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Electronic Effect of Substituents on Hydrodesulfurization of Thiophenes : Reactivity and Selectivity

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Despite the large scale-commercial application of heterogenous catalytic hydrodesulfurization (HDS) to the desulfurization of organo-sulfur compounds in petroleum, very little is known about the various mechanisms likely to be involved in this process. In this work, one possible mechanism of hydrodesulfurization of substituted thiophenes which is based on the electronic effects of the substituents is proposed. Organosulfur compounds studied are: alkylthiophenes, phenyl-thiophenes, pyridylthiophenes and thiophene. Under present conditions (T = 553 K; pH_2 = 50 bar), it is possible to formulate both global relative rate and selectivity hydrogenation/hydrogenolysis for substituted thiophenes. Electronic effects of substituents are responsible of the selectivity and lead to particular modes of adsorption on catalyst: more hydrogenation is observed with an electron-withdrawing substituent which would be adsorbed on an acceptor catalytic site. The hydrogenolysis is facilated by an acceptor substituent, adsorbed on a donor catalytic site.

Key Words: Hydrodesulfurization, Hydrogenation, Hydrogenolysis, Thiophenes.

INTRODUCTION

Hydrotreatment applications for removal of heteroatoms such as sulfur from feedstock are one of the largest processes in the petroleum refining industry. In order to reduce the sulfur content in transport fuels for environnemental protection purpose, regulations are issued[1-4]. The need to meet more stringer standards limiting the emission of SOx in atmosphere, urges a deeper understanding of the mechanism by which sulfur containing compounds are destroyed over hydrodesulfurization (HDS) catalysts.

On typical NiW/alumina hydrotreating catalyst, HDS of a lkylthiophenes shows that β-substitued thiophenes are more reactive than those of α-substituted compounds[5]. Their selectivity hydrogenation/hydrodrodesulfuration depends on the position of the alkyl groups on the thiophenic ring[5].

Hensen *et al.*[6] proposed a mechanism of thiophene hydrodesulfurization on different carbon-supported metal catalysts. Results show that aromatic ring is partially hydrogenated to 2,3-dihydrothiophene. This intermediate can isomerize to 2,5-dihydrothiophene, hydrogenate to tetrahydrpothiophene or desulfurize. The yield

of the partially hydrogenated thiophenes depends on the catalyst used. Large amounts of these intermediate compounds are obtained on Mo/C catalyst, while Rh/C catalyst produces small amounts[6].

However, the product distribution obtained in thiophene and alkylthiophene HDS over typical NiW/alumina catalyst shows that the reaction gives essentially two steps: (i) Hydrodesulfurization (HDS) leading to correspondant diene, by breaking the C_{sp2}-S bond. (ii) Partial hydrogenation followed by total hydrogenation of the thiophenic ring. HDS can occur on both partially or totally hydrogenated sulfur compounds.

Despite the fact that the formation of dienes by direct desulfurization is still questioned, it was concluded that the HDS of thiophene and derivative alkyled compounds occurs through two parallel reactions: (i) Direct desulfurization which yields dienes and alkyled derivatives. (ii) Hydrogenation which gives partially and totally hydrogenated type compounds.

This work examines the electronic effect of alkyl, phenyl and pyridil groups on the HDS of derivative thiophenes under typical hydrotreating conditions. A new reaction mechanism of sulfur compounds in hydrotreating, based on the electronic effect of the substituent (electro-withdrawing or electro-donor) is therefore proposed together with a discussion on how structure and position of a substituent can promote or inhibit one of the two pathways of the reaction. The types of the catalytic centers involved in HDS on NiW/alumina sulfided catalyst are also discussed.

EXPERIMENTAL

The hydrodesulfurization (HDS) of thiophene, alkylthiophenes, phenylthiophenes and pyridylthiophenes was carried out at 553 K, under 50 bar hydrogen pressure and 1 bar H_2S pressure, in a fixed-bed reactor. Decane was used as solvant.

Catalyst: The comercial NiW/alumina hydrotreating catalyst containing 3 % NiO, 11.5 % WO_3 and 85.5 % alumina was sulfided in a mixture of 15 % H_2S and 85 % H_2 under a total pressure of 1 bar. The gas flow was kept at 120 mL/mn, while heating the catalyst at a rate of 8 K/mn.The temperature was then kept at 673 K for 4 h before decreasing at a rate of 8 K/mn until 303 K. After the sulfidation, catalyst was kept 0.5 h under nitrogen medium and conserved in a glass tube.

Sulfur compounds: Thiophene, alkylthiophenes and pyridilthiophenes were purchased from Aldrich, whereas 2-phenylthiophene and 3-phenylthiophene were synthesized since they are not available commercially.

Preparation of 2-phenylthiophene: 40 mL of *n*-butyl lithium (1.5 M in hexane) were added dropwise at 273 K to 8.4 g of thiophene. Anhydrous ether was used as solvant. After 0.5 h of reaction the mixture was brought out into room temperature. 12 mL of iodobenzene and 2 mL of piperidine are then added to the mixture which was heated at 373 K during 2 h. This method leads to 4.2 g of 2-phenylthiophene and 0.8 g of 2,5-diphenylthiophene.

Preparation of 3-phenylthiophene: According to procedure described in the literature[7], 3-phenylthiophene was synthesized in 2 steps:

Dehydratation of 2-phenyl-2-butanol: 16 g of 2-phenyl-2-butanol (0.1 mol) were heated at 503 K in benzene during 5 h with iodine. Yield: 12.6 g of 2-phenyl-2-butene.

Cyclization in presence of sulfur: 9 g of sulfur were added to 12.6 g of 2-phenyl-2-butene and the mixture was heated at 503 K during 7 h. Distillation under a 0.2 mm Hg pressure and 503 K leads to 3.6 g of 3-phenylthiophene.

RESULTS AND DISCUSSION

Under typical hydrotreating conditions only thiophenic ring reacts. Neither hydrogenation nor hydrogenolysis of the substituent was observed under the above mentioned conditions.

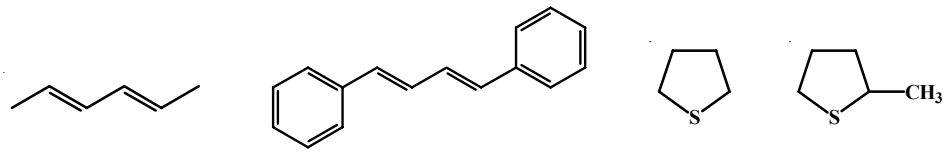
The intermediate products, obtained in hydrodesulfurization (HDS) of substituted thiophenes over typical NiW/alumina catalyst, were analyzed by gas phase chromatography and by coupled GPC/Mass spectra. These intermediates are: (i) a mixture of 2,3-dihydro(substituted)thiophene and 4,5 dihydro(substituted)thiophene, (ii) a totally hydrogenated compound, obtained by hydrogenation of 2,3-dihydrothiophene or 4,5-dihydrothiophene (iii) a mixture of corresponding mono-olefines and hydrocarbons.

Since, the reaction mechanism for the hydrodesulfurization of used model thiophenes is still a matter of great debat, it was suggested that the cleavage of the carbon-sulfur bonds may yiel 1,3-butadiene directly followed by a fast hydrogenation to 1-butene[8]. Furthermore, Devanneaux *et al.*[9] pointed out that tetrahydrothiophene should be considered as an intermediate of the HDS of thiophene and partially hydrogenated thiophenes have also been propsed as possible intermediates[10]). It was found that these thiophenes are more reactive than tetrahydrothiophene[11] which in turn desulfurizes more easily than thiophene[12].

In the present study no diene, product of direct desulfurization, was detected which suggests that it is either not formed or formed and fastly hydrogenated to olefine. In an effort to clarify the reason why the presence of this compound is not detected under present conditions, hydrogenation of **1** and **2** was carried out at 553 K and 70 bar hydrogen pressure. The results show that the two compounds are fastly hydrogenated to corresponding olefines. It is concluded that under present conditions dienes cannot be detected and the cleavage of C_{sp2}-S bond can be a possible step of the HDS of thiophenes.

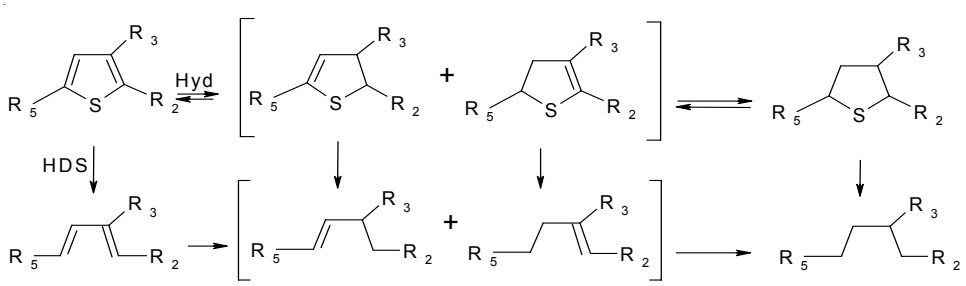
On the other hand, HDS of tetrahydrothiophene (**3**) and 2-methyltetrahydrothiophene (**4**) carried out under the same conditions show that the reaction proceed trough two parallel reactions: (i) dehydrogenation to dihydrothiophene and 2,3-dihydro, 2-methylthiophene, respectively. (ii) direct desulfurization which yields hydrocarbon compounds.

This is in contrast to the study of Markel *et al.*[11] who indeed found that the interconversion of tetrahydrothiophene to 2,3-dihydrothiophene was not detected.



1 **2** **3** **4**

An attempt to deduce from these observations that HDS of thiophenes occurs through two pathways (**Scheme-I**): (i) partial hydrogenation of thiophenic ring followed by total hydrogenation and desulfurization, (ii) direct desulfurization yielding dienes, fastly hydrogenated to olefines.



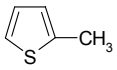
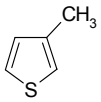
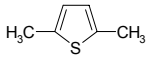
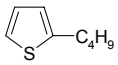
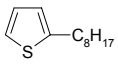
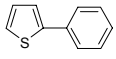
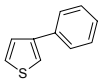
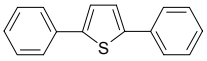
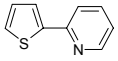
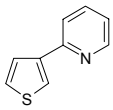
Scheme-I: HDS of thiophenes

Another unresolved issue is the selectivity hydrogeantion/hydrogenolysis of studied thiophenes. The results clearly demonstrate a relation between selectivity and nature of substituent on thiophenic ring. Small amounts of hydrogenated intermediate compounds were detected in HDS of phenylthiophenes comparatively to alkylthiophenes and no hydrogenated pyridilthiophenes were detected in this study (Table-1).

On the basis of the kinetic results it has been established that HDS activity of thiophenes depends on the nature and the position of the substituent on the ring and decreases in order: thiophene < 2-octylthiophene < 2-butylthiophene < 2-ethylthiopheneone < 2-methylthiophene < 3-methylthiophene < 3-pyridilthiophene < 2-pyridilthiophene < 3-phenylthiophene < 2,5-diphenylthiophene (Table-1).

These findings are in accordance with those reported by Miki *et al.*[5] who found that β-alkyl substituted thiophenes are more reactive than those α-substituted. For others[13] the position of the alkyl proups on the ring has no effect on the réactivity of the thiophene. With an insaturated substituent (phenyl or pyridil), the reaction rate of a thiophenic compound is found to be three to nine times higher than that of thiophene (Table-1).

TABLE-1
REACTIVITY AND SELECTIVITY OF SUBSTITUTED THIOPHENES

Sulfur compound	Substituent			Relative rate constants (Hyd + HDS)	Selectivity (conversion = 20 %) (Hyd + HDS(
	R_2	R_3	R_5		
 Thiophene	-H	-H	-H	1	-
 2-Methylthiophene	$-CH_3$	-H	-H	1.4	30
 3-Methylthiophene	-H	$-CH_3$	-H	2.1	20
 2,5-dimethylthiophene	$-CH_3$	-H	$-CH_3$	1.6	50
 2-Butylthiophene	$-(CH_2)_3-CH_3$	-H	-H	1.1	60
 2-Octylthiophene	$-(CH_2)_7-CH_3$	-H	-H	1	80
 2-Phenythiophene	$-(C_6H_5)$	-H	-H	3.3	10
 3-Phenylthiophene	-H	$-(C_6H_5)$	-H	3.0	15
 2,5-Diphenylthiophene	$-(C_6H_5)$	-H	$-(C_6H_5)$	9.0	-
 2-Pyridil,2-thiophene	$-(C_5H_5N)$	-H	-H	4.6	-
 2-Pyridil,3-thiophene	H	$-(C_5H_5N)$	-H	3.2	-

The selectivities to the different hydrothiophene product molecules at a conversion of *ca.* 20 % are summarized in Table-1. Depending on the reactant (methylthiophene, phenylthiophene or pyridilthiophene), contribution of the hydrogenation pathway to the overall HDS was very different. Under present conditions, hydrogenation pathway contributed 60 % to the overall HDS of methylthiophenes while only 20 % to the HDS of the phenylthiophenes. It was also found that the presence of a pyridil group on the thiophenic ring inhibited hardly the hydrogenation of a pyridilthiophene. No hydropyridilthiophene was detected under present HDS conditions. The reaction would occur through direct desulfurization.Then, an attempt is made to deduce from these considerations that low hydrogenation pathway correspond to high hydrogenolysis one and inversely.

To describe the effects of the substituents on the overall HDS of thiophenes, localized (inductive) and delocalized (resonance) effects are considered. The localized effects are represented by the substituent constant σ_I and the delocalized effects by σ_R. These constants reported in Table-2 are positive or negative depending on the electron-withdrawing or electron-donating ability of the substituent[14].

TABLE-2
INDUCTIVE (σ_I) AND RESONANCE (σ_R) SUBSTITUENT PARAMETERS [Ref. 14]

Substituent	H	Methyl $-CH_3$	*n*-Butyl $-(CH_2)_3CH_3$	*n*-Octyl $-(CH_2)_7CH_3$	Phenyl $-C_6H_5$	Pyridil $-C_5H_5N$
σ_I	00.00	-0.04	-0.04	-0.06	+0.15	+0.20
σ_R	00.00	-0.11	-0.12	-0.14	-0.10	+0.23

The results show that strongly electron-donating substituents (methyl and phenyl groups) favour hydrogenation, while hydrogenolysis is favoured by electron-withdrawing substituent (pyridil groups). In other words, the contrasting behaviour observed for the two pathways (hydrogenation and hydrogenolysis) shows the existence of 2 different catalytic sites: one responsible for hydrogenation, associated with an electron-withdrawing character ($\sigma < 0$) favouring adsorption of thiophenes with electro-donor substituents (methyl or phenyl groups), the other one responsible for the C_{sp2}-S bonds associated with an electron-donating character ($\sigma > 0$) favouring adsorption of thiophenes substituted with electron-withdrawing groups. The existence of two catalytic sites have often been proposed in the litterature[15].

The consequences of these observations are important to consider to improve a catalytic system or to define new concepts for new catalysts.

Conclusion

The results presented in this paper and compared with available litterature indicate that the conversion of thiophenes occurs through two pathways:hydrogenation and hydrogenolysis both are almost affected by the nature and the position of the substituent on the ring. The conversion rates (hydrogenation + hydrogenolysis) of thiophene is much lower than the rates of conversion of alkylthiophene, pyrididlthio-

phene and phenylthiophene by a factor of about 1.5; 3 and 4, respectively. This increase in rate constants and the product distribution can result from the electronic properties of the substituents at the α and β-positions of the sulfur atom. Hydrogenation of the thiophenic ring is favoured by highly electro-donating substituents such as alkyl or phenyl groups and inversely, hydrogenolysis of C_{sp2}-S bonds is facilated by highly withdrawing substituents such as pyridil groups. The presence of such correlations is a chemical evidence for the existence of two distinct catalytic sites: one responsible for hydrogenation associated with an electron-withdrawing character and the other one responsible for the hydrogenolysis of C_{sp2}-S bond associated with an electron-donating character. All these assumptions might better explain the mechanism likely to be involved in the HDS process and lead to a better model for a more effective hydrotreating catalyst.

REFERENCES

1. T.G. Kaufmann, A. Kaldor, G.F. Stuntz, M.C. Kerby and L.L. Ansell, *Catal. Today*, **62**, 77 (2000).
2. C. Marcilly, *Stud. Surf. Sci. Catal.*, **135**, 37 (2001).
3. C. Song and X. Ma, *Appl. Catal. (B) Environ.*, **41**, 207 (2003).
4. I.V. Babich and J.A. Moulijin, *Fuel*, **82**, 607 (2003).
5. Y. Miki, Y. Suguimoto and S. Tamadaya, *Sekiyu Gakkaishi*, **36**, 32 (1993).
6. E.J. Hensen, M.J. Vissenberg, V.H.J. De Beer, J.A.R. Vanveen and R. Santen, *J. Catal.*, **163**, 429 (1996).
7. A.S. Brown and M.G. Voronkov, *J. Gen. Chem.*, **17**, 1162 (1947).
8. J.M.J.G. Lipsch and G.C.A. Schuit, *J. Catal.*, **15**, 179 (1969).
9. J. Devanneaux and J. Maurin, *J. Catal.*, **69**, 202 (1981).
10. B.T. Carvill and M.J. Thompson, *Appl. Catal.*, **75**, 249 (1991).
11. E.J. Markel, G.L. Schrader, N.N. Sauer and R.J. Angelici, *J. Catal.*, **116**, 11 (1989).
12. P. Desikan and C.H. Amberg, *Can. J. Chem.*, **42**, 843 (1964).
13. S. Brunet, D. Mey, G. Perot, C. Bouchy and F. Diehl, *Appl. Catal.*, **278**, 143 (2005).
14. H.C. Lee and J.B. Butt, *J. Catal.*, **49**, 320 (1977).
15. S.H. Yang and C.N. Satterfield, *J. Catal.*, **81**, 168 (1983).

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