Available online at www.sciencedirect.com

Catalysis Today 119 (2007) 31–34

www.elsevier.com/locate/cattod

Catalytic performances of platinum doped molybdenum carbide for simultaneous hydrodenitrogenation and hydrodesulfurization

M. Lewandowski [a,*], A. Szymańska-Kolasa [a], P. Da Costa [b], C. Sayag [b]

[a] *Institute of Coal Chemistry of PAS, Sowińskiego 5, 44-121 Gliwice, Poland*
[b] *Laboratoire Réactivité de Surface, UMR CNRS 7609, Casier 178, Université P. & M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France*

Abstract

The hydrotreating activity of molybdenum carbide doped with platinum (0.3 wt.%) was studied and compared to that of a pure, non-modified Mo_2C. 4,6-Dimethyldibenzothiophene (4,6-DMDBT, 300 ppm of S) and carbazole (100 ppm of N) were designated as model compounds and subjected to hydrodesufurization (HDS) and hydrodenitrogenation (HDN) processes either separately or simultaneously. In both cases the molybdenum carbide doped with platinum (Mo_2C-Pt) turns out to be more active than Mo_2C. The increase of the hydrotreating activity, owing to the presence of platinum in molybdenum carbide can be related to the raise of hydrogenation activity of the modified catalyst. The platinum modified molybdenum carbide was stable (*displays a long lifetime*) under HDN and HDS reaction conditions. The predominant reaction products are bicyclohexyl (BCH) for the HDN process or 3,3′-dimethylbiphenyl (3,3′-DMBPh) and methylcyclohexyltoluene (MCHT) for the HDS process, respectively.

Keywords: Molybdenum carbide; Platinum; Hydrodesulfurization (HDS); 4,6-Dimethyldibenzothiophene; Hydrodenitrogenation (HDN); Carbazole

1. Introduction

Transition metal carbides have shown exceptionally high catalytic activity in a number of reactions carried out under hydrotreating conditions [1]. Molybdenum carbide is one of the most frequently studied compound from among the large group of transition metal carbide catalysts. Mo_2C, either bulk or deposited on an inorganic support, shows excellent activity and selectivity in many catalytic processes, especially in hydrodesufurization (HDS) and hydrodenitrogenation (HDN) [1–4].

For several decades the petroleum industry has been under increased pressure from parliaments worldwide to improve quality of diesel fuels with a view of reducing exhaust emissions. The United States Environmental Protection Agency (EPA) has introduced regulations aimed at lowering the amount of sulfur and nitrogen content in diesel fuels from the current 500 to 15 ppm wt. in 2006, and in gasoline from 300 to 30 ppm wt. by 2004 [5] and even to 10 ppm wt. and less, around 2009 [6,7]. On the one hand, HDN is the most complicated hydrotreatment process and little is known about what N-containing organic compounds are the most refractory or about the kinetics of their conversion during the course of the industrial process. On the other hand, organic compounds containing nitrogen are inhibitors of the HDS process. That is why the level of such nitrogen compounds should be reduced to the values below 60 ppm in order to achieve very deep HDS (less than 10 ppm wt. S) [8,9]. Decomposition of both S- and N-containing organic compounds (alkyl derivatives of dibenzo[*b*,*d*]thiophene and carbazole stand for model compounds) requires the use of catalysts performing good hydrogenation capabilities which transition metal carbides are known to display. Therefore, in this study we have examined activities of Mo_2C doped with platinum in HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) and in HDN of carbazole and compare with the activities of pure Mo_2C.

2. Experimental

2.1. Preparation of Mo_2C

Molybdenum carbide (Mo_2C) was prepared by a temperature programmed reaction of MoO_3 with 10 vol.% CH_4/H_2 gas

---

* Corresponding author. Tel.: +48 322380791 (secr.); fax: +48 322312831.
E-mail address: marco@karboch.gliwice.pl (M. Lewandowski).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.08.062

mixture in a flow quartz reactor system. The characterization of the product was accomplished by obtaining XRD pattern, BET measurements and CO chemisorption. Then the temperature was elevated at a linear rate of 0.9 K/min from room temperature to 973 K, at which temperature the sample was held for 1 h. After cooling down the sample to room temperature the sample was passivated in a 1% O_2/He gas flow in controlled operating conditions to form a protective oxide layer on the surface of the carbide.

2.2. *Doping of Mo_2C with Pt and the catalytic tests*

A sample of Mo_2C was impregnated with a water solution of hexachloroplatinic acid to reach 0.3 wt.% of Pt, followed by drying at 383 K. The product was denoted as Mo_2C-Pt.

2.3. *Catalytic test*

The HDS and HDN reactions were performed in a down-flow fixed-bed microreactor in a high-pressure flow system. The catalyst (weight = 0.1 g for HDN reaction, 0.25 g for HDS reaction and simultaneously reaction, grain size 0.25–0.315 mm) was mixed with carborundum at a ratio of the catalyst to SiC = 1/5. The liquid feed 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 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 in which temperature was maintained at 288 K. Finally, this liquid was analysed 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 GC/MS analysis with a capillary column DB5 (30 m × 0.25 mm × 0.25 μm).

The HDS reaction of 4,6-dimethyldibenzothiophene and HDN reaction of carbazole were performed separately or simultaneously at 350 °C, H_2 pressure of 6.0 MPa and the H_2/feed ratio of 600. The liquid feed contained 0.17% of 4,6-DMDBT (300 ppm S) and/or 0.08% of carbazole (100 ppm N) in *o*-xylene. The catalysts were reduced in situ at 723 K (450 °C) for 2 h in dihydrogen atmosphere prior catalytic tests. The catalytic process was conducted for about 100 h. After 100 h, the initial operating conditions were re-set in order to check the deactivation of the catalyst. No deactivation was observed for any of our catalysts.

Before starting any catalytic tests the possibility of solvent conversion was checked. Practically no conversion of solvent was observed in our operating conditions.

3. Results and discussion

X-ray structural analysis of the molybdenum carbide reveals its hexagonal crystallographic structure. The specific surface area equals to 54 m^2/g and amount of adsorbed CO equals to 137 μm/g. The specific surface area and CO chemisorption determinations had not been measured for Mo_2C-Pt as the catalyst sample was reduced in situ in the reactor.

The results of the HDN rate and the conversion of carbazole in the presence of the two catalysts [the pure Mo_2C and the platinum doped Mo_2C (Mo_2C-Pt)] are shown in Fig. 1a. The modification of Mo_2C with 0.3 wt.% of Pt, results in ca. 10% increase of both the substrate conversion and the efficiency of HDN for each of the contact time applied. The HDN reaction of carbazole along the hydrogenation route goes through the intermediate product tetrahydrocarbazole (THC) and leads mainly to bicyclohexyl (BCH) as the final product. According to literature data [10,11], in peculiar operating conditions, hydrogenated carbazole compounds can be observed in traces such as: 1,2,3,4,4a,9a hexahydrocarbazole octahydrocarbazole and perhydrocarbazole beside to high amount of tetrahydrocarbazole. These partly hydrogenated intermediates compounds are very reactive on the route to the removal of N because the C–N bond scission is easier for carbon atoms with sp^3 hybridisation. By comparison, the electronic structure of carbazole is different from that of dibenzothiophene (DBT) as the main product obtained over the same catalyst as a result of HDS of DBT is biphenyl. In the case of carbazole, the intermediate compounds prefer to adsorb on the active site through their aromatic ring.

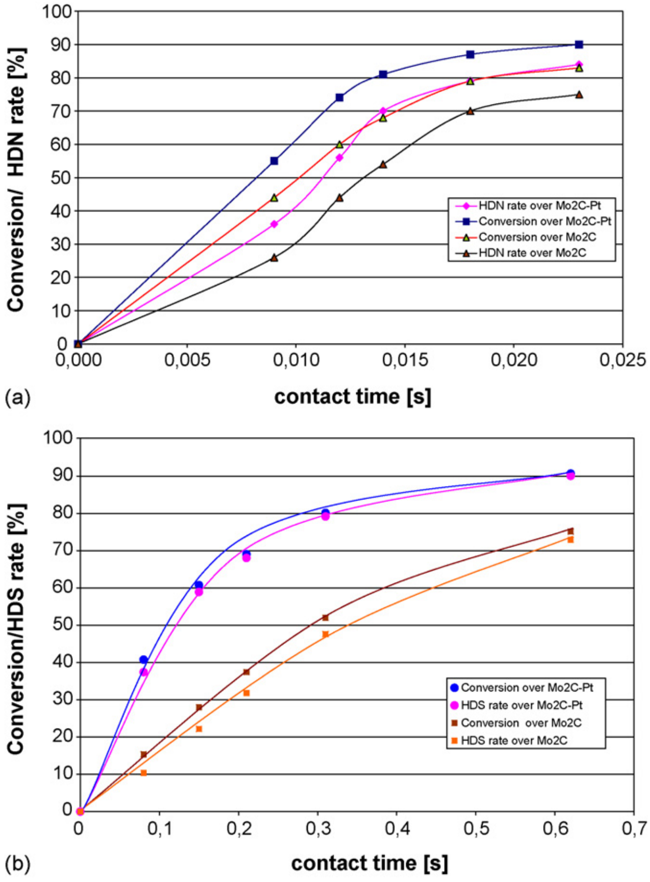

Fig. 1. Conversion and HDN rate (a), and conversion and HDS rate (b) vs. contact time over Mo_2C and Mo_2C-Pt catalysts. HDN and HDS processes performed separately at 623 K and 6 MPa.

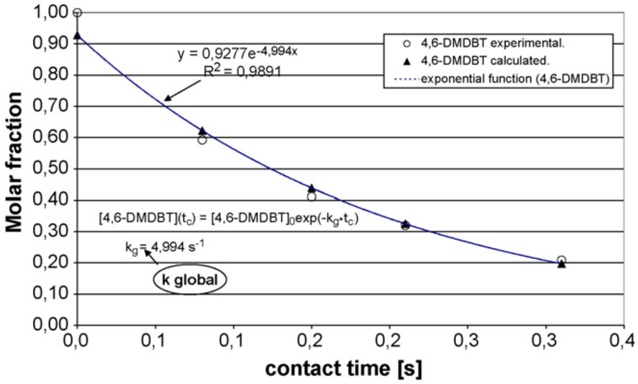

Fig. 2. Correlation between the experimental (○) and the calculated (▲) data of 4,6-DMDBT concentration using the first-order rate laws formulae of global kinetics performed over a Mo_2C-Pt catalyst at 623 K and 6 MPa.

The amount of CHB that forms as the product of direct denitrogenation following the preceding hydrogenation of one aromatic ring of carbazole is small and stands at the level of 3%. One can believe that the increase of BCH during the HDN process over Mo_2C-Pt, is a measure of high catalyst activity [12–14].

Fig. 1b demonstrates both curves of 4,6-DMDBT conversion, and HDS rate for the Mo_2C and the platinum doped Mo_2C samples. The catalytic activity of the modified molybdenum carbide is approximately two times higher for low contact times (<0.31 s) as compared with the activity of Mo_2C. For Mo_2C, a zero-order with respect to 4,6-DMDBT concentration is observed when conversion is below 50%. However, for the Mo_2C-Pt catalyst the shape of the curves of the substrate conversion and the degree of its HDS as a function of contact time, suggests a change of the reaction order from zero- to a first-order with respect to 4,6-DMDBT concentration. Moreover, a very good fit between experimental and calculated data of 4,6-DMDBT concentrations versus contact time has been found (Fig. 2). Based on these results it can be assumed that the HDS rate of the 4,6-DMDBT catalyzed by Mo_2C-Pt is a first-order reaction with respect to the substrate concentration, while for the non-modified Mo_2C catalyst, this rate is independent of the 4,6-DMDBT concentration in the range of contact time studied. The products distribution versus contact time over Mo_2C and Mo_2C-Pt is depicted in Fig. 3a and b. There are two routes of desulfurization, namely the direct desulfurization route (DDS) of 4,6-DMDBT to form 3,3′-dimethylbiphenyl (3,3′-DMBPh) and the hydrogenation route (HYD) leading to the formation of methylcyclohexyltoluene (MCHT) and

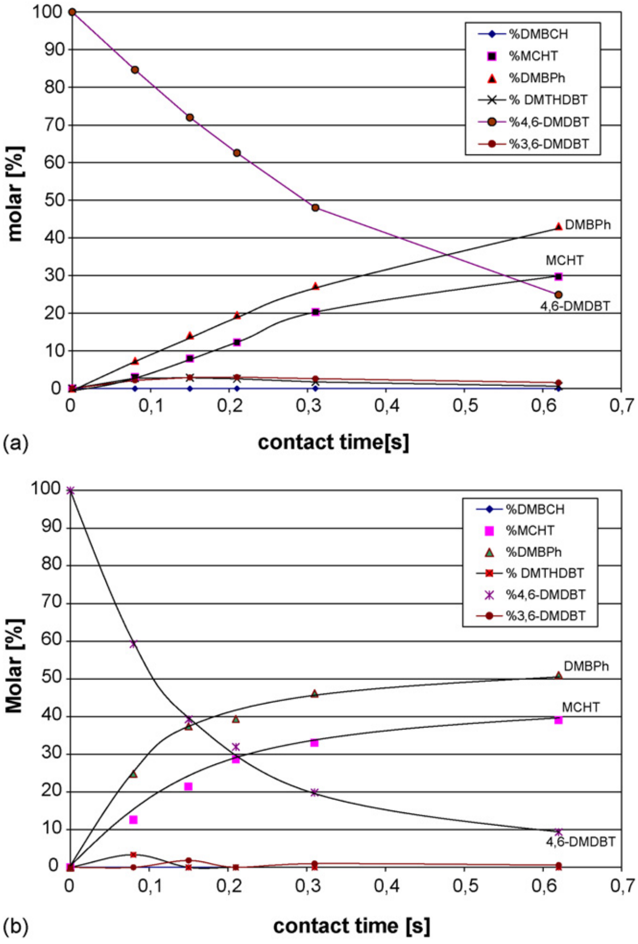

Fig. 3. Products distribution for the HDS of 4,6-DMDBT over: (a) Mo_2C and (b) Mo_2C-Pt at 623 K and 6 MPa.

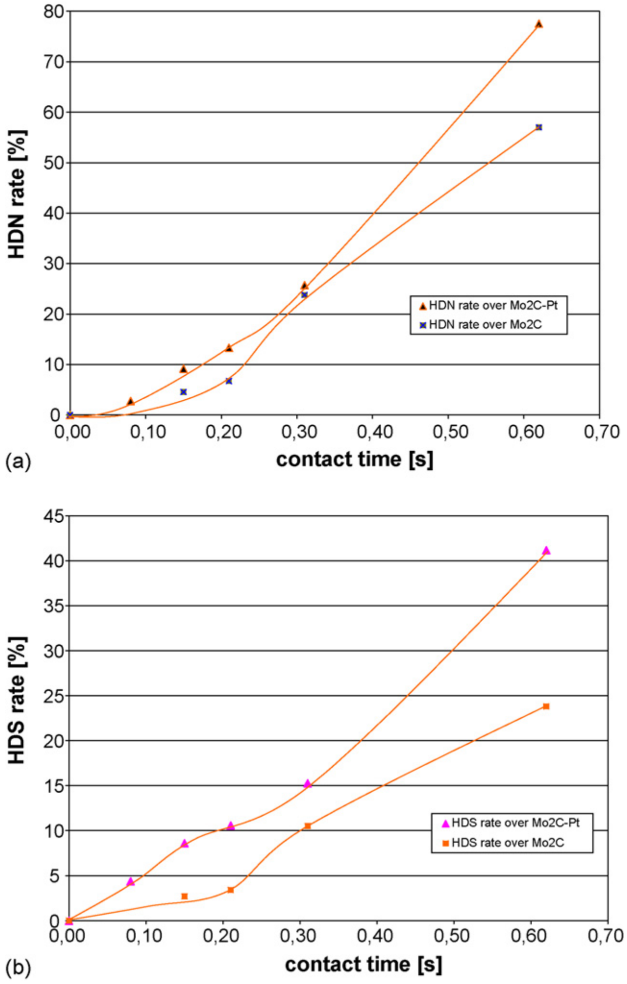

Fig. 4. HDN rate (a) and HDS rate (b) vs. contact time over Mo_2C and Mo_2C-Pt. HDN and HDS processes were performed simultaneously at 623 K and 6 MPa.

3,3′-dimethylbicyclohexyl (3,3′-DMBCH) with 4,6-dimethyltetrahydrodibenzothiophene (4,6-DMTHDBT) as an intermediate product. Comparing the product distribution (Fig. 3a and b) acquired as an effect of HDS process performed in the presence of both catalysts one can ascertain that the higher activity of Mo_2C-Pt is related to the increasing yields of both 3,3′-DMBPh and MCHT.

Fig. 4 presents the HDN (Fig. 4a) and HDS (Fig. 4b) rates, performed when both processes undergo simultaneously, versus contact time over Mo_2C and Mo_2C-Pt. It is well known that N-containing organics strongly inhibit HDS process. These nitrogen compounds or the intermediate products of their denitrogenation compete for active catalyst centers with organic sulfur compounds contributing to their lower conversion and lower degree of desulfurization [15–18]. This phenomenon has been observed also in our studies. The presence of carbazole in a mixture with 4,6-DMDBT dramatically reduces the HDS rate of 4,6-DMDBT. Nevertheless, the Mo_2C-Pt catalyst is still more active than Mo_2C. It is worth noting that for contact times below 0.3 s the HDS rate for both catalysts is reduced to the values below 20% under our applied operating conditions. For longer contact time (from 0.3 to 0.64) a threefold increase of the HDS rate is observed over Mo_2C-Pt, whereas a 14% increase of the HDS rate is observed over Mo_2C (Fig. 4b). Furthermore, a twofold increase of the HDN is observed.

In spite of this, it is well known that Pt is very sensitive to sulfidation [19] but it depends on the amount of sulfur present in the feed, partial pressure of H_2S and operating conditions of the reaction. Based on the studies of Kabe and co-workers [7,20–22] performed with the use of noble metals, a part of the total sulfur can be considered as labile sulfur which precipitates during the HDS reaction. Pt is present in the form of PtS_x ($x = 0$–0.25) when partial pressure of H_2S is below 5.2 kPa (in our case 1.63 kPa) [22]. Therefore, we observed an increased of the yield of 3,3′-DMBPh for Mo_2C-Pt as compared with pure Mo_2C. Another result from Kabe and co-workers studies [7,20–22] revealed that the amount of labile sulfur over noble metal did not change with the temperature although their activity in HDS increased with temperature. This indicates that the mechanism of HDS reaction occurring over noble metal is different from that observed classically over Mo-based catalysts [20].

The other factor responsible for the higher activity of the platinum modified molybdenum carbide might be the spillover of hydrogen formed on the Pt particles deposited over Mo_2C which can play an important role in the HDS process [23]. The increase of the hydrogenation ability due to hydrogen spillover results in the enhancement of the HDN rate because the inhibition resulted the HDS process is diminished.

4. Conclusions

Addition of platinum to Mo_2C enhances its catalytic activity both in the HDS process of 4,6-DMDBT and in the HDN process of carbazole. Moreover, formation of BCH is enhanced during the HDN of carbazole. A higher activity of the Mo_2C-Pt catalyst in HDS of 4,6-DMDBT gives rise to a higher output of 3,3′-DMBPh and MCHT.

The HDS of 4,6-DMDBT catalyzed by platinum-containing molybdenum carbide shows a first-order rate with respect to 4,6-DMDBT concentration, while a zero-order rate is observed when the pure Mo_2C is used. The platinum doping enhances the activity of both (HDS and HDN) processes performed simultaneously.

References

[1] E. Furimsky, Appl. Catal. A Gen. 240 (2003) 1.
[2] P. Da Costa, C. Potvin, J.-M. Manoli, M. Breysse, G. Djega-Mariadassou, Catal. Lett. 86 (2003) 133.
[3] A. Szymańska, M. Lewandowski, C. Sayag, G. Djéga-Mariadassou, J. Catal. 218 (2003) 24.
[4] P. Da Costa, C. Potvin, J.-M. Manoli, B. Genin, G. Djéga-Mariadassou, Fuel 83 (2004) 1717.
[5] X. Wang, P. Clark, S.T. Oyama, J. Catal. 208 (2002) 321.
[6] M. Breysse, G. Djéga-Mariadassou, S. Pessayre, Ch. Geantet, M. Vrinat, G. Perot, M. Lemaire, Catal. Today 84 (2003) 129.
[7] A. Ishihara, F. Dumeignil, J. Lee, K. Mitsuhashi, E.W. Qian, T. Kabe, Appl. Catal. A Gen. 289 (2005) 163.
[8] Y. Sano, K.Y. Choi, I. Mochida, Appl. Catal. B Environ. 53 (2004) 169.
[9] Y. Sano, K.Y. Choi, I. Mochida, Appl. Catal. B Environ. 49 (2004) 219.
[10] M. Nagai, Y. Goto, O. Uchino, S. Omi, Catal. Today 43 (1998) 249.
[11] M. Nagai, Y. Goto, A. Irisawa, S. Omi, J. Catal. 191 (2000) 128.
[12] H.S. Joo, J.A. Guin, Fuel Process. Technol. 49 (1996) 137.
[13] C.J.H. Jacobsen, E. Tornqvist, H. Topsoe, Catal. Lett. 63 (1999) 179.
[14] Z. Vit, J. Ciribulk, D. Gulkova, Appl. Catal. A Gen. 272 (2004) 99.
[15] T.C. Ho, D. Nguyen, J. Catal. 222 (2004) 450.
[16] G.C. Laredo, A. Montesinos, J.A. de los Reyes, Appl. Catal. A 265 (2004) 171.
[17] H. Yang, J. Chen, C. Fairbridge, Y. Briker, Y.J. Zhu, Z. Ring, Fuel Process. Technol. 85 (2004) 1415.
[18] G.C. Laredo, A. Montesinos, J.A. de los Reyes, Appl. Catal. A Gen. 243 (2003) 207.
[19] J. Barbier, E. Lamy-Pitara, P. Marecot, J.P. Boitiaux, J. Cosyns, F. Verna, Adv. Catal. 37 (1990) 279.
[20] W. Qian, Y. Yoda, Y. Hirai, A. Ishihara, T. Kabe, Appl. Catal. A Gen. 184 (1999) 81.
[21] T. Kabe, W. Qian, Y. Hirai, L. Li, A. Ishihara, J. Catal. 190 (2000) 191.
[22] E.W. Qian, K. Otari, L. Li, A. Ishihara, T. Kabe, J. Catal. 221 (2004) 294.
[23] M. Sugioka, Y. Kanda, T. Kobayashi, Y. Uemichi, Mem. Muroran. Inst. Tech. 54 (2004) 41.