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Hydrodesulfurization of dibenzothiophene on NiMo/γ-Al_2O_3 washcoated monoliths

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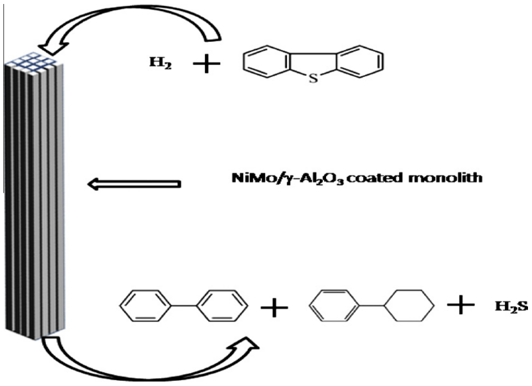
HIGHLIGHTS

- Optimum metal loading was determined for hydrodesulfurization of dibenzothiophene on NiMo/γ-Al_2O_3 catalyst.
- Higher catalyst size showed pore diffusional resistances.
- Catalyst dispersion decreased with metal loading.
- NiMo/γ-Al_2O_3 washcoated on monoliths was fully utilized with no external or internal mass transfer resistances.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrodesulfurization of dibenzothiophene, dissolved in n-hexadecane, was conducted in the temperature range of 548–593 K at 10 MPa pressure in a conventional packed bed reactor for two different catalyst sizes and on monoliths washcoated with different metal loadings. The monolith catalysts were made by washcoating using NiMo/γ-Al_2O_3 catalysts prepared by incipient wetness and uniform well-adhered washcoats were obtained by calcination after each dipping–air blowing–drying cycle. The MoO_3 loading of the powder catalyst was varied from 12.0 to 24.3 wt.%, keeping the MoO_3/NiO wt. ratio fixed at 6. With an increase in metal loading, the surface area, pore volume and the concentration of weak acidic sites decreased, whereas the metal particle size and the concentration of acidic sites of intermediate strength increased. The highest conversion was obtained with the catalyst containing 18.6 wt.% MoO_3 and 3.21 wt.% NiO. The effectiveness factor of the larger size catalyst (average size: 1.5 mm) varied from 0.61 to 0.71 at 593 K. The rate constants (calculated on the basis of metal loading) for the monoliths were in good agreement with those obtained in a packed bed, implying that all the catalyst was utilized in the monoliths. After a 72 h run at 593 K and 10 MPa, the concentration of strong acidic sites increased but there was no change in the activity or product distribution.

1. Introduction

In recent years, the availability of low sulfur crude oils is diminishing and the remaining hydrocarbon reserves consist mostly of heavy crudes that contain relatively higher concentrations of polluting sulfur, oxygen and nitrogen compounds. On the other hand, the allowable limit of sulfur in transportation fuels is being continuously reduced. Presently, in USA, the sulfur content of diesel should be below 15 ppm and the allowable limit is expected to be lowered further [1].

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The most commonly used process for reducing the sulfur content of petroleum fractions is hydrodesulfurization (HDS). Though several catalysts have been reported, $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ are the catalysts of choice [2–4]. HDS is a multiphase reaction which requires high temperature and pressure and is usually conducted in co-current, downflow packed bed reactors. The advantages of such a reactor include high volumetric catalyst loading and the ability to handle high throughputs without flooding. However, it suffers from several disadvantages such as high pressure drop, flow maldistribution, pore diffusional limitation and partial wetting of the catalyst. Moreover, with such a flow arrangement, the H_2S concentration increases along the reactor length and inhibits the removal of the more refractory sulfur compounds remaining near the reactor exit. To overcome the shortcomings of packed bed reactors, monoliths have emerged as a promising option. Monoliths are assembly of large number of parallel channels, separated from each other by a thin wall. Depending on the requirement, the channel cross-section can be circular, square or hexagonal [5]. Monoliths possess certain advantages in comparison to packed bed reactors, which includes lower pressure drop, higher mass transfer rates, negligible pore diffusional limitation, high tolerance to plugging and easier scale-up. Moreover, monoliths permit countercurrent operation without flooding problems [6,7].

Out of the different types of sulfur compounds present in diesel, dibenzothiophene and alkyl substituted dibenzothiophenes are the most difficult to desulfurize because of their bulky molecular structure and the steric hindrance associated with alkyl substituted groups [8]. To reduce the sulfur content to below the allowable limit, it is necessary to develop HDS catalysts and reactors with improved activity, selectivity, and stability.

Very limited published information is available for HDS on monoliths, especially at high pressures. The kinetics of HDS of dibenzothiophene was investigated in the temperature range of 543–573 K and a hydrogen pressure of 6–8 MPa on CoMo deposited on a γ-Al_2O_3 monolith but no comparison was made with a packed bed reactor [9]. Ismagilov et al. [10] used Pt supported on zeolite-containing (65% zeolite; 35 wt.% Ca-monlmorillonite) monoliths for the HDS of diesel fuels at a temperature of 573 K and a total pressure of 6 MPa. The crushed catalyst had a higher hydrogenation activity that was attributed to intragranular diffusional limitations on the monolith catalyst. It should be mentioned that monoliths made of γ-Al_2O_3 and zeolites are not available commercially. Several modeling studies have shown the advantages of monolith reactors over conventional reactors for HDS and hydrogenation reactions [11–13].

In this study, the HDS of dibenzothiophene (DBT) has been investigated in the temperature range of 548–593 K and a pressure of 10 MPa on ceramic monoliths coated with Ni–Mo/γ-Al_2O_3 and on powdered catalysts of two different sizes. Moreover, the effect of metal loading (at a constant Ni/Mo ratio) on the conversion of DBT has been evaluated for the monolith and trickle bed reactor. The catalysts were characterized using X-ray diffraction (XRD), surface area using nitrogen adsorption, transmission electron microscopy (TEM), X-ray fluorescence spectroscopy (XRF), temperature-programmed reduction (TPR), temperature programmed desorption of NH_3 (NH_3-TPD) and Raman spectroscopy.

2. Experimental details

2.1. Preparation of NiMo/γ-Al_2O_3 catalysts

The NiMo/γ-Al_2O_3 catalysts of three different metal loadings were prepared by incipient wetness impregnation method. The MoO_3 loading was varied from 12 to 24.3 wt.% whereas the MoO_3/NiO weight ratio in all the catalysts was kept the same at 6. The metal precursor salts used were ammonium heptamolybdate and nickel nitrate. The catalysts were prepared by dissolving 3 g of citric acid in 14 ml of water followed by addition of the required amounts of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$. The contents were stirred till a clear solution was obtained. The solution thus prepared was slowly added to 20 g of Al_2O_3 placed in a rotary evaporator. The catalyst was dried at 353 K under vacuum till the support was free-flowing. The catalyst sample was then dried at 393 K for 1 h followed by calcination of the dried sample at 823 K for 2 h. The powder thus obtained was pelletized, crushed, sieved and the fractions between 0.25 and 0.3 mm (denoted as NiMo 1, NiMo 2 and NiMo 3) and 1.4–1.6 mm (denoted as NiMo 4, NiMo 5 and NiMo 6) retained for use.

2.2. Washcoating of monoliths

Deposition of the catalyst on the monoliths can be done either by first depositing the active metal on the support and then washcoating the monolith with the slurry of the supported catalyst, or by a two-step procedure, in which the monolith is first washcoated with only the support and then the active metal is deposited on the washcoated support. Mogalicherla and Kunzru [14] found that for Pd/Al_2O_3 catalysts, the catalyst dispersion reduced with washcoated loading using the two step procedure and there was a possibility of nonuniform metal deposition. Therefore, for this study, the monoliths were washcoated with slurry of NiMo/γ-Al_2O_3.

NiMo/γ-Al_2O_3 catalysts, prepared using the procedure detailed in Section 2.1 were used for washcoating the 400 cpsi (cells per square inch) cordierite monoliths (Corning, USA). The monolith pieces were approximately 30 cm in length containing 16 channels and a square cross section of 0.5 cm × 0.5 cm. These pieces were machined from larger diameter monolith blocks. The preparation of monolith catalyst was done in two steps. First, the desired composition of supported NiMo/γ-Al_2O_3 catalyst was prepared using the incipient impregnation method followed by deposition of the NiMo/γ-Al_2O_3 on the channel walls using slurry washcoating method [15].

Initially, the as-received monolith was heated for 6 h at 773 K followed by ultra-sonication for 1 h to remove any adsorbed impurities. Then, the initial weight of monolith was measured.

The average size of the NiMo/γ-Al_2O_3 powder catalyst was reduced from 50 μm to 3 μm by wet ballmilling for 24 h in a Planetary mono mill (Pulverisette 6, Fritsch, Germany). Concentrated nitric acid was added to adjust the pH of the slurry to ~3.0 during milling. The milled alumina was dried in an oven at 393 K for 10 h and the soft agglomerates stored for further experiments. The washcoating slurry was prepared by adding the milled alumina powder to water containing colloidal alumina (used as a binder) and again milled for 2 h. The monolith was then dipped vertically in this slurry and the slurry rose through the channels of the monolith due to capillary action. Dipping time was fixed at 4 min. The monolith was removed from the slurry and the excess slurry removed from the channels by blowing compressed air. Then the monolith was dried at 393 K for 4 h followed by calcination at 773 K for 6 h. The change in weight of the monolith was measured to determine the amount of washcoat deposited on the channels. For achieving higher loadings, the dipping–air blowing–drying-cal cination cycle was repeated till the desired loading was obtained. The final washcoat loading of the supported catalyst on the monolith was between 10.2 and 13.0 wt.% of bare monolith weight.

The adherence of the washcoat was measured by subjecting the coated monolith to ultrasonication in acetone for 1 h at an intensity of 33 kHz. In all cases, the weight loss was less than 0.5 wt.% of the washcoat loading.

Since the pH during washcoating is maintained around 3, there is a possibility of the metals leaching out in the slurry. The leaching