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ScienceDirect
Applied Catalysis B: Environmental 81 (2008) 244–250
APPLIED CATALYSIS B: ENVIRONMENTAL
www.elsevier.com/locate/apcatb

Reactive adsorption of sulfur compounds in diesel on nickel supported on mesoporous silica

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Received 30 July 2007; received in revised form 14 December 2007; accepted 15 December 2007
Available online 27 December 2007

Abstract

Sulfur compounds in commercial diesel were selectively removed by reactive adsorption using metallic nickel nanoparticles supported on mesoporous silica. Nanosize nickel particles were supported on mesoporous silica SBA-15 and KIT-6 by impregnation of nickel nitrate and subsequent reduction. X-ray diffraction and transmission electron microscopy study revealed that the maximum nickel concentration achieved was 30 wt% for both the substrates, before particle agglomeration sets. Under these conditions, the best dynamic adsorption capacity observed was 1.7 mg/g at 10 ppmw S breakthrough level with a high sulfur diesel (240 ppmw) on 30 wt% Ni/SBA-15. For a low sulfur diesel (11.7 ppmw), the corresponding result was 0.47 mg/g for the same adsorbent at 0.1 ppmw S breakthrough level, which is suitable for fuel cell applications.

Keywords: Reactive adsorption; Desulfurization; Nickel nanoparticle; Mesoporous silica

1. Introduction

The production of transportation fuel with low sulfur concentration has been a major concern in petroleum industry due to the stringent statutory environmental regulations imposed by the government worldwide [1,2]. For example, the Korean government has already announced a plan to reduce the upper limit of sulfur concentration in diesel to 10 ppmw by 2009 [2]. To date, conventional hydrodesulfurization (HDS) to convert the sulfur compounds into hydrogen sulfide using Co–Mo/Al_2O_3 or Ni–Mo/Al_2O_3 catalysts has been a major desulfurization process which failed to meet expected sulfur regulation, while HDS with unsupported transition metal sulfide still seems to be the only practical solution to achieve low sulfur diesel less than 10 ppmw [3–5]. However, further reduction of sulfur concentration by HDS, to less than 1 ppmw, is still a challenging research target. In addition to the environmental aspect, the demand for ultra-low sulfur diesel (ULS-diesel), less than 0.1 ppmw, has been growing due to the fuel cell applications. Transportation fuels, such as gasoline, jet fuel, and diesel, are ideal fuels due to their high energy density, ease of storage and transportation, and established distribution network. However, their sulfur concentration must be less than 0.1 ppmw to protect the deactivation of catalysts in reforming process and electrodes in fuel cell system [6].

Recently, adsorptive desulfurization has been reported to be a complementary and alternative technique for HDS [7]. Metal ion exchanged Y zeolites showed high selectivity and capacity for sulfur compounds using π-complexation between metal ion and sulfur compounds [7–10]. However, their selectivity and capacity for sulfur compounds varied depending on the fuel composition, such as aromatic and moisture concentrations [11]. Unlike π-complexation, the reactive adsorption of sulfur compounds, adsorption assisted by chemical reaction between metal particles and adsorbates, was reported on metallic nickel supported on silica, which could lower sulfur level in model diesel or fractionated jet fuel to below 10 ppmw [12–14]. In reactive adsorption, fuel composition is not expected to affect the selectivity and adsorption capacity for sulfur compounds, because specific bond formation reaction between sulfur atom and metal in adsorbent is the main driving force for sulfur compounds adsorption. Our group explored the possibility of the production of low sulfur diesel using nickel particles supported on mesoporous silica SBA-15 and observed that the

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doi:10.1016/j.apcatb.2007.12.014

surface status of nickel particles played a critical role in reactive sulfur adsorption [15,16].

The present paper describes the results of the extension of the above studies to achieve ULS-diesel with sulfur levels less than 0.1 ppmw from commercial diesel feedstock.

2. Experimental

2.1. Chemicals

All chemicals were used as received without further purification. Pluronic 123 (P123), tetraethoxysilane (TEOS), *n*-butanol, and tetrahydrofuran (THF) were obtained from Aldrich. Hydrochloric acid solution (HCl) and nickel nitrate hexahydrate were obtained from Junsei. Two grades of commercial diesel, high sulfur diesel (HS-diesel) and low sulfur diesel (LS-diesel) with 240 and 11.7 ppmw, respectively, were purchased from gas station near Daejeon.

2.2. Preparation of adsorbents

Mesoporous silica SBA-15 and KIT-6 were synthesized based on the methods reported elsewhere [17,18]. For the synthesis of SBA-15, 2.0 g of P123 was dissolved in 15 g of deionized water and 80 g of 2 M HCl solution. Then, 4.25 g of TEOS was added and this mixture was stirred for 5 min and then kept at 308 K for 1 day, followed by aging for another 24 h at 373 K. The solid product was filtered without washing, dried in an oven at 373 K, and subsequently calcined in O_2 flow for 4 h at 823 K. For the synthesis of KIT-6, typically, 3.2 g of P123 and *n*-butanol were dissolved in 116 g of deionized water and 6.3 g of 35 wt% HCl solution under stirring at 305 K. TEOS was added into the resultant solution at 308 K and the magnetic stirring was continued for 24 h at the same temperature. Subsequently, the mixture was placed in an oven at 373 K for 24 h. The remaining steps in synthesis procedure were the same as for SBA-15. On SBA-15 and KIT-6, $Ni(NO_3)_2{\cdot}6H_2O$ dissolved in THF was impregnated by incipient wetness method. THF is better than deionized water in terms of the nickel particle dispersion [15]. The solids thus obtained were dried in an oven at 373 K with N_2 purging for 1 h and then reduced in hydrogen gas flow at 873 K for 4 h. The resultant samples were designated as Ni/SBA-15 and Ni/KIT-6, respectively.

2.3. Characterization of the adsorbents

The BET surface area, pore volume and pore size distribution of calcined mesoporous silica (SBA-15 and KIT-6) were measured by nitrogen adsorption at 77 K using a Micromeritics (ASAP 2010) surface area measurement apparatus. Pore size distribution was calculated by Barrett–Joyner–Halenda (BJH) method. X-ray powder diffraction (XRD) patterns and transmission electron microscopy (TEM) images of Ni/SBA-15 and Ni/KIT-6 were obtained using Rigaku Miniflex (Cu Kα radiation (λ = 0.15406 nm) at 30 kV) and EM912 EF-TEM operated at 120 kV in Korea Basic Science Institute.

2.4. Breakthrough experiments

A constant flow liquid metering pump was used to feed diesel to experimental set-up for the breakthrough test. One gram of adsorbent was packed in a stainless steel column with 4 mm inner diameter and 300 mm length. Total bed volume occupied by 1.0 g of adsorbent was 2.7 ml. Appropriate particle size in the range 37–44 μm, was obtained by sieving the materials. Tubular furnace was equipped for heat treatment and temperature maintaining. The moisture in hydrogen gas was removed prior to use by 3A zeolite. The feed flow rate was maintained at 0.2 ml/min. Thus mean residence time of the fluid was 13.5 min and liquid hourly space velocity (LHSV) was 4.44 h^{-1}. The sulfur concentration of eluted diesel was measured by a total sulfur analyzer (9000LLS, Antek). Quantitative analysis of sulfur compounds in the diesel feeds were performed using HP 6890 series gas chromatograph (GC), equipped with SUPELCO 24158 SPB-1 SULFUR capillary column and a flame photometric detector (FPD). Identification of the sulfur compounds was carried out using the standard model compound solutions.

For the breakthrough test with HS-diesel, 10 ppmw was taken as the criterion for sulfur breakthrough. We defined two adsorption capacity terms as follows. When the sulfur concentration of eluted diesel reaches 10 ppmw, the volume of eluted diesel so far was defined as the breakthrough volume, based on which the breakthrough sulfur adsorption capacity was estimated. On the other hand, total sulfur adsorption capacity was defined as the integrated area between the breakthrough curve and the straight line, representing the initial sulfur concentration of the feed.

3. Results and discussion

3.1. Properties of adsorbents

Fig. 1 displays the low angle X-ray diffraction patterns of calcined mesoporous silica SBA-15 and KIT-6. Based on the

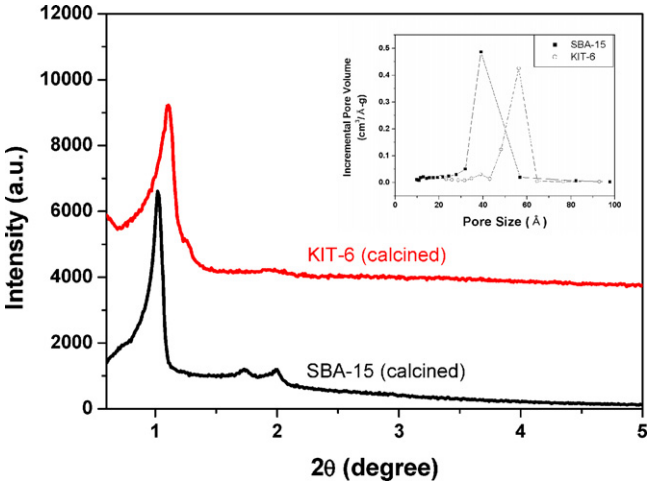

Fig. 1. X-ray diffraction patterns of SBA-15 and KIT-6: low angle region for mesopore characterization (inset shows pore size distributions of calcined SBA-15 and KIT-6 by BJH method).