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Adsorption of thiophenes out of hydrocarbons using metal impregnated nanocrystalline aluminum oxide

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Abstract

Adsorption of thiophene and its derivatives was carried out using silver impregnated nanocrystalline metal oxides, with special emphasis on aluminum oxide. A modified nanocrystalline aluminum oxide was prepared by an impregnation method and characterized. The adsorption experiments were carried out for thiophene, benzothiophene, dibenzothiophene and 4,6-dimethyl dibenzothiophene. Incorporation of soft Lewis acid sites such as silver ion is necessary for the adsorption of thiophene related molecules. The modified adsorbent was found to retain its adsorption characteristics even after compaction and it can be used for adsorption again after regeneration by heating at modest temperatures. The adsorption properties of the silver impregnated aluminum oxide (prepared by aerogel procedure) (Ag-AP-Al_2O_3) were compared with several other high surface area materials (>200 m^2/g). Detailed characterization studies showed that the active site in Ag-AP-Al_2O_3 is the Ag^+ ion coordinated to carbonate. Metallic silver nanoparticles do not appear to be effective in thiophene adsorption.

Keywords: Adsorption; Desulfurization; Thiophene; Nanocrystalline aluminum oxide; Silver; Silver carbonate

1. Introduction

Desulfurization, removal of organosulfur compounds, is an important operation in petroleum refining [1]. The sulfur compounds present in the fuels are of serious environmental concern since combustion of the sulfur containing fuels produces SO_2. Also, sulfur compounds are poisons for catalysts used in automobiles, e.g. group VIII metal catalysts. For fuel cell applications, using gasoline as a feed, the sulfur compounds in the hydrocarbons need to be reduced to less than 0.1 ppmw to avoid catalyst poisoning [2]. Hence a considerable effort is being made to remove the organosulfur molecules from the fuel to obtain sulfur free or ultra-low-sulfur fuel. The EPA Legislation Tier II requires substantial reductions in sulfur content from the current levels of hundreds of ppm to 30 ppm (gasoline) and 15 ppm (diesel) by 2006 [3]. This legislation would require a rapid development of new methodologies in order to achieve such a large reduction in sulfur content in a relatively shorter period. Traditionally, hydrodesulfurization (HDS) with a Co–Mo/Al_2O_3 or Ni–Mo/Al_2O_3 catalyst and hydrogen has been used to remove the sulfur compounds from fuels and this process requires stringent conditions such as high temperatures and high pressures [4]. The HDS process is efficient in removing thiols, sulfides, and disulfides but it is not adequate for the removal of aromatic thiophenes and their derivatives. The sulfur compounds that remain after the HDS process are thiophene, benzothiophene,

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dibenzothiophene and their alkylated derivatives. So, alternative technologies are of particular interest to obtain sulfur free fuels.

Several non-HDS based desulfurization technologies have been proposed in the literature. Desulfurization based on a bio-catalytic process in which a genetically engineered bacteria converts the sulfur in the petroleum products to sulfates has been reported [5]. Homogeneous nickel and platinum complexes are reported to be effective in desulfurizing alkylated dibenzothiophenes [6]. Oxidative desulfurization using hydrogen peroxide and formic acid has been reported by Scarsella et al. [7]. Extraction of dibenzothiophenes from petroleum feed stocks using a ruthenium complex has been reported by Angelici et al. [8]. Extraction of dibenzothiophene with ionic liquids and oxidation of dibenzothiophene to a sulfone in a liquid biphasic system has been reported [9]. A new technology using ultrasound in which the thiophenic compounds are oxidized in an ultrasonic reactor to form sulfoxides and sulfones which are subsequently removed by solvent extraction has also been reported [10].

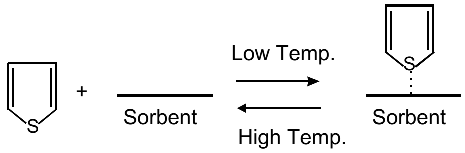
One of the new approaches for desulfurization is by selective adsorption of thiophenes on adsorbents and this method might be the most economical way for the removal of thiophenes. There is an ongoing effort to invent new adsorbents to remove the thiophenes from fuels via π-complexation [11], van der Waals and electrostatic interactions [12], reactive adsorption [13] or chemisorption [14]. The fuel is brought in contact with a solid adsorbent which selectively adsorbs sulfur containing compounds. Desulfurization by adsorption, however, faces two major challenges; (i) to develop adsorbents with a high capacity and (ii) to find adsorbents that selectively adsorb the sulfur compounds (mainly aromatic) over other aromatic and olefinic compounds present in the fuel. During the past few years, there has been enormous amount of research done on the use of such sorbents for liquid fuel desulfurization. Commercially available sorbents such as zeolites, activated carbon and activated alumina have all been involved in these studies. Activated alumina (Alcoa Selexsorb) has been used in an adsorption process by Irvine [15]. The zeolites used for adsorption include 5A, 13 X, various ZSM's (e.g. ZSM-5) and ion-exchanged zeolites (Cu^{2+}–zeolite–Y, Ag^{+}–zeolite–Y). Weitkamp et al. [16] and King et al. [17] used ZSM-5 zeolite as a sorbent to adsorb thiophene using fixed-bed breakthrough experiments. The thiophene capacities were fairly low (1–2 wt.%) in all the above cases.

A transition metal based adsorbent loaded on a porous solid support such as MCM-41 has been reported to be able to reduce the sulfur content in the fuel from 500 ppm to less than 1 ppm [18]. Ma and co-workers have reported desulfurization based on a transition metal compound supported on silica gel with 5.0 wt.% loading of the metal compound [19]. It has been reported that silver salts adsorbed on amorphous silica or mesoporous SBA-15 silica can extract dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-Me_2DBT) from simulated petroleum feedstocks [20].

A family of new adsorbents based on the principles of chemical complexation has been proposed by Yang et al. [21]. Chemical complexation bonds are generally stronger than van der Waals interactions, but weak enough to be reversible by moderate changes in temperatures/pressures. These authors have reported, based on π-complexation, that Ag–zeolite–Y, Cu–zeolite–Y and Ni–Zeolite–Y are highly selective towards thiophene adsorption and that Cu^{+} and Ag^{+} zeolite Y can adsorb sulfur compounds from commercial fuels with high sulfur capacities and selectivities at ambient temperatures and pressures [21]. Desulfurization of a model and real jet fuel (JP-8) over Ce-exchanged zeolite with a capacity of 10 mgS/g of adsorbent has been reported recently [14]. Also, removal of dibenzothiophene from a model diesel fuel by adsorption on carbon aerogels has been reported and the capacity is close to 11 mg S/g [22]. Nanostructured W_2C on high surface area carbon materials has been reported to adsorb thiophene effectively [23]. Collins et al. have reported the removal of sulfur after oxidation of the thiophenic compounds using H_2O_2, an acid catalyst and a phase-transfer agent, and subsequent adsorption of the oxidized products on silica gel [24]. An interesting adsorbent based on a hybrid of catalyst and sorbent, *S Zorb*, has been commercialized by Conoco Philips Petroleum Company [3].

None of the reported studies, to the best of authors' knowledge, have used nanocrystalline metal oxides as the adsorbents for desulfurization. There exists a need to develop improved adsorbents which (i) have enhanced sorption capacity, (ii) can be produced with a low cost, (iii) can be easily regenerated and (iv) have the capability to remove all the organosulfur compounds. Moreover, the adsorption process should be carried out under milder conditions (ambient temperatures/pressures) and should be cost effective without using any hydrogen (Scheme 1).

Nanocrystalline metal oxides are of current interest and they constitute a novel family of inorganic porous materials [25]. They generally possess high surface areas and readily form aggregates either in powder or consolidated pellet forms [26]. The metal oxide nanocrystals



Scheme 1. A schematic of adsorption of thiophene molecules on a model adsorbent.