Influence of different hydrocarbon components in fuel on the oxidative desulfurisation of thiophene: Deactivation of catalyst

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HIGHLIGHTS

- Oxidation of thiophene in five different model fuels was studied using TS-1 as catalyst.
- Fresh and used catalysts were analyzed to confirm the deposition of hydrocarbons and sulfur.
- Five model fuels were prepared by mixing n-octane, benzene and cyclohexane with thiophene in iso-octane.
- A deactivation based kinetic model is proposed.

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ABSTRACT

Oxidation of thiophene in five different model fuels was studied using TS-1 as catalyst and the influence of different hydrocarbon components in the model fuels on the oxidation and catalyst deactivation were observed in a batch process. The model fuels were prepared by dissolving thiophene at a particular concentration in iso-octane and then adding different types of hydrocarbons such as, a naphthene, a paraffin, an alkane and an aromatic one by one into the basic model fuel. Fresh as well as used catalysts were analyzed in BET, FTIR, XPS and EDS to confirm the deposition of different hydrocarbons as well as sulfur on the catalyst surface. The effects of different process variables on the reaction under catalyst deactivation were noted. Deactivation kinetics for the catalytic reaction was proposed including evaluation of process parameters at different temperatures. The activation energy of the reaction with deactivation of catalyst was found to be 19.13 kJ/mol.

1. Introduction

Environmental concerns have driven people of today's world to use fuel of very low sulfur content. Automobile emission with sulfur oxide gases now-a-days compels to make strict regulation by all the developed and developing countries on the limit of sulfur content in the combustion fuels. According to U.S. guidelines, the latest sulfur level in gasoline should be kept less than 15 ppmw [1] and according to EURO IV standard the maximum sulfur content in gasoline and diesel have been restricted to 50 ppm since April 1, 2010 [2] in some selected cities in India. Hydrodesulfurisation (HDS) is the conventional process practised in refinery for removal of sulfur compounds from petroleum cuts. As this process suffers from some disadvantages, such as, difficulty to remove refractory sulfur compounds, and high severity

operation with the use of valuable hydrogen gas [3], people are prone to search some alternative desulfurisation processes which may surpass the drawbacks of HDS. In this search, oxidative desulfurisation (ODS) is found to be one of the interesting and easier processes and a handsome amount of research work have already been done on this field [4–7].

The work which have been done in ODS are mostly concerned about using either different types of oxidizing agents [8–13], or different catalysts [14–17] or application of ODS on different sulfur substrates [9–11]. Almost all work was done with either a model fuel containing a sulfur compound dissolved in a solvent or with a light petroleum cut. No work has been found which deals with the effect of different hydrocarbon components of a cut on the removal of a sulfur compound by ODS and how the catalyst is being deactivated in the process. Deactivation of catalyst may occur by poisoning, fouling, thermal degradation, vapor compound formation accompanied by transport, vapor–solid and/or solid–solid reactions, and attrition/crushing [18]. The probable reason for deactivation in ODS process may be due to the poisoning by

either sulfur or hydrocarbon deposition on catalyst surface. Poisons are usually substances whose interaction with the active sites is very strong and irreversible and in this respect the increasing poisoning activity for sulfur species, is $H_2S > SO_2 > SO_4^{2-}$ [19]. Deactivation by sulfur poisoning and carbon deposition of steam reforming catalyst of n-hexadecane on a rhodium/nickel catalyst supported on γ-alumina has been reported. TEM–EDS of used catalysts showed adsorption of sulfur on the surface of Ni crystallites and a large carbon deposition was observed during steam reforming of sulfur-bearing fuel [20]. The deactivation of Pt/Ba/Al$_2$O$_3$ catalyst by SO$_2$ and the regeneration of the sulfated catalyst under hydrogen and other gas mixtures have been studied with characterization of catalyst [21]. Deactivation of a commercial chromia–alumina catalyst was investigated by using a VOC containing chlorohydrocarbons and it has been concluded that the catalytic activity and selectivity were dependent on the type of feed stream and the reactor design [22]. Cu–Zn oxide catalyst was reported to be deactivated in the methanol synthesis process where the deactivation is observed to be delayed by the incorporation of Zn in the catalyst which forms zinc sulfide and sulfate, thus extending the catalyst life [23]. Deactivation of Pt catalyst supported on γ-alumina by benzothiophene as sulfur contamination in tetralin hydrogenation reaction was investigated and the characterization of fresh and sulfur-poisoned catalysts was reported [24].

As petroleum fraction is a mixture of different hydrocarbons, the present work was aimed to find out the effects of different types of hydrocarbons, such as, alkane, naphthene, olefin and aromatic, on the oxidation of thiophene in model fuel. Different model fuels of different hydrocarbons compositions have been prepared with a definite amount of thiophene (TH) content. In this ODS process, commercial titanium silicate-1 (TS-1) and tertiary butyl hydroperoxide (TBHP) were used as catalyst and oxidant respectively. The deactivation of catalyst was studied and deactivation kinetics was proposed. Table 4 showed the comparison among the different catalysts on thiophene removal.

2. Experimental

2.1. Materials

Thiophene, n-octane and TBHP were procured from Spectrochem Private Ltd., India; cyclohexane, iso-octane, benzene and dimethyl sulfoxide (DMSO) were obtained from Merck Specialities Pvt. Ltd., India and TS-1 was purchased from Sud Chemie India Ltd.

2.2. Methods

The reaction was done in a 100 ml glass reactor fitted with a glass stirrer and condenser, kept in a water bath whose temperature was maintained within ±1 °C accuracy by using a temperature controller cum indicator.

Desired quantity of the thiophene was dissolved in several combinations of hydrocarbons to prepare five types of model fuels. The compositions of model fuels are as follows;

Model fuel 1: Thiophene in iso-octane, model fuel 2: Thiophene in a mixture of iso-octane and benzene at mole ratios of iso-octane to benzene 2:0.25, 2:0.5 and 2:1, model fuel 3: Thiophene in a mixture of iso-octane and cyclohexane at mole ratios of iso-octane to cyclohexane 2:0.25, 2:0.5 and 2:1, model fuel 4: Thiophene in mixture of iso-octane and n-octane at mole ratios of iso-octane to n-octane 2:0.25,2:0.5 and 2:1, model fuel 5: Thiophene in mixture of iso-octane, benzene, cyclohexane, n-octane at mole ratio of 2:1:1:1. In each model fuel iso-octane was taken as a common hydrocarbon as, iso-octane may represent gasoline and the thiophene content was kept at 540 ppmw. The reaction was done by

using 40 ml of model fuel, a definite amount of catalyst TS-1 and TBHP, at a particular temperature of 50 °C under stirring. Samples were withdrawn at definite interval of time for analysis.

The progress of reaction was studied by the analyzing reaction sample in high performance liquid chromatography (Perkin Elmer, Series 200) with reversed phase Agilent SB C-18 column and a Perkin Elmer Series 200 UV/VIS detector set at 254 nm. The mobile phase used was 90% methanol in water.

2.3. Catalyst characterization

Commercial TS-1 catalyst was characterized by BET analysis in Quantachrome-Autosorb-1 (Model: AS1 MP/Chemi-LP, USA) instrument, Fourier Transform Infrared Spectroscopy (FTIR), (Model Perkin Elmer spectrum 100) in the spectral range of 400–4000 cm^{-1} and Transmission Electron Microscopy-Energy Dispersive Spectroscopy (TEM-, JEOL Ltd., Tokyo, Japan, EDS-Oxford Instruments Analytical, England). Surface composition of TS-1 catalyst was characterized by PHI 5000 XPS from physical electronics equipped with a monochromatic Al X ray source (1486.6 eV, 350 W).

3. Results and discussion

The BET surface area of fresh and used catalysts were determined and presented in Table 1.

It has been observed from the table that the surface area of fresh catalyst is determined to be 412 m^2/g, whereas, the surface area of the used catalyst decrease moderately with reaction. This may be due to the poisoning of some catalyst active sites by the reaction components.

The FTIR analytical results of fresh TS-1 and TS-1 after being used in the reaction of model fuel 2, 3 and 4 are shown in Fig. 1 in the region between 450 and 4000 cm^{-1}. The strong vibration band appeared at the range of 1400–1000 cm^{-1} for all used TS-1 is assigned to SO$_2$ and SO groups of sulfur compounds. Moreover, the 1456 cm^{-1} and 2951 cm^{-1} vibration bands which are also observed for all used TS-1 are assigned to alkane (C—H) bond bending and stretching. Vibration bands at 3100 cm^{-1} and 1453 cm^{-1} are assigned to aromatic (C—H) and aromatic (C═C) bonds which are found for the TS-1 used in model fuel 2 [32]. Hence, it is clear that the oxidized sulfur containing product and hydrocarbons, who are sharing their respective peaks, are deposited on the used catalyst surfaces.

The TEM-EDS data of pure TS-1 and used TS-1 in the reaction are shown in Figs. 2a and 2b. It is observed from figure that, sulfur is deposited on the catalyst surface, which may be one of the prominent causes of catalyst deactivation. From Table 2 it is shown that the main elemental composition of pure TS-1 are silicon, oxygen and titanium but in the case of spent TS-1 catalyst another two new elements are present along with Ti and Si. Hence, it may be inferred that Carbon and sulfur deposition occurred on the catalyst surface which prevent the catalyst to work as efficiently as pure one.

XPS analysis of pure and used TS-1 catalysts are shown in Figs. 3a and 3b. It has been observed from EDS analysis of TS-1

Table 1
Surface area of fresh and used TS-1 catalyst.

Sample	Surface area (m^2 g^{-1})
Fresh TS-1	411.92
TS-1 used for model fuel 1	340.73
TS-1 used for model fuel 2	301.78
TS-1 used for model fuel 3	294.16
TS-1 used for model fuel 4	314.70
TS-1 used for model fuel 5	301.17