

Reduction of surface nitrates by hydrogen as a key step in H₂ assisted HC-SCR over Ag-Al₂O₃

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Introduction

The Ag-Al₂O₃ system for selective catalytic reduction of NO_x with hydrocarbons (HC-SCR) has been intensely studied during the last two decades. Using long-chain hydrocarbons as reductant [1], especially with the addition of small amounts of hydrogen [2] has been shown to move the active window towards lower temperatures, making the system very interesting for real applications. Many suggestions have been made regarding the promotion of NO_x reduction by hydrogen during HC-SCR [3]. In this work flow reactor studies and kinetic modeling [4] has been combined with results from *in-situ* DRIFTS spectroscopy, to elucidate a key feature of this hydrogen effect.

Materials and Methods

The catalyst used in the flow reactor studies consisted of 3.5 wt% Ag on Al₂O₃, prepared by a single step sol-gel method and washcoated onto a cordierite monolith. The monolith was placed in a quartz glass tube in a flow reactor operated with a GHSV of 30000 h⁻¹. The feed gas concentrations of NO, O₂, octane, H₂ and the feed temperature were varied systematically between high and low levels of 315 to 815 ppm, 2 to 7%, 150 to 250 ppm, 0.1 to 1% and 250 to 350°C, respectively. Experiments with different feed conditions were carried out in series with switching between reactant feed concentrations to allow transient responses to be observed.

A kinetic model was formulated. The model accounted for adsorption of reactants, desorption of products and surface reactions. Nitrate species poisoning the catalyst surface was a key feature of the kinetic model and the role of hydrogen was to reduce surface nitrate species to nitrites. Note that several causes for the promotion of NO_x reduction by hydrogen addition have been proposed, however in this model the included step was the reduction of nitrate surface poisons [3].

To further elucidate the role of hydrogen, *in-situ* DRIFT (diffuse reflection infrared Fourier transform) spectroscopy measurements were carried out using a BioRad FTS 6000 spectrometer. The powder samples were exposed to 1000 ppm NO and 8% O₂ (in Ar), and transient experiments with addition/removal of 1000 ppm H₂ were performed at 250°C. The evolution of surface species during the transient experiments was followed by DRIFTS for 15 min (2 scans/min at a resolution of 1 cm⁻¹).

Results and Discussion

Upon introduction of NO and O₂, the DRIFT spectra show peaks at 1608, 1560 (with a shoulder at 1580) and 1540 cm⁻¹, which can be attributed to nitrate species, and 1298 cm⁻¹, that likely are due to nitrite species. When H₂ is added to the feed gas the peaks at 1610,

1560 and 1540 cm⁻¹ decrease, while the other peaks are unchanged or increase slightly. Thus, it is likely that one of the functions of H₂ is to remove nitrate species from the catalyst surface.

The formation of stable nitrates, poisoning the catalytic surface, subsequently reduced by hydrogen, is a key feature of the model. Changes due to variations in the feed are well reproduced in general, especially the poisoning effects of higher NO feed concentrations, presumably due to nitrate formation, and the strong promotion of NO_x reduction by introduction of hydrogen.

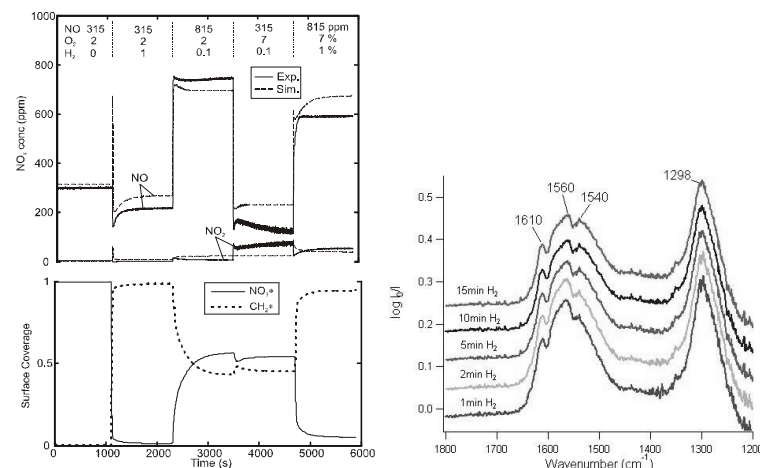


Figure 1. Left: Experimental and simulation transient results from varying NO, O₂ and H₂ feed concentrations. Constant feed conditions: 350°C and 250 ppm n-octane. Right: DRIFT spectra of NO_x surface species in the presence of hydrogen.

Significance

Theoretical and experimental elucidation of one of the key features of the hydrogen effect in H₂ assisted HC-SCR, the reduction of stable surface nitrates by hydrogen, is presented.

References

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