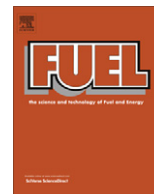


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Adsorptive desulfurization of diesel by regenerable nickel based adsorbents

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HIGHLIGHTS

- ▶ NiMCM-41 and NiY were demonstrated as regenerable diesel sulphur adsorbent.
- ▶ Sulphur level was brought down to below 50 ppm from a 450 ppm 'S' refinery diesel.
- ▶ The process conditions are milder in comparison to conventional HDS processes.
- ▶ The H₂ requirement of the present process is also lower than conventional processes.
- ▶ Adsorbent regeneration conditions were optimized based on TPO study.

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ABSTRACT

An experimental investigation on a vapor phase adsorptive desulfurization process for diesel is described based on NiMCM-41 and NiY as sulphur selective adsorbents. Under optimized conditions [pressure 4 bar (absolute) and temperature 350 °C] the NiMCM-41 adsorbent could bring down the sulphur concentration to a 50 ppm level from a concentration of 450 ppm in a refinery diesel, and about 20 ml of diesel could be treated per gram of adsorbent. With a diesel feed of 150 ppm sulphur, the same adsorbent could bring the sulphur down to 15 ppm level and about 14 ml of the feed could be treated per gram of the adsorbent. The performance of NiY is slightly better than NiMCM-41. Around 25 ml diesel feed could be treated per gram NiY adsorbent in bringing down the sulphur levels from 450 ppm to <50 ppm. Both these adsorbents are regenerable under controlled oxidation with air at ~450 °C without noticeable loss in the sulphur removal capacity. The regeneration conditions were established based on a temperature programmed oxidation (TPO) study on spent diesel adsorbents.

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1. Introduction

Nowadays one of the key parameters for transportation fuel quality is its sulphur content [1]. In India diesel is the main transportation fuel. Europe and USA are also gradually shifting towards a diesel economy due to higher energy efficiency of diesel. With increasing demand of diesel there is also a growing concern about the pollution associated with diesel vehicle exhaust. Worldwide, the sulphur levels for diesel are being tightened through legislation because catalytic converters fitted in diesel driven vehicles are highly susceptible to sulphur poisoning, which in turn leads to harmful vehicular emissions such as SO_x, NO_x and carcinogenic poly aromatic hydrocarbons. In USA the Environmental Protection Agency (USEPA) has mandated 15 ppmw sulphur for highway diesel since 2006 [2]. Europe also envisaged EU-wide changeover to 10 ppm sulphur in diesel for road transport. Other developed

countries such as Japan and Canada have also followed similar regulations [3]. In India the existing two tier system for fuel quality called Bharat Stage specifications (BS) had introduced the BS-IV grade diesel in thirteen major cities since April 2010, which required a reduction of sulphur from the earlier 350 ppm level (BS-III) to 50 ppm (BS-IV). The rest of the country is presently being supplied with BS-III diesel [4].

In future the countrywide change over to BS-IV grade diesel will require enormous investments in Indian refineries if current catalytic hydrodesulfurization (HDS) based technologies are to be used. Catalytic hydrodesulfurization (HDS) by CoMoS or NiMoS based catalysts are the established processes in petroleum refineries for the production of desulfurized transportation fuels like gasoline, diesel and jet fuels. However deep HDS for ultra low sulphur diesel production (ULSD) becomes uneconomical, when a sulphur level <50 ppmw is targeted [5,6]. This is because sulphur species such as dibenzothiophene and substituted dibenzothiophenes (e.g. 4,6 dimethyl-di-benzothiophene) present in this concentration range are highly refractory in nature and require high severity operations (high H₂ pressure, high temperature) to break the C–S bond. The

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catalyst activity also needs to be boosted by few orders of magnitude if conventional refinery HDS infrastructure is to be utilized without revamp. The severity of operating conditions and increased requirement of high purity hydrogen for ULSD production also makes the process a leading contributor in the overall refinery carbon footprint.

There is thus an urgent need for an energy efficient, low cost and greener deep desulphurization process for diesel. Several alternative greener desulfurization pathways have been proposed in recent years based on mainly solvent extraction, oxidative desulfurization and adsorption [7]. The adsorption based approaches appear particularly attractive due to their simpler flow sheet and less hydrogen requirement. There are several reports on diesel sulphur removal using different adsorbents such as activated carbon [8], metal exchanged zeolites [9–11], metal oxides [12] and mesoporous materials [13]. Most of these studies have focused on testing of new adsorbent materials for their desulfurization performance. The adsorbent regeneration aspects are carried out by either solvent elution or by thermal treatment and reports are often sketchy. In studies where the adsorbent is thermally regenerated, as in the recent reports on use of nickel based adsorbents for deep adsorptive desulfurization of transportation fuels, the adsorption is generally at ambient temperatures with thermal regeneration at much higher temperatures, so that there is a large temperature swing involved [10,11]. This makes the process operationally difficult to implement. Also very limited focus has been given on studying diesel desulfurization performance over multiple adsorption–regeneration cycles which will be important in establishing the long term adsorbent regenerability and hence viability of an adsorptive desulfurization process. Among the few studies reported was the Conoco–Phillips's one on the development of a fluidized bed adsorption process for diesel along the same line as their gasoline desulfurization process, which was based on proprietary mixed oxide based sorbents [14]. Their approach is based on a concept called reactive sorption where sulphur-containing molecules were selectively adsorbed, including sterically hindered molecules like 4,6 dimethyl-dibenzo-thiophene, and the sulphur atom was then split from the molecule and retained on the adsorbent while the hydrocarbon gets desorbed. The process is claimed to require milder operating conditions (Pressure: 19–35 bar; Temperature: 371–427 °C) in comparison to catalytic HDS. However the process is yet to be established commercially.

In the present paper we report an experimental investigation on a vapor phase adsorptive desulfurization process for diesel using NiMCM-41 and NiY as sulphur selective adsorbents. Controlled high temperature air oxidation was used to regenerate these adsorbents and the optimum conditions for such regeneration were identified from independent TPR/TPO studies on the spent adsorbents.

2. Experimental

2.1. Adsorbent preparation

2.1.1. NiY

NiY was prepared by ion exchanging NaY (Si/Al = 2.5, Süd Chemie) three times with 1.72 M Ni(II) aqueous solution under reflux conditions keeping nickel ion in exchange solution four times the calculated ion exchange capacity of NaY. The detailed preparation procedure was reported elsewhere [15,16]. ICP analysis showed a nickel content of 8.8 wt% which corresponds to ~97% Ni²⁺ exchange.

2.1.2. NiMCM-41

The SiMCM-41 support for nickel loading was precipitated from a gel of the molar composition: SiO₂:C₁₆H₂₉N(CH₃)₃Br:H₂O =

1:0.4:68. Sodium Silicate (Assay 10% NaOH, 27% SiO₂) was used as the silica source. The siliceous MCM-41 were loaded with 8.8 wt% Ni (same Ni content as in NiY) by the incipient wetness impregnation method using required amount of Ni(NO₃)₂·6H₂O salt, solubilized in THF, as a precursor of Ni. The light green solid obtained was calcined in a furnace at 550 °C for 14 h (heating rate 1 °C/min).

2.1.3. Adsorbent forming

Extrudates of the calcined NiMCM-41 and NiY were formed by mixing γ -alumina as binder. The amount of γ -alumina added was 30 wt% of the total mixture. A thick paste was formed by adding the required amount of 3 vol% acetic acid into the above mixture with thorough mixing. This paste was then pressed through a hand extruder to form cylindrical shaped extrudates which were dried at 100 °C overnight and then calcined at 500 °C for 5 h. Finally the particle size of the extrudates was brought down to about 1.5 mm length by cutting with a sharp razor blade.

2.2. Adsorbent characterization

The adsorbent materials after nickel loading were characterized for surface area, pore volume and pore size distribution in a Micromeritics Tristar instrument by measuring nitrogen adsorption desorption isotherms at –196 °C and applying the BET, BJH isotherm model at the appropriate P/Po region.

2.3. Fixed bed adsorption breakthrough experiments

The adsorption breakthrough experiments were carried out in an automated adsorber system schematically shown in Fig. 1. The unit has the provision of in situ thermal regeneration/activation of spent adsorbent under oxidizing and reductive atmosphere. For adsorption breakthrough experiments, 10 g of adsorbent was packed inside the stainless steel (SS 316 grade alloy) made adsorber column of 19 mm I.D. positioned inside a three zone tubular furnace. An HPLC pump was used to pump diesel feed from a reservoir to the adsorber through a liquid preheater which served to vaporize the feed. The diesel vapors leaving the preheater were mixed with a H₂–N₂ gas mixture (50 vol% H₂) or pure H₂ and entered the adsorber from the bottom. Vapors exiting the adsorber were cooled and taken to a high pressure gas–liquid separator. Condensed liquid (desulphurised product) was withdrawn from the separator with a liquid level control by a Liquid Control Valve (Badger Instruments, USA) and analysed for sulphur content, while uncondensed vapors were vented under pressure control through a pressure control valve (Badger Instruments, USA), as shown in Fig. 1. Three thermocouples axially placed inside the adsorber column were used to monitor the temperatures. Prior to the first adsorption experiment the adsorber column was heated at 350 °C in the presence of flowing dry nitrogen for 2 h in order to remove any moisture present in the adsorbent bed. The detailed adsorption conditions are given in Table 1.

Analysis of the diesel feed and product sulphur was done by the X-ray fluorescence technique (Spectrofinix) using sulphur calibration curves made with the help of known sulphur solutions in 0–1000 ppm sulphur range. These solutions were prepared by dissolving measured amount of dibenzothiophene in *n*-hexadecane.

2.4. Regeneration experiments

After each adsorption experiment the bed was regenerated by following a three step protocol (Table 1). In the first step, the bed was purged by dry nitrogen at 350–450 °C for 30 min at ambient pressure in order to purge out hydrocarbon vapors from the void space of the adsorbent bed. The second step was oxidative regen-

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