

MECHANISTIC INVESTIGATIONS ON THE ADSORPTION OF ORGANIC SULFUR COMPOUNDS OVER SOLID ADSORBENTS IN THE ADSORPTIVE DESULFURIZATION OF TRANSPORTATION FUELS

S.Velu, Xiaoliang Ma and Chunshan Song*

Clean Fuels and Catalysis Program, The Energy Institute, and
Department of Energy and Geo-Environmental Engineering,
The Pennsylvania State University,
209 Academic Projects Building, University Park, PA 16802
E-mail: csong@psu.edu

Introduction

The deep removal of organic sulfur compounds from gasoline, diesel and jet fuel to produce ultra-clean transportation fuels, particularly for fuel cell applications, is becoming a paramount issue in recent years because the sulfur content in the fuel needs to be reduced to < 1 ppmw. Adsorptive desulfurization is a promising approach to produce fuel cell grade gasoline and diesel at relatively low temperature and low pressure without using hydrogen gas, and advantageous compared to the conventional hydrodesulfurization method that uses high temperature and high hydrogen pressure.¹

Adsorptive desulfurization is based on the ability of a solid adsorbent to selectively adsorb organic sulfur compounds from liquid transportation fuels. Since these fuels consist of various thiophenic sulfur compounds together with considerable amount of aromatics and olefins, the selective removal of sulfur compounds is challenging. A new concept developed at Penn State University known as selective adsorption for removing sulfur (PSU-SARS) is being explored in our laboratory with a variety of adsorbents based on various materials such as zeolites, metal compounds, and mixed metal oxides.¹⁻³

In order to develop a selective adsorbent for removing sulfur compounds, it is necessary to understand the nature of interaction between sulfur compounds and adsorbents. Thiophene has two pairs of electrons on S atom. One pair of electrons is in the six-electron π system and the other lies in the plane of the ring. Consequently, thiophene can act as either an n-type donor by donating the lone pair of electrons of the sulfur atom to the metal (direct S—M bond) or as a π -type donor by utilizing the delocalized electrons of the aromatic ring to form a π -complex with the metal or metal ion. At least eight different coordination geometries of thiophene are known in organometallic complexes and they include direct S—M bond, π -complex formation and geometries involving both direct S—M bond and π -complexes.^{1,4} This indicates that thiophenic sulfur compounds can be removed from the transportation fuels either by the formation of direct S—M bonds or by π -complexation. However, in the later, aromatics and olefins in the fuel may compete and this would decrease the selectivity for the adsorption of sulfur compounds.

The objective of the present study is to investigate if the direct S—M interaction or π -complex formation is involved in the adsorption of thiophenic sulfur compounds on the given adsorbent. And also to understand which type of interaction (direct S—M interaction or π -complex formation) is favorable for the selective adsorption of only sulfur compounds without adsorbing aromatics and olefins present in the fuel. For this purpose, a model fuel containing thiophene (aromatic sulfur compound), tetrahydrothiophene (non-aromatic sulfur compound), benzene (non-sulfur aromatic) and 1,5-hexadiene (non-sulfur olefin) as shown in Scheme-1 has been prepared and used as a feed. Adsorbents based on zeolites, mixed metal oxides, supported metal compounds, etc have been tested. Since Ag-exchanged zeolite is known to form π -

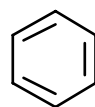
complexes with aromatics and olefins,⁵ it is considered as representative for adsorption of sulfur by π -complexation. The observed results are corroborated with electron density on S atom and C—C bond order of the sulfur compounds, aromatic and olefin derived from computer simulation. Understanding the mechanism of sulfur adsorption in this study will be very useful to develop selective adsorbents for removing sulfur from transportation fuels for refinery and fuel cell applications.



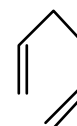
Thiophene



Tetrahydrothiophene



Benzene



1,5-hexadiene

Scheme 1. Adsorbates added to n-decane solvent in the preparation of a model fuel

Experimental

Zeolites containing various metal ions were prepared either by ion exchange or impregnation of NH₄Y-zeolite with a SiO₂/Al₂O₃ molar ratio = 5 as described earlier.³ Mixed metal oxide and supported metal adsorbents were prepared by co-precipitation and impregnation, respectively. The model fuel containing thiophene, tetrahydrothiophene as sulfur compounds, each 270 ppmw on the sulfur basis, in n-decane was prepared. About 270 ppmw of benzene and 270 ppmw of 1,5-hexadiene were also added to the fuel. The adsorptive desulfurization was performed using a flow apparatus as described elsewhere.¹⁻³ Analysis of treated fuel was performed using an Antek 9000 Series Sulfur Analyzer as well as a GC equipped with a flame ionization detector. Computer-aided molecular orbital calculations were performed using CAChe and MOPAC as described earlier.⁶

Results and Discussion

Figure 1 shows the breakthrough curves for the adsorptive desulfurization of the model fuel used in the present study over Ag-exchanged Y-zeolite. As can be seen, all the compounds, namely thiophene, tetrahydrothiophene, benzene and 1,5-hexadiene are completely adsorbed. The breakthrough points for the adsorption of benzene, thiophene and 1,5-hexadiene are about 22, 28, and 50 g, respectively. Tetrahydrothiophene was not detected in the treated fuel even after 50 g of fuel treatment. These results indicate that Ag-exchanged Y-zeolite forms π -complexes with benzene, 1,5-hexadiene and thiophene and that the π -complexation with 1,5-hexadiene being stronger than that with benzene and thiophene. The absence of tetrahydrothiophene in the treated fuel indicates that Ag-exchanged zeolite also makes direct S—M bond and this is even more stronger compared to the π -complexation with 1,5-hexadiene or thiophene. Since thiophene has a pair of electrons in the plane of the ring, it could form a direct S—M bond and π -complexation simultaneously.^{1,2} In such case, the adsorption of thiophene could be much more stronger than that of tetrahydrothiophene because of the simultaneous involvement of both types of bonding interactions. However, the observed results indicate that thiophene involves mainly π -complexation using delocalized electrons of the aromatic ring rather

than a direct S—M bond with Ag-exchanged zeolite. This is because the electron density on S atom of the thiophene is only 5.696 compared 6.042 in tetrahydrothiophene as calculated from computer simulation, implying that the S—M bond between the adsorption site and thiophene is much weaker than that between the adsorption site and tetrahydrothiophene.

The initial concentration of benzene was around 270 ppmw. However, its concentration in the outlet reached up to 700 ppmw after reaching the saturation value. This indicates that benzene initially adsorbed is desorbed during the course of the adsorption under the present experimental conditions. Similar result has also been observed in the adsorption of thiophene and this further substantiates that probably only π -type interaction exists between thiophene and Ag-exchanged zeolite.

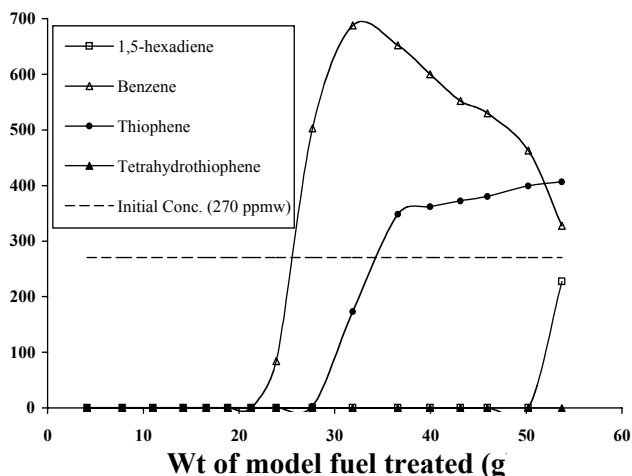


Figure 1. Breakthrough curves for the adsorption of thiophene, tetrahydrothiophene, benzene and 1,5-hexadiene in n-decane over Ag-exchanged Y-zeolite at 80°C. Wt of adsorbent: 3.5 g; LHSV = 12 h⁻¹. The outlet conc. of thiophene and tetrahydrothiophene are on the sulfur basis.

The adsorption of aromatics and olefins along with sulfur compounds by π -complexation would deteriorate the quality of transportation fuels. The competitive adsorption of aromatics and olefins with sulfur compounds would also decrease the selectivity and adsorption capacity. In fact, it has been found from our earlier experiments that the presence of about 10 wt % of toluene in a model gasoline fuel decreases the adsorption capacity of Ag-exchanged zeolite by about 20 times.⁷ Similarly, the presence of olefin decreases the capacity by about 6 times.

Figure 2 shows the breakthrough curves for the adsorptive desulfurization of the model fuel over a Ni-based supported metal adsorbent. Unlike that observed over Ag-exchanged Y-zeolites, only sulfur compounds (thiophene and tetrahydrothiophene) are removed over this adsorbent. The outlet concentrations of benzene and 1,5-hexadiene are very close to that present in the feed, indicating that they are not adsorbed at all. These results suggest that sulfur compounds are adsorbed by the direct S—M bond formation rather than by π -complexation over the Ni-based supported metal adsorbent. It is also interesting to note that the breakthrough curve of thiophene coincides with that of the tetrahydrothiophene and this indicates that these two compounds interact with the adsorbent to the same extent although there is a considerable difference in the electron density on S atom between these two sulfur compounds.

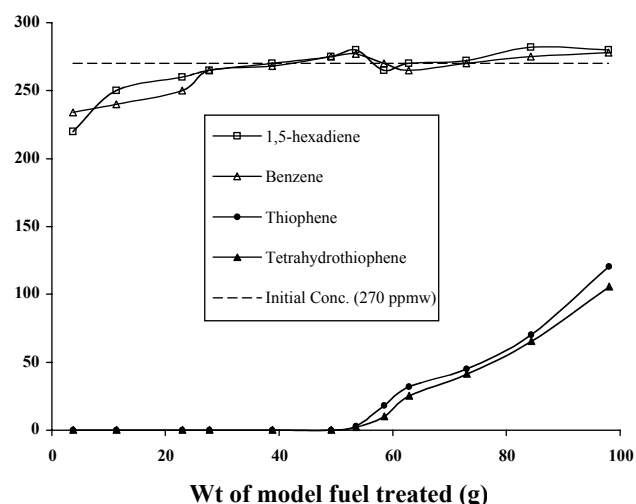


Figure 2. Breakthrough curves for the adsorption of thiophene, tetrahydrothiophene, benzene and 1,5-hexadiene in n-decane over Ni-based supported metal adsorbent at 80°C. Wt of adsorbent: 4.5 g; LHSV = 12 h⁻¹. The outlet conc. of thiophene and tetrahydrothiophene are on the sulfur basis.

Various other adsorbents such as mixed oxides derived from hydrotalcite-like anionic clays, transition metals supported on mesoporous materials, etc have also been tested in the present study. Based on the results obtained, better adsorbents selective for removing only sulfur compounds have been selected for the adsorptive desulfurization of real gasoline, diesel and jet fuel.

Conclusions

Depending on the nature of adsorbent used, thiophenic sulfur compounds form either π -complexes using delocalized electrons of the aromatic ring or a direct S—M bond using the lone pair of electrons of the sulfur atom present in the plane of the ring. While thiophene is removed by π -complexation over adsorbents such as Ag-exchanged zeolites, it is removed by the direct S—M interaction over Ni-based supported metal adsorbent.

Sulfur removal by π -complexation is less selective due to the competitive adsorption of aromatics and olefins present in the transportation fuels. On the other hand, sulfur compounds can be selectively removed by the direct S—M interaction.

Acknowledgements. This work was supported in part by the US department of Energy and in part by the US department of Defense.

References

- (1) Song, C.; Ma, X. *Applied Catalysis B: Environmental*, **2003**, 41, 207.
- (2) (a) Ma, X.; Sun, L.; Song, C. *Catal.Today*, **2002**, 77, 107; (b) Song, C. *Catal.Today*, **2002**, 77, 17.
- (3) Velu, S.; Ma, X.; Song, C. *Submitted for publication*.
- (4) Reynolds, M.A.; Guzei, A.; Angelici, R.J. *J.Am.Chem.Soc.* **2002**, 124, 1689.
- (5) Takahashi, A.; Yang, R.T.; Munson, C.L.; Chinn, D. *Langmuir*, **2001**, 17, 8405.
- (6) Song, C.; Ma, X.; Schmitz, A.D.; Schobert, H.H. *Appl.Catal. A*, **1999**, 182, 175.
- (7) Velu, S.; Watanabe, S. Ma, X.; Song, C. *Preprints-Am.Chem.Soc., Division of Petroleum Chemistry*, **2003**, 48, 56.