

## Time-Resolved Ultraviolet Raman Spectroscopy of Coke Formation

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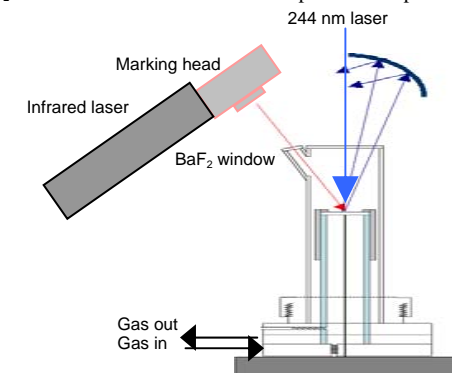
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### Introduction

H-MFI suffers from deactivation due to carbonaceous buildup (coke) during the methanol-to-gasoline reaction. UV-Raman spectroscopy allows *in-situ* analysis of reaction products during coke formation[1]. However, heating and cooling was slow (minutes), and coke formation was too fast for real-time UV-Raman measurements. With an infrared laser, heating and cooling are much faster,  $10^{-6}$  to  $10^{-3}$  s. After heating, products and intermediates are trapped inside the zeolite pores and unable to react or desorb. Using this pulse-quench sequence intermediates can be detected by UV-Raman spectroscopy.

### Materials and Methods

The fluidized bed reactor for UV-Raman was modified for IR heating through a BaF<sub>2</sub> side window [2]. A 9.3 micron CO<sub>2</sub> laser was directed onto the sample via computer-controlled beam steering mirrors (Fig. 1). The IR laser power was in the range 0.25-2.5 w. Zeolite powder (100 mg) was calcined at 600°C for 2 hours in pure oxygen. After cooling to 25°C in helium the zeolite was dosed with 100 μL of methanol through a bubbler. After 10 min. the zeolite was heated by systematically increasing laser power (increasing reaction temperatures). Raman spectra were measured with 244 nm excitation after calcination, after dosing, and during heating. The UV laser was aimed at a different position than the IR laser. Helium gas flow and mechanical vibration were used to stir the bed, avoid laser damage, and carry the sample from the IR laser beam to the UV laser beam.

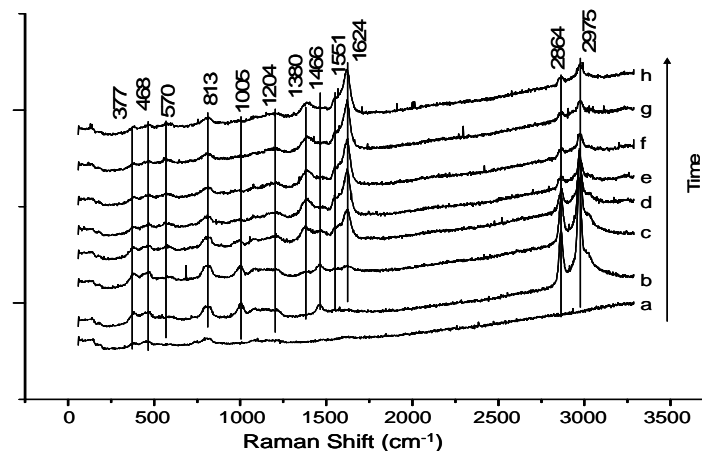


**Figure 1.** Fluidized bed modified with side-arm and infrared laser

### Results and Discussion

Infrared laser heating is a successful approach to forming coke within zeolite pores (Fig. 2). With increasing laser power, reactants disappear and products appear. No product desorption is detectable by mass spectrometry. The reaction temperature can be estimated from the beam power and zeolite thermal properties. From this estimation, a 1% increase in

laser power is equivalent to a 100°C increase in temperature. These temperatures are consistent with reaction products seen in conventional heating experiments. Peaks at 1005, 1466, 2864 and 2975 cm<sup>-1</sup> are due to methanol, and peaks at 377, 466, 813, and 1100-1200cm<sup>-1</sup> are due to zeolite [3]. Methanol and zeolite peaks decrease due to reaction and optical self-absorption, respectively. The peak at 1551 cm<sup>-1</sup> signals the presence of polyolefins with 6-8 repeat units. Peaks at 1380 and 1624 cm<sup>-1</sup> show that naphthalene forms initially, but changes in their relative intensity indicate formation of higher aromatics. Small peaks near 710, 1080, 1310, and 1495 cm<sup>-1</sup> are detectable, and work is in progress on chemical identification. The absence of product desorption implies polyaromatic formation takes place inside the pores and not on the external surface of the zeolite.



**Figure 2.** Progressive infrared laser heating of a methanol dosed H-MFI catalyst: (a) after calcination, (b-g) after at least 800 seconds of IR heating at linearly increasing temperatures from approximately 125-625°C respectively, (h) at different position on sample after final heating.

### Significance

Rapid heating and quenching allows trapping of reaction intermediates and monitoring by *in-situ* Raman spectroscopy. The absence of product desorption indicates that all observed reactions, including coke formation, take place in the zeolite pores.

### References

1. Chua, Y. T.; Stair, P. C. *Journal of Catalysis* 213, 39-46 (2003).
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3. Li, J.; Xiong, G.; Feng, Z.; Liu, Z.; Xin, Q.; Li, C. *Micro. and Meso. Mater.* 39, 275-280 (2000).