# Sulfur Removal via Selective Adsorption using Organic Framework Supported Molybdenum Carbides

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## Introduction

The selective adsorption[1] of organosulfur compounds directly from liquid fuels has several advantages over traditional hydrodesulfurization (HDS) processes. Metal organic framework (MOF) materials are promising materials for use as sorbents[2] because of their very high surface areas (can exceed 4000 $m^2/g$ [3]), however, these materials do not possess sites with strong affinities for the organosulfur compounds[4] Consequently, the organosulfur compounds are easily leached from the MOF surface. Molybdenum carbides have been shown to possess[5] strong affinities for organosulfur compounds. Depositing nanoscale molybdenum carbides onto high surface area MOF supports could produce sorbents with high capacities and affinities for the organosulfur compounds left in transportation fuels including diesel and JP-8.

## Materials and Methods

Molybdenum was dispersed onto MOF-5 via a wetness impregnation technique using $Mo(CO)_6$ as a precursor. The $Mo(CO)_6$ was dissolved in pentane then added to MOF-5 in a dropwise fashion. This impregnated MOF-5 was dried at room temperature then pyrolyzed at 300 ºC in 5% $H_2/N_2$ overnight. The impregnation process was repeated several times to achieve the desired loading. The resulting sorbents were characterized to determine key structural and compositional properties. A ¼" stainless steel tube reactor was used for the desulfurization experiments; these experiments were carried out at ambient conditions. Organosulfur compounds including benzothiophene, 3-methyl benzothiophene, di-benzothiophene (DBT), and dimethyl dibenzothiophene, in iso-octane were employed. Benzene, naphthalene, and toluene were added for some experiments. The effluent was analyzed using a gas chromatograph equipped with sulfur specific flame photometric and flame ionization detectors.

## Results and Discussion

Surface areas for the *a*$MoC_x$/MOF-5 (where *a* represents the number of impregnations) were as high as 1800 $m^2/g$, and up to 19.6 wt% of Mo was deposited onto the MOF-5 support. Pore size distributions for the fresh MOF-5 and *a*MoCx//MOF materials were very similar. The slight surface area loss was likely due to blockage of the micropores by the catalyst precursor, but not to collapse of the pore structure.

The *a*$MoC_x$/MOF-5 materials were effective sorbents. Selected results for DBT adsorption from simulated fuels containing benzene and naphthalene, are summarized in Figure 1 and Table 1. The selectivity factor is defined as the breakthrough capacity for DBT divided by that for naphthalene. Breakthrough occurred in the following order: benzene > naphthalene > DBT. The *a*$MoC_x$/MOF-5 materials possessed higher breakthrough capacities than MOF-5. The addition of small amounts of aromatic compounds had little effect on the sulfur adsorption capacities. However, high aromatic concentrations (20 wt%) caused a significant decrease in the sulfur breakthrough capacity as well as the selectivity.

## Significance

As much as 20 wt% of Mo have been successfully dispersed onto MOF-5 supports. The resulting materials had very similar pore structures as the parent MOF-5 and their surface areas exceeded 1800 $m^2/g$. The resulting materials possessed high selectivities and breakthrough capacities for key organosulfur compounds, even in presence of aromatic compounds, and hold promise for use in removing sulfur from transportation fuels.

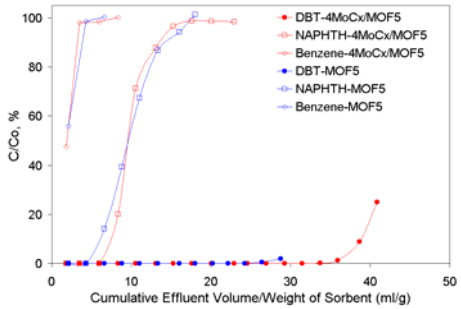


**Figure 1**. Breakthrough curves for DBT on selected sorbents (feed: 52 ppmwS, 700 ppmw of naphthalene and 1000 ppmw of benzene in *iso*-octane with space velocity of $1.6hr^{-1}$).

**Table 1**. Summary of experimental results for selected sorbents at room temperature.

| Sorbent | Sulfur Conc. (ppmw) | Aromatics Concentration (ppmw) | | Breakthrough Capacity | | |
|---|---|---|---|---|---|---|
| | | Naphthalene | Benzene | $S_{DBT}$ (mmolS/g) | Naphthalene (mmol/g) | Selectivity factor |
| MOF5 | 35 | 0 | 0 | 0.014 | - | - |
| | 52 | 700 | 0 | 0.029 | 0.017 | 5.7 |
| | | | 1,000 | 0.027 | 0.016 | 5.6 |
| 4MoCx | 35 | 0 | 0 | 0.025 | - | - |
| | 52 | 700 | 0 | 0.037 | 0.015 | 8.0 |
| | | | 1,000 | 0.035 | 0.023 | 5.2 |
| | | | 200,000 | 0.004 | 0.006 | 2.3 |

## References

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