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Comparison of molybdenum carbide and tungsten carbide for the hydrodesulfurization of dibenzothiophene

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Abstract

The molybdenum and tungsten carbides (Mo_2C and W_2C) were synthesized, characterized and tested in hydrodesulfurization (HDS) of dibenzothiophene (DBT). The phase purity of these catalysts was established by X-ray diffraction (XRD), and the surface properties were determined by N_2 BET specific surface area (Sg) measurements, CO chemisorption and high-resolution transmission electron microscopy (HRTEM). The activities of catalysts were determined during the HDS of DBT at a temperature of 613 K and under a 6 MPa total pressure. Both molybdenum and tungsten carbides were active in HDS of DBT. The reactivity studies showed that molybdenum carbide was more active than tungsten carbide related to weight. However, W_2C was shown to possess stronger hydrogenating properties.

Keywords: Molybdenum carbide; Tungsten carbide; Hydrodesulfurization; Dibenzothiophene

1. Introduction

Hydroprocessing refers to a variety of catalytic hydrogenation processes that saturate heteroatomatic rings and remove S, N, O and metals from different petroleum streams in a refinery [1]. In order to further decrease sulfur level, a second stage hydrotreating process can be imagined where more active catalysts, i.e. treating highly refractory molecules, would be used [2,3]. The literature data suggest that the transition metal carbides and nitrides (TMC and TMN) can meet these expectations. The bulk and supported molybdenum carbide (Mo_2C) and tungsten carbide (W_2C) phases were successfully synthesized by means of temperature-programmed reaction of the corresponding oxides [2,4–8]

Dibenzothiophene (DBT) structures and their alkyl derivatives are the typical sulfur containing refractory compounds present in feed stocks [9,10]. Most of the work concerning hydrodesulfurization (HDS) of dibenzothiophene deal with commercial catalysts such as alumina supported sulfides molybdenum and tungsten promoted with cobalt and nickel [11–14] whereas for over bulk or supported TMC catalysts, data are scarce [2,5]. Therefore, in the present work, the HDS of a high concentration of DBT over bulk Mo_2C and W_2C was first studied in a large conversion range. The results obtained underlined a difference in activity and in selectivity in HDS of DBT for both catalysts.

2. Experimental

2.1. Materials

MoO_3 (Fluka, ≥99.5%) and WO_3 (Fluka, ≥99.5%) were used as precursors for the preparation of the catalysts. The gases employed were H_2 (Air Liquide, Custom grade C, purity > 99.995%), He (Air Liquide, Custom grade C, purity > 99.995%), O_2 (Air Liquide, Custom grade C, purity > 99.5%) and CH_4 (Air Liquide, Custom grade N30, purity > 99.9%). For the catalytic tests, the chemicals employed were: dibenzothiophene (Fluka, ≥98%) and decaline (Fluka, ≥98%).

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2.2. Synthesis of bulk Mo_2C and W_2C

Molybdenum and tungsten carbides were synthesized via a temperature-programmed reaction of MoO_3 or WO_3 using a 10 vol.% CH_4/H_2 mixture. Molybdenum or tungsten precursor (3 g) was placed on a fritted plate in a quartz reactor and was carburized at a volume hourly space velocity (VHSV) of about 85 h^{-1}. For molybdenum trioxide the temperature was increased linearly from 300 K at a rate of 53 K h^{-1} to a final temperature of 973 K which was held for 1 h. For tungsten trioxide the temperature was increased linearly from 300 to 923 K at a rate of 45 K h^{-1} and was held at 923 K for 1 h. The reactor was then cooled down to room temperature (RT) in the carburizing gas mixture. After cooling the gas flow was stopped and the carbide sample passivated in 1 vol.% O_2/He. The passivation of carbides is performed to avoid bulk oxidation of the samples when exposed to air.

2.3. Characterizations

The passivated catalysts were characterized by X-ray diffraction (XRD), CO chemisorption, BET surface area measurements and high-resolution transmission electron microscopy (HRTEM). Structural characterization of carbides, were carried out by X-ray diffraction using a SIEMENS D-500 automatic diffractometer with the Cu Kα monochromatized radiation. CO chemisorption was used to titrate the hydrogenating sites in the sample. The in situ CO uptake was measured right after the synthesis without exposing the samples to air or to the passivating mixture. Pulses of a known quantity of CO gas (17 μmol) were introduced at regular intervals through a sample at RT with the He carrier gas stream (40 mL min^{-1}) passing over the samples. The specific surface area (Sg) of the samples was determined on a constant volume adsorption apparatus (Quantachrome–Quantasorb Jr) by the N_2 BET method. High-resolution transmission electron microscopy was carried out on fresh and used carbides. The HRTEM study was performed using a JEOL 200 CX electron microscope.

2.4. Kinetic study of HDS of DBT

The HDS of DBT was conducted with a down flow fixed-bed microreactor in a high-pressure flow system. The catalyst (density = 1.5 g cm^{-3}, weight = 0.6 g, grain size = 0.25 to 0.315 mm) was mixed with carborundum (SiC) at a ratio of catalyst to SiC = 1/5. The liquid feed, consisting of 1.5 wt.% DBT in decaline, was fed to the reactor by means of a high-pressure piston pump. The hydrogen flow (30–360 cm^{-3} min^{-1}) and total pressure were controlled by a mass flow controller and a back-pressure regulator, respectively. The temperature of the oven was regulated using a temperature controller.

The kinetic study was carried out at a total pressure of 6 MPa at temperature 613 K, with H_2/feed volume ratio of 600 and contact times (t_c) ranging from 0.07 to 0.8 s. The contact time (t_c) was defined as follows: t_c (s) = catalyst volume (cm^3)/(H_2 flow + feed flow) (cm^3 s^{-1}). The liquid products of the reaction were collected every hour in the condenser maintained at 288 K. Finally, this liquid was analyzed by gas chromatography (HP 4890) using a capillary column (HP1, 30 m × 0.25 mm × 0.25 μm) and a FID detector. The product identification was confirmed by both GCMS analysis (Finnigat Mat Model 800, capillary column DB5, 30 m × 0.25 mm × 0.25 μm) and injection of the standards.

3. Results and discussion

3.1. Characterization of the catalyst

The XRD patterns of the synthesized and passivated molybdenum and tungsten carbides correspond to the lattice planes of the hexagonal compact phase (hcp) β-Mo_2C and hexagonal compact phase W_2C structures (Fig. 1). The specific surface areas of the bulk materials were 33 and 13 m^2 g^{-1} for Mo_2C and W_2C, respectively. The experimental CO uptakes of the samples were 142 and 70 μmol g^{-1} for Mo_2C and W_2C, respectively.

The nitrogen adsorption–desorption isotherm of the Mo_2C is shown in Fig. 2a. According to Brunauer [15] the shape of the isotherm of nitrogen adsorption indicates that it can be classified as type II. On the other hand, the presented adsorption–desorption hysteresis loop of Mo_2C catalyst may be classified as type A according to De Boer's or H1 according to the IUPAC classification [16,17]. The hysteresis loop of the present studied Mo_2C leads to the conclusion that the type A may be assigned to the presence of tubular capillaries with different shapes, opened at both ends or to the formation of a porous network. The relatively high value of p/p_o = 0.55 indicates a great number of larger pores (meso and/or macroporous). The pore size

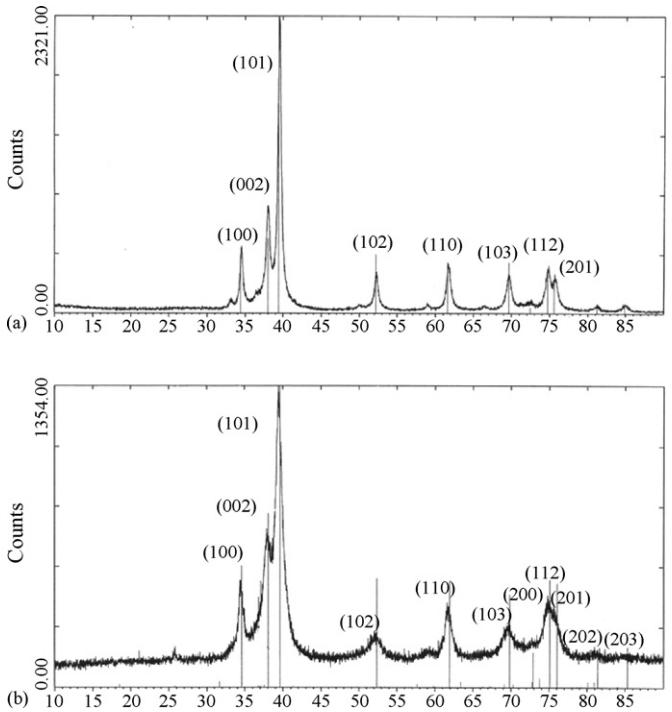
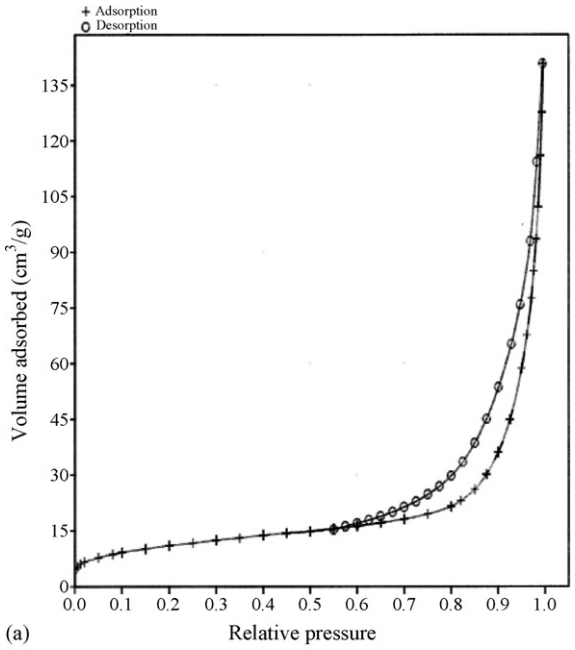


Fig. 1. X-ray diffraction patterns of bulk molybdenum carbide and tungsten carbide. (a) β-Mo_2C, (b) W_2C.



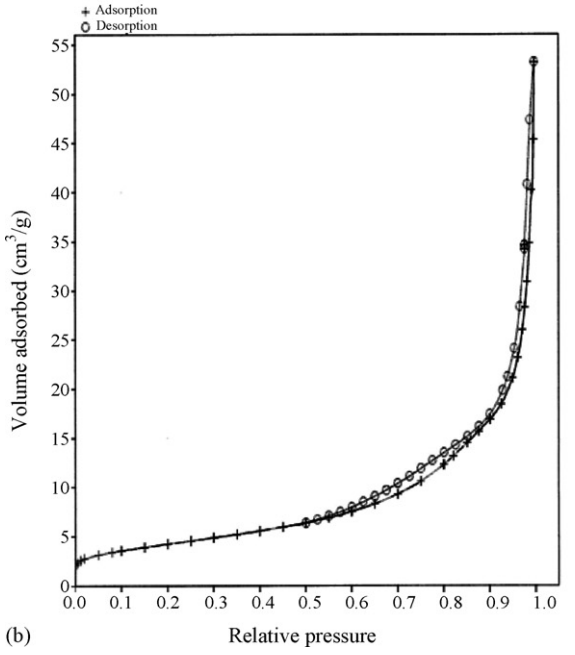
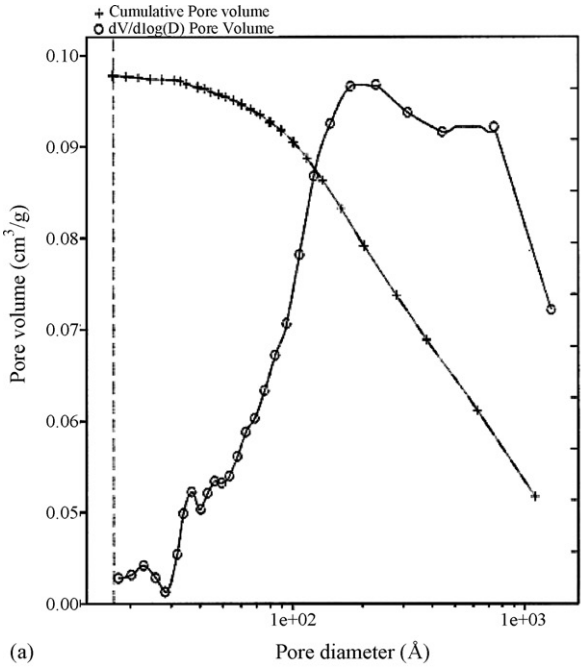


Fig. 2. Adsorption–desorption curves for: Mo_2C (a) and W_2C (b).



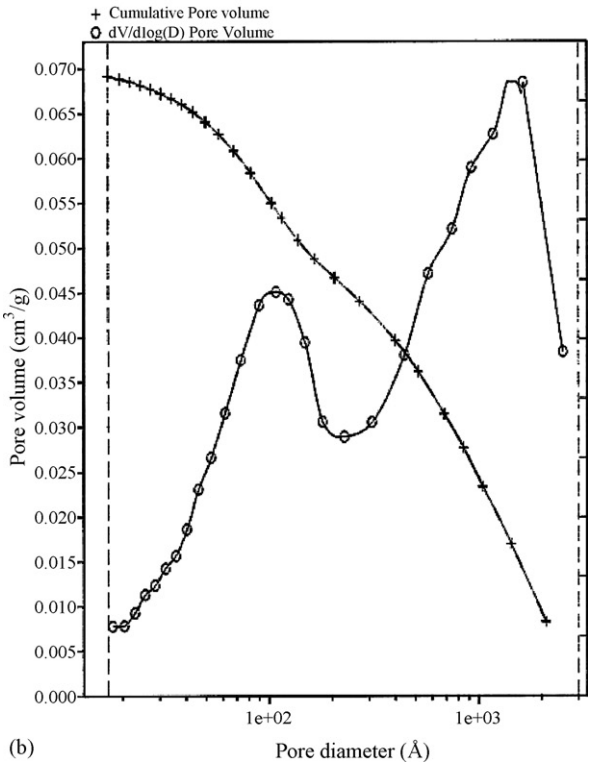


Fig. 3. Pore-size distribution (BJH method) for: Mo_2C (a) and W_2C (b).

distribution for Mo_2C is illustrated in Fig. 3a. Most of the pore volume comes from mesopores (20–500 Å) with a maximum for pore diameter of 200 Å. Practically, Mo_2C has mainly mesopores and relatively small amount of macropores.

The nitrogen adsorption–desorption isotherm of W_2C is presented in Fig. 2b and the pore size distribution in Fig. 3b. As well as for Mo_2C the nitrogen adsorption isotherm can be classified as type II [15] and the adsorption–desorption hysteresis loop may be classified as type A or H1 [16,17]. As for Mo_2C also, $p/p_o = 0.55$ indicates a great number of larger pores.

However, the shapes of adsorption–desorption loop differ for the two carbides. For tungsten carbide the distance between adsorption and desorption curves is much narrow than in the case of molybdenum carbide. It suggests that W_2C is rather a macroporous material compared to Mo_2C. Pore-size distribution (Fig. 3b) showed two local maxim: 100 Å in the range of mesopores and 1100 Å for macropores range. The distribution curve suggests that tungsten carbide possesses mainly macropores and relatively small amount of mesopores in opposition with Mo_2C.

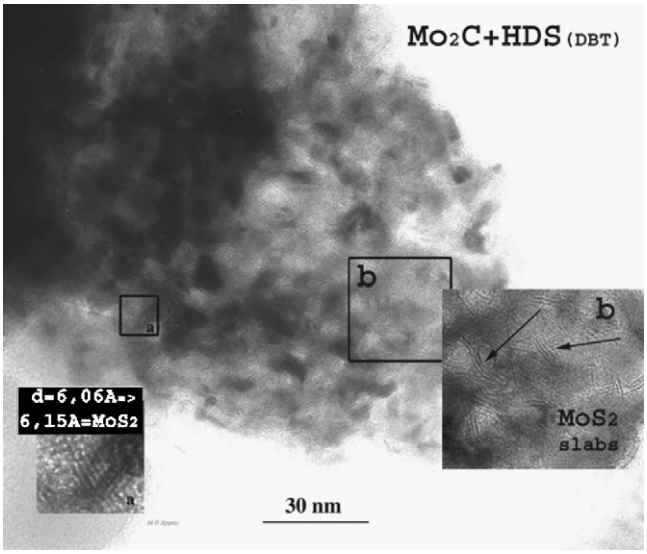


Fig. 4. TEM micrographs of MoS_2 (a and b) on Mo_2C surface after HDS of DBT.

For both carbides very small amount of micropores are measured. As a conclusion, the pore system produced during the synthesis of the carbides catalysts should allow the diffusion of relatively large heterocompounds such as DBT, alkyl derivatives of DBT and carbazoles to the active centers and then the diffusion of the final products.

The HRTEM analysis of the catalyst after the HDS of DBT process, where the feed contained high level of sulfur, exhibited the presence of MoS_2 crystallographic phase, on the surface of the molybdenum carbide. Indeed, on the TEM patterns (Fig. 4a), the slabs characteristic to molybdenum disulfide were observed. An inter planar distance of 0.60 nm was measured (Fig. 4a), corresponding to the (0 0 2) plane of the hexagonal phase of 2H-MoS_2 [JCPDS: No. 37–1492, 18]. Concerning tungsten carbide slabs of WS_2 were also observed after the HDS process. These slabs visible in Fig. 5 (d = 6.06 to 6.13 Å) can be attributed to the (0 0 2) plane of the 2H-WS_2

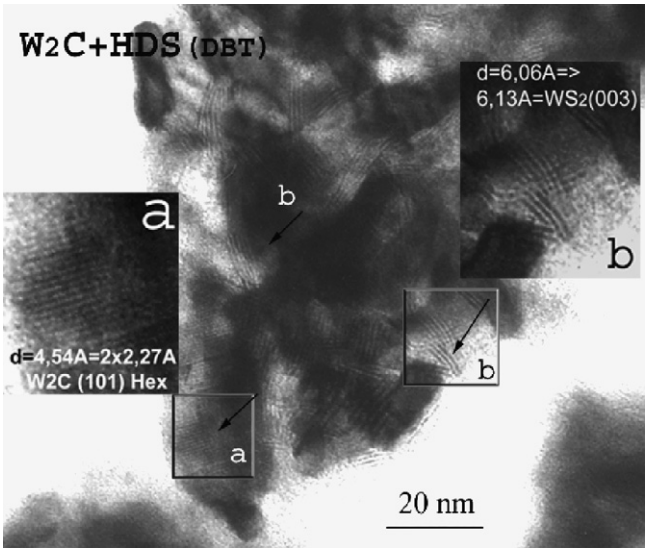


Fig. 5. TEM micrographs of WS_2 (b) on W_2C (a) surface after HDS of DBT.

rhombohedral phase [19]. These results suggest that for both catalysts a surface sulfurization occurred to some extend in the operating conditions of the catalytic tests. However, the crystallographic structure of the catalysts was maintained as the hexagonal phase of carbide (Fig. 5a, d = 4.54 Å = 2 × 2.27 Å ⇒ W_2C (1 0 1) [JCPDS: No. 035–0776]). Agerter et al. [20] observed a superficial sulfurization of Mo_2C/Al_2O_3 and Mo_2N/Al_2O_3 during the HDS of thiophene, without a change in the crystallographic structure of the catalysts as well. Dhandapani et al. [2] also observed a modification of the carbides surface by sulfur, during HDS of DBT, and carbosulfides were identified. On the other side, according to the literature [18,19,21] it is possible to form sulfocarbide during the preparation of bulk WS_2 and MoS_2 by decomposition of the organic thiosalts.

3.2. Distribution of products and intermediates: reaction network of the HDS of DBT over bulk molybdenum and tungsten carbides

The distribution of products and intermediates analysed during the HDS of DBT over bulk carbides Mo_2C and W_2C are presented in Table 1. Total conversions of dibenzothiphene and HDS rates are also presented for a temperature of 613 K and contact time of 0.27 and 0.53 s for Mo_2C and W_2C, respectively.

Data presented in Table 1 concern comparable total conversion of DBT for both catalysts. Therefore, for W_2C the contact time is twice longer than for Mo_2C. The major products of desulfurization of DBT were biphenyl (BPh) and cyclohexylbenzene (CHB). A small amount of partial hydrogenated product of DBT, tetrahydrodibenzothiophene (THDBT) could be also detected. Taking both the total conversion of DBT and HDS rate into consideration (Table 1) it can be concluded that Mo_2C shows higher activity in comparison with W_2C in the HDS process of DBT. However, comparing the hydrogenating selectivity (calculated as ratio of yields CHB/BPh—0.5 for Mo_2C and 1.4 for W_2C) of both catalysts, it comes that W_2C possesses stronger hydrogenation properties. At comparable conversions, the concentration of cyclohexylbenzene for W_2C was 35%, whereas for Mo_2C it was only 19%.

On the contrary, the concentration of the aromatic product, such as biphenyl, was 38% for Mo_2C and 25% for W_2C.

On the basis of detected products and literature data, a reaction scheme of HDS of dibenzothiophene over both bulk molybdenum carbide and tungsten carbide is proposed on Scheme 1, where undetected sulfur containing intermediates products, are presented. Hydrodesulfurization of DBT occurs following two parallel routes: hydrogenation (HYD) and direct desulfurization (DDS). Bicyclohexyl was never observed in our process conditions.

The concentration of DBT and of its products versus contact time and catalysts are presented in Fig. 6. It confirms the higher activity of Mo_2C compared to W_2C. Over Mo_2C, the conversion of DBT reached 100% for contact times shorter than 0.8 s (Fig. 6a), while for W_2C only 78% at t_c = 0.8 s (Fig. 6b). The higher activity of molybdenum carbide, in comparison with tungsten carbide, can result from the higher specific surface

Table 1
Distribution of intermediate and products (mol%) during the HDS of DBT over bulk Mo_2C and W_2C at 613 K and 6 MPa

	mol%	
	Mo_2C (t_c = 0.27 s)	W_2C (t_c = 0.53 s)
1—Sulfur containing compounds: tetrahydrodibenzothiophene (THDBT)	5	4
2—Direct desulfurization (DDS, Scheme 1): biphenyl (BPh)	38	25
3—Hydrogenation (HYD, Scheme 1): cyclohexylbenzene (CHB)	19	35
DBT conversion [%] (1 + 2 +3)	62	64
HDS [%] (2 + 3)	57	60

area of Mo_2C, as well as the larger amount of active centers (CO chemisorption) taking part in the HDS reaction of DBT. The yield of BPh over molybdenum carbide is almost 1.5 times as much as over tungsten carbide (Table 1). We can suppose that

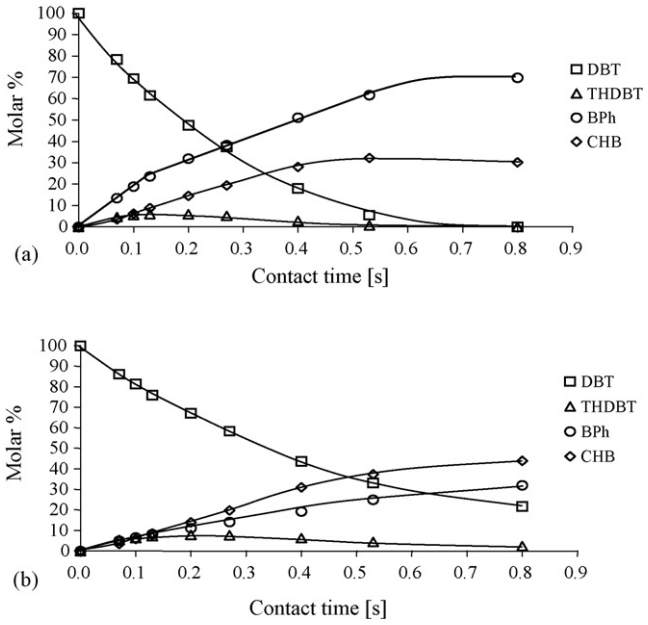
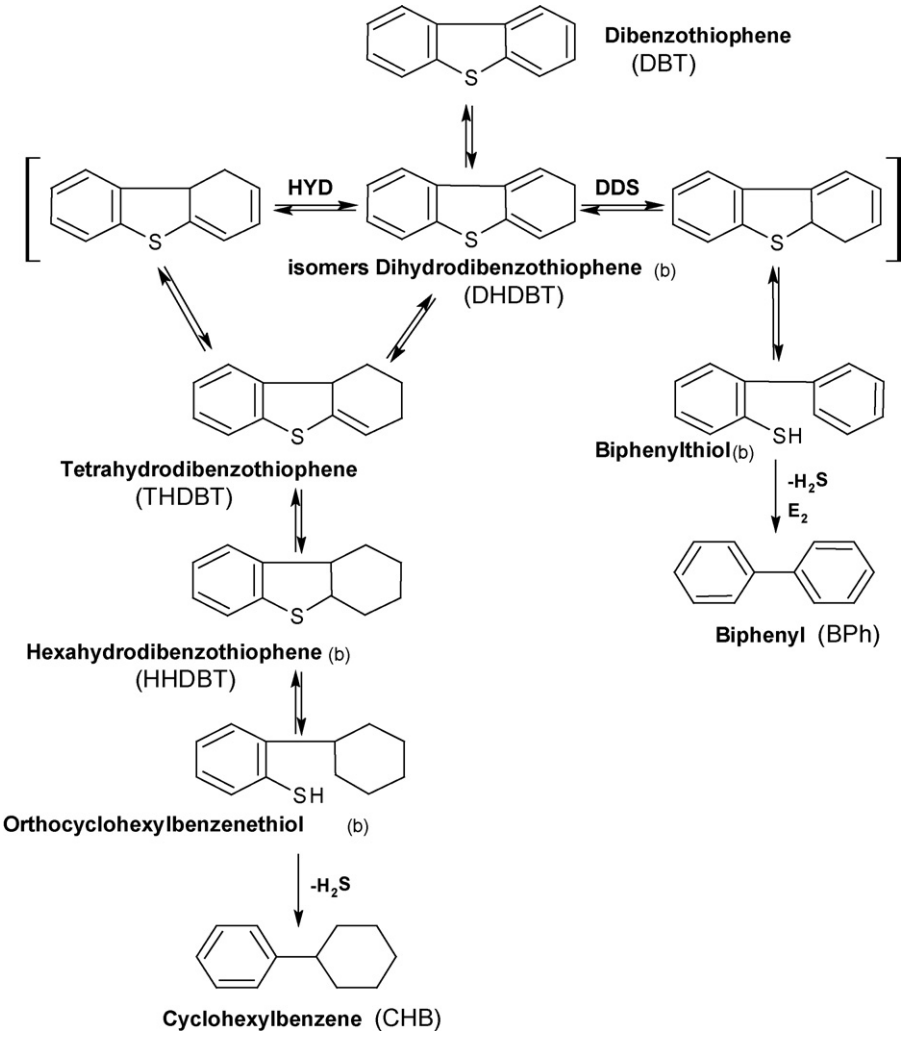


Fig. 6. Distribution of DBT, intermediates and products observed during the HDS of DBT vs. contact time over bulk Mo_2C (a) and W_2C (b) at 613 K.



Scheme 1. Reaction pathway of the HDS of dibenzothiophene over bulk Mo_2C and W_2C. '(b)' denotes undetected sulfur containing compounds.

the main route for W_2C is hydrogenation route, where cyclohexylbenzene is the final product of reaction. However, the direct desulfurization route or hydrogenation of BPh to CHB as secondary reactions are possible [22]. For Mo_2C, the favored route is the direct desulfurization route. However, hydrogenation route occurs in a smaller degree. Therefore, W_2C possesses stronger hydrogenation properties than Mo_2C.

Molybdenum carbide is more active than tungsten carbide related to weight. However, tungsten carbide is more active when conversion is expressed per unit of surface area—calculated values are 7.68×10^{-3} μmol s^{-1} m^{-2} for W_2C and 3.60×10^{-3} μmol s^{-1} m^{-2} for Mo_2C, respectively. Also the calculated values of chemisorption of CO m^{-2} of specific surface area are higher for W_2C than for Mo_2C (5.38 and 4.30 μmol m^{-2}, respectively). Moreover, the hydrogenation activity of W carbide is greater than that of Mo carbide. This is consistent with more efficient activation of hydrogen.

4. Conclusion

Both carbides have a meso and macroporous structure. Both molybdenum and tungsten carbides had an high activity in hydroprocessing in our operating conditions, with HDS conversion reaching 100%. However, it was found that Mo_2C had better activity than W_2C for HDS of dibenzothiophene related to weight. But in other side, intrinsic activity (per unit of surface area) is higher for W_2C. The composition of DBT takes place through two parallel pathways, a direct desulfurization pathway leading to biphenyl, the other hydrogenation pathway leading to cyclohexylbenzene. On the Mo_2C catalyst the DDS pathway was predominant whereas on the W_2C catalyst, HYD was the main pathway. The DDS/HYD selectivity during the HDS of DBT over Mo_2C was twice as much as over W_2C. It suggests that the W_2C catalyst has stronger hydrogenating properties than Mo_2C.

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