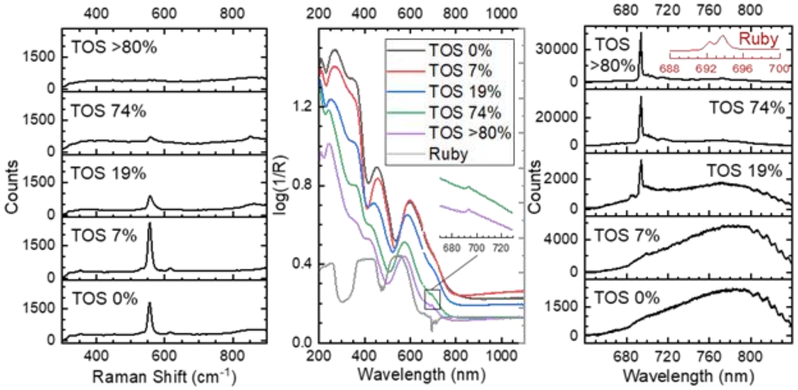

Figure 1. Spectral evolution of a CrO_x/Al_2O_3 catalyst with TOS. *Left)* Raman spectroscopy. *Middle)* UV-VIS diffuse reflectance spectroscopy plotted as pseudo-absorbance. The inset highlights a new transition observed at 694 nm in the 74% and >80% TOS spectra. *Right)* Emission spectroscopy. The red inset shows the emission spectrum of a synthetic ruby.

Significance

In comparison to traditional methods that focus on signal loss and disappearance of the Cr_2O_3 spectral features, this work presents a niche approach to direct detection of the onset and acceleration of Cr^{3+} solid state diffusion; a critical physical deactivation pathway that limits the lifetime of the CrO_x/Al_2O_3 propane dehydrogenation catalyst used in the commercial Catofin process.

References

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