Catalysis Today 141 (2009) 99–102

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Adsorptive desulfurization of diesel on activated carbon and nickel supported systems

V. Selvavathi [a,*], V. Chidambaram [a], A. Meenakshisundaram [a], B. Sairam [a], B. Sivasankar [b]

[a] Research and Development Center, Chennai Petroleum Corporation Limited, Chennai, India
[b] Department of Chemistry, Anna University, Chennai, India

ARTICLE INFO

Article history:
Available online 1 July 2008

Keywords:
Adsorptive desulfurization
Carbon A
Carbon B
Dibenzothiophenes
4-Methylbenzothiophene
4,6-Dimethyl-dibenzothiophene
Adsorption capacity

ABSTRACT

Adsorptive desulfurization (ADS) process was studied for the refractory sulfur compounds viz., dibenzothiophene (DBT), 4-methylbenzothiophene (4MDBT) and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) present in diesel fuel (Gas oil). Two commercially available activated carbons A and B and modified forms of the same by HNO_3 treatment and Ni supported systems were used for the adsorption studies. The modified activated carbon samples A and B showed better adsorption capacity when compared with that of as received activated carbon samples and metal supported systems.

1. Introduction

The maximum allowable sulfur content in highway diesel fuel is reduced to less than 15 ppmw in 2006 in the US and will be less than 10 ppmw by 2010 in the EU. Bringing down the sulfur level of diesel to less than 50 ppmw by catalytic hydrodesulfurization appears difficult due to the steric hindrance exhibited by the more refractory sulfur compound viz., 4,6-dimethyl-dibenzothiophene.

Alternatively, an innovative process is adsorptive desulfurization. Development of new adsorbents with high sorption capacity, selectivity and regenerability is the key to an efficient adsorptive desulfurization process. It is known from literature that acid treatment of activated carbon increases adsorption capacity [1].

The adsorption performance of carbon material depends on their surface physical and chemical properties. In this study we examined two commercially available activated carbons A and B, modified forms of A and B, nickel loaded on modified activated carbons, alumina, silica and Y-zeolite samples. The surface physical properties were characterized by BET. The adsorption selectivity of the carbon materials and other adsorbents for adsorptive desulfurization of diesel fuel are discussed on the basis of experimental results obtained in this study.

2. Experimental and methods

2.1. Modification of activated carbon

Powder forms of both the commercial carbon samples were modified by treating with HNO_3 followed by argon treatment in order to alter the surface functional groups and surface area.

3. Characterization

3.1. Feedstock

The total sulfur content of diesel feedstock was determined by X-ray fluorescence spectrophotometer. The different types of sulfur compounds present in the feed diesel were analyzed using Varian GC-PFPD-CP-3800 analyzer and the chromatogram is given in Fig. 1. It is inferred from GC-PFPD chromatogram that the main Sulfur compounds present in diesel feed are 11 ppm of 4-MDBT, 128 ppm of 4,6-DMDBT, 31 ppm of other C_2DBTs, 110 ppm of C_3DBTs and 10 ppm of C_3 + DBTs [2]. The feedstock was characterized for other properties like density, viscosity, aniline point, pour point and flash point and are given in Table 1.

3.2. Adsorbents

The textural characteristics of adsorbents were characterized by adsorption/desorption of nitrogen using Quantachrome Auto-

* Corresponding author. Tel.: +91 44 25944048; fax: +91 44 25941338.
E-mail addresses: vselvavathi@cpcl.co.in, vselvavathi@yahoo.co.in (V. Selvavathi).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.05.009

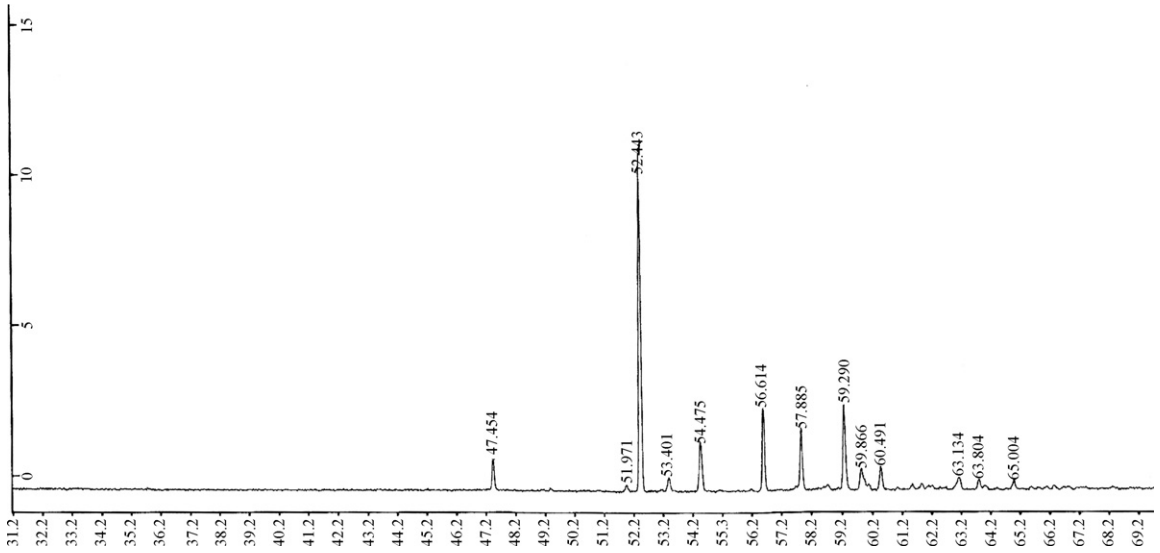

Fig. 1. GC-PFPD for diesel feed stock.

Table 1
Characteristics of the diesel feed and product

Characteristics	Diesel feed	Diesel product (modified carbon A at 0.4 LHSV)
Flash point (°C)	102.2	103.5
Aniline point (°C)	75.0	83.5
Viscosity at 40 °C (Cst)	4.55	4.31
Pour point (°C)	+3	+3
Total sulfur (ppm)	290	27
Density (g/cc)	0.8495	0.8412
Diesel index	59	65

sorb-1-C surface area and pore size distribution analyzer. The characteristics of the adsorbents are given in Table 2.

4. Adsorption studies

4.1. Adsorption using model compound

To validate the adsorptive desulfurization of refractory sulfur compounds using activated carbon, sulfur free Liquid Paraffin Oil (LPO) doped with 50 ppm of DBT, 125 ppm of 4-MDBT and 125 ppm of 4,6-DMDBT model refractory sulfur compounds was used as feed. The adsorption experiment was conducted using modified activated carbon 'A' in a stainless steel column at 0.4 LHSV. GC-PFPD chromatograms of the model compound feed and the product obtained after adsorption are given in Figs. 2 and 3 respectively. It is observed from the GC-PFPD chromatogram (Fig. 3) that the model refractory sulfur compounds are completely adsorbed.

4.2. Adsorptive studies using industrial feedstock

In the present study, dehydrodesulfurized (DHDS) diesel fuel from Chennai Petroleum Corporation Ltd. was taken as the feedstock for adsorptive desulfurization. The total sulfur content of the feedstock was 290 ppm.

The adsorbents were tested in a fixed bed flowing system with a stainless steel column. The adsorption conditions were controlled at Liquid Hourly Space Velocities (LHSVs) of 0.4, 0.7, 1.0, 1.3 and 1.6 at room temperature. The product diesel eluted was analyzed for total sulfur content and types of sulfur compounds.

5. Results and discussion

Using modified carbon 'A' at 0.4 LHSV the sulfur content in product diesel was reduced up to a level of 27 ppm.

Table 2
Characteristics of the adsorbents

Types of adsorbents	Surface area (m^2/g)	Pore volume (cm^3/g)	Adsorption capacity (mgS/gm of Ads.)	Adsorption capacity ($mgS/m^2/g$ of Ads.)
Carbon A	939	0.588	0.45	4.79×10^{-4}
Modified carbon A (350 °C)	1014	0.65	1.2	1.18×10^{-3}
Modified carbon A (600 °C)	1106	0.71	1.6	1.45×10^{-3}
Modified carbon A (800 °C)	1080	0.68	1.5	1.39×10^{-3}
Carbon B	882	0.40	0.31	3.51×10^{-4}
Modified carbon B (350 °C)	953	0.47	0.91	9.55×10^{-4}
Modified carbon B (600 °C)	1048	0.52	1.05	1.0×10^{-3}
Modified carbon B (800 °C)	1022	0.51	0.99	9.69×10^{-4}
Ni/carbon A	980	0.48	0.81	8.26×10^{-4}
Ni/carbon B	914	0.42	0.58	6.35×10^{-4}
Silica	461	0.36	0.27	5.86×10^{-4}
Alumina	322	0.21	0.18	5.59×10^{-4}
HY-zeolite	570	0.19	0.14	2.46×10^{-4}
Ni/silica	371	0.28	0.23	6.20×10^{-4}
Ni/alumina	262	0.17	0.11	4.2×10^{-4}
Ni/HY-zeolite	350	0.14	0.07	2.0×10^{-4}

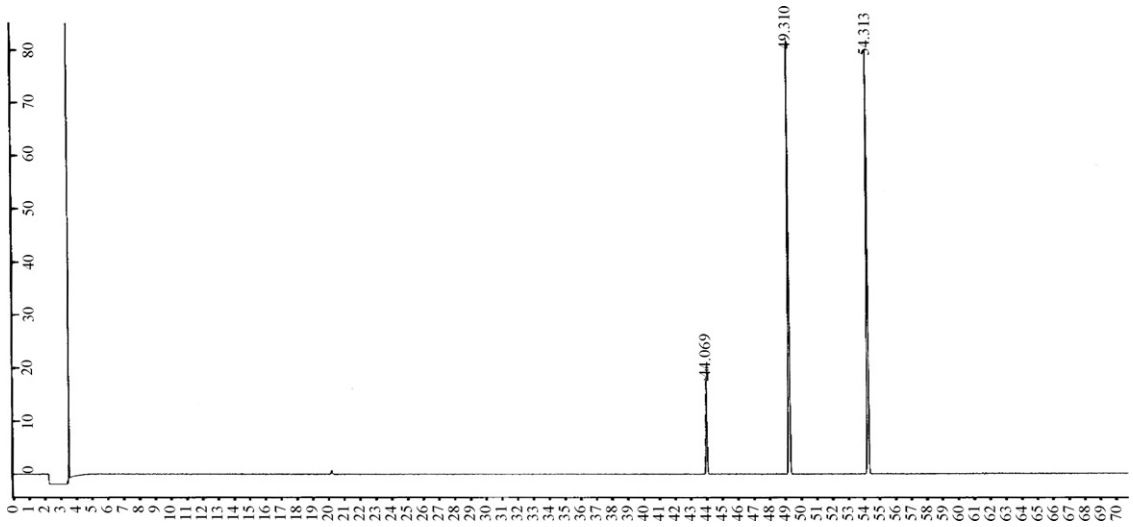

Fig. 2. GC-PFPD chromatogram for the model compound feed.

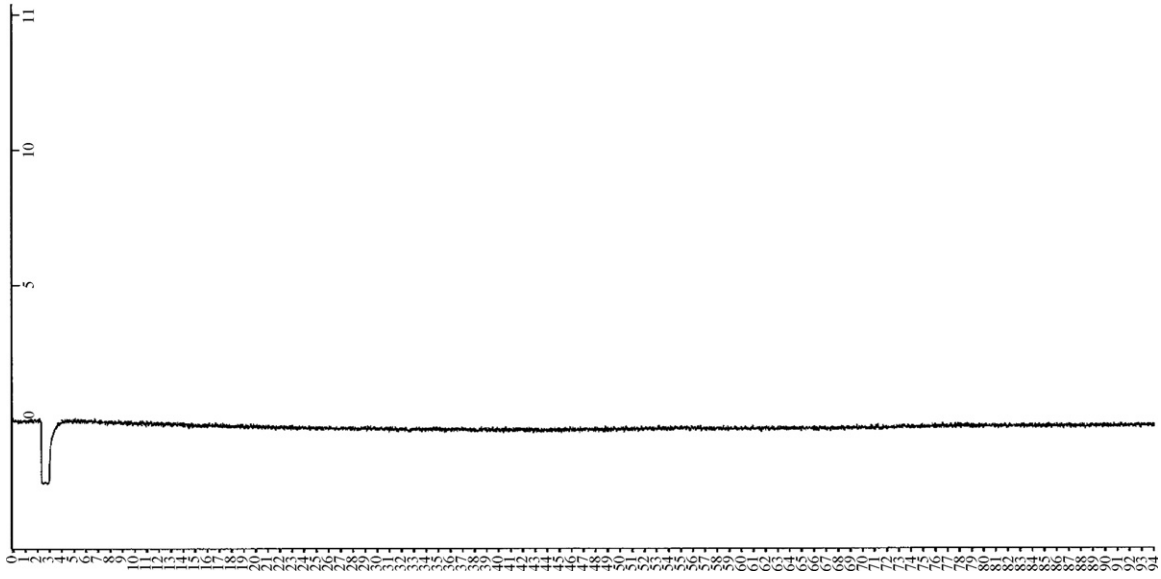

Fig. 3. GC-PFPD for the model compound product.

5.1. Effect of modification temperature

It was found that nitric acid treated carbon followed by argon treatment at 600 °C could result in maximum surface area. It has been shown that nitric acid treatment results in the alteration of its nature of surface functional groups as well as the surface area of carbon samples [3]. From Table 2, it is deduced that modified carbons 'A' and 'B' showed maximum surface area when they were calcined at 600 °C.

5.2. Effect of nitric acid and argon treatment

The modification of the carbon by acid and argon treatment on the surface functionalities was studied by FT-IR and the results are given in Fig. 5.

HNO_3 treatment followed by Ar activation resulted in an increase in the intensity of the bands centered around 1080 and 1450 cm^{-1} indicating an increase in the amounts of oxygen surface functional groups namely phenolic (C–O stretching and O–H bending). The intensity of the band centered around 1630 cm^{-1} also showed a steep raise indicating enhancement in the aromatic C=C groups (carbonization). The presence of aliphatic CH_2 stretching is evidenced only in carbon 'A' treated with HNO_3 and activated in Ar atmosphere.

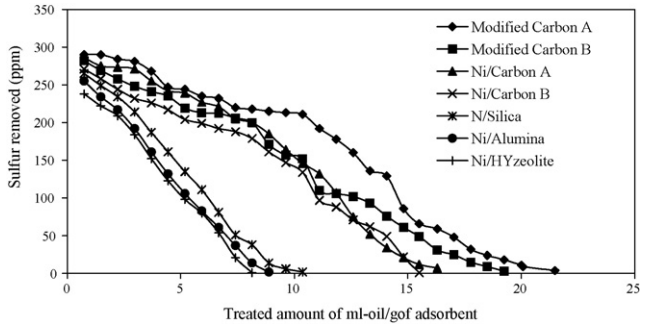

Fig. 4. Comparison of all the adsorbents at 0.4 LHSV (h^{-1}).

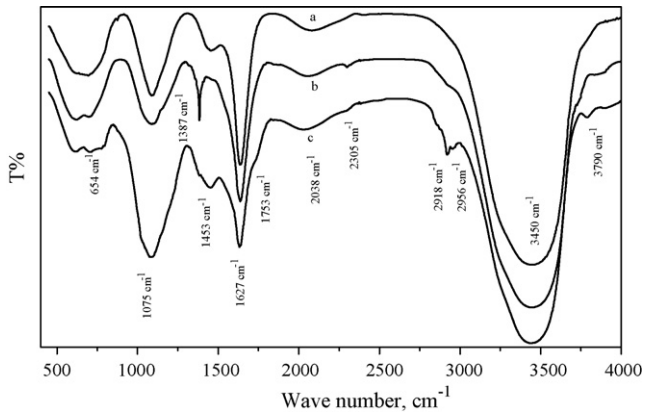

Fig. 5. FT-IR spectra of (a) modified carbon A as received, (b) modified carbon treated with nitric acid and (c) modified carbon A treated with nitric acid followed by Ar activation.

5.3. Comparative study on the adsorption capacity of the adsorbents

The adsorption capacity of modified commercial activated carbons is high compared to that of nickel supported systems. The reduction in adsorption capacity arises due to occupation of the pores by the metal ions, which effectively reduces the adsorption of bulky molecules and also due to steric hindrance exhibited by the alkyl groups in 4,6-DMDBT [4].

Adsorption capacities are generally reported both in per gm basis and per unit surface area basis. In our work the adsorption capacity trend for both basis is same and hence we have reported only based on mass. The comparison based on mass and surface area is given in Table 2. The comparison of all the adsorbents at 0.4 LHSV is given in Fig. 4.

Under the same experimental conditions employed, it was found that the breakthrough capacity was 2.83 mg S/g of adsorbent (mg/g) for model compounds whereas it was about 0.83 mg S/g for the diesel feedstock. The results pertain to modified carbon A which has the highest breakthrough capacity among the systems studied. The breakthrough capacity for commercial gasoline using Cu (I) HY zeolite was reported 0.22 mg/g [5].

The adsorptive capacity of activated carbons for the sulfur compounds has to be associated with the type of π–π interactions as well as due to refunctionalisation of carbon surfaces for favorable interaction with sulfur compounds. The carbon systems easily adsorb highly refractory substituted dibenzothiophenes as compared to thiophenes as seen by the GC-PFPD results. This indicates that the methyl groups enhance the adsorption affinity or interaction probably through increasing the electron density or π–π interaction of the aromatic systems.

The adsorption capacities of different adsorbents used in this study are given in Table 2. The adsorption capacity of different adsorbents decreases in the order: modified activated carbon 'A' > modified activated carbon 'B' > Ni/modified carbon 'A' > Ni/modified carbon 'B' > Ni/silica > Ni/alumina > Ni/HY zeolite.

6. Conclusion

The studies using model compounds suggest that adsorptive desulfurization of more refractory sulfur compounds is possible on modified activated carbon systems.

Different carbon materials exhibit significantly different adsorption capacities and selectivities for sulfur removal, which depends not only on the textural properties of the carbon materials but also on the surface functional groups. Trend for adsorption selectivities for various adsorbents increases in the order, carbon A (modified) > carbon B (modified) > Ni/carbon A > Ni/carbon B > Ni/silica > Ni/alumina > Ni/HY-zeolite.

References

[1] A. Zhou, X. Ma, C. Song, Preprints, ACS Div. Petrol. Chem. 49 (3) (2004) 329.
[2] V. Selvavathi, A. Meenakshisundaram, B. Sairam, B. Sivasankar, Petrol. Sci. Technol. 26 (2008) 208–216.
[3] S.A. El-molla, G.A. El-Shobaley, S.A. Sayed Ahmed, Chin. J. Catal. 28 (2007) 611.
[4] X. Ma, S. Velu, J.H. Kim, C. Song, Appl. Catal. B: Environ. 56 (2005) 137.
[5] A. Zhou, X. Ma, C. Song, J. Phys. Chem. B 110 (2006) 4699.