



Investigating role of sulphur specific carbon adsorbents in deep desulphurization



Sandip V. Patil^a, Laxmi Gayatri Sorokhaibam^a, Vinay M. Bhandari^{a,*}, D.J. Killedar^b, Vivek V. Ranade^a

^a Chemical Engineering & Process Development Division, CSIR-National Chemical Laboratory, Pune 411 008, India

^b Shri G.S. Institute of Technology and Science, Indore 452003, India

ARTICLE INFO

Article history:

Received 10 April 2014

Accepted 9 July 2014

Available online 14 July 2014

Keywords:

Thiophene

Desulphurization

Adsorption

Fuel

Pollution

ABSTRACT

Adsorptive desulphurization of model fuel (thiophene in isooctane) was studied by using sulphur specific carbon based adsorbents, SHIRASAGI GH2x 4/6 and SRCx 4/6, in an attempt to obtain insight into the adsorptive behaviour of sulphur moiety on the modified surfaces. Both adsorption equilibria and adsorption kinetics have been reported. Characterization of the modified adsorbents was carried out using scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction (XRD) and surface area analyser. Adsorption experiments along with characterization results highlight potential for higher sulphur adsorption on the modified adsorbents. Substantially higher capacities for adsorption of thiophene were obtained, ~ 5.5 and $\sim 20 \text{ mg g}^{-1}$ of sulphur for SHIRASAGI GH2x 4/6 and SRCx 4/6 respectively. Experimental investigations reveal possible influence of Al/Si ratio, 12.46 and 9.35 in GH2x and SRCx respectively that can have implication in adsorption behaviour. It was found that surface modification plays important role in enhancing sulphur removal capacity as compared to conventional carbon adsorbents. A plausible mechanism to account for surface interactions and role of surface modification has been proposed. The higher mesopore volume along with higher oxygen content is believed to influence preferential adsorption of thiophenic sulphur by SRCx. The work also indicated specific role of Al and Si content in the carbon matrix. The utility of these adsorbents and higher sulphur removal capacity has also been confirmed using synthetic mixture of refractory sulphur compounds such as benzothiophene, dibenzothiophene along with thiophene.

© 2014 Elsevier Ltd. All rights reserved.

Introduction

The ever increasing stringent environmental regulations require sulphur content in transportation fuels to be reduced drastically. Whereas the earlier environmental norms allowed sulphur content in diesel and gasoline to be 500 and 300 ppm respectively, the existing norms require this to be brought down nearly 10 fold i.e. 15 and 30 ppm respectively [1–3]. Gasoline, an attractive option for application in fuel cells, also has limitations due to stringent requirement of sulphur content well below 1 ppm to avoid poisoning of catalyst. In such cases, adsorptive desulphurization can be one of the most promising processes for deep desulphurization to meet the challenge. Understanding surface interactions and surface modifications can substantially aid development in this regard.

The removal of sulphur compounds during petroleum refining operations to obtain different fuel fractions is not straightforward and becomes increasingly more and more difficult with lowering of sulphur concentrations. The three important fuel fractions namely gasoline, diesel and jet fuel contain variety of sulphur compounds. Generally, gasoline contains mercaptans, sulfides, disulfides, thiophene, alkylated derivatives of thiophene and benzothiophene while the sulphur compounds in the diesel comprise mainly of alkylated benzothiophenes, dibenzothiophene and its alkylated derivatives. Conventionally, hydrodesulphurization (HDS) [4] is used to bring down sulphur concentration in liquid fuels. However, with existing stringent norms for drastically lower sulphur concentrations, HDS processes have severe limitations in bringing down sulphur concentrations to desired levels both technically and economically. Hydrodesulphurization process requires suitable catalyst for removal of sulphur compounds and operates at high temperatures of the order of 450°C and high pressures of the order of 20–40 atm. The removal of these sulphur compounds, including refractory sulphur compounds by HDS process to meet the desired levels would demand more than 3 fold increase in the catalyst

* Corresponding author: Tel.: +91 020 25902171; fax: +91 2025893041.

E-mail addresses: laxmigayatri1@gmail.com (L.G. Sorokhaibam), vm.bhandari@ncl.res.in (V.M. Bhandari).

Nomenclature

a_L	Langmuir theoretical adsorption capacity, mg g^{-1}
AC	activated carbon
ADS	adsorptive desulphurization
b_L	Langmuir adsorption constant, L mg^{-1}
BDS	biodesulphurization
BT	benzothiophene
C_e	liquid phase concentration at equilibrium, mg L^{-1}
C_0	liquid phase initial concentration, mg g^{-1}
C_s	Solid phase concentration of sulphur at equilibrium, mg L^{-1}
DBT	dibenzothiophene
GH2x	SHIRASAGI GH2x 4/6 adsorbent
HDS	hydrodesulphurization
K_F	Freundlich adsorption coefficient, $(\text{mg} \cdot \text{g}^{-1})(\text{L} \cdot \text{mg}^{-1})^{1/n_F}$
n_F	Freundlich constant
q_e	solid phase concentration at equilibrium, mg g^{-1}
$q_{e,\text{cal}}$	calculated equilibrium adsorption capacity
$q_{e,\text{exp}}$	experimental equilibrium adsorption capacity
R_L	Langmuir dimensionless constant separation factor
SRCx	SHIRASAGI SRCx 4/6 adsorbent
T	thiophene

volume/reactor size and as a consequence, rise in cost of operation of this high temperature and high pressure process. HDS method may also lead to decrease in fuel efficiency due to decrease in octane number [5] of the fuel resulting from saturation of aromatic or olefinic groups in meeting the new stringent specifications. It is therefore instructive to evaluate alternate solutions to this problem and possible alternatives include adsorptive desulphurization [6], biodesulphurization [7–9] and oxidative desulphurization [10–12].

The need for practically sulphur free fuels like gasoline needed for fuel cell application has necessitated the scope not just for development of newer methods but for more techno-economically feasible options like adsorption process that operate at ambient temperature and pressure conditions. Deep desulphurization considerations have provided impetus for research in different technological platforms, and adsorptive desulphurization seems to be a promising one. Adsorptive separations also have limitations in sulphur removal, mainly due to low capacity for sulphur removal, difficulty in removing refractory sulphur compounds and poor understanding of surface interactions that play crucial role in sulphur removal. This in turn requires improved understanding of adsorption behaviour of various sulphur compounds on different adsorbent surfaces, modification of surfaces, extent and efficacy of newer materials/modifications in deep desulphurization.

Adsorptive desulphurization (ADS) can remove sulphur compounds through physisorption, chemisorption or π complexation. Adsorption process using porous forms of activated carbons [13] and modified adsorbents can be an excellent technique that may integrate with the existing HDS process to meet the threshold limit of sulphur content in diesel and other fuels. The advantages of conventional adsorption process and issues with other processes make it imperative to study production of ultra-low sulphur fuels using adsorption and newer adsorbents. Apart from this, ADS method does not impart impurity and fuel composition remains essentially unchanged. The typical adsorption process is expected to offer selective removal of sulphur compounds under ambient conditions with ease of operation/process control and economically achieve removal of sulphur compounds from the

transportation fuels with greater efficiency. The ease of regeneration with minimum requirement of chemical or energy is crucial for satisfactory implementation of this technology. A number of sorbents starting from simple activated carbons [14] to π -complexation adsorbents have been reported in the literature with varying degree of success, though unsatisfactory in most cases. Sorbents impregnated with transition metals like Ni [15], Fe [16], Cu [17], Zn, Mn [18], Pd, Vn [19] and Ce have also been reported. Ion exchanged zeolites have been found to be promising adsorbents with sulphur removal capacity of 42 mg g^{-1} using model fuel of benzothiophene, dibenzothiophene and 4,6-dimethyl dibenzothiophene [2]. Hernández-Maldonado and Yang [20] showed that Cu-Y and Ag-Y zeolites have good capacity for thiophene sulphur removal from benzene and *n*-octane mixtures. Researchers have worked with solid adsorbents like activated carbon, Ag-loaded nanofibrous membranes [21], zeolites, polymeric adsorbents etc. for several separation/purification applications including industrial applications due to their high surface area and good adsorption capacity. In this regard, though a large number of adsorbents with different matrix, porous structure and adsorbent capacity are available for commercial use, the selection for any particular application is not an easy process and not straightforward. It is where the role of surface functional groups has to be investigated wherein certain functional groups affect the interaction with specific or polar adsorbate. Sulphur is known to be slightly polar in nature and this aspect of sulphur may be exploited for successful desulphurization of transportation fuels like diesel. This is also expected to provide insight into effective regeneration strategy that is difficult in most cases as of today. The selection of the present adsorbents, GH2x and SRCx for desulphurization application was envisaged in the light of polarity interactions for obtaining improvement in desulphurization performance.

Experimental

Materials, reagents and methods

Thiophene (99.9% purity, Loba Chemicals), isooctane (99.9% purity, Loba Chemicals), benzothiophene (95%, Fluka) and dibenzothiophene (98%, Sigma–Aldrich) were used without further purification. Modified carbon based adsorbents SHIRASAGI GH2x 4/6 and SHIRASAGI SRCx 4/6 procured from Japan EnviroChemicals Ltd. were used for liquid phase adsorption of thiophene from isooctane and also for synthetic fuel mixture. Pelletized Norit activated carbon procured from Aldrich was also used in the experimental investigation. The samples were analysed for sulphur removal using total sulphur analyser, TN-TS 3000 (Thermoelectron Corporation, Netherlands) and also with Gas Chromatograph (Agilent GC 7980) equipped with CPSil 5CB for sulphur as column ($30 \text{ m} \times 320 \times 4 \mu\text{m}$) in conjunction with flame photometric detector. Helium was used as a carrier gas with flow rate of 1.25 mL min^{-1} and split ratio of 10:1. The injector temperature employed was 250°C with injection volume of $1 \mu\text{L}$ and total analysis time of 40 min. The oven temperature was ramped at 5°C min^{-1} from 40 to 100°C and $40^\circ\text{C min}^{-1}$ to 230°C . Reproducibility of the experimental results was checked and was found satisfactory.

Adsorption studies

Equilibrium adsorption studies were carried out at 30°C using standard procedures. Known volume of solution – predetermined concentration was equilibrated with known weight of the adsorbent in the range of 0.05–1 g per 10 mL of model fuel (initial concentration of 442.5 mg L^{-1} of total sulphur using thiophene as sulphur containing component in iso-octane). Equilibration time of

Download English Version:

<https://daneshyari.com/en/article/221984>

Download Persian Version:

<https://daneshyari.com/article/221984>

[Daneshyari.com](https://daneshyari.com)