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Selective adsorption of nitrogen compounds using silica-based mesoporous materials as a pretreatment for deep hydrodesulfurization

J.C. García-Martínez[a,*], H.A. González Uribe[a], M.M. González-Brambila[a], J.A. Colín-Luna[a], Y.E. Escobedo-García[b], A. López-Gaona[c], L. Alvarado-Perea[d]

[a] Universidad Autónoma Metropolitana Azcapotzalco, Departamento de Energía, Área de Análisis de Procesos, Av. San Pablo 180, Col. Reynosa, CP. 02200, Ciudad de México, Mexico

[b] Universidad Autónoma de Zacatecas, Maestría en Ciencias de la Ingeniería-Doctorado en Ingeniería Aplicada, Ramón López Velarde 801, Calle Camino a la Bufa, Col. Centro, CP. 98000, Zacatecas, Zac, Mexico

[c] Universidad Autónoma Metropolitana Iztapalapa, Departamento de Química, Av. San Rafael Atlixco 186, Col. Vicentina, CP. 09340, Ciudad de México, Mexico

[d] Universidad Autónoma de Zacatecas, Unidad Académica de Ciencias Químicas y Maestría en Ciencias en la Ingeniería Química, Campus UAZ Siglo XXI, Zacatecas, Zac, Mexico

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ABSTRACT

The adsorption of quinoline (Q) and dibenzothiophene (DBT)—model compounds for nitrogen and sulfur in diesel fuels—over mesoporous SBA-15, SBA-16, and MCM-41 was studied. The Langmuir model was suitable for describing the adsorption of nitrogen-containing compounds from a simulated diesel fuel. A pseudo-second-order kinetic model better fitted the Q adsorption data than a first-order rate model when describing the adsorption rates on all materials. Comparison of the adsorption of Q and DBT confirmed that the nitrogen compound was selectively removed, and MCM-41 was found to have better adsorption characteristics than SBA-15 and SBA-16. DBT was not adsorbed in any experiment. The adsorbents were characterized using N_2-physisorption, powder X-ray diffraction, and high-resolution transmission electron microscopy to describe the morphologies of the adsorbents. The characterization results revealed that the specific area and the structure of the adsorbent are key parameters required to explain the adsorption process.

1. Introduction

In recent years, worldwide legislation on the sulfur content in diesel fuels has become more stringent because of air pollution due to exhaust gas from diesel engines. The nitrogen content in diesel feedstocks used to obtain fuel is very important because nitrogen-containing compounds inhibit the active sites of the catalyst used for the hydrodesulfurization (HDS) reaction [1]. In particular, basic nitrogen compounds such as quinoline (Q) can strongly adsorb on the acidic sites of various catalysts used in petroleum refining processes, resulting in poisoning of the active sites [1]. The production of ultra-low sulfur diesel (ULSD) (below 10 ppmw of sulfur) is motivated by the need for using new emission-control technologies that are sensitive to sulfur (e.g., EURO VI norms). In general, novel catalysts and process concepts have been regarded as solutions for cheaper and cleaner fuel [2–4]. The hexagonal cylindrical pore structured SBA-15 was utilized in the HDS reaction in another work [3], and the mesoporous materials MCM-41 and Ti-MCM-41 were utilized in hydrotreating reactions [4]. Hence, mesoporous materials can be suitable adsorbents for treating the sulfur and nitrogen heterocompounds contained in diesel fuel.

It is known that adsorptive desulfurization and adsorptive denitrogenation are competitive methods [5] that can be applied for desulfurization/denitrogenation to obtain an ultra-low level (15 ppmw sulfur content). They are also crucial for recent applications such as fuel cells. Because adsorption usually depends on the performance of the adsorbent, the search for a suitable adsorbent is very important. The main requirements for an effective adsorbent include ease of preparation, mild operating conditions, high porosity, easy regeneration, and environmental feasibility [6]. Several kinds of adsorbents have been used to remove nitrogen- and sulfur-containing compounds from fuels. The materials used for adsorptive desulfuration and denitrogenation include activated carbons (ACs) [7–10], mesoporous silica, alumina and related materials [11–13], zeolites [14–16], and SBA-15-supported nickel(II) [17].

The catalysts used for processing refinery streams via isomerization, reforming, catalytic cracking, and hydrocracking are very sensitive to nitrogen compounds; hence, removal of these compounds from the streams prior to processing has been the focus of considerable attention

* Corresponding author.
E-mail address: jgarciam@correo.azc.uam.mx (J.C. García-Martínez).

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