

# Spectroscopic and computational study of Cr and Mo oxide nanostructures in ZSM-5 for methane dehydroaromatization

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## Introduction

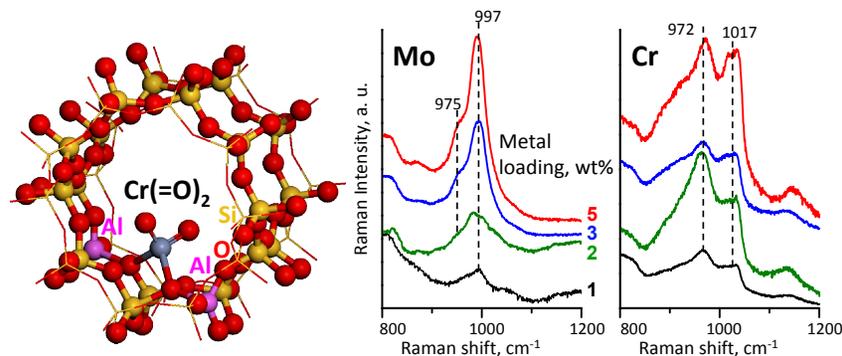
Methane conversion into valuable aromatic products represents a highly desirable route for conversion of natural gas into liquid fuels and chemical feedstocks. Cr and Mo catalysts supported on ZSM-5 are actively studied for methane dehydroaromatization with benzene as the main product. Cr-based catalysts are usually less active than Mo/ZSM-5. However, addition of Cr to Mo/ZSM-5 can improve both activity and benzene selectivity. The current study is the first investigation of the initial structure of Cr and Mo/ZSM-5 with *operando* Raman spectroscopy, UV-vis measurements and density functional theory (DFT) calculations.

## Materials and Methods

Cr and Mo/ZSM-5 catalysts with variable Si/Al atomic ratios (15-140) and variable metal loadings (1-5 wt%) were prepared by incipient wetness impregnation. The catalysts were calcined at 500°C and tested for methane activation (flow of 1.5 mol% CH<sub>4</sub> in He) at 500-750°C by simultaneously collecting *operando* Raman spectra and online mass spectra of reaction gases. The catalysts were also characterized with UV-vis diffuse reflectance spectroscopy. Gradient-corrected spin-polarized DFT calculations were performed with cluster models using the DMol3 code in Materials Studio software by Accelrys and with a periodic full ZSM-5 unit cell using plane wave VASP code.

## Results and Discussion

UV-vis spectra for Cr/ZSM-5 exhibit two main bands at ~245 and 350 nm. Similar spectra were reported previously for Mo/ZSM-5 and assigned to two oxide species with isolated Mo atoms based on a comparison with reference Mo compounds [1]. DFT calculations suggest that both of these species are Mo(=O)<sub>2</sub> dioxo nanostructures that are bridge-bonded to zeolite framework oxygen, but located on different Al framework sites. One species is located



**Figure 1.** Dioxo Cr(=O)<sub>2</sub> species bridge-bonded through framework oxygen to two Al sites in ZSM-5.

**Figure 2.** Raman spectra (442 nm excitation) for Mo/ZSM-5 and Cr/ZSM-5 with Si/Al=15 after calcination at 500°C.

on a single Al site and another on two Al sites in proximity. Similarly to Mo, Cr forms two dioxo nanostructures. The dioxo structure [Cr(=O)<sub>2</sub>]<sup>2+</sup> on two Al sites in an Al-Si-Si-Al arrangement is shown in Fig. 1. Calculated vibrational frequencies for the symmetric stretch of the two dioxo Cr and Mo models match the corresponding Raman band pairs in Fig. 2.

The major difference between supported Cr and Mo species is in the preferential occupation of Al framework sites. The Mo dioxo species preferentially occupy two Al sites at low Si/Al ratios and low metal loadings when a sufficient number of these double Al sites are available (Raman band at 997 cm<sup>-1</sup> in Fig. 2). With increasing Mo loading (Fig. 2) and Si/Al ratio (not shown for brevity), Mo species also begin to occupy less preferable single Al sites (band at 975 cm<sup>-1</sup>). As a result, the intensities of the Raman bands at 975 and 997 cm<sup>-1</sup> for Mo species on these two sites, a single Al or two Al atoms in proximity, change with the Mo loading and Si/Al ratio. In contrast, the intensity ratio of the similar Raman bands at 972 and 1017 cm<sup>-1</sup> for Cr species in Fig. 2 stays practically constant, indicating that Cr is equally likely to be stabilized on different Al sites. Furthermore, additional measurements show that at high Si/Al ratios when the ZSM-5 framework does not have enough anchoring Al sites, Cr and Mo species can be stabilized on sites without Al on the outer surface of the zeolite (Raman band for Mo/ZSM-5 at 985 cm<sup>-1</sup> and UV-vis band at 450 nm for Cr/ZSM-5 for Si/Al=140). A lack of Al anchoring sites also forces agglomeration of isolated Cr and Mo species into crystalline nanoparticles (UV-vis band at 600 nm for Cr/ZSM-5).

## Significance

A combination of *operando* spectroscopic characterization and DFT calculations with vibrational analysis for the first time provides information on the structure and activity of Cr and Mo/ZSM-5 at the molecular level.

## References

1. Tian, H., Roberts, C.A. and Wachs, I.E., *J. Phys. Chem. C* 114 (33), 14110 (2010).