Ain Shams University
Faculty of Science
Chemistry Department

Metal Organic Framework-Graphene Nano-Composites for Desulfurization Process

Thesis Submitted for

Ph.D. Degree of Science
(Chemistry)
By

Aya Mostafa Ibrahim Mtloob

M.Sc. in Chemistry

(Organic Chemistry 2016)

To
Chemistry Department
Faculty of Science
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Abstract

The combustion of fossil fuels containing sulfur compounds emits some of the sulfur oxides which considered a harmful influence on human health and the surrounding environment as well as the economy. Elimination of the sulfur compounds in the transportation fuel can be achieved by utilizing different desulfurization processes for the fuel products, which is commonly carried out using the catalytic hydrogen processing approaches (hydrodesulfurization), or by using different desulfurization process such as; oxidative and or adsorptive desulfurization. Adsorptive desulfurization is based on the ability of a solid adsorbent to selective adsorb organosulfur compounds from refinery streams which is depending on the interaction mechanism between the sulfur compounds and adsorbents.

In this work, adsorptive desulfurization (ADS) process was applied to model oil (thiophene derivatives dissolved in dodecane) using metal organic framework (MOF) and/or metal organic framework graphene hybride nonocomposites (MOF/Gr) as adsorbents.

Three MOFs {Cu-MOF, Fe-MOF, and Cr-MOF} have been prepared by green solvothermal method.

The structure formation was systematically controlled according to the changing in the ratio of metal source and the organic ligand from 1:1 to 4:1 molar ratio. Then, the MOF sample

with 2:1 molar ratio was selected to prepare MOF/Gr hybrid nano-composite by the same method (solvothermal). The structure of MOF/Gr samples was systematically controlled according to MOF: GO wt. ratio from 1:1 to 9:1. The sample with 9:1 wt. ratio was selected to prepare Fe-MOF/Gr and Cr-MOF/Gr.

All of the prepared MOFs and MOF/Gr samples have been characterized by applying different techniques such as: XRD, FTIR, BET, HRTEM, and XPS.

Adsorptive performance of the MOF and MOF/Gr adsorbents were investigated for the removal of DBT under various conditions such as time (30- 300 min), temperature (25- 60ºC) and the amount of adsorbent (0.05- 0.2 g). After adsorption, sulfur removal % reach to 70, 62 and 57 % for Cu-MOF, Fe-MOF, and Cr-MOF respectively. And 92, 95.6, and 96.9% for Cu-MOF/Gr, Fe-MOF/Gr and Cr-MOF/Gr respectively as measured by gas chromatography (GC-FPD).

Therefore, MOF/Gr shows superior removal efficiency compared to the parent MOF due to the high functional group occupied on the composite material (heterogeneous surfaces), that established new active centers to interact with aromatic sulfur compound. Also, the kinetic study clarifies that the adsorptive desulfurization data of DBT were fitted to a pseudo second-order reaction. This suggests that the overall sulfur adsorption is most likely to be controlled by chemisorption process.

Finally, the adsorptive desulfurization of MOF/Gr adsorbent

was extended to different substrates thiophene (TH) and 4,6-dimethylbenzothiophene (4,6-DMDBT) and diesel fuel under the optimum conditions.

Key words: *Metal organic frame work, Graphene, Solvothermal method, Desulfurization process, Adsorptive desulfurization*

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