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Review Paper

Investigating Metal Organic Frameworks in Adsorptive Desulfurization

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1. ABSTRACT

Investigating methods to remove sulfur compounds from fuel is one of the most important and vital issues in the oil industry. Adsorptive desulfurization is known as one of the most promising desulfurization methods due to its low energy consumption. Metal-organic frameworks are a new family of porous materials with tunable structure and function. High specific surface area and porosity, adjustable pore size, and most importantly, high selectivity of metal-organic frameworks towards sulfur compounds, are among the features that distinguish this adsorbent from other adsorbents such as metal oxides, zeolites and carbon compounds, and they show higher adsorption capacities than other adsorbents due to the proper interaction with sulfur compounds. In this study, the application and mechanisms of MOF in adsorptive desulfurization was investigated. The dominant mechanisms in the adsorptive desulfurization process over metal-organic frameworks are π complexation, acid-base interaction, direct sulfur-metal interaction, and Van der Waals forces.

Keywords: Metal-Organic Framework, Adsorptive Desulfurization, Sulfur Compounds, Adsorptive Mechanism.

2. INTRODUCTION

Fossil fuels are the most common source of energy used worldwide. However, the release of dangerous and toxic chemicals during their use is an important threat to human society as well as the environment. Crude oil, gasoline, diesel, jet fuel, and fuel oil are fossil fuels that contain sulfur compounds that produce dangerous oxides such as SOx during combustion. The released sulfur dioxide reacts with rainwater and air humidity and produces acid rain. Hydrodesulfurization (HDS) is a widely used current technology in petroleum refineries to remove sulfur from petroleum fractions. Over the last two decades, several alternative sulfur removal methods are reported. Among them, the top five technologies are (1) biodesulfurization (BDS), (2) pervaporation desulfurization (PDS), (3) adsorptive desulfurization (ADS), (4) extractive desulfurization (EDS), and (5) oxidative desulfurization (ODS). Adsorptive desulfurization is promising method that uses a low temperature and pressure operating conditions and does not need costly hydrogen. Absorptive desulfurization is an easy and cheap method in terms of operation, and its development to industrial mode is simpler and more affordable than other methods. Since absorptive desulfurization mainly depends on the absorption capacity of the material, the choice of adsorbent is very important. A wide variety of adsorbents based on metal oxide, zeolite, metal organic framework (MOF), and carbon was examined for desulfurization. The selectivity of adsorbents to sulfur compounds depends on the physical (van der Waals force) or chemical (sigma and pi bonds) interaction between the adsorbent or target molecules (sulfur) and the active sites on the surface of the adsorbent [1].

The incorporation of metals, and acid or alkali treatments significantly enhance the adsorption capacity of adsorbents by increasing active sites on the surface for π complexation, acid-base, and direct sulfur-metal interactions [2].

Among the various new materials that have been designed and synthesized in the past few years, metal-organic frameworks are a promising option for a wide range of applications due to their high porosity, high surface area, and availability of active sites. Metal-organic frameworks are a new generation of nanoporous coordination polymers that are formed by the accumulation of metal ions or metal clusters as coordination centers and organic ligands as connectors of these centers. These organic-inorganic composite frameworks show a very high adsorption capacity in gas or liquid

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phases. Due to the wide variety of metals and potential ligands, the number of possible structures of organometallic frameworks is practically infinite [3].

3. RESULTS AND DISCUSSION

3.1. Desulfurization using metal-organic framework

Metal-organic frameworks have gained increasing attention from researchers around the world as adsorbents in the recent decade due to their unique and advantageous characteristics such as high pore volume, large surface area, multiple topologies, designable crystalline structure, adjustable pore size, and surface chemistry. Adsorption studies of aromatic sulfur compounds have been investigated by various research groups with different types of metal-organic frameworks for obtaining low-sulfur liquid fuels. A list of adsorptive desulfurization results in the liquid phase using different metal-organic frameworks is presented for the adsorption of benzothiophene (BT) in Table 1 and the adsorption of dibenzothiophene (DBT) in Table 2. In Table 3, adsorption of BT, DBT, and 4,6-dimethyldibenzothiophene (4,6-DMDBT) using different metal-organic frameworks for varying experimental conditions are shown [4].

Table 1. MOFs as adsorbents for benzothiophene (BT).

Adsorbent	Conditions or Remarks	Adsorption Capacity (mmol/g)
MIL-53(Cr)		0.60
MIL-53(Al)	*n*-Octane solvent, 298 K	0.26
MIL-47(V)		1.6
NENU-511	*i*-Octane solvent, 298 K	2.2
NENU-512		1.4
NENU-513	*n*-octane	1.1
NENU-514		1.0
Zr(BTC)	liquid fuel	290 mg/g
ZIF-8		45
MIL-100(Fe)		114
MIL-101(Cr)		35.77%
MIL-100(Fe)		20.76%
MOF-74(Ni)	*n*-octane	76.97
MIL-101		36.4
UiO-66		19.83
HKUST-1		18.2

Table 2. MOFs as adsorbents for dibenzothiophene (DBT).

Adsorbent	Conditions or Remarks Solvent, Temperature (K)	Adsorption Capacity
NENU-511		2.6 mmol/g
NENU-512		2.2 mmol/g
NENU-513	*i*-Octane	2.0 mmol/g
NENU-514		1.9 mmol/g
HKUST-1		7.7 mgS/g
MIL-101(Cr)		32.5 mgS/g
ZIF-8		45 mgS/g
MIL-100(Fe)		114 mgS/g
MOF-101	*n*-octane	52.4 mg/g
MIL-100(Fe)		35.77%
MIL-101(Cr)		20.76%
MOF-74(Ni)		85.05%
MOF-505		39.2%
MOF-199	dodecane	90%

Table 3. MOFs as adsorbents for BT, DBT, and 4,6-dimethyldibenzothiophene (4,6-DMDBT).

Adsorbent	Adsorbate (SCC)	Conditions or Remarks Solvent, Temperature (K)	Adsorption Capacity (mmol/g)
UMCM-152		*i*-Octane, 298 K	1.8, 2.6
UMCM-153	DBT/DMDBT		2.8, 1.2
MIL-101(Cr)			0.20/0.17
MIL-100(Fe)		Octane, 298 K	0.20/0.25
HKUST-1			0.57/0.28
MOF-505	BT/DBT/DMDBT	*i*-Octane, 298 K	0.38/0.21/0.13
UMCM-150			0.30/0.45/0.19
HKUST-1			0.19/0.24/0.08

3.2. Effects of process parameters on adsorptive desulfurization

3.2.1. Contact time

The contact time has a great influence on the adsorption efficiency of any adsorbent. Generally, with an increase in the contact time, the adsorption capacity of an adsorbent increases until it reaches its equilibrium [5].

3.2.2. Initial sulfur content of feedstock

Langmuir (1) and Freundlich (2) isotherms describe the uniform monolayer adsorption, and the heterogeneous adsorption, respectively [5].

3.2.3. Adsorbent dosage

Generally, the percentage of adsorption or sulfur removal increases with increasing adsorbent dosage due to the increasing number of accessible active sites [5].

3.2.4. Adsorption temperature

With increasing temperature, the rate of adsorption is expected to increase as sulfur compounds move faster through pores of adsorbents and overcome the activation energy barrier [5].

4. Future perspectives

Very few reports are available on the application of adsorbents for desulfurization of real fuels. A variety of adsorbents such as metal oxide, zeolite, carbon, and metal-organic framework have shown promising adsorption capacities with model sulfur compounds. The real feedstock contains a wide variety of non-sulfur compounds including aromatics and nitrogen compounds. These compounds hinder adsorption of sulfur compounds through competitive adsorption. More studies are required to develop adsorbents, which can selectively adsorb sulfur compounds in real fuels.

5. CONCLUSION

Sulfur compounds present in fuels are toxic and extremely dangerous for the environment and human health. Adsorptive desulfurization is a promising low-cost method of removing organic sulfur compounds by adsorption under ambient conditions. Metal-organic frameworks provide reasonable performance due to their ultrahigh porosity. The development of low-cost selective ADS adsorbents is an ongoing area of research.

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