COMPETITIVE ADSORPTION REMOVAL OF SULPHUR COMPOUNDS IN GASOLINE USING X ZEOLITE

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Summary

The paper presents the results of sulphur removal from gasoline in a ternary system, i.e. benzene, 3-Methylthiophene (3-MT)/ Benzothiophene (BT) and isooctane. These results indicate that the presence of aromatic compounds strongly reduces the efficiency of the removal of sulphur in gasoline. Moreover, it is found that the exchanged zeolite exhibits higher activity than the original and the type of sulphur containing compound plays an important role in the adsorption of sulphur in gasoline. A discussion on the obtained results is also presented.

Key words: *Adsorption, removal of sulphur, zeolite, gasoline.*

1. Introduction

As a positive attempt to cope with the alarming degradation of air quality in today's industrialised world, many environmental regulations have been issued, exerting a great deal of control over the enormous emissions discharged from the relentless operation of billions of transportation means and factories, in which sulphur oxides remain a major concern. Nowadays, most of the sulphur compounds are removed from petroleum-based feedstocks by the hydrodesulphurisation (HDS) process which usually operates at severe conditions, such as elevated temperature (300 - 340°C) and high pressure (20 - 100atm). This process can reduce the sulphur content in gasoline to less than 30ppmw. However, it is difficult to reduce the sulphur content in diesel to less than 15ppmw. In order to enhance the efficiency of the sulphur removal process to meet the required standards, the reactor volume or the catalyst activity must be at least three times larger than those currently used in refineries [1]. Such an increase in the reactor volume will unfavourably affect operating cost and capital. Moreover, another major problem associated with the deep HDS of gasoline is the significant reduction of octane number due to the saturation of aromatics and olefins in naphtha from fluid catalytic cracking, which also means higher hydrogen consumption. Obviously, more effective and affordable methods to produce ultra low levels of sulphur compounds in transportation fuels are needed.

There are several new techniques which have been developed as alternatives to conventional HDS. One of these is the adsorption process, which is considered to be a promising major advanced economical desulphurisation process due to its ambient operating conditions. However, a great challenge for this approach is to select a suitable sorbent of high selectivity and sulphur capacity. A wide variety of sorbents are commonly used for adsorption purposes such as activated carbon, silica-based sorbents, zeolites, and metal exchanged/impregnated activated carbon/zeolites/mesoporous materials [2 - 5]. Yet the capacity reported was not satisfactorily high. During 2003 and 2004, Hernandez and co-workers [6] found that adsorbents based on Y-Zeolites exchanged with Ni, Cu or Ag cations have good capacity for thiophene adsorption in benzene via strong π-complexation bonding, which is stronger than Van der Waals interaction but can be easily broken by manipulating temperature and pressure.

In our previous study [7], in a binary system, it was found that the concentration of the exchanged metal in the zeolite and the type of sulphur containing compound strongly influenced the removal of sulphur compounds in gasoline. The present study deals with ternary systems of isooctane, benzene, and 3-MT/BT using Ni^{2+} exchanged zeolite as adsorbent.

2. Experimental section

The experimental process was described in detail in [7]. Briefly, batch liquid adsorption experiments were carried out in a 15cm^3 vial. The ratio of fuel to adsorbent was fixed at 85 [8] with constant stirring. The equilibrium time was set at 8h [9]. Once the system reached equilibrium, samples were withdrawn by using syringe and then analysed by gas chromatography (HP 5890 Series 2) with FID detector and HP-5 column (30m x 0.32mm x 0.25mm film thickness).

3. Results and discussion

3.1. Effect of aromatic content on sulphur compounds adsorption

As discussed above, in view of large aromatic content (benzene used as the model aromatic compound), we believed that there was a competition between aromatic (benzene) and sulphur (3-MT orBT) compounds getting adsorbed on zeolites. In order to obtain a clearer picture on the effect of aromatics in the desulphurisation of transportation fuels, experiments using a small range of benzene concentration (0 - 15% by weight) in a solution of isooctane and 2,000ppmw (0.2% by weight) sulphur containing compound (3-MT and BT) content were conducted. NiX zeolite with the highest metal loading (7.48%wt Ni) and the original NaX zeolite were chosen for testing. The results are shown in Figs.1 and 2.

Results in Figs.1 and 2 illustrated a dramatic reduction in the sulphur uptake with increasing aromatics concentration. The drastic drop on adsorption capacity was found to be approximately 85% for 3-MT and 80% for BT at benzene concentration of 6%. As benzene concentration increased further, the further reduction in adsorption capacity was not significant. The influence of aromatic content could be explained from the fact that benzene can compete with 3-MT and BT for entering zeolite pores and adsorbing on the active sites of the zeolite. Even with benzene presented as co-adsorbate, the exchanged zeolite still exhibited a higher affinity towards sulphur compounds than the original one. In other words, the interaction between sulphur compounds and the exchanged zeolite seemed to be ruled by π-complexation. Therefore, it could be safely concluded that the π-complexation sorbent is more favourable in desulphurisation application.

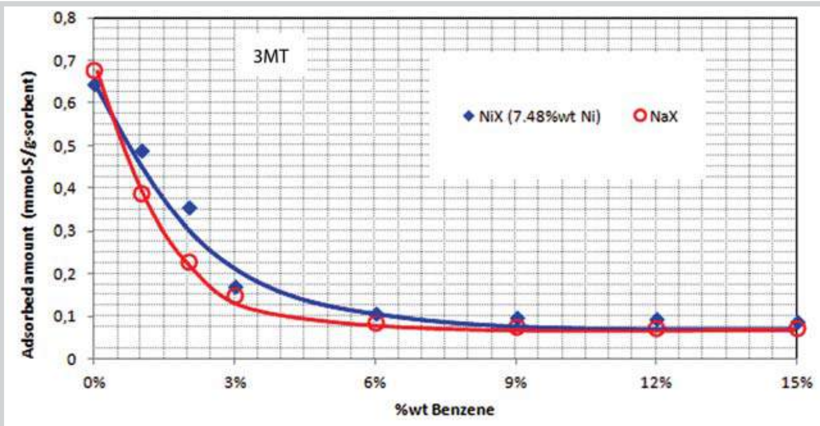

Fig.1. *Effect of competitive benzene adsorption on 3-MT adsorption on NiX (7.48%wt Ni) and NaX*

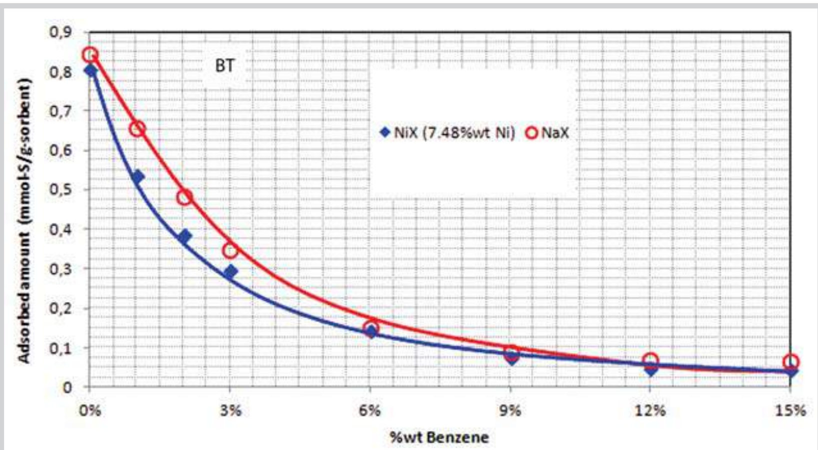

Fig.2. *Effect of competitive benzene adsorption on BT adsorption on NiX (7.48%wt Ni) and NaX*

3.2. Competitive adsorption between sulphur compounds and benzene on zeolites

Results for sulphur compounds and benzene adsorption on NiX (7.48%wt Ni) and original NaX zeolites from different concentrations of benzene (0 - 15% by weight) in solution of isooctane and 2,000ppmw sulphur containing compound content are presented in Table 1 and 2 giving more insights about the impact of aromatics on the sulphur removal process. In addition, Table 1 and 2 also show selectivity (given in terms of number of moles of sulphur compounds and benzene adsorbed on zeolites) for sulphur compounds and benzene, helping to estimate how sulphur compounds were more favoured over benzene in mixture solution.

As seen from Table 1 and Fig.3, in case of low aromatic content (2%wt), the selectivity of 3-MT and BT over benzene was 1.40 and 1.37, respectively, for π-complexation sorbent (NiX zeolite). Meanwhile, at this benzene concentration, for original zeolite (NaX), the selectivity was 0.42 for 3-MT and 0.90 for BT. This result confirmed the beneficial effect of exchanged zeolite on the adsorption selectivity of sulphur compounds in the presence of

***Table 1.** Selectivity of 3-MT over benzene in ternary system using NiX (7.48%wt Ni) and NaX zeolites*

Zeolite	Benzene content (%wt)	Absorbed 3-MT (mmol/g-sorbent)	Adsorbed Benzene (mmol/g-sorbent)	Selectivity ($S_{3MT/Benzene}$)
NiX (7.48%wt Ni)	0%	0.645	-	-
	1%	0.492	0.161	3.06
	2%	0.356	0.254	1.40
	3%	0.173	0.506	0.34
	6%	0.108	0.561	0.19
	9%	0.098	0.549	0.18
	12%	0.095	0.589	0.16
	15%	0.091	0.585	0.16
NaX	0%	0.681	-	-
	1%	0.389	0.298	1.28
	2%	0.230	0.478	0.42
	3%	0.150	0.556	0.27
	6%	0.087	0.594	0.15
	9%	0.078	0.607	0.13
	12%	0.074	0.607	0.12
	15%	0.075	0.635	0.12

***Table 2.** Selectivity of BT over benzene in ternary system using NiX (7.48%wt Ni) and NaX zeolites*

Zeolite	Benzene content (%wt)	Absorbed BT (mmol/g-sorbent)	Adsorbed Benzene (mmol/g-sorbent)	Selectivity ($S_{BT/Benzene}$)
NiX (7.48%wt Ni)	0%	0.842	-	-
	1%	0.657	0.145	4.48
	2%	0.482	0.350	1.37
	3%	0.350	0.475	0.74
	6%	0.150	0.695	0.22
	9%	0.089	0.702	0.13
	12%	0.070	0.768	0.09
	15%	0.065	0.750	0.09
NaX	0%	0.805	-	-
	1%	0.538	0.272	1.95
	2%	0.387	0.422	0.90
	3%	0.298	0.518	0.58
	6%	0.144	0.634	0.23
	9%	0.075	0.718	0.10
	12%	0.048	0.744	0.06
	15%	0.046	0.766	0.06

benzene. The high values of selectivity at low benzene concentration (up to 2%wt) also implied that sulphur compounds have higher strengths of π-complexation bonds than benzene. However, when increasing the aromatic content, experimental data showed a significant decrease of selectivity and an effective shifting of the balance to benzene. These less-than-one values imply that zeolites are more subjective to be occupied by benzene than by sulphur compounds at this high level of benzene concentration. It could be explained that at these concentrations, despite sulphur compound's high strength of π-complexation bonds, the surface of zeolite had been completely saturated by benzene molecules, leaving very few active sites available for sulphur compounds to be bound. However, at any benzene concentration, the selectivity of sulphur containing compound over benzene of the exchanged sorbent (NiX) is higher than that of the original one (NaX).

Considering the effect of sulphur-containing compound on the removal of sulphur from gasoline (Fig.3, Table 1 and 2), the type of sulphur-containing compounds strongly affected the adsorption capacity of the studied zeolites. As it can be seen, at low concentration of benzene, the adsorbent showed higher selectivity to BT than 3-MT. However, at high concentration of benzene (higher than 6%wt), there was not much difference between the 3-MT selectivity and BT selectivity. This result was in good consistence with our previous results in binary systems where the higher affinity of the aromatic ring played crucial role in the adsorption of S-containing compound.

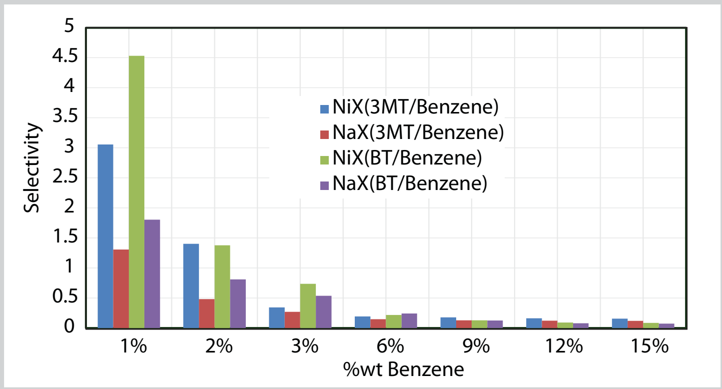

Fig.3. *Adsorption selectivity of adsorbents at different benzene concentrations*

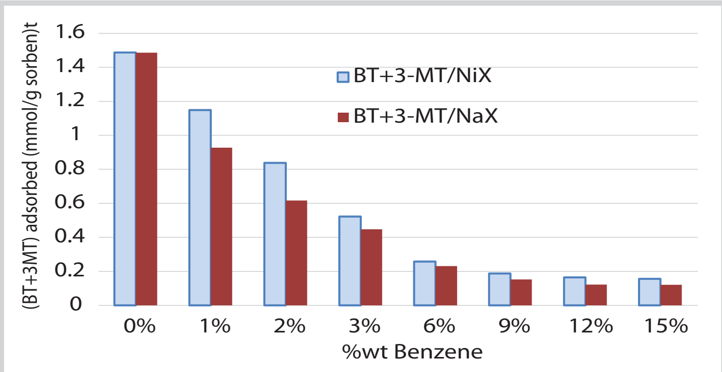

Fig.4. *Effect of Benzene adsorption on BT+3MT adsorption on NiX (7.48%wt Ni)*

As a first step to illustrate the effect of benzene adsorption on the removal of sulphur-containing compounds in gasoline, the total amount of BT and 3-MT adsorbed on zeolites in the presence of benzene is depicted in Fig.4. It can be seen that, the total amount of BT and 3-MT adsorbed is the same on both zeolites when there is no Benzene in the system. This can be explained by the saturation of adsorbate on the adsorbent because the adsorption time was kept quite long. The benefit of π-complexation in the sorbent (NiX) is observed at any concentration of benzene in the system, especially in the range of 1 to 6 %wt.

4. Conclusions

The presence of aromatic compounds strongly influences the adsorption of sulphur containing compound on NaX and NiX zeolites. The adsorption capacity decreases with increasing benzene concentration. The rate of decrease is especially high at low benzene concentrations (less than 3%). However, when the concentration of benzene reaches a certain level, the rate of sulphur-containing compound adsorption only decreases slightly.

Similar to binary systems, the adsorption of sulphur on the studied zeolites depended on the type of S-containing compounds. The capacity to adsorb BT is higher than 3-MT, which might be the result of higher affinity of the aromatic rings in the BT structure.

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