

## Mechanisms of hydrocarbon poisoning of a urea SCR catalyst

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### Introduction

Control of NO<sub>x</sub> emissions from diesel or lean burn gasoline engines is a technical barrier that must be overcome if the fuel efficiency advantages of these engines are to be fully realized. Urea Selective Catalytic Reduction (SCR) catalysts are a promising solution for minimizing NO<sub>x</sub> emissions while maintaining high overall vehicle efficiency. Aftertreatment systems based on these catalysts are starting to see commercial application, but a few unresolved issues could prevent urea SCR systems from meeting increasingly stringent emissions regulations and customer durability requirements. Catalyst poisoning by residual hydrocarbons in engine exhaust [1] is one of these unresolved issues. The goal of this study is to use flow reactor experiments combined with surface spectroscopy to develop a mechanistic understanding of how hydrocarbons interact with a commercial-intent urea SCR catalyst.

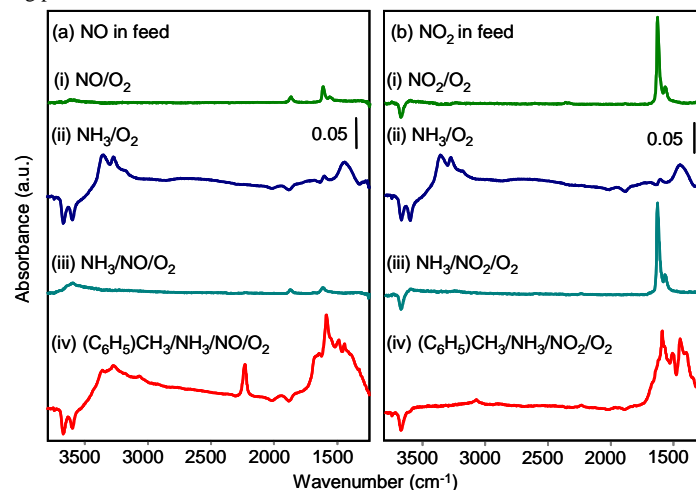
### Materials and Methods

The experiments were performed on an iron-zeolite catalyst obtained from Umicore Autocat USA. Flow reactor experiments were conducted on a monolith core sample to quantify hydrocarbon (HC) adsorption capacity, rates of HC oxidation and HC SCR reactions, and the impact of various HCs on NH<sub>3</sub> SCR NO<sub>x</sub> conversion. An in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) apparatus, described fully in [2], was used to identify surface adsorbates and reaction intermediates under conditions similar to those used in the flow reactor experiments. A small piece of the Umicore Fe zeolite SCR catalyst was ground to a powder, placed on a 10mm x 10 mm aluminum substrate, and loaded into the sample chamber of the DRIFTS reactor. Gases were flowed continuously over the sample at a flow rate of 100 cm<sup>3</sup>/min (STP).

### Results and Discussion

Figure 1 shows an example of the results obtained in this investigation. It contains a series of DRIFT spectra obtained with the Fe zeolite SCR catalyst exposed to various mixtures of O<sub>2</sub>, NH<sub>3</sub>, NO, NO<sub>2</sub>, and toluene. Spectrum a-i was obtained after exposure to 350ppm NO+14% O<sub>2</sub> at 200°C. The catalyst surface was cleaned (14% O<sub>2</sub>, 500°C, 30 min) and the remaining three spectra in panel a (ii-iv) were collected sequentially, all at 200°C. First, the catalyst was saturated with 140 ppm NH<sub>3</sub> + 14% O<sub>2</sub>, and spectrum a-ii was collected. The prominent features above 3000 cm<sup>-1</sup> (on the left side of the spectrum) are of particular interest. The positive peaks can be attributed to adsorbed NH<sub>3</sub> species; the negative peaks are due to displacement of hydroxyl groups by the adsorbed NH<sub>3</sub>. Upon addition of 350 ppm NO to the feed stream (spectrum a-iii), these features disappear. The adsorbed NH<sub>3</sub> disappears from the surface because it is being consumed by the NH<sub>3</sub> SCR reaction. Spectrum a-iv was taken 20 minutes after introducing 50 ppm toluene into the feed gas. The NH<sub>3</sub> features at around 3300 cm<sup>-1</sup> have reappeared, indicating that toluene inhibits consumption of NH<sub>3</sub> by the SCR reaction. NH<sub>3</sub> adsorption is obviously not hindered by the presence of the toluene, so it can be

concluded that toluene does not poison the SCR catalyst by blocking NH<sub>3</sub> adsorption sites. Spectra collected at 300°C look very similar to the ones shown here, indicating that the same poisoning process occurs at 300°C.



**Figure 1.** DRIFT spectra of Umicore Fe zeolite SCR catalyst at 200°C under (a-i) 350 ppm NO/14% O<sub>2</sub>; (a-ii) 140 ppm NH<sub>3</sub>/14% O<sub>2</sub>; (a-iii) 140 ppm NH<sub>3</sub>/350ppm NO/14% O<sub>2</sub>; (a-iv) 50ppm toluene/140 ppm NH<sub>3</sub>/350 ppm NO/14% O<sub>2</sub>; (b-i) 350 ppm NO<sub>2</sub>/14% O<sub>2</sub>; (b-ii) 70 ppm NH<sub>3</sub>/14% O<sub>2</sub>; (b-iii) 70 ppm NH<sub>3</sub>/350ppm NO<sub>2</sub>/14% O<sub>2</sub>; (b-iv) 50ppm toluene/70 ppm NH<sub>3</sub>/350 ppm NO<sub>2</sub>/14% O<sub>2</sub>

Figure 1(b) shows the results of a similar experiment that was conducted with NO<sub>2</sub> instead of NO in the feed. Like NO, NO<sub>2</sub> reacts with the adsorbed NH<sub>3</sub>, and the NH<sub>3</sub> spectral features disappear (spectrum c-iii). However, in this instance, we do not see an increase in adsorbed NH<sub>3</sub> with the addition of toluene to the feed gas (spectrum c-iv)—the toluene is not inhibiting the SCR activity of the catalyst when NO<sub>2</sub> is in the feed. We can conclude that toluene prevents NO oxidation to NO<sub>2</sub> by poisoning the Fe active sites. The presentation will discuss correlations between the DRIFTS and flow reactor experiments, the effects of other hydrocarbons (ethylene and propane), and the impacts of H<sub>2</sub>O and CO<sub>2</sub> in the feed gas.

### Significance

Understanding the mechanisms by which hydrocarbons poison urea SCR catalysts will enable accurate modeling of catalyst performance and durability and could lead to the identification of operating strategies and formulations that mitigate hydrocarbon poisoning.

### References

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2. T.J. Toops, D.B. Smith, W.P. Partridge, *Appl. Catal. B: Environmental* 58, 245 (2005).