Ain Shams University
Faculty of Science
Chemistry Department

# *Green Desulfurization of some Petroleum Organic Sulfur Compounds Using Nano Layered Materials Loaded with {$Mo_{132}$} Nanoball*

*Thesis Submitted for*

*Ph.D. Degree of Science*
(Chemistry)
*By*

***Asmaa Ahmed Abdelrahman Ahmed***

**M.Sc. in Chemistry**

(Inorganic Chemistry 2013)

*To*
*Chemistry Department*
*Faculty of Science*
*Ain Shams University*
*Cairo, Egypt*

**2018**

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Asmaa Ahmed Abdelrahman

## ***Aim of the work***

This study has aimed to produce ultra-low sulfur diesel fuel via oxidative desulfurization process. Two kinds of polyoxometalate - graphene oxide composites were used:

A- **{$Mo_{132}$}/GO composite.**

B- **{$Fe_{30}Mo_{72}$}/GO composite.**

The structural and chemical properties of the prepared materials were characterized using Fourier-transform infrared spectroscopy (FT-IR) , X-ray diffraction (XRD) ,UV-vis., Raman spectroscopy, HR-TEM, TGA and SBET techniques.

So the plane of this work can be presented according to the following sequences:

1- Preparation and characterization of graphene oxide (GO).

2- Preparation of polyoxymolybdate nanoballs{$Mo_{132}$}.

3- Preparation of metal substituted polyoxymolybdate nanoball{$Fe_{30}Mo_{72}$}.

4- Preparation of polyoxomolybdate and metal substituted polyoxymolybdate nanoballs graphene nanocomposite.

5- Characterization of the prepared materials and composites with conventional techniques.

6- Study the efficiency of the prepared material on oxidative – desulfurization of petroleum organosulfur compounds.

7- Optimization of reaction conditions including (reaction temperature, $H_2O_2$ ratio (O/S) molar ratio, catalyst weight and time).

8- Application of the more active prepared materials on petroleum fraction (gas oil) feed stock.

9- Characterization of spent catalysts and reuse for several time.

| Abbrev. | Description |
|---|---|
| 2D | 2-dimensional |
| 3D | 3-dimentional |
| A (in Arrhenius equation) | (Pre-exponential factor) |
| AC | Activated carbon |
| ADS | Adsorptive desulfurization |
| ASA | Amorphous silica-alumina |
| BDS | Biodesulfurization |
| BET | Brunauer-Emmett-Teller |
| BN | Boron nitride |
| BT | Benzothiophene |
| CNT | Carbon nano tube |
| DBT | Dibenzothiophene |
| DDS | Direct desulfurization pathway |
| DMDBT | Dimethyldibenzothiophene |
| DMF | Dimethylformamide |
| DTA | Differential thermal analysis |
| $E_a$ | The activation energy (KJ/mol) |
| EDS | Extractive desulfurization |

| | |
|---|---|
| EPA | Environmental protection agency |
| EPODS | Extraction and photocatalytic oxidative desulfurization |
| g-$C_3N_4$ | Graphitic carbon nitride |
| GO | Graphene oxide |
| GPH | Graphene prepared by conventional Hummers' method |
| GPP | Graphene prepared by phosphoric acid |
| HDS | Hydrodesulfurization |
| HYD | Hydrogenation pathway |
| ICP | Inductive coupling plasma |
| IUPAC | International Union of Pure and Applied Chemistry |
| K | Rate constant of pseudo-first order |
| Me CN | Acetonitrile |
| MIPs | Molecularly imprinted polymers |
| MS | Mechanical stirring |
| MIL | Materials of Institute Lavoisier |
| MOF | Metal-Organic Framework |
| NMP | N-methylpyrrolidone |
| NMR | Nuclear magnetic resonance |
| O/S | The $H_2O_2$/DBT molar ratio |

| | |
|---|---|
| ODH | Oxidative-dehydrogenation |
| ODS | Oxidative desulfurization |
| OSC | Organic sulfur compounds |
| POMs | Polyoxometalates |
| ppm | Part per million |
| R | Universal gas constant |
| $R^2$ | Regression coefficient |
| rGO/ZrP | Reduced graphene oxide /zirconium phosphate |
| RT | Room temperature |
| $S_0$ | The initial sulfur concentration |
| SEM | Scanning electron microscope |
| $SO_x$ | Sulfur Oxides |
| St | The sulfur concentration at reaction time (t) |
| T | Temperature (K) |
| TBHP | Tertbutyl hydroperoxide |
| TEM | Transmission electron microscopy |
| TGA | Thermal gravimetric analysis |
| TMs | Transition metals |
| UV/VIS | Ultra-violet/visible |

| | |
|---|---|
| XPS | X-ray photoelectron spectroscopy |
| XRD | X-ray diffraction |
| XRF | X-ray fluorescence spectroscopy |