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# Carbon black composites—supports of HDS catalysts

P. Gheek [a], S. Suppan [a], J. Trawczyński [a,*], A. Hynaux [b],
C. Sayag [b], G. Djega-Mariadssou [b]

[a] *Wrocław University of Technology, 50-344 Wrocław ul. Gdańska 7/9, Poland*
[b] *University Pierre et Marie Curie, Laboratorie Reactivite de Surface, UMR CNRS 7609, Casier 178,*
*4 Place Jussieu, 75252 Paris Cedex 05, France*

**Abstract**

HDS activity of sulfided Mo (W) catalysts supported on carbon black composites (CBC) is affected by kind of functional groups present on the CBC surface. Oxidation of CBC with $(NH_4)_2S_2O_8$ produce functionalities with the highest acid strength and corresponding catalyst exhibits the highest HDS activity. Sulfided W/CBC is less active in thiophene HDS than corresponding Mo counterpart. The rate of thiophene HDS over Mo/ ''basic'' CBC does not depend on the method of Mo deposition.

*Keywords:* Carbon black composites; Hydrodesulfurization; Catalyst

## 1. Introduction

Molybdenum- and tungsten-based catalysts, promoted with Co (Ni) have been commonly used in refineries for oil fractions hydrodesulfurization (HDS) [1]. Carbon supported sulfides of Mo (W) exhibit a higher HDS activity than these ones supported on conventional carriers like $Al_2O_3$ or $SiO_2$ [2]. Carbon-based carriers show many advantages (high specific surface area, controlled both pores structure and surface properties, low interaction with active phase precursor, easy metal recovery from the catalysts spent, reduced coking propensity), however, they also exhibit drawback due to narrow pore structure inaccessible to large molecules containing sulfur. One can enlarge the volume of meso- and macropores by burning off the carbon material but this process worsens mechanical resistance of the carrier. CBC-based materials are free from these disadvantages: possess high mechanical resistance and their porosities depend on the particle size of the initial carbon black [3].

Many authors have investigated the relation between the surface chemistry, the method of active phase precursor deposition and the activity of corresponding catalyst [1], nevertheless the effect of the method of deposition of active phase precursor, especially on carriers different from alumina has not been intensively studied. The functional groups on the surface of active carbon are very different in their nature depending on the carbon source and the method of activation [4]. The chemistry of the surface of carbon materials can be controlled by treating them with oxidizing agents. Vazquez et al. have found that hydrodenitrogenation activity of both Mo- and W-based catalysts strongly depends on the preparation method and on the used precursor of active phase [5]. Calafat et al. studied the effect of the carrier oxidation on the HDS of thiophene on carbon supported Mo (Ni, NiMo) [6]. They observed that introduction of oxygen functional groups increases O–Ni interaction during impregnation—HDS activity of Ni catalysts can be increased by acidic treatment of the carrier. Moreno-Castilla et al. have shown that the treatment with $(NH_4)_2S_2O_8$ produce acidic groups with higher acid strength than the treatment with $HNO_3$, however, this last procedure results in higher concentration of acidic surface groups than oxidation with $(NH_4)_2S_2O_8$ [7]. Activation of carbon with water steam develops basic character of its surface [8].

The aim of this work is to gain a better insight into the role of functionalities developed on the CBC surface on the HDS activity of sulfided Mo (W) catalysts. The effects of the composition (and strength) of surface groups and the method of active phase precursor's deposition on the activity of these catalysts have been studied.

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* Corresponding author.
*E-mail address:* janusz.trawczynski@pwr.wroc.pl (J. Trawczyński).

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## 2. Experimental

### 2.1. Preparation

Details of CBC synthesis are described elsewhere [9]. Shortly, it was prepared according to Schmitt et al. from mechanical mixture of carbon black "Carbex-330" and polyfurfuryl alcohol [10]—a mixture was extruded ($d = 1.2$ mm), dried and carbonized under argon flow at 973 K. Resulted "raw" CBC (sample C) was activated either by boiling in concentrated $HNO_3$ for 0.5 h (C–N) or with a saturated solution of $(NH_4)_2S_2O_8$ in 1 M $H_2SO_4$ (1 g of CBC/10 ml of solution) at 298 K for 24 h then washed with distilled water until there were no sulfates in the washing water (C–S). Gasification with water steam was performed at 1073 K up to 20% of burn-off (C–W).

Oxidic precursors of the Mo catalyst were supported on the carriers (particle size = 0.3–0.6 mm) using the following methods: incipient wetness impregnation (IWI), non-dry impregnation (NDI), equilibrium–deposition–filtration (EDF) [11] or slurry impregnation SI [12].

Following volumes of the ammonium heptamolybdate (POCh, p.a.) in the solution of 10 vol.% of acetone in water were used: 0.05 ml (IWI), 0.30 ml (NDI) and 3.0 ml (EDF) per 1 $m^2$ of support's surface area. Samples prepared by both NDI and EDF methods were allowed to equilibrate for 24 h, with occasionally shaking. After the equilibration, contents of non-adsorbed Mo in the filtered solution, was determined by ICP method. The adsorption isotherms were measured at 298 K.

The SI was performed by soaking the carrier in the suspension of $MoO_3$ (Fluka, p.a.) in distilled water: either 0.3 or 3.0 ml of $H_2O$ per 1 $m^2$ of support's surface area was used. The mixture was heated under a reflux condenser at the temperature of boiling point for 48 h. Then, the water solution and non-adsorbed $MoO_3$ was separated from the catalysts, dried at 383 K and the resulting powder was weighed. All prepared oxidic forms of catalysts were dried at 383 K for 24 h.

Three atoms of W/$nm^2$ of carrier surface area was supported by using IWI method from ammonium tungstate solution.

### 2.2. Characterization

Specific surface area was determined by $N_2$ adsorption at 77 K using an Autosorb-1 apparatus. Chemical properties of the surface of the carriers prepared were determined by titrations with bases of different strength following the method of Boehm [13] and with HCl to determine the total surface basicity. Mass titration of aqueous slurries was used to determine the pH of the point of zero charge ($pH_{PZC}$) according to the procedure proposed by Noh and Schwartz [14].

Tests of thiophene HDS were carried out in a gradientless stainless steel microreactor with an internal recycle flow system, at 673 K and at atmospheric pressure. Test conditions: 1.0 g of catalyst (0.3–0.6 mm), flow from 3.6 to 45.0 $dm^3$/h of the thiophene/hydrogen (2.6 mol%) mixture. The reaction products were analyzed by means of gas chromatography.

## 3. Results and discussion

The surface properties of activated carbons essentially depends on their heteroatom content, especially on the content of surface oxygen complex. They determine the charge of the surface, its hydrophobicity, and the electronic density of the graphene layers. When a carbon is immersed in an aqueous solution, it develops a surface charge that comes from the dissociation of surface groups or the adsorption of ions from solution and carbons are positively charged below their $pH_{PZC}$ and negatively charged above this pH. The charge of surface depends on the pH of solution and the characteristics of the carbon surface [15]. Properties of the prepared materials (Table 1) are in good agreement with this general rule. Oxidation with $HNO_3$ leads to material with slightly increased specific surface area and developed acidic functionalities on the surface. In comparison to raw C carrier, sample C–N shows acidic value of $pH_{PZC}$. Oxidation with $(NH_4)_2S_2O_8$ does not considerably affect surface area of the initial carrier however it develops strong acidic sites on the surface. Steam activated carrier exhibits well developed surface area and basic character of the surface.

The changes in the acid–base character caused by activation procedures were studied by Boehm's titration measurements (Table 1). Titration with basic solutions is regarded as approximate probe of acidic surface groups: NaOH reacts with all functionalities possessing acidic character, $Na_2CO_3$ detects carboxyl and f-lactonic groups and $NaHCO_3$ carboxyl ones. It is assumed that the results of neutralization with hydrochloric acid represents the concentration of surface basic groups [13].

Raw carrier C exhibits small content of basic sites and nearly 10 times higher content of acidic sites with the weakest strength (Table 1). Gasification with water steam (C–W) develops basic sites and inconsiderable decreases the number of acidic ones in comparison to raw carrier. Activation with either nitric acid or $(NH_4)_2S_2O_8$ develops acidic sites at the cost of basic ones. Nitric acid (C–N) produces 0.62 mequiv./g of acidic sites—0.23 mequiv./g of them are sites which react with $NaHCO_3$

Table 1
Specific surface area, $pH_{PZC}$ and acid–base properties of studied materials

| Carrier | $S_{BET}$ ($m^2$/g) | $pH_{PZC}$ | Neutralization of acidic/basic surface sites (mequiv./g) | | | |
|---|---|---|---|---|---|---|
| | | | HCl | NaOH | $Na_2CO_3$ | $NaHCO_3$ |
| C | 84.9 | 9.98 | 0.030 | 0.29 | 0 | 0 |
| C–W | 162 | 11.4 | 0.137 | 0.28 | 0 | 0 |
| C–N | 85.0 | 1.75 | 0.005 | 0.62 | 0.02 | 0.23 |
| C–S | 80.5 | 1.42 | 0 | 1.04 | 0.12 | 0.89 |

Table 2
Effect of the activation procedure on the rate of thiophene HDS over Mo (W) catalysts (3 atoms Me/nm$^2$) prepared by IWI method (mol thiophene)/(mol Me s)

| Carrier | Mo | W |
|---|---|---|
| C | 4.2 | 2.8 |
| C–N | 7.8 | 3.4 |
| C–W | 14.5 | 9.6 |
| C–S | 15.8 | 6.7 |

(carboxylic acids). At the same time the amount of basic sites distinctly decreases. In similar way oxidation with $(NH_4)_2S_2O_8$ affects both the amount of acidic and basic sites, however, shares of the three types of acidic groups are different—this type of oxidation produces strong acidity (carboxylic groups) on the CBC surface.

Presented results are in agreement with conclusions of Moreno-Castilla et al. who found that during oxidation of carbon with $(NH_4)_2S_2O_8$ carboxyl groups (with the highest acid strength) are formed on the surface [7]. It can be supposed that different functional groups developed on the surface of carriers studied confer them distinct properties of interaction with the catalyst precursor.

Results of determination of catalytic activity of sulfided catalysts in thiophene HDS are presented in Table 2. Catalysts supported on the activated CBC are more active in this reaction than these ones on raw CBC. In general, Mo-based catalysts are more active in thiophene HDS than corresponding W-based ones. It is known that degree of tungsten sulfidation is crucial for catalytic performance of the W-based catalysts [16]. Scheffer et al. has found that owing to the weak interaction existing between active phase and the carbon support, sulfidation of carbon supported catalysts is more efficient [17] so one would expect that modification of this interaction could improve activity of W-based catalysts. However, it appeared that studied tungsten containing catalysts are not as sensitive to procedure of carrier activation as Mo-based ones. These results once more confirm, that sulfidation behaviour and catalytic activity of W- and Mo-based catalysts are different.

Catalysts supported on the carrier with basic character (C–W) exhibit higher rate of thiophene HDS than these ones supported on ‘‘acidic’’ C–N one. This can effect partially be explained by higher surface area of the former material. Activation with $(NH_4)_2S_2O_8$ does not develop surface area of the CBC (Table 1), nevertheless Mo supported on this carrier exhibits somewhat higher rate of thiophene HDS than those ones supported on C–W. These results suggest that, in general, the chemical character of the CBC carrier surface affects the efficiency of the supported catalyst in thiophene HDS. Activity of Mo catalysts containing 0.5–10 atoms Mo/nm$^2$ strongly depends on the Mo content (Fig. 1) and in the whole range of composition basic carrier secure higher activity of corresponding catalysts than the acidic one.

Surface functionalities affect on the adsorption of Mo (W) ions from aqueous solution during the catalyst preparation. The ions containing active metal are anchored to surface complexes during this process [11,12]. Character (acidic or basic) and strength of surface complexes affects the structure of metal ions and process of their deposition on the carbon surface. Both C–N and C–S carriers show acidic character (and approximately close specific surface area). However, rate of thiophene HDS over Mo/C–S is more than two times higher than this one over Mo/C–N. The same effect is observed for W-based catalysts. It seems that such big difference in activity of both catalysts have to be related with the differences in the structure of acidic groups on the surface of their carriers. Surface groups of the C–S carrier are mainly carboxylic ones and they are more acidic than functionalities on the surface of C–N (Table 1). So, it can be concluded that strong acidic character of the surface of carbon carrier advantageously affects the HDS activity of sulfides of Mo (W), supported on this material. Such conclusion implies also that the method of deposition of Mo can influence on the activity of the catalyst. This assumption was verified here for the basic carrier.

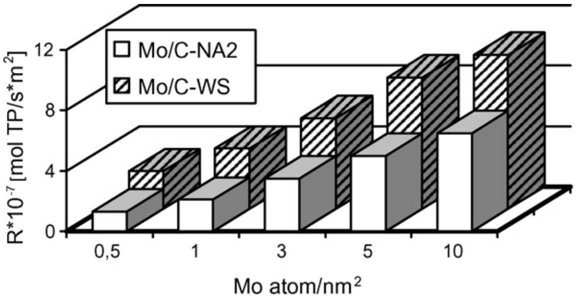

Fig. 1. Effect of the content of Mo deposited by IWI method on C–W and C–N carriers on the rate of thiophene HDS (mol thiophene)/(s m$^2$).

The adsorption capacity of Mo on C–W is equal ca. 5 mmol Mo/m$^2$ (EDF method) what corresponds to ca. 3 Mo atoms/nm$^2$ of its surface area (Fig. 2). Similar amount of Mo can be loaded on C–W by using NDI technique. Deposition from the slurry of $MoO_3$–water (SIM method) allowed to load (on the same carrier) ca. 4 Mo atoms/nm$^2$ independently on the C–W/water ratio (0.3 or 3.0 ml/m$^2$).

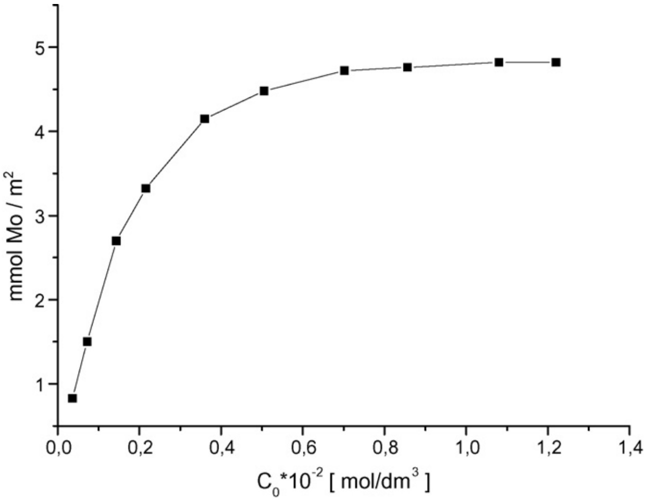

Fig. 2. The amount of Mo deposited on the C–W vs. Mo concentration in the initial solutions. $T = 298$ K.

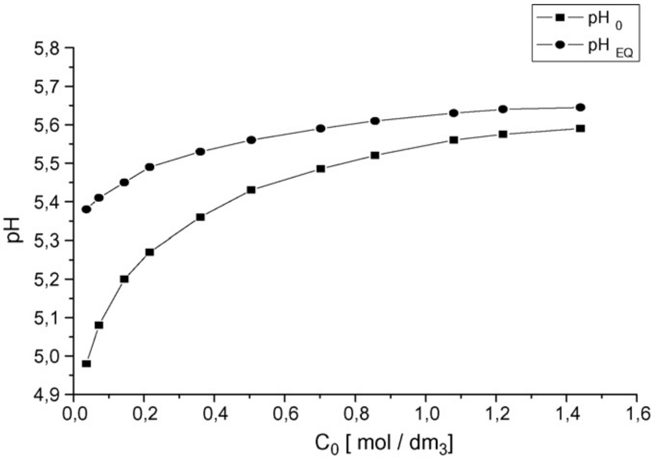

Fig. 3. The dependence of the pH of ammonium heptamolybdate solution before ($pH_0$) and after ($pH_{EQ}$) EDF on the concentration of solution (C–W carrier).

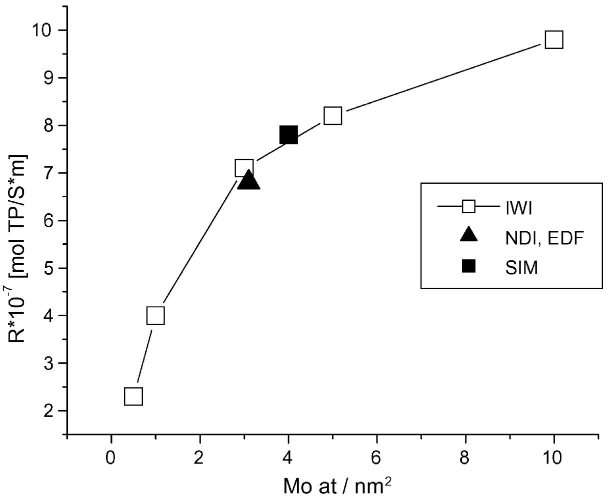

Fig. 4. The rate of thiophene HDS activity over Mo/C–W prepared by different techniques as a function of the Mo concentration.

In Fig. 3 the variation of the pH value of ammonium heptamolybdate solution before ($pH_0$) and after ($pH_{EQ}$) Mo deposition during the EDF process is plotted. The $pH_0$ increases with the concentration of the Mo solution; in the same time the $pH_{EQ}$ also increases in spite of molybdenum anions adsorption. This phenomenon can be explained by neutralization of the negative charge of C–W surface by positive ions from the impregnation solution what results in the increasing of the pH value under equilibrium process. It can be supposed that two competitive processes proceed between the C–W surface and the impregnation solution: (i) adsorption of Mo anions on the surface, and (ii) neutralization of the negatively charged functionalities on the C–W surface by positive ions from the solution. The neutralization of C–W surface is competitive to molybdenum deposition and can be responsible for the relatively low amount of Mo loaded on the C–W by EDF method.

In Fig. 4 the rates of thiophene HDS over Mo/C–W catalysts prepared by studied techniques are shown. A clear correlation between the reaction rate and Mo content exists for all catalysts. That means that the rate of HDS does not depend on the method of Mo deposition but on the surface chemistry of the carrier.

## 4. Conclusions

1. HDS activity of sulfided Mo (W) catalysts supported on activated CBC is affected by the kind of functional groups developed on the carrier surface during its activation. Activation with $(NH_4)_2S_2O_8$ produce carboxyl groups (with the highest acid strength) and corresponding catalyst exhibits the highest HDS activity.
2. Tungsten sulfides supported on activated CBC are in general less active in HDS of thiophene than corresponding molybdenum counterparts.
3. The rate of thiophene HDS over Mo catalysts supported on the ‘‘basic’’ CBC does not depend on the method of Mo deposition.

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## References

[1] H. Topsoe, B.S. Clausen, F.E. Massoth, in: J.R. Anderson, M. Boudart (Eds.), Hydrotreating Catalysis, vol. 11, Science and Technology, Springer, Berlin, 1996.
[2] J.C. Duchet, E.M. van Oers, V.H.J. de Beer, R. Prins, J. Catal. 80 (1983) 386.
[3] E. Broniek, G. Djega-Mariadassou, J. Kaczmarczyk, C. Sayag, T. Siemieniewska, S. Suppan, J. Trawczyński, Proc. IVth Inter. Conf. ‘‘Catal. and adsorption in fuel processing and environ. protection’’, Wrocław, September 18–21, (2002), p. 377.
[4] A.F. Perez-Cadenas, C. Moreno-Castilla, F.J. Maldonado-Hodar, J.L.G. Fierro, J. Catal. 217 (2003) 30.
[5] P. Vazquez, L. Pizzio, M. Blanco, C. Caceres, H. Thomas, R. Arriagada, S. Bendezu, R. Cid, R. Garcia, Appl. Catal. A: Gen. 184 (1999) 303.
[6] A. Calafat, J. Laine, A. Lopez Agudo, J. Palacinos, J. Catal. 162 (1996) 20.
[7] C. Moreno-Castilla, M.V. Lopez-Ramon, F. Carrasco-Marin, Carbon 38 (2000) 1995.
[8] J. Trawczyński, S. Suppan, C. Sayag, G. Djega-Mariadassou, Fuel Process. Technol. (2002), pp. 77–78, 317–324.
[9] S. Suppan, J. Trawczyński, J. Kaczmarczyk, G. Djega-Mariadassou, A. Hynaux, C. Sayag, Appl. Catal. A: Gen. 280 (2005) 209.
[10] J.L. Schmitt, P.L. Walker Jr., G.A. Castellion, US patent 3,978,000 (1976).
[11] L. Karakonstantis, K. Bourikas, A. Lycourghiotis, J. Catal. 162 (1996) 295.
[12] L. Kaluža, M. Zdražil, Carbon 39 (2001) 2023.
[13] H.P. Boehm, Adv. Catal. 16 (1966) 179.
[14] J.S. Noh, J.A. Schwartz, Carbon 28 (1990) 675.
[15] C. Moreno-Castilla, Carbon 42 (2004) 83.
[16] H.R. Reinhoudt, R. Troost, A.D. van Langeveld, S.T. Sie, J.A.R. van Veen, J.A. Moulijn, Fuel Process. Technol. 61 (1999) 133.
[17] B. Scheffer, P. Arnoldy, J.A. Moulijn, J. Catal. 112 (1988) 516.