

Deep desulfurization of diesel by adsorption over Ni/ZSM-5

K.K.Sarda and K.K.Pant*

Department of Chemical Engineering

Indian Institute of Technology Delhi-110016, India

*Corresponding Author: E.mail: kkpant@chemical.iitd.ac.in

Introduction

Environmental restriction regarding the quality of transportation fuels and the emissions from them are the most important issues. Because of more stringent regulations and fuel specifications regarding development of better method for deep-desulfurization of fuels are important. There has been recent interest in developing adsorbents for selective desulfurisation by adsorption. Mercaptans, thiophenes, sulfides that are present in diesel are linear compounds and hence easy to remove by adsorptive desulfurisation process but benzothiophenes, dibenzothiophene, 4-MDBT, 4,6-DMDBT are cyclic compounds, are difficult to remove due to very high steric hinderence.^[1-5]

Desulfurization by adsorption is based on the ability of a solid sorbent to selectively adsorb organosulfur compounds from refinery streams. The pi complexation bonds are stronger than those formed by Vander Waals interactions, but they are also weak enough as to be broken by traditional engineering means, such as increasing temperature and/or decreasing pressure. Therefore, this provides opportunities for tailoring and developing new adsorbents for processes where selective adsorption is needed, such as in the case of sulfur removal from fuels.^[6-7]

Although research has been carried out using various sorbents, there is not a single sorbent identified for the removal of sulfur compounds. It was reported in literature that Cu, Ni, Mo and Ag based sorbents have given satisfactory results for desulfurization. However details of sorbent preparation and characterization are not revealed. There is also a need to understand the mechanism of adsorption of various compounds of sulfur on the surface.

Experimental

The adsorbents prepared in this work were based on Nickel over ZSM-5 support. Incorporation of Ni into the zeolite framework was done using liquid-phase ion-exchange method at room temperature. Different amount of Nickel was loaded on to the support. Ni(I)-ZSM-5 adsorbent was prepared by ion-exchanging ZSM-5[(Si/Al)=20] with Ni(NO₃)₂ aq. solution for 24hours. This solution is heated in oven for 18 hours at 110 °C and then calcined at 550 °C for 4 hrs.

Results & Discussion

To study the effectiveness of the adsorbent on sulfur removal experiments were carried out in batch. Desulfurization process depends on the overall activity of metal as well as support material. Effect of Si/Al ratio of ZSM -5 on sulfur removal is given in Table 1. As the silica to alumina ratio increases the acidity of ZSM-5 decreases. Also the pore size of the catalyst is different for different silica to alumina ratio. These two factors affect the desulfurization process. The maximum % sulfur removal was observed for the zeolite with silica to alumina ratio (SAR) of 20. As silica to alumina ratio decreases the acidity of ZSM increases. Therefore it can take the lone pair of sulfur compounds easily and hence more the sulfur removal. Also for the ZSM 20 the constraint index is 0.5 that is less than 2 hence it has large pore size hence it can remove variety of sulfur compounds present in diesel sample according to their size. As there were many types of sulfur compounds present in diesel hence it is not feasible to adsorb all kind of sulfur compounds. Hence oxidative desulfurization was used to further remove the sulfur compounds from the diesel. Removal by oxidation was also studied for diesel in a batch process.

Table 1: Effect of varying Silica to Alumina ratio(SAR) in ZSM on sulfur removal [T= 27 °C, P= 1 atm, Initial sulfur content = 350 ppm]

Weight of Sorbent (gm.)	% Removal of Sulfur for ZSM (SAR20)	% Removal of Sulfur ZSM SAR 34	% Removal of Sulfur ZSM SAR 45	% Removal of Sulfur ZSM SAR 200	Amount of sulfur adsorbed per gm of sorbent (mg/gm)			
					ZSM (SAR 20)	ZSM (SAR 34)	ZSM (SAR 45)	ZSM (SAR 200)
2	30	25	25	20	0.52	0.43	0.43	0.35
2.5	35	30	27.5	23.75	0.49	0.42	0.38	0.33
3	40	32.5	32.5	30	0.46	0.37	0.37	0.35
3.5	42.5	40	38.75	35	0.42	0.4	0.38	0.35
4	42.5	40	38.75	35	0.37	0.35	0.33	0.3

For the ZSM (SAR20) the constraint index is 0.5 that is less than 2 that indicates that it has large

pore size hence it can remove variety of sulfur compounds present in diesel sample according to there size. ZSM (Si/Al (SAR) = 20) has shown highest sulfur removal because of its acidic in nature. The pore size of the SAR 20 catalyst is high as its constraint index is low 0.5. (<2) and its surface area is 500 m²/g.^[15] Hence ZSM (SAR=20) was used for further investigation studies in batch process.

Effect of wt % of Ni on ZSM (SAR20) and H₂O₂ dosing:

Removal of sulfur was highest (76%) at 8 wt % of Ni . Removal of sulfur first increased and then decreased because initially when the amount of Ni was increased in the sorbent the adsorption sites also increased. As shown in the Figure 1, after 8 wt. % of Ni there was a decrease because the desulfurization process was dependent on the overall activity of the catalyst as a whole.

Highest sulfur removal was obtained with Ni (8 wt % of Ni).

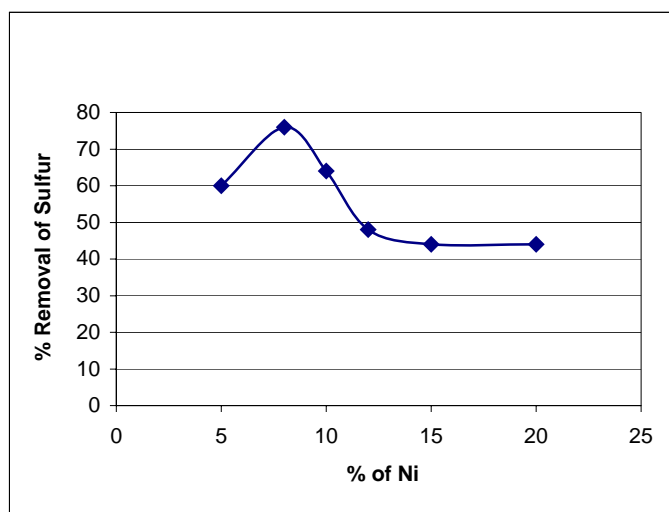


Fig. 1: % Removal of sulfur from commercial diesel v/s wt % of Ni ON ZSM 5

Effect of H₂O₂ concentration is also presented in Fig. 2. In a batch process, 1.2 gm of sorbent is added in 10 ml of model diesel sample. Hydrogen peroxide (6 % w/v solution) concentration in the sample was 1.0 ml per 10 ml of the diesel sample. Experiments were carried out at 27 °C and pressure. Initially when the H₂O₂ dose increased sulfur removal increased and than it reached to a constant value. This was because the amount of sulfur compounds present in the diesel sample that reacted with H₂O₂ was constant. When initially the amount of H₂O₂ increased then there were more chances for sulfur compounds to react with H₂O₂. But after this amount of sulfur compounds present in the diesel is the limiting factor for this reaction.

To perform these experiments model diesel was prepared using calculated amount of thiophene, dibenzothiophene, benzyl mercaptan and dibutylsulfide in isooctane. Amount of above mentioned sulfur compounds was taken in such a way that finally they accounted for 400 ppm of sulfur in the final model sample. Maximum removal of sulfur compounds with Ni-ZSM and H₂O₂ is observed because Ni removes the hindered sulfur compounds such as thiophene, benzothiophene whereas H₂O₂ is effective in removing linear compounds such as mercaptan and dibutyl sulfides. To study the effect of H₂O₂ 30% w/v solution of H₂O₂ is used and the results are given in Fig. 9.

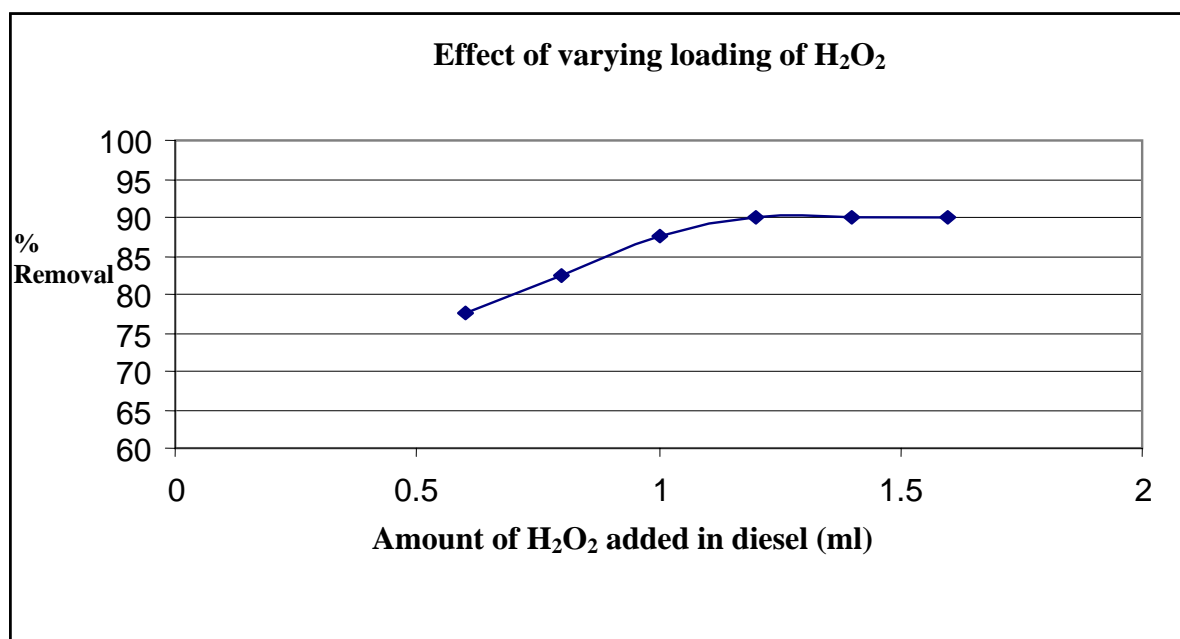


Fig. 2: Effect of H₂O₂ dose with constant loading of Ni-ZSM

The removal observed with 3.0 gm of Ni-ZSM (8%) was approximately 76%. Sulfur removal increased as the concentration of H₂O₂ up to a constant value. This is because the amount of sulfur compounds present in the diesel sample that can react with H₂O₂ is constant. The combination is effective because Ni has strong molecular orbital that can attract the hindered sulfur compounds and H₂O₂ can remove the linear sulfur compounds by converting them to sulfones.

Column Experiments

Effect of bed height on sulfur removal:

Batch process has given satisfactory results with approximately 90% sulfur removal with Ni-ZSM (8 wt % of Ni) and Hydrogen peroxide (6% w/v solution). Column experiments were

carried out with varying amount of weight of sorbent in the column. The experimental conditions were as follows: sorbent: Ni-ZSM-5 (SAR20), adsorbent dose 2-8 g; T:27 °C; flow rate 0.2-2.0 ml/min.; Initial sulfur in diesel: 350 ppm.

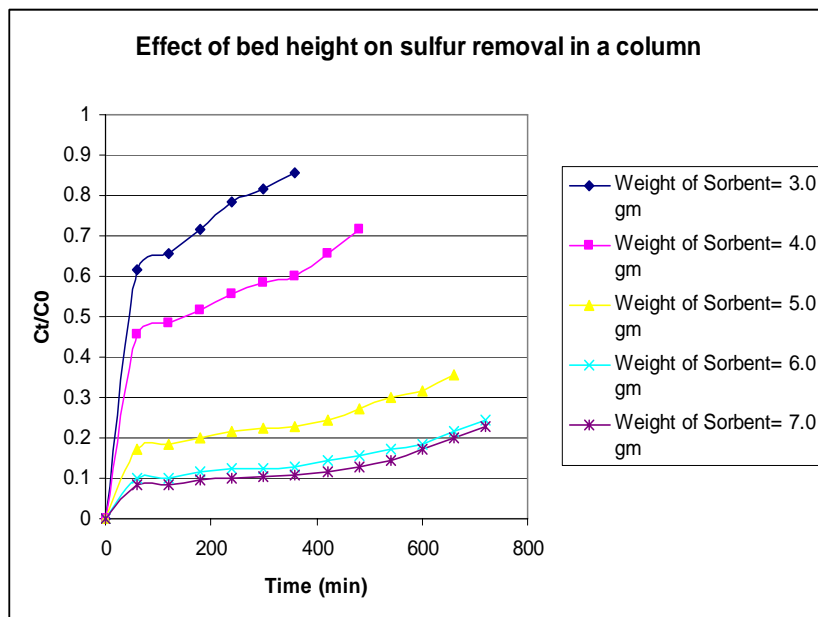


Fig 3: Effect of bed height on sulfur removal in column [$H_2O_2 = 5$ ml, Flow Rate = 0.2 ml/min, T= 27 °C, P= 1 atm, Initial sulfur content = 350 ppm]

It can be seen from Figure 3 that as the bed height increases the sulfur removal increase and then it reached to a maximum value after that there was no effect of further increase in the bed height. This was because as the sorbent amount increased the sorption sites increased. Hence the sulfur removal increased. But after the maximum there was no effect of increase of sorption sites as sorption capacity of the sorbent comes into picture.

Effect of flow rate on sulfur removal:

Column experiments were carried out with increasing the flow rate of diesel in the column. Ni-ZSM (8 wt % of Ni and Si/Al =20) was used as sorbent and flow rate was varied from 0.2 ml/min to 2.0 ml/min. It can be seen from the Figure 4 that as the flow rate increases the sulfur removal decrease. This was because as the flow rate increased the contact time between the diesel and sorbent decreased. Hence the sulfur was not able to come in contact with diesel and hence the adsorption decreased.

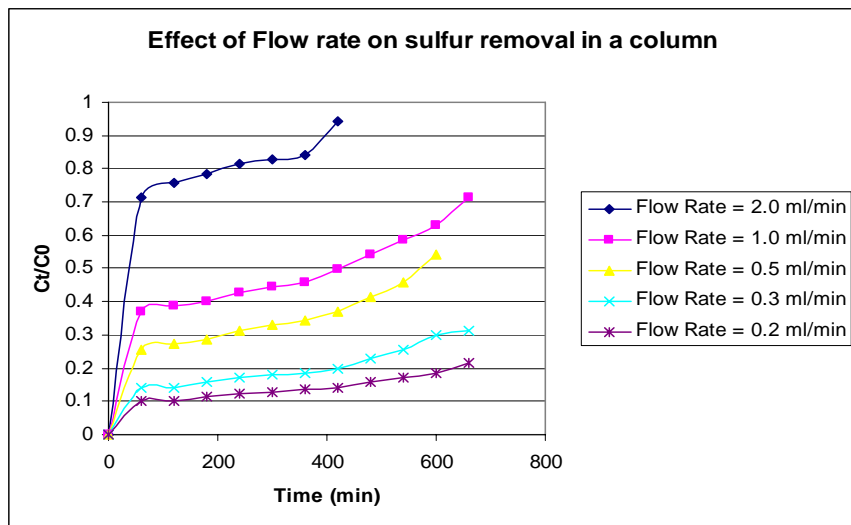


Fig. 4 Effect flow rate of diesel on sulfur removal in column [Weight of Ni-ZSM = 6 gm, H₂O₂ = 5 ml, T= 27 °C, P= 1 atm, Initial sulfur content = 350 ppm]

Experiments were also carried out with increasing the flow rate of diesel in the column. Catalyst bed was initially saturated with H₂O₂. Ni-ZSM (8 wt % of Ni and Si/Al =20) was used as sorbent and flow rate was fixed at 0.3 ml/min. On increasing the concentration of H₂O₂ the % sulfur removal increased. This was because as the concentration of H₂O₂ increased the amount of oxidant present in the sorbent increased and hence there was more oxidation of the linear sulfur compounds.

Conclusion

Among the various ZSM-5 catalysts with varying silica to alumina ratio, ZSM (Si/Al =20) was found to be most effective. A detailed investigation of Ni-ZSM [(Si/Al) =20] has confirmed high adsorption capacity (4.8mg S/g adsorbent) of sulfur. Ni-ZSM [(Si/Al) =20] was found to be very effective on the removal of sulfur compounds from commercial diesel. In the batch study Ni-ZSM and H₂O₂ has also shown approximately 90% removal of sulfur. 8%Ni-ZSM with H₂O₂ has shown more than 90% removal of sulfur from commercial diesel in the column study.

References

1. Babich V., Moulijn J. A.; '*Deep desulfurisation of oil refinery stream*' Applied Sciences, 136, (1); 2002, 262-268
2. C. Song ; '*Clean Fuels and Catalysis Program*'; Applied Catalysis; 41, (1-2); 207-238
3. Molinari D.; '*Oxidation and Functionalization: Classical and Alternative Routes and Sources*'; DGMK-Conference, Milan; 2005
4. Bhandari V. M., Chang H. K., Park U. G., Han S. S., Cho H. S. and Kim J. N.; '*Desulfurisation of diesel using ion exchanged zeolite*'; Chemical Engineering Science; 61,(8); 2006; 2599-2608,
5. Richardeau D., Joly C., Canaff C., Magnoux P., Guisnet M. and M. Thomas; '*Adsorption and reaction over HFAU zeolites of thiophene in liquid hydrocarbon solutions*'; Applied Catalysis; A 263; 2004; 49–61.
6. Xue M., Chitrakar R., Sakane K., Hirotsu T., Ooi K., Yoshimura Y., Toba M. and Qi F.; '*Preparation of cerium-loaded Y-zeolites for removal of organic sulfur compounds from hydrodesulfurized gasoline and diesel oil*'; Journal of Colloid and Interface Science; 298 (2006); 535-542
7. Song C. , Sun L. , Xiaoliang M.; '*Active carbon based desulfuriser*'; Catalysis Today; 77,(1); 2002; 107-116
8. Arturo J. Hernández-Maldonado, Frances H. Yang, Gongshin Qi, Ralph T. Yang; '*Desulfurization of transportation fuels by p-complexation sorbents; Cu(I)-, Ni(II)-, and Zn(II)-zeolites*'; Applied Catalysis; 1 56 (2005); 111–126
9. A. Marafi , A. Al-Hindi, A. Stanislaus; '*Deep desulfurization of full range and low boiling diesel streams from Kuwait Lower Fars heavy crude*'; Fuel Processing Technology; 88 (2007); 905–911
10. Jinbo Gao, Shouguo Wang, Zongxuan Jiang, Hongying Lu, Yongxing Yang, Fei Jing, Can Li; '*Deep desulfurization from fuel oil via selective oxidation using an amphiphilic peroxotungsten catalyst assembled in emulsion droplets*'; Journal of Molecular Catalysis; 258 (2006); 261–266
11. Farhan Al-Shahrani , Tiancun Xiao , Simon A. Llewellyn , Sami Barri c, Zheng Jiang , Huahong Shi , Gary Martinie , Malcolm L.H. Green; '*Desulfurization of diesel via the H₂O₂ oxidation of aromatic sulfides to sulfones using a tungstate catalyst*'; Applied Catalysis; 73 (2007); 311–316
12. G. McKay, H.S. Blair and J.R. Gardner; '*Adsorption of dyes on chitin Equilibrium studies*'; J. Applied Polymer Science; 27 (1982); pp. 3043–3047