Epoxides assisted synthesis of MOF MIL-101-Cr and its application as high selective adsorbent of Organic Nitrogen Hetero Molecules present in diesel fuel

J. Ascención Montoya de la Fuente *[1], Rodolfo Mora Vallejo[1], Edith Meneses Ruiz[1], Paz del Angel Vicente[1], Heriberto Díaz Velazquez[1] and Roberto García de León[1]

1 *Instituto Mexicano del Petróleo, Dirección de Investigación y Posgrado, Eje central 152 Norte, 07730, México D.F, México*

* amontoya@imp.mx, rdeleon@imp.mx

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1. Introduction

Materials called metal organic framework (MOFs) have gained increasing interest in recent years. These materials develop unusual high porosity that extends from the microporous to the mesoporous size, they also offer some predictability in synthesis due to the combination of metal ions with preferred coordination geometry and ligands with defined connectivity. Their nanostructure, high surface to volume ratio, and the possibility of tuning their crystal structure [1]. The MOF´s are a novel class of materials that exhibit high potential of application in important areas, such as selective adsorption of Organic Nitrogen Molecules present in diesel units feedstocks, as it has been recently shown [2].

In this work we report a simple synthesis of the MOF MIL-101-Cr structure using Porpylen Oxide in absence of the toxic HF to obtain a mesoporous thermally stable structure [3]. However, in order to reach a high yield of the MOF structure and as well as an adequate crystallite size, some synthesis parameters were modified. In addition, the MOF MIL-101-Cr characterization by TEM studies overcoming their beam sensitivity is reported as well as its performance on high selective adsorption of organic nitrogen compounds (NOC´s) present in diesel fuel.

2. Experimental

Hydrothermal synthesis: The Chemicals, $Cr(NO)_3.6H_2O$, terephthalic acid, Propylen oxide and Acetone were purchased from Aldrich. In a typical synthesis, in a 1 liter beaker Teflon, 660 ml of demineralized water were added, constant magnetic stirring at room temperature was initiated, and then 22.174 g of terephtalic acid (H_2BDC) were added and stirred for 10 minutes. Pulses with SONICS Vibra Cell with 80% amplitude was applied for an effective time of 6 minutes to improve the solubility of H_2BDC, and 52.879 g of $Cr(NO)_3.6H_2O$ was added and the solution was stirred by 20 min, finally 1.9388 g of Propylen Oxide were added and the solution was stirred for 10 minutes. The final solution was poured into a Tefon-lined autoclave vessel (1000 ml) and sealed. The Parr reactor was closed to start the hydrothermal treatment for 24 hours at 180°C, 200 rpm and autogenous pressure. In order to improve the yield of MOF MIL-101-Cr and its crystallinity, the effect of using various amounts of acetone for washing was studied as well as the reaction time from 12 to 24 hours.

Characterization: In order to control the morphology and porosity, MOF MIL-101-Cr was synthetized as described elsewhere [3]. Characterization was carried out by TEM using a TITAN 80-300, transmission electron microscope and by SEM using a Nova-200 Nanolab, scanning electron microscope.

Selective Nitrogen molecules Adsorption; The intrinsic and selective nitrogen-molecules adsorption capacity of the MOF's samples was evaluated in a screening high throughput approach using a liquid dispensing robot, CAVRO, equipped with temperature control and stirring. A series of MOF's in powder shape were weighted (0.5 g) into a 40 ml glass vials, and pretreated at 150°C during 24 h, then using the robot, 20 ml of the diesel were added under stirring at 30°C, the adsorption time was of 90 min. Once the adsorption finished a 1 ml sample was taken from the liquid and total Nitrogen remaining content was determined on an Antek by Pack analyzer. Adsorption experiments were performed in a packed column at atmospheric pressure and room temperature (described as IMP-NitSorb Adsorption Process) [4].

3. Results and discussion

In the present work high purity MOF MIL-101-Cr was synthetized, with controlled micro and mesoporosity according to the synthesis parameters, BET surface area ranged from 2,500 to 3,500 m^2/g, pore volume from 1.1 to 2.2 cm^3/g and pore diameter from 15 to 55 nm.

Figure 1a. shows SEM image of MOF MIL-101-Cr aggregates, they comprise particles with sizes from 50 to 300 nm, mainly; and it seems, they have a layer-type morphology. These particles were observed by TEM and they correspond to single crystals with MOF MIL-101-Cr structure, such as it is observed in Figure 1.b. In this case, the (111) plane (FFT inset) with a planar distance of 44.4 Å is observed, which is in accordance with the XRD measurements. Although MOF MIL-101-Cr is very sensitive to the electron beam, we were able to obtain HRTEM images at 300 kV, by fine-tuning low dose electron beam interacting over nanocrystals.

It was found that the MOF MIL-101-Cr possess a high selectivity adsorption properties and it is able to remove nitrogen organic compounds from real diesel fuel units feedstock at levels of 80% in continuous process, figure 1 c. The adsorbent is able to process up to 250 bbl/Ton per each adsorption cycle and it can be regenerated to 100% of its adsorption capacity.

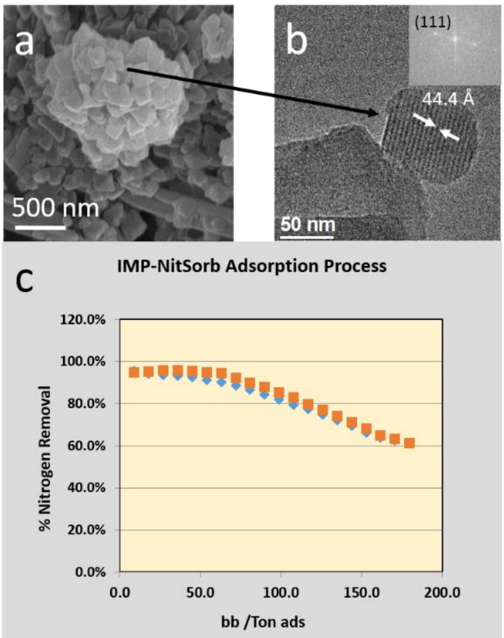

Figure 1 a) SEM image of MOF, b) TEM image of MOF MIL-101-Cr, showing the (111) plane, characteristic of this material, c) Nitrogen Organic Compounds (total nitrogen) removed from diesel in a continuous process.

4. Conclusions

The MOF MIL-101-Cr material has been synthetized using propylene oxide and the mesoporosity depeds on the amount of epoxide. The MOF MIL-101-Cr was applied as a high selectivity adsorbent in a continuous adsorption process for removing at least 80% of the total Nitrogen Organic Compounds present in feedstock gasoil as a pretreatment to the HDS process to obtain ULSD. The impact upon reaction conditions and catalytic performance has been measured using a micro reactor system.

References

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