Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Catalysis Today 119 (2007) 3–6

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Kinetic study of the deep hydrodesulfurization of dibenzothiophene over molybdenum carbide supported on a carbon black composite: Existence of two types of active sites

A. Hynaux [a], C. Sayag [a,*], S. Suppan [b], J. Trawczynski [b], M. Lewandowski [c], A. Szymanska-Kolasa [c], G. Djéga-Mariadassou [a,*]

[a] *University Pierre and Marie Curie, Laboratory Réactivité de Surface, CNRS, UMR 7609, Casier 178, 4 Place Jussieu, 75252 Paris Cedex 05, France*
[b] *Institute of Chemistry and Technology of Petroleum and Coal, Wroclaw University, Gdanska 7/9, 50-344 Wroclaw, Poland*
[c] *Institute of Coal chemistry PAS, Sowinskiego 5, 44-102 Gliwice, Poland*

Abstract

Hydrodesulfurization (HDS) is part of the hydrotreating process, which is an ensemble of several reactions (HDN, HDO, HDS, etc.) taking place simultaneously at the industrial scale. Only sulfur is currently submitted to drastic Europeans specifications and conventional commercial catalysts cannot reach the specifications at low cost. This paper presents the behavior of a potential substitute catalyst tested for the deep HDS of a model molecule such as the dibenzothiophene (DBT). The substitute is molybdenum carbide supported on a mesoporous carbon black composite of surface area 240 $m^2\ g^{-1}$. A global kinetic study of the deep HDS of DBT (300 ppm S) was performed at 623 K and 5.0 MPa and a global kinetic model was proposed as well as global rate constants were calculated to obtain theoretical plots of concentration versus contact time to compare with the experimental data. The kinetic model and global kinetic orders were confirmed as an acceptable correlation was found between calculated and experimental data. Furthermore, the determination of the global kinetic orders indicated that two types of active sites must be present on the surface in order to explain the observed results.

Keywords: Hydrodesulfurization; Dibenzothiophene; Molybdenum carbide; Carbon support; Kinetics; Modelization

---

1. Introduction

Hydrodesulfurization (HDS) is one of the most important petroleum refining processes. Because of increasing stringent environmental regulations, the development of new HDS catalysts is necessary. The amount of sulfur, which is at present inferior to 50 ppm, should not exceed 10 ppm in diesel fuels in 2009 (Directive 2003/17/EC). The conventional commercial catalysts used in HDS are still alumina supported sulfided Co(Ni)Mo. They are very active but, highly refractory sulphur containing molecules still remain after the hydrotreating process.

Molybdenum carbides and nitrides could be potential candidates to proceed to deep HDS in a second stage process. Indeed, they exhibit hydrogenating properties similar to those of noble metals [1] and they are sulphur-tolerant in the presence of low sulphur level [2]. It was reported by several authors [3–6] that these materials could exhibit similar or higher HDS activity than sulfided Mo/Al_2O_3 or $Co(Ni)Mo/Al_2O_3$. Lee and Boudart [3] found that unsupported α-MoC_{1-x} and sulfided Mo/Al_2O_3 had a comparable activity towards the HDS of thiophene. Sajkowski and Oyama [4] claimed that alumina supported β-Mo_2C catalyst had an HDS activity per active site over two times greater than that of a commercial $NiMo/Al_2O_3$ catalyst towards a coal gas oil feed containing 116 ppm of sulfur, 3580 ppm of nitrogen and 0.35% of oxygen. Nagai et al. [5] have shown that alumina supported Mo_2N was 1.1–1.2 times more active than a sulfided Mo/Al_2O_3 in the HDS of thiophene. Aegerter et al. [6] have compared thiophene HDS activity of Mo_2C/Al_2O_3, Mo_2N/Al_2O_3 and sulfided Mo/Al_2O_3 catalysts. They found that HDS activities (expressed in μmol thiophene/mol Mo/s)

---

* Corresponding authors. Tel.: +33 1 44273624/4914.
E-mail addresses: csayag@ccr.jussieu.fr (C. Sayag), djega@ccr.jussieu.fr (G. Djéga-Mariadassou).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.08.053

of the catalysts increased according to the trend: sulfided Mo/Al_2O_3 < Mo_2N/Al_2O_3 < Mo_2C/Al_2O_3. In a more recent work [7], it was found that carbon black composite (CBC) supported molybdenum carbide and molybdenum or cobalt sulfides had same range reaction rates for the HDS of thiophene.

Alumina is the most widely used support material for commercial hydrotreating catalysts. However, the full sulfidation of the oxide precursor is difficult to obtain because of the alumina-oxide precursor interaction. Substituting alumina support by carbon, which is a more inert material, led to promising results [8–12]. For example, Duchet et al. [8], Arnoldy et al. [11] have shown that sulfided Mo activities for thiophene HDS increased following the trend: sulfided Mo/Al_2O_3 < sulfided Mo/SiO_2 < sulfided Mo/C. This trend was also observed with sulfided rhenium [11], tungsten [8], Ni(Co)Mo [12–14]. Moreover, according to Mordenti et al. [15], the use of a carbon support could drastically simplify the synthesis of the transition metal carbide (TMC). Indeed, carburization could be carried out in pure H_2, as the carburizing agent is formed by reaction between the carbon support and the hydrogen carrier gas. Such protocol, also avoided the formation of polymeric carbon on the surface of Mo_2C [15]. On the contrary, the classical method of TMC synthesis (temperature programmed reaction between an oxide precursor and a mixture of hydrogen and carbon-containing gases), usually led to a polymeric carbon surface contaminated TMC formed by pyrolysis of the carbon-containing gases.

From these considerations, molybdenum carbide was chosen as the active phase and was supported over a mesoporous carbon material such as a carbon black composite (CBC). Dibenzothiophene was for the first time used to undergo HDS over the above catalytic system. Recent literature can be found concerning the kinetic study of deep HDS of DBT but over sulfided Ni–Mo or Co–Mo supported over alumina [16–18], mesoporous silica [19] or carbon materials [20]. The present work is dedicated to the study and modeling of the global kinetic of the deep HDS of DBT over a carbon black composite supported molybdenum carbide in the presence of a low amount of sulfur (300 ppm). Global reaction orders were determined as well as global rate constants. The existence of two types of active sites on the surface of the molybdenum carbide is suggested in order to explain the obtained results.

2. Experimental

The CBC support was prepared according to Schmitt et al. [21], from soot (carbon black Printex 90, DEGUSSA) and a binder (polyfurfurylic alcohol) and will be denoted ‘‘C’’. This carbon material was impregnated with ammonium heptamolybdate dissolved in a 10 vol.% acetone/H_2O mixture, using the incipient wetness impregnation method. The impregnation was carried out in one step at 10 wt.% Mo and was followed by drying at 383 K for 16 h. Next, this sample was carburized according to the following protocol [15]: Temperature was raised from room temperature to 973 K at a rate of 33 K h^{-1} and then left for 2 h at 973 K under a flow of hydrogen of 20 L h^{-1} g^{-1}. The sample was finally quenched in hydrogen down to room temperature and will be denoted as Mo_2C/C.

The catalyst was characterized by X-ray diffraction (XRD), nitrogen physisorption at 77 K, elemental analyses, CO chemisorption and high resolution transmission electron microscopy (HR-TEM). All these methods are detailed in Ref. [22].

The dibenzothiophene hydrodesulfurization was carried out in a dynamic high-pressure nanoflow reactor (7 mm i.d., 235 mm length) heated in an oven. The catalyst (0.25 g), sieved between 180 and 355 μm, was diluted with 1.25 g of SiC. In order to ensure a plug flow pattern, the following operating conditions were fulfilled: $D/d_p > 10$ and $L/d_p > 50$ [23] (D and L are, respectively, the inside diameter and the length of the reactor and d_p is the catalyst particles diameter). The catalyst was activated ‘‘in situ’’ prior to catalytic runs at atmospheric pressure in pure hydrogen at 723 K for 2 h. After activation, the pressure was increased to 5.0 MPa, the temperature was decreased to 623 K. The liquid feed (consisting of DBT diluted in *n*-hexadecane—300 ppm S) was introduced in the system by means of a Gilson piston pump (model 307). The sulfur concentration used in this work is close to that of a real feed stock, which was already submitted to a preliminary hydrotreating step. The pressure was regulated using a backpressure regulator (Brooks 5866) and the gas flow rate was controlled by a mass flow controller (Brooks 5850 TR). Reactants and products were analyzed by off-line gas chromatography with an Agilent Technology 6890N instrument equipped with a Supelco SPB 1 capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. The contact time (t_c) was defined as the ratio ‘‘catalyst volume/total flow’’. It was changed by varying the flow rate of the liquid as well as the gaseous reactant one, while keeping their ratio constant and equal to 1/600. The steady state was reached after 4–6 h, and after 5 days of operation no catalyst deactivation was observed.

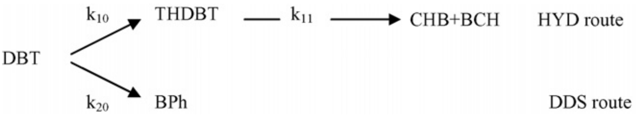
3. Results and discussion

3.1. Characterization of the active phase

Elemental chemical analysis data indicated a molybdenum content superior to what was expected (15 wt.% instead of 10 wt.%). As previously observed [22], this is due to a loss of carbon from the support during the carburization step. A suitable surface area of 240 m^2/g and pores of 35 nm diameter in the mesoporous range were measured for the synthesized sample. The mesoporosity, corresponding mainly to the intergranular spaces between the spherical soot particles, will allow a better accessibility of large molecules to the active sites. XRD patterns of the catalyst confirmed the presence of only the expected hexagonal molybdenum carbide phase (β-Mo_2C, PDF 35-0787) as the carbon supported active phase. Measurements by HR-TEM indicated that the Mo_2C particle size distribution was very large up to 50 nm and was distributed heterogeneously on the support. In order to compare the sample with the bulk molybdenum carbide [24], the number of metallic sites was expressed per gram of Mo_2C and not per gram of catalyst. CO titration of the supported catalyst gave a value of 317 μmol CO/g_{Mo_2C}, i.e. 35% less than what was obtained with a bulk material synthesized under similar operating conditions [24]. After the catalytic test in presence of 300 ppm of sulphur (DBT), the HR-TEM study of the sample did not exhibit the presence of molybdenum sulfide, usually characterized by MoS_2 slabs.

3.2. Global kinetic study and modeling of HDS of DBT

The experimental concentrations of DBT, intermediate and products detected during the HDS of DBT over the supported catalyst, are represented versus contact time in Fig. 1 (symbols). From this plot, it can be observed that the HDS pathway of DBT followed two parallel routes, as described by Houalla et al. [25], represented by the following scheme.



The hydrogenation route (denoted HYD) goes to cyclohexylbenzene (CHB) and bicyclohexyl (BCH) through tetrahydrodibenzothiophene (THDBT), and the direct desulfurization route (denoted DDS) leads to biphenyl (BPh). The major product of the reaction was BPh indicating that the DDS route was favored. The sequential hydrogenation of BPh can be neglected as long as sulfur compounds are still present in the feed in significant amounts because of a competitive adsorption between both molecules [26]. The dehydrogenation of CHB was also not considered as this reaction is not thermodynamically favored in our operating conditions (623 K, 5.0 MPa). The global kinetic study over Mo_2C/C (Fig. 1), exhibited an interesting feature. Indeed, the appearance rate of the unsaturated product (BPh) being linear up to 80% conversion, the global reaction order with respect to DBT along the DDS route should be zero. Along the HYD route, a global first order reaction with respect to DBT was assumed. The HYD route could be described as a sequence of first order successive steps. Indeed, the THDBT concentration goes through a maximum as it should the case for the intermediate while concentration of reactant decreases (DBT) and concentration of final product increases (CHB + BCH). The global rate constants $k_{10} = 0.3\ s^{-1}$, $k_{11} = 20.4\ s^{-1}$ and $k_{20} = 9.2 \times 10^{-3}$ mol $L^{-1}\ s^{-1}\ s^{-1}$ were determined from the experimental data and used to recalculate the concentrations of all products using the following theoretical equations [27]:

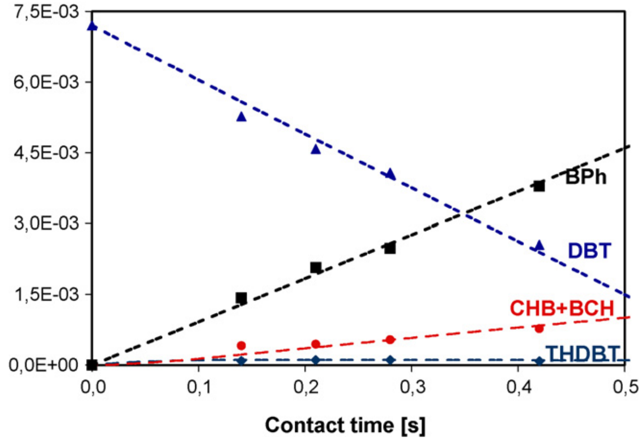


Fig. 1. Reactant, intermediate and products concentrations distribution vs. contact time for the hydrodesulfurization of dibenzothiophene over Mo_2C/C at 623 K and 5.0 MPa. The experimental data are represented by the symbols and calculated data are represented by the dotted lines. DBT: dibenzothiophene; THDBT: tetrahydrodibenzothiophene; BPh: biphenyl; CHB: cyclohexylbenzene; BCH: bicyclohexyl.

$$[\mathrm{Bph}]_t = k_{20}t \qquad (1)$$

$$[\mathrm{THDBT}]_t = [\mathrm{DBT}]_0\left(\frac{k_{10}}{k_{11}-k_{10}}\right) \times (\exp(-k_{10}t) - \exp(-k_{11}t)) \qquad (2)$$

$$[\mathrm{CHB}+\mathrm{BCH}]_t = [\mathrm{DBT}]_0\left(1 - \left(\frac{k_{11}}{k_{11}-k_{10}}\right)\exp(-k_{10}t) + \left(\frac{k_{10}}{k_{11}-k_{10}}\right)\exp(-k_{11}t)\right) \qquad (3)$$

$$[\mathrm{DBT}]_t = [\mathrm{DBT}]_0\exp(-k_{10}t) - k_{20}t \qquad (4)$$

Eq. (1) is the classical equation describing the concentration of a product formed through a zero order elementary step. Eqs. (2)–(4) are the classical equations describing, respectively, the concentrations of intermediate, products and reactant participating in the reaction composed of two successive first order elementary steps. Simulation of the kinetic curves is presented in Fig. 1 (dotted lines) and a good correlation can be observed between the calculated (dotted lines) and the experimental data (symbols). Hence, the global reaction orders with respect to DBT for the HYD and DDS routes could be validated as well as an interesting conclusion could be drawn out. Indeed, since a global zero order reaction along the DDS route is observed it means that the active sites working for the DDS route are kept saturated by DBT in the all range of contact time used in our work. Nevertheless, products formed through the HYD route are observed. This implies that different active sites exist, are free and can perform the HYD route. Thus, two types of active sites exist over Mo_2C/C: sites working for the HYD route and other sites acting along the DDS route.

4. Conclusions

These preliminary results indicated that a Mo_2C/C can proceed to the deep hydrodesulfurization of dibenzothiophene in the presence of 300 ppm of sulfur. Global rate constants could be calculated from the global kinetic study. Furthermore, global reaction orders could be confirmed from the proposed modeling of the kinetic curves as an acceptable correlation was found between calculated and experimental data. Besides, the global kinetic study of the HDS of DBT over Mo_2C/C exhibited an interesting feature. Indeed, the two parallel routes of the HDS reaction network, i.e. HYD and DDS routes, proceeded according to a first and a zero global order reaction with respect to DBT, respectively. Such findings implies the existence of two types of active sites on the surface of molybdenum carbide supported on carbon black composite. One active sites works by the HYD route and another one working along the DDS route.

References

[1] R.B. Levy, M. Boudart, Science 181 (1973) 541.

[2] P. Da Costa, J.L. Lemberton, C. Potvin, J.M. Manoli, G. Pérot, M. Breysse, G. Djéga-Mariadassou, Catal. Today 65 (2001) 195.

[3] J.S. Lee, M. Boudart, Appl. Catal. 19 (1985) 207.

[4] D.J. Sajkowski, S.T. Oyama, Appl. Catal. A 134 (1996) 339.

[5] M. Nagai, T. Miyao, T. Tuboi, Catal. Lett. 18 (1993) 9.

[6] P.A. Aegerter, W.W.C. Quigley, G.J. Simpson, D.D. Ziegler, J.W. Logan, K.R. McCrea, S. Glazier, M.E. Bussell, J. Catal. 164 (1996) 109.

[7] S. Suppan, J. Trawczynski, J. Kaczmarczyk, G. Djéga-Mariadassou, A. Hynaux, C. Sayag, Appl. Catal. A 280 (2005) 209.

[8] J.C. Duchet, E.M. van Oers, V.H.J. de Beer, R. Prins, J. Catal. 80 (1983) 386.

[9] Z. Vit, Catal. Lett. 13 (1992) 131.

[10] B. Dhandapani, S. Ramanathan, C.C. Yu, B. Frühberger, J.G. Chen et, S.T. Oyama, J. Catal. 176 (1998) 61.

[11] P. Arnoldy, E.M. van Oers, V.H.J. de Beer, J.A. Moulijn, R. Prins, Appl. Catal. 48 (1989) 241.

[12] H. Farag, D.D. Whitehurst, K. Sakanishi, I. Mochida, Catal. Today 50 (1999) 9.

[13] H. Farag, I. Mochida, K. Sakanishi, Appl. Catal. A 194–195 (2000) 147.

[14] J. Laine, M. Labady, F. Severino, S. Yunes, J. Catal. 166 (1997) 384.

[15] D. Mordenti, D. Brodzki, G. Djéga-Mariadassou, J. Solid State Chem. 141 (1998) 114.

[16] G.F. Froment, Catal. Today 98 (1–2) (2004) 43.

[17] C. Lopez-Garcia, M. Roy-Auberger, T. Chapus, F. Baco, Preprints of symposia, Am. Chem. Soc. Div. Fuel Chem. 48 (2) (2003) 61.

[18] P. Steiner, Fuel Process. Technol. 79 (1) (2002) 1.

[19] Y. Wang, Z. Sun, A. Wang, C. Li, X. Li, B. Zhao, P. Yao, Comput.-Aided Chem. Eng. 15B (2003) 1228 (Process Systems Engineering).

[20] H. Farag, I. Mochida, K. Sakanishi, App. Catal. A 194–195 (2000) 147.

[21] J.L. Schmitt, P.L. Walker Jr., G.A. Castellion, US Patent 3,978,000 (1975).

[22] C. Sayag, M. Benkhaled, S. Suppan, J. Trawczynski, G. Djéga-Mariadassou, Appl. Catal. A 275 (2004) 15.

[23] J.F. Le Page, Applied Heterogenous Catalysis, Technip, Paris, 1987.

[24] J.S. Choi, G. Bugli, G. Djéga-Mariadassou, J. Catal. 193 (2000) 238.

[25] M. Houalla, N.K. Nag, A.V. Sapre, D.H. Broderick, B.C. Gates, AIChE J. 24 (1978) 1015.

[26] P. Da Costa, C. Potvin, J.-M. Manoli, J.L. Lemberton, G. Perot, G. Djéga-Mariadassou, J. Mol. Catal. A 184 (1–2) (2002) 323.

[27] M. Boudart, G. Djéga-Mariadassou, Kinetics of Heterogeneous Catalytic Reactions, Princeton University Press, Princeton, NJ, 1984.