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Catalysis Today 119 (2007) 35–38

CATALYSIS TODAY

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Comparison between tungsten carbide and molybdenum carbide for the hydrodenitrogenation of carbazole

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Abstract

The activity of molybdenum and tungsten carbides in hydrodenitrogenation (HDN) of carbazole was studied. Transition metal carbides (Mo_2C and W_2C) were synthesized using the temperature-programmed reaction of the appropriate oxide precursor (MoO_3 and WO_3) with the following gas mixture: 10 vol.% CH_4/H_2. The structure of the catalysts was characterized using X-ray diffraction, CO chemisorption, high resolution transmission electron microscopy (HRTEM) and BET surface area measurements. From the HRTEM analysis, it could be concluded that the tungsten carbide was thioresistant in our operating conditions (50 ppm of S, pressure = 6 MPa, $553 < T < 653$ K, H_2/feed volumic ratio = 600). In the case of Mo_2C, molybdenum sulphide was observed as single slabs. The activity of catalysts was determined during the hydrodenitrogenation of carbazole at the wide range of temperature (553–653 K) and under a 6 MPa total pressure of H_2. The comparison of tungsten carbide and molybdenum carbide has shown higher activity of Mo_2C than W_2C at the same condition. However, W_2C leads to higher amount of isomers of main products, and have higher hydrogenation activity.

Keywords: Molybdenum carbide; Tungsten carbide; Hydrodenitrogenation; Carbazole

1. Introduction

Hydrodenitrogenation (HDN) has received relatively less attention in the literature than hydrodesulfurization (HDS), but several reviews are available regarding the HDN process [1,2]. N-containing compounds are well known inhibitors of the HDS process among others such as cracking and hydrocracking [3]. Therefore, the HDN process should be carefully studied. The most of the works deal with the HDN of indole [4–8]. Carbazole, as the most resistant nitrogen-containing compound, has been studied to a small extent [9–12].

The objective of this investigation was to compare the reactivity of bulk tungsten carbide (W_2C) and bulk molybdenum carbide (Mo_2C) for carbazole hydrodenitrogenation in a large range of conversion (from 10 to 100%) and temperature (553–653 K). As a preliminary study, the concentration of nitrogen used was relatively high (0.4 wt.% of carbazole in *o*-xylene). The study of HDN of carbazole over bulk Mo_2C was previously published elsewhere [9]. The present work only reports the study of HDN of carbazole over W_2C where the activities of both catalysts are compared.

2. Experimental

2.1. Materials

MoO_3 (Fluka, ≥99.5%) and WO_3 (Fluka, ≥99.5%) were used as precursors for the preparation of 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: carbazole (Fluka, 98%), *o*-xylene (Fluka, ≥98%) and dimethyl-disulfide (Fluka, ≥98%).

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doi:10.1016/j.cattod.2006.08.039

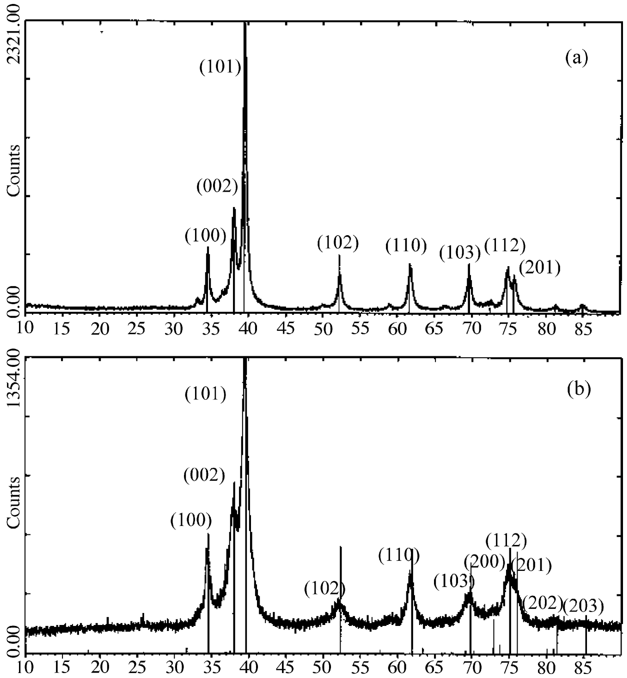

Fig. 1. X-ray diffraction patterns of bulk molybdenum carbide and tungsten carbide (a) β-Mo_2C and (b) W_2C.

2.2. Preparation of bulk Mo_2C and W_2C

Molybdenum and tungsten carbides were synthesized via the temperature-programmed reaction of MoO_3 or WO_3 using a 10 vol.% CH_4/H_2 mixture. 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. Finally, the reactor with sample was quickly cooled down to room temperature (RT) in the carburizing gas mixture. The gas flow was switched to a 1 vol.% O_2/He gas mixture in order to passivate the carbide.

2.3. Characterization

The passivated catalysts were characterized by XRD,BET surface area measurements and high-resolution transmission electron microscopy (HRTEM) and CO chemisorption was performed on the fresh catalysts as indicated below.

The X-ray powder diffraction (XRD) was carried out with a Siemens D-500 diffractometer using monochromatic Cu Kα radiation. Specific surface areas of the catalysts were determined from N_2 adsorption at 77 K by the conventional BET method using a Quantachrome–Quantasorb Jr apparatus. High-resolution transmission electron microscopy (HRTEM) was carried out on carbides before and after catalytic tests. The HRTEM study was performed using a JEOL 200 CX electron microscope. The CO uptake was performed ‘‘*in situ*’’, i.e. in the synthesis reactor without exposing the fresh carbide to air or to the passivating mixture. Pulses of a known quantity of CO (17 μmol) were injected at regular intervals into the sample at RT in a stream of He (40 mL min^{-1}).

2.4. Kinetic study of HDN of carbazole

The HDN of carbazole was measured in a down flow fixed-bed microreactor, described in detail elsewhere [9]. The kinetic study was carried out at a total pressure of 6 MPa at temperatures between 553 and 653 K, with a H_2/feed volumic ratio of 600 and contact times (t_c) ranging from 0.07 to 0.8 s. The liquid products of the reaction were collected every hour at 288 K and 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 (Finnigan MAT Model 800, capillary column DB5, 30 m × 0.25 mm × 0.25 μm and HP5890-HP5971A, capillary column PONA, 50 m × 0.20 mm × 0.5 μm) and injection of the standards. At each temperature, the carbides were stabilized ‘‘*in situ*’’ for 10 h with a mixture of 70 ppm of DMDS/*o*-xylene in the hydrogen carrier gas (60 mL min^{-1}) at the temperature of the process and at a total pressure of 6 MPa.

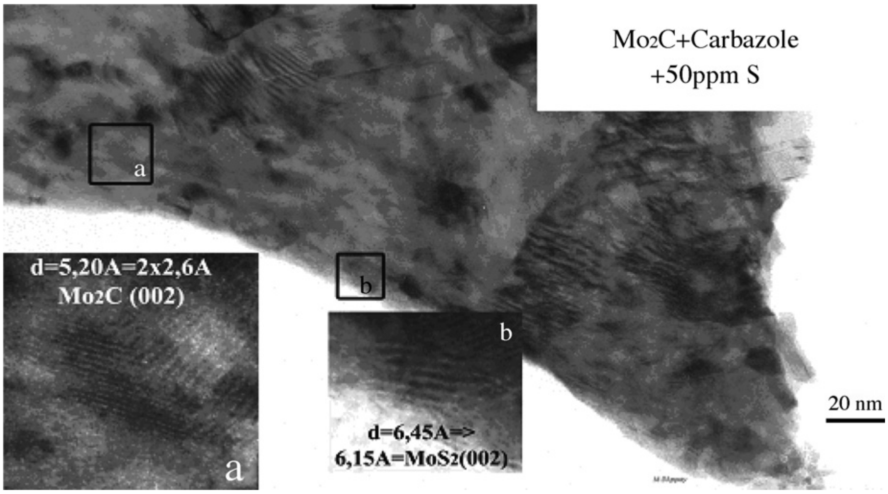

Fig. 2. TEM micrographs of molybdenum carbide after the HDN of carbazole. Identification of crystallographic phases was performed: (a) Mo_2C and (b) MoS_2.

3. Results and discussion

3.1. Characterization of the catalyst

The passivated molybdenum carbide and tungsten carbide exhibited a BET surface area of 33 and 13 $m^2\ g^{-1}$, respectively. The amount of adsorbed CO per 1 m^2 is higher for W_2C than for Mo_2C and is equal to 5.4 μmole CO and 4.3 μmole CO, respectively. XRD data confirmed the presence of the expected molybdenum and tungsten carbides active phases. The hexagonal compact phase (hcp) of molybdenum carbide, β-Mo_2C, was the only phase observed (Fig. 1a). Similar results were obtained in the case of the hexagonal compact phase (hcp) of tungsten carbide, W_2C as shown in Fig. 1b. Concerning samples after catalytic test, the TEM study indicated that slabs of MoS_2 could be scarcely observed (Fig. 2). In this case, it was assumed that superficial sulfidation could occur, but to a small extent, whereas concerning W_2C, the TEM study did not underlined any WS_2 slabs (Fig. 3) Thus, the initial crystallographic structures of the carbides remained after catalytic tests. Sajkowski and Oyama [13] reported, that carbides and nitrides were stable in the presence of 800 ppm of sulphur. Da Costa et al. [14] also reported that on the surface of Mo_2C/Al_2O_3 and WC/Al_2O_3, the corresponding sulfides phases were not observed, after hydrogenation of tetraline in the presence of 200 ppm of sulfur.

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

In agreement with the products observed a reaction scheme of the HDN of carbazole over both bulk molybdenum carbide and tungsten carbide is proposed and presented in a previous paper concerning HDN of carbazole over Mo_2C [9]. The main observed HDN product was bicyclohexyl (BCH) and its isomers (methylcyclopentylcyclohexane, hexylcyclohexane.) with a small amount of cyclohexylcyclohexene (CHCHe). The second detected product was cyclohexylbenzene (CHB) with its isomers (methylcyclopentylbenzene, cyclopentylphenylomethane, *n*-hexylbenzene). The distribution of products for both carbides clearly indicated the differences of their activity, particularly concerning the amount of isomers. However, for both catalysts, biphenyl (BPh) was not formed, indicating that the direct denitrogenation route (DDN) did not occurred.

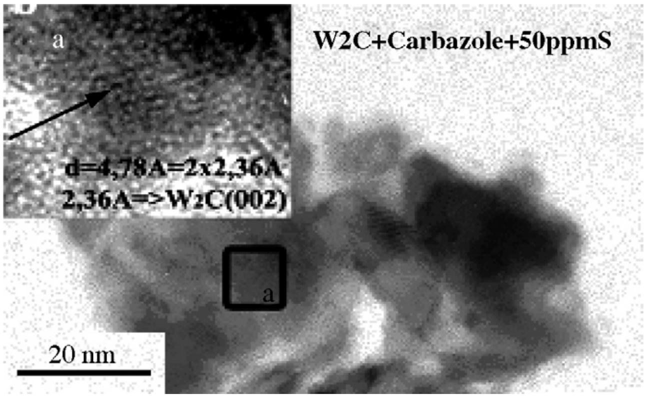

Fig. 3. TEM micrographs of a tungsten carbide after the HDN of carbazole. Identification of crystallographic phases was performed: (a) W_2C.

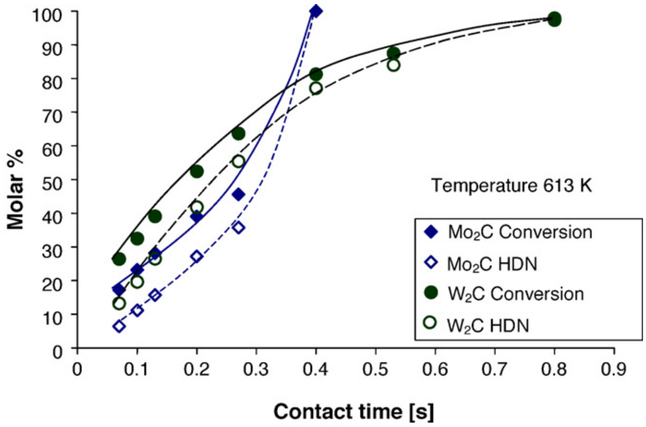

Fig. 4. Conversion of carbazole and HDN rate over both Mo_2C and W_2C at 613 K, 6 MPa vs. contact time.

Conversion of carbazole and HDN percent presented in Fig. 4 show that activity of W_2C was 10% higher for short contact

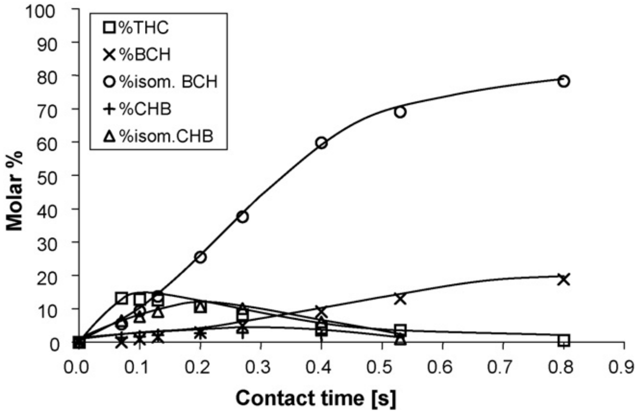

Fig. 5. Distribution of intermediates, and products versus contact time detected during the HDN of carbazole over bulk W_2C at 613 K and 6 MPa.

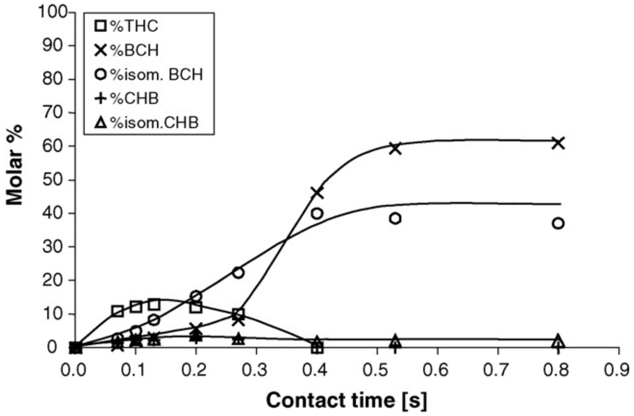

Fig. 6. Distribution of intermediates, and products vs. contact time detected during the HDN of carbazole over bulk Mo_2C at 613 K.

times ($t_c < 0.3$ s), whereas above 0.3 s the activity of Mo_2C was significantly higher than that of W_2C in our operating conditions. Conversion of carbazole and HDN percent curves for W_2C increased proportionally with contact time and reached 100% above 0.8 s, whereas for molybdenum carbide this was already reached at a contact time of 0.4 s. Besides, the calculated activation energies of the hydrogenation step of carbazole correlate these observations. Indeed, an activation energy of 123 kJ mol^{-1} was calculated for W_2C which is higher than that of Mo_2C (86.6 kJ mol^{-1} [9]).

Figs. 5 and 6 present the distribution of products of HDN of carbazole over W_2C and Mo_2C, respectively. The same products were detected whatever the carbide but with a different selectivity. For both catalysts, BCH and its isomers were the main products but the total amount of isomers were significantly higher over W_2C. Cyclohexylbenzene and its isomers were present in small quantity at short contact times. Therefore, the hydrogenating route of HDN of carbazole over W_2C and Mo_2C was more favoured. Differences between both catalysts appear in the selectivity between BCH and its isomers. The isomerization to a larger extent occurs on W_2C. The isomerization reactions observed during HDN of carbazole process mean that both carbides are bifunctional catalysts. Therefore, they possess acidic and metallic active sites as required in the isomerization reactions of cycloalkanes [15].

4. Conclusion

Both synthesized carbides possessed hexagonal compact phase (hcp) characterized by XRD. TEM characterization does not reveal the presence of sulfides on the surface of W_2C after the HDN of carbazole in the presence of sulfur (50 ppm), at 6 MPa and temperature ranging from 553 to 653 K, whereas it was the case for Mo_2C for which superficial traces of MoS_2 could be detected.

Tungsten carbide and molybdenum carbide are active catalysts in HDN of carbazole in the presence of a low amount of sulfur (50 ppm). The main route of HDN of carbazole over W_2C and Mo_2C is the hydrogenation route (HYD) which leads mainly to BCH and its isomers. However, in the case of W_2C the isomers of BCH are the major products. The presence of isomerization reactions indicate that tungsten carbide and molybdenum carbide are bifunctional catalysts where W_2C possesses the strongest hydrogenation (metallic function) and isomerisation properties.

Acknowledgements

We want to thank Dr. Patricia Beaunier and Dr. Marie-Dominique Appay for providing the TEM micrographs and the crystallographic measurements, respectively. CNRS and PAN are greatly acknowledged for financial supports.

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