

Characteristics of sulfur removal by silver-titania adsorbents at ambient conditions

Sachin Nair · Bruce J. Tatarchuk

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Abstract Sulfur capacity of SiO_2 , TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ structures was investigated. Thermal treatment of TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ in air increased their respective sulfur capacity by 67 and 43%. Sulfur capacity was associated with surface acidity and the improvement attributed to the formation of bronsted acid sites. Addition of 4wt% transition metals further enhanced the sulfur capacity of TiO_2 with Ag indicating the highest increase. Comparison of sulfur capacity of Ag/ TiO_2 with other adsorbents was made using JP5 fuel with sulfur concentration of 1172 ppmw. Ag/ TiO_2 adsorbent demonstrated a saturation sulfur capacity of 8.20 mg/g. A significant loss in sulfur capacity was observed between real and model fuel compositions. Various factors resulting in this loss was investigated such as the effect of additives, competitive adsorption and the structure of sulfur heterocycles.

Keywords Adsorptive desulfurization · Fuel additives · Surface acidity · Competitive adsorption

1 Introduction

Sulfur removal is an essential step in the production of refined hydrocarbon fuels. The demand for more efficient sulfur removal technologies is on the rise due to tightening sulfur regulations, decline in the supply of sweet crude and increasing supply of bitumen derived feed-stocks. Sulfur removal also has gained prominence due to the introduction

of fuel cells for power generation. The extremely low sulfur tolerance of electro-catalysts makes sulfur removal an inevitable part of such power systems. The most prevalent and industrially relevant sulfur removal technology is hydro desulfurization (HDS). Alternative sulfur removal processes such as catalytic oxidation (Mei et al. 2003; Wang et al. 2007a, 2007b), biological removal (Grossman et al. 1999; Klein 1999; Ma et al. 2006; McFarland et al. 1998; Zakharyants et al. 2005) and membrane separation are being pursued for when HDS is inefficient or cost-prohibitive. Another emerging alternative is adsorptive removal of sulfur in liquid feeds. These technologies maybe employed for mobile applications or stationary units where HDS operation is not feasible.

Several compositions have been reported to be effective for adsorptive desulfurization of fuels at ambient conditions. A number of transition metal oxides have been employed for this purpose (Gislason et al. 2004; Khare 2001; Morton et al. 2004a, 2004b, 2004c; Price et al. 2003; Simon et al. 2004; Sughrue et al. 2003). Ni in its reduced metallic form (Kim et al. 2006; Ma et al. 2005; Velu et al. 2005b), supported chloride salts of Cu and Pd (Hernández-Maldonado et al. 2005b; Wang et al. 2006), zeolitic structures ion exchanged with Cu, Ag, Ce, Ni have also been shown to be effective (Bhandari et al. 2006; Hernández-Maldonado et al. 2005b; Hernández-Maldonado and Yang 2004a; Hernández-Maldonado and Yang 2003, 2004c; King and Li 2006; Velu et al. 2003; Xue et al. 2006); particularly Y type zeolites (Bhandari et al. 2006; King and Li 2006; Takahashi et al. 2001a; Takahashi and Yang 2001b; Yang et al. 2003, 2004). Among support structures, SiO_2 , Al_2O_3 (Hernández-Maldonado and Yang 2004b; Jeevanandam et al. 2005; Kim et al. 2006) and activated carbon (Hernández-Maldonado and Yang 2004b; Kim et al. 2006) are the most common. Sulfur capacity of CuY zeolite over diesel fuel (430 ppmw sulfur) was

S. Nair · B.J. Tatarchuk (✉)
Department of Chemical Engineering, Auburn University,
Auburn, AL 36849, USA
e-mail: tatarbj@auburn.edu

0.167 mmol/g (Hernández-Maldonado et al. 2004a). Palladium halide adsorbents over JP5 fuel (~1200 ppmw sulfur) demonstrated a breakthrough sulfur capacity of 0.065 mmol/g and saturation capacity of 0.284 mmol/g (Wang et al. 2006).

Recently we developed Ag/TiO₂ adsorbents that demonstrated high capacity for sulfur aromatics in fuels at ambient conditions (Nair and Tatarchuk 2010; Tatarchuk et al. 2008). The adsorbent was thermally regenerable in air over multiple cycles demonstrating a consistent sulfur capacity of 8.5 mg/g over 10 adsorption/regeneration cycles for JP5 fuel (~1200 ppmw sulfur). Breakthrough studies using fuels with varying sulfur speciation indicated that sulfur capacity was affected by fuel chemistry. A significant variation in selectivity between sulfur heterocycles was noted for the Ag/TiO₂ adsorbent. Oxide phases of Ag were also identified at the adsorption interface as there was no pre-reduction step during adsorption. This was another unique attribute of the adsorbent composition.

Sulfur removal using Ag based adsorbents maybe possible through three mechanisms; the formation of a sulfide on the surface (Lavrenko et al. 2006; Salas et al. 2002; Satokawa et al. 2005, 2007), strong chemisorption (Benard et al. 1965; Rovida and Pratesi 1980, 1981), physisorption or a combination thereof. These mechanisms differ by the strength of interaction between the sulfur heterocycle and the active center. Multi-layer sulfide formation is a possible mechanism as observed in the tarnishing of silver objects in air. High selectivity for trace amounts of sulfur in fuels also suggests strong chemisorption as a possible mechanism of sulfur removal. Sulfur removal may result from physical adsorption through van der Waal's interactions between sulfur heterocycle and active center as a majority of industrial adsorption processes are designed based on physical adsorption.

A marked loss in sulfur capacity was observed between real and model fuels. Sulfur capacity also varies with fuel chemistry especially in the presence of jet fuel additives such as oxygenates and metal deactivators. Variation in the aromatic content and the presence of contaminants also influences the performance of sulfur adsorbents. Elucidating the reason for such loss in sulfur capacity not only facilitates the design of better adsorbents or guard beds to remove deactivating agents but also provide a better understanding of nature of the active centers. Higher sulfur capacity of CuCl₂- γ -Al₂O₃ compared to Cu-Y zeolite has been attributed to the higher selectivity towards oxygenates such as ethanol and MTBE compared to sulfur aromatics (Hernández-Maldonado et al. 2005a). A few compositions reported for adsorptive desulfurization was prepared and tested to provide a comparison to the performance of Ag/TiO₂. The adsorbents were prepared using supports of identical particle size, tested using JP5 fuel (~1200 ppmw

sulfur) at similar flow conditions. Variation in performance from reported data would gauge the influence of factors such as fuel chemistry, particle size and pretreatment steps on sulfur capacity.

Fuel additives impact the performance of sulfur adsorbents more so than the natural variation in fuel chemistry between the different fuels. Additives such as metal deactivators and corrosion inhibitors are designed to interfere with the activity of metallic components. Additives are fuel soluble chemicals added in small amounts to enhance or maintain properties important to fuel performance or fuel handling. Anti-oxidants, metal deactivators, static dissipaters, corrosion inhibitors, icing inhibitors, biocides, thermal stabilizers are common additive components in jet fuels. A fuel system icing inhibitor (FSII) is generally used to prevent the formation of ice at low temperatures encountered at high altitudes, and thus is an essential component of jet fuels. The only FSII approved for Jet A, Jet A1 and US military fuels is di-ethylene glycol monomethyl ether (di-EGME). Metal deactivators are generally used to inhibit the catalytic activity of metals such as copper and zinc against possible oxidation reactions. Alfa-alfa 1-methylethylenediimino-di-ortho-cresol is a common metal deactivator. Electrical conductivity enhancers are used to dissipate static electricity formed due to friction. The only additive currently approved for use in jet fuel is Stadis[®] 450 whose composition is proprietary. Oxygen in the small amounts of air dissolved in the fuel attacks the reactive compounds in the fuel. Antioxidants prevent this initial attack that can potentially set off a chain of oxidation reactions. Natural antioxidants found in straight run fuels are removed by hydrotreating processes making antioxidants more necessary for treated fuels. The maximum allowed concentration is 24 mg/L. The approved antioxidants for aviation fuel are hindered phenols such as 2,6-Di-tert-butyl-4-methylphenol (Bacha et al. 2000). Breakthrough studies using model fuels comprising of fuel additives and contaminants were carried out to establish the negative influence of these components on the Ag/TiO₂ adsorbent.

Sulfur adsorption has been generally attributed to the interaction of transition metals with π electron cloud on sulfur aromatics. Variation in sulfur speciation of fuels has been noted to influence the performance of sulfur adsorbents (Nair and Tatarchuk 2010). This was attributed to the variation in π electron density between sulfur heterocycles. Delocalization of π electrons is influenced by the number of aromatic rings on the aromatic. π complexation have been used to explain sulfur capacity of Cu-Y type zeolites. Variation in electron density of aromatic ring brought about by the sulfur atom has been attributed to the higher selectivity. The lone pair of electrons on the sulfur atom conjugates with π electrons on the aromatic ring. The d orbitals on the Cu atom back donate electron density to anti-bonding π orbitals (π^*)

of the sulfur rings resulting in π bonding between the solute and Cu atoms (Yang et al. 2004). Similarly, higher HDS activity of benzothiophene (BT) has been attributed to the non-uniform electron distribution compared to dibenzothiophene (DBT) (Song and Ma 2004). Adsorptive desulfurization selectivity has been observed to increase with increasing electron density on the sulfur atom (Ma et al. 1995). The influence of the number of aromatic rings associated with the sulfur molecule on desulfurization performance was established for Ag/TiO₂ adsorbent. This data would indicate the influence of π electron interactions on sulfur adsorption.

The role of acidic centers has been established for a myriad of industrially relevant heterogeneous reactions. Acidic centers are generally categorized as either Lewis or Bronsted. Lewis acid sites (LAS) are coordinatively unsaturated centers which are electron acceptors arising from breaking of crystal lattice at the surface. Bronsted acid centers (BAS) are either hydroxyl groups (bridging or otherwise) with sufficiently mobile protons or coordinated water or H₃O⁺ ions and are proton donors. Surface acidity has been linked to the photocatalytic activity of TiO₂; influenced by surface area, crystal structure and density of surface OH groups (Kobayakawa et al. 1990). Basic OH groups has been identified on TiO₂ surfaces as well (Boehm 1966). Basic functional groups on activated carbons have been reported to be involved in methane adsorption (Contreras et al. 2009) and oxygen/carboxylic groups for water vapor adsorption (Fletcher et al. 2007). Therefore the role of surface functional groups in sulfur removal by TiO₂ based adsorbents need to be assessed.

When establishing the sulfur capacity of adsorbents with active metal species, sulfur capacity of the blank support structures need be considered as well. Blank supports are ideally tested for sulfur capacity following treatment steps as during the preparation of adsorbents with dispersed metals. Synthesis stages such as impregnation, drying and high temperature treatments influence the concentration of surface functional groups and support pore structure. Sulfur capacity of supports prior to the introduction of active metals has been reported by a few researchers. Kim et al., reported adsorption of several aromatics over activated γ -Al₂O₃ and activated carbon following pretreatment in flowing N₂ at 200°C for 2 h (Kim et al. 2006). Sulfur capacity of activated carbon (16.29 mg/g) was significantly higher than that of γ -Al₂O₃ (2.41 mg/g) using a model fuel composition of ~300 ppmw total sulfur. Velu et al., reported sulfur capacity of HY zeolite obtained by calcination of NH₄Y zeolite at ~500°C (Velu et al. 2003) to be comparable to Y type zeolites ion exchanged with Cu, Ce etc. A comparison of sulfur capacities was also reported by Takahashi et al., between Cu-Y and Na-Y zeolites (Takahashi et al. 2001a). These studies indicate that a good part of the sulfur capacity of an adsorbent may reside in the virgin support structure. The nature of interactions between sulfur molecules and the active

Table 1 Properties various supports/adsorbents used for adsorptive desulfurization

Support	Vendor	Grade	BET surface area [m ² /g]	Pore volume [cc/g]
TiO ₂	St. Gobain Nor Pro	Type 1	153	0.46
SiO ₂	Grace Davison	Grade 21	319	0.80
γ -Al ₂ O ₃	Alfa Aesar	Catalyst support	256	1.20
Cu-Y	Strem Chemicals	Molecular sieve	472	0.37
Selexorb	BASF	CDX	411	0.39

centers on the support may vary from the interactions with active metals. Therefore sulfur capacities of TiO₂ Al₂O₃ and SiO₂ dried and calcined at 450°C were studied.

In this article, efforts were made to differentiate the sulfur capacity of the support structures from that of the metal loaded samples. The influence of various transition metal components on sulfur capacity was studied. Comparison of sulfur capacity of Ag/TiO₂ was made with other reported compositions for adsorptive desulfurization. The influence of fuel additives, structure of sulfur molecules and the effect of competitive adsorption was also studied for Ag/TiO₂ adsorbent.

2 Experimental

2.1 Adsorbent preparation

TiO₂, SiO₂ and γ -Al₂O₃ were crushed and sieved to a size of 1.4–0.85 mm and dried in a convection oven for at least 6 h at 110°C prior to use (Table 1). Wet impregnation was used to deposit the transition metals on the support using the corresponding nitrate (99.9% purity from Alfa Aesar Co) solutions in water. The resulting particles were then dried at 110°C for 6 h followed by calcination in air at 400°C for 2 h. Metal weight loading on the sorbent was typically maintained at ~4%. Support blanks were prepared using identical synthesis procedures as for metal loaded samples, the only difference being that impregnation was carried out with dilute HNO₃ of identical concentration. The adsorbents were tested once cooled to ambient temperature without any pretreatment.

Cu-Y zeolite was tested prepared using liquid phase ion exchange as reported previously (King and Li 2006; Takahashi et al. 2001a). The adsorbent was pretreated in flowing (ultrapure) He at 450°C for 2 hours *in situ* prior to desulfurization studies. PdCl₂ on γ -Al₂O₃ composition was prepared using thermal dispersion techniques (Hernández-Maldonado et al. 2005a; Xie and Tang 1990). The adsorbent was pretreated in (ultrapure) He at 350°C (ramped to

temperature at 1 deg/min) and held at temperature for 2 h prior to testing for sulfur capacity. Selexorb CDX (1.4 mm spherical particles) was obtained from BASF Inc. and tested following pre-treatment in air at 250°C for 2 h.

2.2 Adsorbent breakthrough performance

The breakthrough characteristics of the adsorbents were determined in a packed column configuration where the challenge fuel flowed from the bottom of the bed to the top. 10.0 g of sorbent was used in all the breakthrough studies. The bed (16 mm ID) was contained in a quartz tube supported on both ends by quartz wool. No effort was made to flush the bed with a sulfur-free solvent to remove trapped air. The fuel flow rate (typically 0.5 ml/min) was maintained by peristaltic pump. The bed output was sampled at regular intervals for analysis of sulfur content. The concept of $t_{1/2}$ was used to estimate the saturation capacity for cases where sulfur removal was not carried out to bed exhaustion. Here the symmetry of breakthrough curve was considered and sulfur capacity estimated from the approximation

$$\int_0^{t_{sat}} q_t dt = q_{t_{1/2}} t_{1/2}$$

Here q represented the sulfur capacity (mg/g), t_{sat} the saturation time (min), $t_{1/2}$ the time for outlet sulfur concentration to reach half the inlet, $q_{t_{1/2}}$ the sulfur capacity at $t_{1/2}$ point.

2.3 Challenge fuels

JP5 with a total sulfur content of 1172 ppmw was obtained from NAVSEA Philadelphia. Model fuels consisting of 3500 ± 10 ppmw thiophene [T] (99.5% Arcos Organics), methyl thiophene [MT] (98% Alfa Aesar), benzothiophene [BT] (97% Arcos Organics), dibenzothiophene [DBT] (98% Alfa Aesar Co.), 4,6 dimethyl dibenzothiophene [4,6 DMDBT] (97% Sigma Aldrich.) in n-octane (97% Arcos Organics) were used for breakthrough tests to study the effect of structure of sulfur aromatics on adsorption. Model fuel with benzothiophene (3500 ± 10 ppmw) and 15 ppmw of antioxidant 2,6-Di-tert-butyl-4-methylphenol (>99.0% Sigma-Aldrich), 15 ppmw of metal deactivator Alfa-alfa 1-methylethylenediimino-di-ortho-cresol (>99.0% Sigma-Aldrich), Ethanol 15.0 Vol% and 100 ppmw water representing fuel additives/ contaminants were also tested for the effect on sulfur capacity.

2.4 Analysis of sulfur

Sulfur content was analyzed using an Antek 9000VS Total Sulfur Analyzer. The instrument was calibrated using standards prepared from dilutions of both real fuels as well as

sulfur heterocycles in n-octane. The lower detection limit of the instrument was observed to be 200 ppbw. A Varian CP3800GC equipped with a Pulsed Flame Photometric Detector (PFPD) containing a sulfur specific optical filter was used as well. The GC column employed was a Restek cross-board column of length 30 m, inner diameter of 0.25 mm and 0.25 µm df. The PFPD detector was calibrated using standards as described earlier. The injector operated at split ratios between 0 and 80 using a 1 µl injection volume. The lower detection limit of the PFPD was observed to be 20 ppbw total sulfur with the injector in split-less mode.

3 Results and discussion

3.1 Sulfur capacity of supports

Sulfur capacity of supports such as SiO₂, Al₂O₃ and TiO₂ are generally established as received or following a simple drying procedure. These steps are carried out to ensure removal of surface moisture and adsorbed organic volatiles. Our work indicated that the supports often exhibit significant adsorption capacity for sulfur when taken through a series of thermal treatments. Addition of metals has been shown to enhance the sulfur capacity of supports such as Cu on Y Type zeolites, Pd on Al₂O₃ and so on. Interactions of sulfur molecules with the support structure maybe varied from that with incorporated metals.

A comparison of sulfur capacity was thus made for TiO₂, Al₂O₃ and SiO₂ that were dried (110°C/6 h) and blank samples that were impregnated with dilute HNO₃, dried (110°C/6 h) and calcined (450°C/2 h) in air. Breakthrough of benzothiophene in a model fuel (3500 ppmw in n-octane) using untreated (dried) samples are shown in Fig. 1. Sulfur capacity of dried TiO₂, SiO₂ and Al₂O₃ were minimal (Table 1). Breakthrough data for blank samples showed a marked improvement in sulfur capacity for Al₂O₃ and TiO₂ samples, while SiO₂ demonstrated a minor loss in sulfur capacity (Fig. 2).

Therefore the thermal treatment was responsible for the generation of active centers for sulfur capture on Al₂O₃ and TiO₂ structures. Such improvement in sulfur capacity may result from the loss or modification of strongly bound ad-molecules on the surface, generation of oxygen vacancies or incorporation of surface functional groups. Generation of surface acidity from bronsted sites may also be considered. This was suggested by the distinct behavior of SiO₂ compared to Al₂O₃ and TiO₂. Previous reports have indicated the absence of surface acidity on SiO₂ surfaces compared to Al₂O₃ and TiO₂. The OH groups on SiO₂ has been observed to be weakly basic or neutral compared to more acidic OH groups on Al₂O₃ (Rajagopal et al. 1995). Decomposition of water molecules on TiO₂ surfaces to form surface hydroxyls

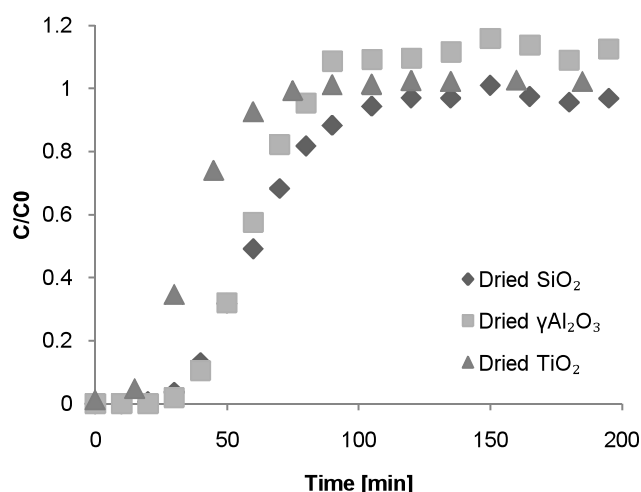


Fig. 1 Breakthrough of benzothiophene (3500 ppmw)/n-octane for dried TiO_2 , dried SiO_2 and Dried $\gamma\text{-Al}_2\text{O}_3$; dried at 110°C for 6 h

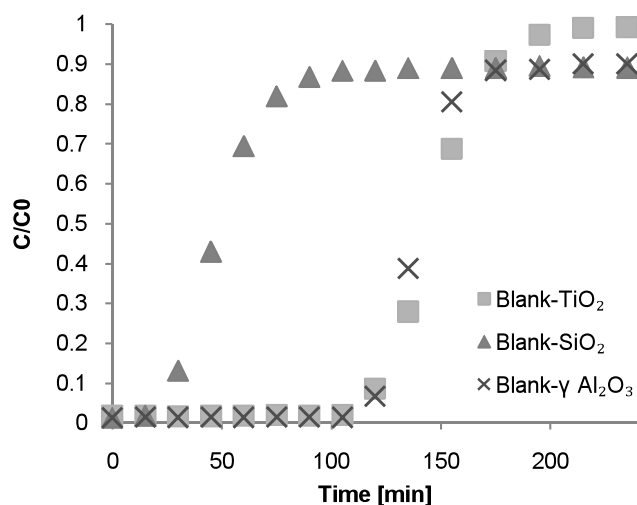


Fig. 2 Breakthrough of benzothiophene (3500 ppmw)/n-octane for Blank TiO_2 , Blank SiO_2 and Blank $\gamma\text{-Al}_2\text{O}_3$

have been reported (Du et al. 2009). Generation of bronsted acidity on TiO_2 surfaces dependent on preparation conditions have been reported (Doolin et al. 1994). OH group concentration on Al-Y zeolites has been observed to maximize at a calcination temperature of 350°C and decrease beyond 550°C (Rajagopal et al. 1995). These reports indicate that active bronsted acid sites may be formed from decomposition of adsorbed water molecules during the calcination step on Al_2O_3 and TiO_2 and not on SiO_2 .

3.2 Comparison of Sulfur capacity of various transition metals and Ag supported on TiO_2

Liquid phase sulfur adsorbents generally contain transition metal components. Therefore they exhibit an inherent affinity for sulfur heterocycles and rely on metal-sulfur aromatic

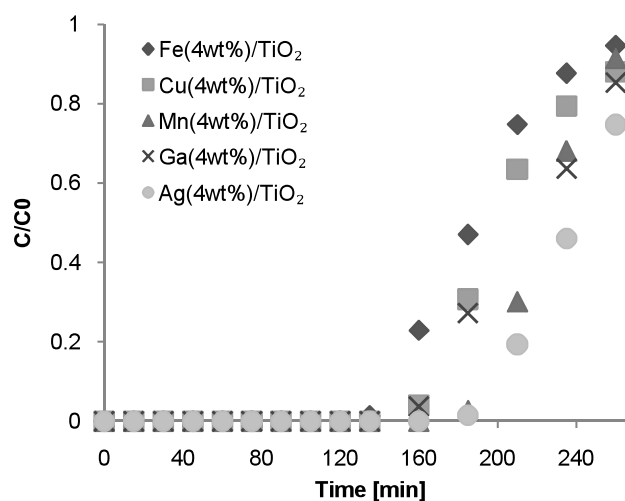


Fig. 3 Breakthrough of benzothiophene (3500 ppmw)/n-octane for 4%wt of various metals shown supported on TiO_2 , dried ($110^\circ\text{C}/6\text{ h}$) and calcined ($400^\circ\text{C}/2\text{ h}$)

Table 2 Sulfur capacity of 4wt% of various transition metals supported on TiO_2 estimated from breakthrough of Benzothiophene ($3500 \pm 10\text{ ppmw}$) in n-octane

	Breakthrough time [min]	Breakthrough capacity* [mg/g]	$t_{1/2}$ [min]	Saturation capacity [mg/g]
Fe	134	23.5	187	32.7
Ga	151	26.4	215	32.6
Cu	151	26.4	198	34.7
Mn	180	31.5	222	38.9
Ag	183	32.0	238	41.7

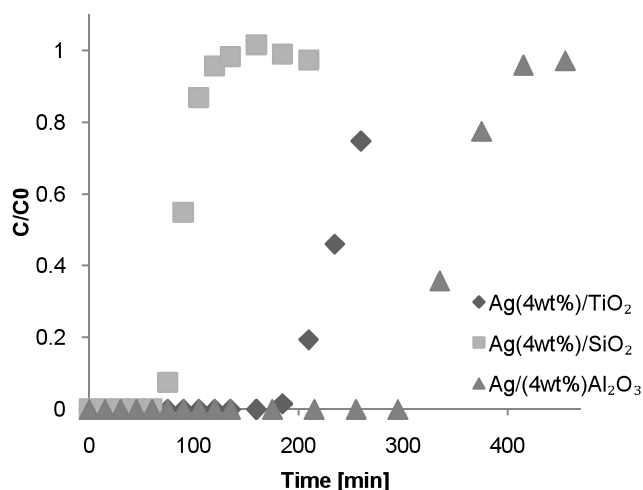
* At 20 ppmw threshold

interaction. Therefore these materials go through reduction (or auto-reduction) pretreatment (Hernández-Maldonado et al. 2004b; Kim et al. 2006; Takahashi et al. 2001a; Velu et al. 2005a). However, our previous work indicated a higher sulfur uptake for supported Cu, Ni, Mn and Ag (without reduction step) on SiO_2 (Nair and Tatarchuk 2010). Preliminary characterization of the metal phase indicated the presence of oxide phase. Detailed analysis of the physiochemical properties of these materials are being carried out and will be presented in the future publications. Among the metals tested Ag demonstrated the highest sulfur affinity. It was also observed that TiO_2 was a more stable support compared to SiO_2 under conditions for thermal regeneration. Here Fe, Cu, Mn, Ga and Ag were dispersed on TiO_2 at a weight loading of 4% and sulfur affinity established from breakthrough of benzothiophene ($3500 \pm 10\text{ ppmw}$) in n-octane shown in Fig. 3. The sulfur capacities estimated from the breakthrough data are presented in Table 2. Ag demonstrated a

Table 3 Sulfur capacity of Blank and Ag loaded TiO₂, Al₂O₃ and SiO₂

	Dried		Blank		4wt% Ag loaded	
	Breakthrough capacity* [mg/g]	Saturation capacity [mg/g]	Breakthrough capacity* [mg/g]	Saturation capacity [mg/g]	Breakthrough capacity* [mg/g]	Saturation capacity [mg/g]
TiO ₂	2.10	6.1	13.6	18.3	32.0	41.7
Al ₂ O ₃	5.25	10.0	13.9	17.4	35.9	43.4
SiO ₂	4.20	10.7	1.9	6.2	7.4	12.1

* At 20 ppmw threshold

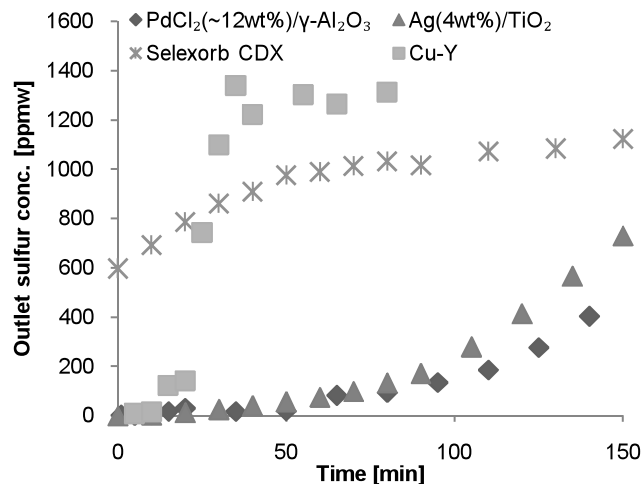
**Fig. 4** Breakthrough of benzothiophene (3500 ppmw)/n-octane for Ag(4wt%)/TiO₂, Ag(4wt%)/ γ -Al₂O₃ and Ag(4wt%)/SiO₂

saturation sulfur capacity of ~ 42 mg BT/g followed by Mg at ~ 39 mg/g and the others.

Breakthrough data for γ -Al₂O₃, TiO₂ and SiO₂ dispersed with 4wt% Ag is shown in Fig. 4. The addition of Ag improved the sulfur capacity of supports, including SiO₂ as listed in Table 3. Therefore, the Ag phase consisted of active adsorption centers independent of TiO₂. Even though the Ag loading was 4wt% on all the samples, improvement in sulfur capacity with the addition of Ag was higher for Al₂O₃ compared to TiO₂. This was attributed to the higher specific surface area of Al₂O₃. Variation in surface acidity with addition of metal ions to a support has been reported in the past. The generation of new bronsted sites and simultaneous decrease in lewis sites on Al₂O₃ surfaces with increasing MoO₃ loading has been reported (Rajagopal et al. 1995). Thus addition of Ag and changing surface acidity of TiO₂ and Al₂O₃ was attributed to the higher sulfur capacity of Ag loaded samples.

3.3 Performance comparisons

For performance evaluation of some reported adsorbents, breakthrough tests were conducted on Cu ion-exchanged

**Fig. 5** A comparison of desulfurization performance of Ag(4wt%)/TiO₂, PdCl₂(~ 12 wt%)/Al₂O₃, Cu-Y zeolite, Ag(4wt%)/TiO₂ and Selexorb CDX using JP5 fuel with 1172 ppmw sulfur at identical testing conditions and particle size**Table 4** A comparison of sulfur capacity obtained from breakthrough data for Ag(4wt%)/TiO₂, CuY-type zeolite, and PdCl₂(~ 12 wt%)/Al₂O₃ using JP5 fuel (1172 ppmw sulfur) as challenge

Adsorbent	Breakthrough time [min]	Breakthrough capacity* [mg/g]	$t_{1/2}$ [min]	Saturation capacity [mg/g]
Selexorb CDX	–	–	0	0.20
Cu-Y	10	0.58	25	1.50
PdCl ₂ / γ -Al ₂ O ₃	50	2.88	165	9.67
Ag/TiO ₂	30	1.73	140	8.20

* At 20 ppmw threshold

Y-type zeolite, PdCl₂(~ 12 wt%)/Al₂O₃, Ag(4wt%)/TiO₂ at similar conditions. The breakthrough performance of the adsorbents is shown in Fig. 5 and sulfur capacities listed in Table 4. Ag(4wt%)/TiO₂ demonstrated a breakthrough capacity of 1.73 mg/g compared to 2.88 mg/g by PdCl₂(~ 12 wt%)/Al₂O₃ at 20 ppmw breakthrough threshold. Breakthrough sulfur capacity of Cu-Y was 0.58 mg/g

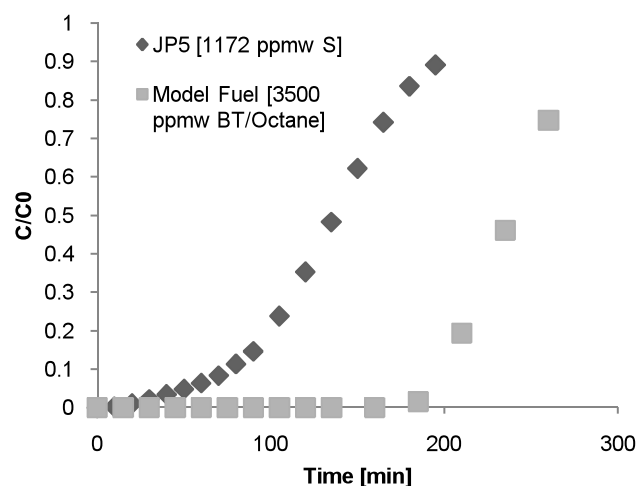


Fig. 6 Breakthrough of sulfur in JP5 (1172 ppmw) compared to that of benzothiophene (3500 ppmw) in octane using the Ag(4wt%)/TiO₂

while Selexorb CDX demonstrated negligible capacity. Among the tested adsorbents, Ag(4wt%)/TiO₂ maybe preferred due to the simple synthesis procedure, absence of activation steps and more importantly facile thermal regenerability using air as a stripping medium (Nair and Tatarchuk 2010; Tatarchuk et al. 2008).

Loss in sulfur capacity of various adsorbents has been reported while using real fuels as challenge. Comparison of breakthrough between JP5 fuel and benzothiophene (3500 ± 10 ppmw) in a model fuel composition for Ag(4%)/TiO₂ at similar test conditions is shown in Fig. 6. It may be observed that the adsorbent exhibited higher sulfur capacity for the model fuel compared to JP5. The breakthrough curve was sharper in the case of model fuel which was attributed to transport issues with real fuel. The factors that result in the lower breakthrough performance maybe arise from the chemistry of natural fuels which includes competitive adsorption between a multitude of sulfur aromatics, sulfur-free aromatics and the presence of additives in the fuel. The impact of some of these components in fuel on the performance of Ag/TiO₂ was further explored.

3.4 Additives

Several components in a fuel might be responsible for lowering the sulfur capacity of adsorbents. The competition from non-sulfur containing aromatics would be significant source as many fuels contain up to 16% aromatic compared to a maximum of a few percent of sulfur. Another factor would be additives present in fuels such as oxygenates, antioxidants, antistatic agents, metal deactivators etc. Understanding the effect of additives on sulfur adsorption process not only addresses the practical issue of application of such adsorbents for use on real fuels but also address the chemical nature of interactions at adsorption interface.

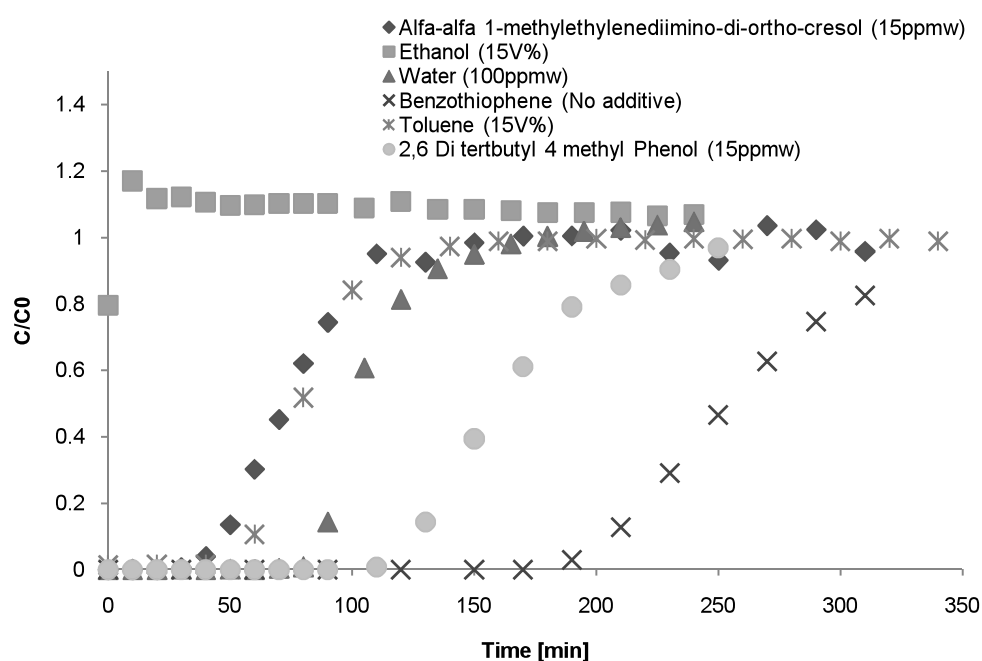
Model fuels containing three components were prepared for this study. The first component was benzothiophene (3500 ± 10 ppmw). The second component was a fuel additive and n-octane was the solvent. Breakthrough of benzothiophene was used to determine the effect of the second component on desulfurization using Ag(4wt%)/TiO₂. The additives/contaminants studied were ethanol (15% Vol) used as an oxygenate in fuels, Alfa-alfa 1-methylethylenediimino-di-ortho-cresol [MD] (15 ppmw) used as a metal deactivator, 2,6-Di-tert-butyl-4-methyl phenol [AO] (15 ppmw) used as an antioxidant and water (100 ppmw), a common contaminant.

From the breakthrough data presented in Fig. 7, it was observed that additives reduced the sulfur capacity of the adsorbent. Ethanol in the fuel completely deactivated the sorbent. Therefore for fuels with added ethanol, these adsorbents may not be applicable. The MD also led to reduction in sulfur capacity. This may be attributed to the interference of hydroxyl group of alcohol/cresol with benzothiophene or active centers on the surface. The marked difference between ethanol and toluene (both 15Vol%) in the fuels indicated the same effect. A comparison of sulfur capacity of the adsorbent in the presence of toluene indicated the significant impact of aromatic content of fuels on adsorbent performance. The effect of AO was not as marked as that of MD (both at 15 ppmw) even though both contain phenolic groups. This was attributed to the presence of nitrogen atom in the diimino groups on MD. The MD molecule is therefore more basic in comparison with AO and therefore considered to strongly interact with surface acidic groups. Trace amounts of water molecules have been known to form H₃O⁺ ions with bronsted centers (Kulkarni and Muggli 2006; Richardson and Benson 1957). This interaction may explain the loss in sulfur capacity in the presence of water.

3.5 Competitive adsorption

Model fuel compositions are generally used as challenge fuels in the evaluation of sulfur adsorbents as they eliminate issues with real fuels such as competitive adsorption between sulfur species, other aromatics and fuel additives. However, competitive adsorption maybe used to gain insight on mechanism of sulfur adsorption. Breakthrough characteristics would not only clarify the primary interactions between the sorbent and solute molecules but also indicate the secondary interactions between surface ad-layers. Breakthrough of three sulfur heterocycles viz. thiophene (0.572 g/l), benzothiophene (0.913 g/l) and dibenzothiophene (1.253 g/l) were observed using Ag/TiO₂ sorbent in a model fuel composition; the total sulfur concentration was 0.08 mol/l. For primary interactions between the sulfur atom and the sorbent, this study would isolate the effect of the structure of sulfur aromatic during competitive adsorption.

Fig. 7 The breakthrough of benzothiophene (3500 ppmw) for Ag(4wt%)/TiO₂ using model fuels also containing (i) 15 ppmw of antioxidant 2,6-Di-tert-butyl-4-methylphenol (ii) 15 ppmw of metal deactivator Alfa-alfa 1-methylethylenediimino-di-ortho-cresol (iii) Ethanol 15.0 Vol% (iv) 100 ppmw water and (v) Toluene 15 Vol%



Multi-component sorption has been classified as quite a formidable subject handled by elaborate models, rules of thumb and extensive experimentation. Computer simulations have been hampered by complex theory, lack of suitable equilibrium data or prediction methods for multiple components. Therefore only qualitative inferences will be attempted here. If each component of the mixture is assumed to follow Henry's law, then each component maybe considered to propagate independent of others resulting in a sequence of discontinuous and sharp fronts during both adsorption and desorption. Generally light components breakthrough initially followed by heavy components. Lighter and intermediate components may rise above its feed concentration. This behavior is predominant in systems following the Langmuir adsorption model (Diran 1997).

This characteristic behavior of systems following the Langmuir model was also noted for the case of BT and DBT (Fig. 8). BT broke through prior to DBT and the concentration remained 20% above the inlet, typical of multi-component adsorption. The observation explained by the displacement of adsorbed BT molecules by DBT. This was also indicated by the lowering of BT concentration from 1.6 C° to 1.2 C° simultaneous to the breakthrough of DBT. Therefore prior to breakthrough, DBT replaced BT on the surface.

Thiophene despite being the lightest component and breaking through before BT and DBT, did not follow the expected trend. Once the outlet concentration approached ~50% of inlet, further breakthrough did not occur within the duration of the experiment. This observation maybe explained by the variation in size between the solute molecules. Even though thiophene broke through initially

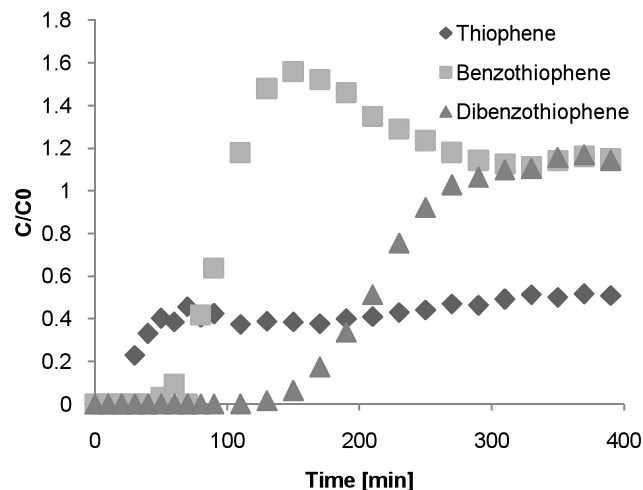


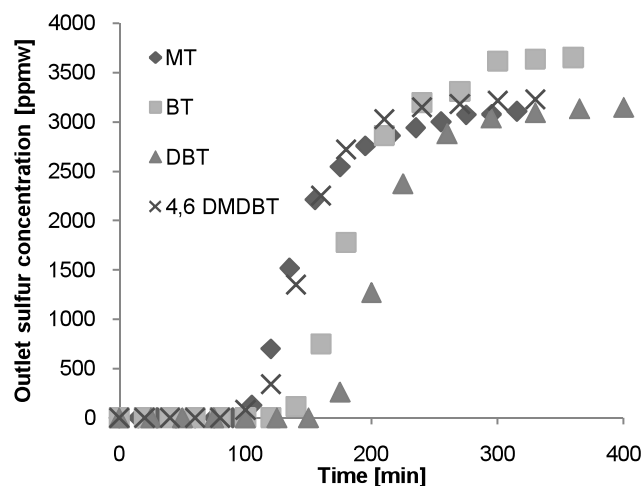
Fig. 8 Breakthrough of thiophene (0.572 g/l), benzothiophene (0.913 g/l) and dibenzothiophene (1.253 g/l) for Ag (4wt%)/TiO₂ from a model fuel containing all three species in n-octane; total sulfur content of ~0.08 mol/l

due to the lower strength of interaction with the sorbent, it was able to access active centers amid larger molecules of BT and DBT on the surface. Multi-component sulfur adsorption using the Ag/TiO₂ sorbent thus followed the general characteristics of the Langmuir model. BT and DBT were removed more efficiently than thiophene. The odd behavior of thiophene was associated with its molecular size. Early breakthrough of sulfur using real fuels compared to model fuels may therefore be attributed to competition among solute molecules. Eliminating interactions among the solutes makes the analysis of the adsorption system simpler.

Table 5 Sulfur capacity of the Ag(4wt%)/TiO₂ sorbent for various sulfur aromatics during individual and competitive adsorption

	Thiophene/M-thiophene 3500/807.9 ± 10 ppmw (mg T-MT/g)		Benzothiophene 3500/1289.5 ± 10 ppmw (mg BT/g)		Dibenzothiophene 3500/1769.7 ± 10 ppmw (mg DBT/g)	
	Breakthrough capacity*	Saturation capacity	Breakthrough capacity*	Saturation capacity	Breakthrough capacity*	Saturation capacity
Competitive adsorption	0.286	–	2.28	5.02	8.14	17.23
Individual adsorption	11.15	29.12	14.86	35.93	18.59	39.64

* At 20 ppmw threshold

**Fig. 9** Breakthrough of methyl thiophene (MT), benzo thiophene (BT), dibenzothiophene (DBT) and 4,6 dimethyl dibenzothiophene for Ag(4%)/TiO₂ in a model fuel with identical sulfur concentration of 0.08 mol/l

Therefore breakthrough of individual sulfur aromatics was also pursued.

3.6 Structure of sulfur aromatic

The structure of the sulfur heterocycle with respect to the number of aromatic rings as well as the presence of alkyl side chains affects the interactions with adsorption centers on the adsorbent. Challenge fuels with methyl thiophene (MT), benzo thiophene (BT), dibenzothiophene (DBT) and 4,6 DMDBT in n-octane were tested for desulfurization performance using the Ag (4wt%)/TiO₂ sorbent. Sulfur concentration of the fuels was 0.08 mol/l. Breakthrough characteristics are indicated in Fig. 9. The sulfur capacity was observed to vary as MT < 4,6 DMDBT < BT < DBT. Therefore the presence of aromatic ring (π electron density) increased the interaction between the sulfur species and the adsorption centers as observed in the earlier case of multi-component adsorption. A significant loss in capacity was observed for 4,6 DMDBT compared to DBT. The lowering of sulfur capacity as a result of methyl groups on 4,6

DMDBT was attributed to the reduction in π electron density on the aromatic ring. From the above data it was noted that larger aromatics are generally more effectively removed with π electron interaction playing a significant role.

Several distinctions can be drawn between the individual and multi-component breakthrough behavior of these sulfur aromatics. Sulfur capacity was higher for species during the individual adsorption due to higher equilibrium sorbent capacity at higher sulfur concentrations (Table 5). Sulfur concentration reached a plateau at levels below the feed concentration in the individual adsorption before rising to the inlet levels. However the outlet levels were noted to rise above the inlet concentration during multi-component adsorption.

The role of surface acidity on the activity of these sulfur adsorbents is being currently pursued in our laboratories. The effect of thermal treatments on surface acidity and corresponding changes in sulfur capacity is being investigated using NH₃ adsorption, titration of bronsted sites and temperature programmed desorption of NH₃. These findings will be presented in future publications.

4 Conclusions

Sulfur adsorption using Ag/TiO₂ adsorbent was attributed to surface acidity arising from bronsted centers. Acidic surfaces such as TiO₂ and γ -Al₂O₃ demonstrated considerable sulfur capacity compared to neutral surfaces such as SiO₂. Addition of bronsted sites by transition metal oxides increased sulfur capacity of all supports. Ag/TiO₂ demonstrated comparable sulfur capacities with other reported adsorbent compositions. Fuel additives were found to have a negative impact on the sulfur adsorption. Interaction of basic additives with acidic adsorption centers was attributed for deactivation of the adsorbent. Competitive adsorption demonstrated that the lighter sulfur aromatics breakthrough initially followed by heavier components. The displacement of lighter molecules was also observed. The adsorbent demonstrated higher capacity for sulfur molecules with the higher number of aromatic rings indicating the significance of π electron interactions at the adsorption interface.

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