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Supported molybdenum carbides lie between metallic and sulfided catalysts for deep HDS

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Hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene on alumina-supported Mo_2C has been studied. These catalysts are stable and active under deep HDS conditions (0–250 wt ppm S). However, although they are well known to have hydrogenation properties, they lead preferentially to a non-hydrogenated product of the HDS reaction: dimethylbiphenyl. For the same reaction, supported platinum and sulfided molybdenum oxide lead to the hydrogenated products dimethyldicyclohexyl and methylcyclohexyltoluene, respectively. The ranking of HDS activity is as follows: $MoS_2/Al_2O_3 < Mo_2C/Al_2O_3 < Pt/SiO_2$.

KEY WORDS: deep hydrodesulfurization; molybdenum carbide; hydrogenation properties; metallic and sulfided catalysts.

1. Introduction

Interest in the deep hydrodesulfurization (HDS) of gas oils has been increased by the regulation of sulfur and polyaromatics in diesel fuels in the European Union [1]. The deep HDS and hydrogenation of refractory S-containing compounds will continue to present problems to refiners. At low levels of sulfur in gas oil fuels, conventional alumina-supported sulfided nickel–molybdenum oxide catalysts become inefficient. In recent years new catalysts have been developed to transform refractory compounds. Most of these catalysts are modified nickel or cobalt/molybdenum-based sulfides [2–8]. Y-Zeolite materials have been used as supports to first isomerize 4,6-dimethyldibenzothiophene (4,6-DMDBT) to a less refractory compound, leading to better HDS activity [3,4]. Segawa *et al.* [5] used a mixed $TiO_2–Al_2O_3$ support instead of pure alumina and found better catalytic performance for deep HDS of gas oil. Kwak *et al.* [6,7] modified classical catalysts by addition of phosphorus or fluorine, both promoters enhancing catalytic activity by modifying the acid–base properties of the materials. Other supports such as carbon can be used in the HDS of 4,6-DMDBT; Sakanishi *et al.* [8] found it to be more active at high temperature (613 K) than commercial NiMo/alumina catalysts. Noble metal-based catalysts can also replace commercial catalysts [9–12]. The use of transition metal carbides or nitrides instead of noble metals can be envisaged. It has been recognized that molybdenum carbides and nitrides show high activity in hydrodenitrogenation (HDN) or HDS reactions, and high resistance to poisoning [13–18]. However, few studies have dealt with deep HDS, using compounds such as 4,6-DMDBT, well known to be one of the most refractory compounds in diesel feedstocks [17,19]. The aim of the present work was to compare, for a typical deep HDS reaction at a very low sulfur level, the activity and the stability of alumina-supported molybdenum carbide with that of alumina-supported sulfided molybdenum oxide and of a supported platinum catalyst.

2. Experimental

2.1. Materials

The support consists of γ-alumina extrudates provided by Procatalyse (specific surface area $S_g = 205\,m^2\,g^{-1}$, total pore volume $V_p = 0.7\,cm^3\,g^{-1}$). Ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Fluka), was used as precursor for the carbide synthesis. Gases employed were methane, Ar, O_2 and H_2 (all supplied by Air Liquide, 99.995%).

2.2. Catalyst preparation

2.2.1. Molybdenum carbide catalyst

Alumina-supported molybdenum material (10% w/w Mo) was prepared using the incipient wetness method. Extrudates once impregnated were dried at 393 K for 12 h. Supported carbides were prepared by temperature-programmed reaction (TPR) using a modification of the procedure described elsewhere [20]. Carbide synthesis was divided into two steps. First the impregnated extrudates were heated in flowing argon (flow rate $60\,cm^3\,min^{-1}$) and held at 673 K for 8 h. The material was then carburized by TPR in flowing CH_4/H_2 (20%

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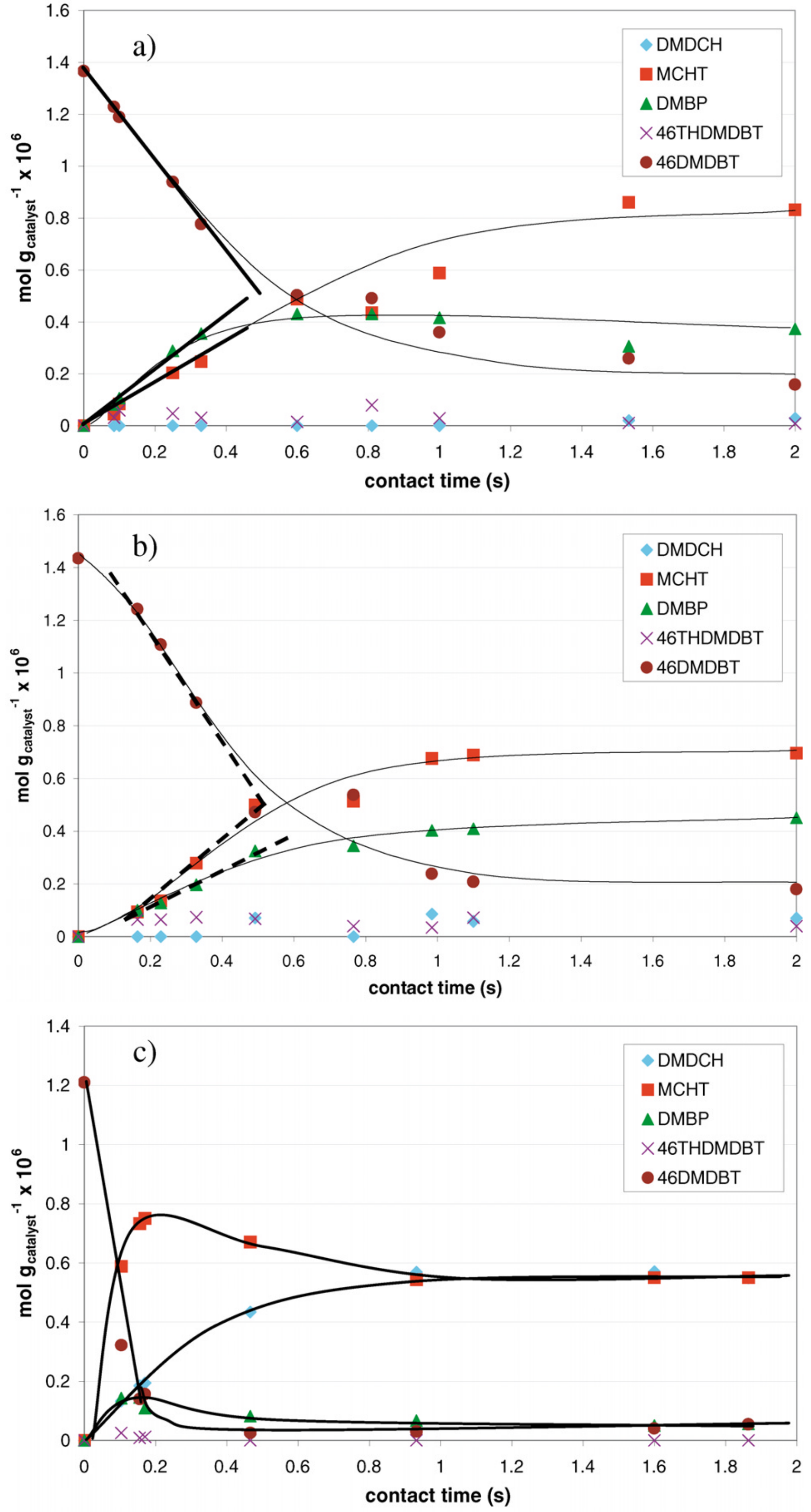

Figure 1. HDS of 4,6-DMDBT. Moles of reactant and products versus contact time; reaction at 613 K and 4 MPa total pressure: (a) alumina-supported carbide, (b) alumina-supported sulfide, (c) silica-supported platinum.

v/v mixture, total flow rate $60\,\mathrm{cm^3\,min^{-1}}$), the temperature being raised linearly from 673 to 950 K. At this final temperature the CH_4/H_2 flow was switched to hydrogen and the material was cooled to room temperature. Hydrogen was then switched to an O_2/Ar mixture (1% v/v) for a passivation step ($170\,\mathrm{cm^3\,min^{-1}}$ for 1 h). Extrudates of supported carbides were ground and sieved to between 0.25 and 0.4 mm before characterization or catalysis experiments Before reaction, 0.4 g of supported carbides were pretreated *in situ*, at 423 K and 4 MPa in flowing hydrogen ($16.7\,\mathrm{cm^3\,min^{-1}}$ for 1 h), to remove the passivation layer. The reaction mixture was then introduced and the temperature raised to the temperature of reaction.

2.2.2. Sulfided molybdenum- and platinum-based catalysts

Alumina (specific surface area $240\,\mathrm{m^2\,g^{-1}}$)-supported molybdenum oxide (10.2% w/w Mo) provided by Procatalyse was also investigated. This material was sulfided *in situ* by a mixture of 5% v/v dimethyldisulfide in *n*-heptane, at 3 MPa hydrogen partial pressure and 4 MPa total pressure. The H_2S and *n*-heptane partial pressures were 0.125 and 0.75 MPa, respectively. The sulfiding feed was injected at a starting temperature of 423 K, then raised to 623 K at $5\,\mathrm{K\,min^{-1}}$. After 14 h the temperature was lowered to 613 K, and the sulfiding feed replaced by the reaction mixture. Silica (Degussa)-supported Pt (1% w/w Pt) catalyst was prepared by cationic exchange of $Pt(NH_3)_4^{2+}$ [21]. After exchange the catalyst was calcined in pure O_2 ($1\,\mathrm{L\,min^{-1}\,g^{-1}}$) up to 573 K, at $1\,\mathrm{K\,min^{-1}}$, then up to 673 K at $0.2\,\mathrm{K\,min^{-1}}$ and held at this temperature for 2 h. It was then reduced *in situ* at 773 K in H_2 ($1\,\mathrm{L\,min^{-1}\,g^{-1}}$) at atmospheric pressure. The temperature was reduced to 423 K and hydrogen replaced by the reaction mixture.

2.3. Characterization

Powder X-ray diffraction (XRD) was carried out using a Siemens model D-500 diffractometer with CuKα radiation. Measurements were performed for 2θ ranging from 10 to 110°. High-resolution transmission electron microscopy (HRTEM) was performed to determine the particle size of the molybdenum carbide supported on alumina and to check the dispersion. HRTEM studies were carried out using a JEOL-JEM 100 CXII apparatus associated with a top-entry device and operating at 100 kV. Energy dispersive spectroscopy (EDS) was performed with the same apparatus using a LINK AN 10000 system, connected to a silicon–lithium diode detector, and multichannel analyzer. EDS analyses were obtained for large domains of samples ($150\times200\,\mathrm{nm^2}$ to $400\times533\,\mathrm{nm^2}$). The Mo and C contents of the catalysts were determined by chemical analysis at the Service Central d'Analyses of the CNRS.

2.4. Hydrodesulfurization of 4,6-dimethyldibenzothiophene

Hydrodesulfurization of 4,6-DMDBT was carried out in a flow reactor at 613 K and a total pressure of 4 MPa; decalin was used as solvent, the mixture being injected by a high-pressure pump (Gilson, model 307). Under standard reaction conditions the various partial pressures were: 4,6-DMDBT, 0.001 MPa; decalin, 0.888 MPa; hydrogen, 3.111 MPa. The reactor effluents were condensed, and liquid samples were collected about every hour and analyzed by gas chromatography. Analyses were carried out using a Varian 3400 chromatograph equipped with a 50 m DB17 capillary column (J&W Scientific) with temperature programming from 373 to 503 K ($10\,\mathrm{K\,min^{-1}}$). The partial pressure of H_2S depended on the HDS conversion and ranged from 0 to 0.0009 MPa, the latter corresponding to 90% conversion of 4,6-DMDBT. The ratio of H_2 flow/liquid feed flow was set to 500. The contact time (t_c) was calculated from the total flow rate (4,6-DMDBT, decalin and hydrogen) and the catalyst volume.

Kinetics were studied with contact times up to 2 s. The amounts of 4,6-DMDBT reacted and of products obtained were calculated from the conversion of the reactant and the formation of products at each contact time. The results presented in figure 1 correspond to a time on stream of at least 2 h for each data point.

3. Results and discussion

3.1. Alumina-supported molybdenum carbides for deep HDS of 4,6-DMDBT

The molybdenum carbide phase is well dispersed on the support, because no particles were observed by TEM or detected by XRD. Moreover, the Mo/Al ratio given by EDS is always constant and equal to 0.7, in agreement with the theoretical value; these results are in agreement with those for molybdenum carbide catalysts described elsewhere [22].

The major products of 4,6-DMDBT HDS are 3,3′-dimethylbiphenyl (DMBP) and 3-(3′-methylcyclohexyl)toluene (MCHT). 4,6-Tetrahydrodimethyl-dibenzothiophene (4,6-THDMDBT) was detected as a minor product (figure 1(a)). Under our conditions, the HDS of 4,6-THDMDBT is very rapid and MCHT appears to be a primary product. For contact times greater than 1.5 s, 3,3′-dimethyldicyclohexyl (DMDCH) was also detected, as shown in figure 1(a). The major products of reaction (MCHT and DMBP) are then independent, as already reported for these reactions [3,19]. A scheme of the reaction is shown in figure 2(a).

Alumina-supported molybdenum carbide catalysts are stable under HDS conditions; no deactivation was observed during any of the kinetic studies. In figure

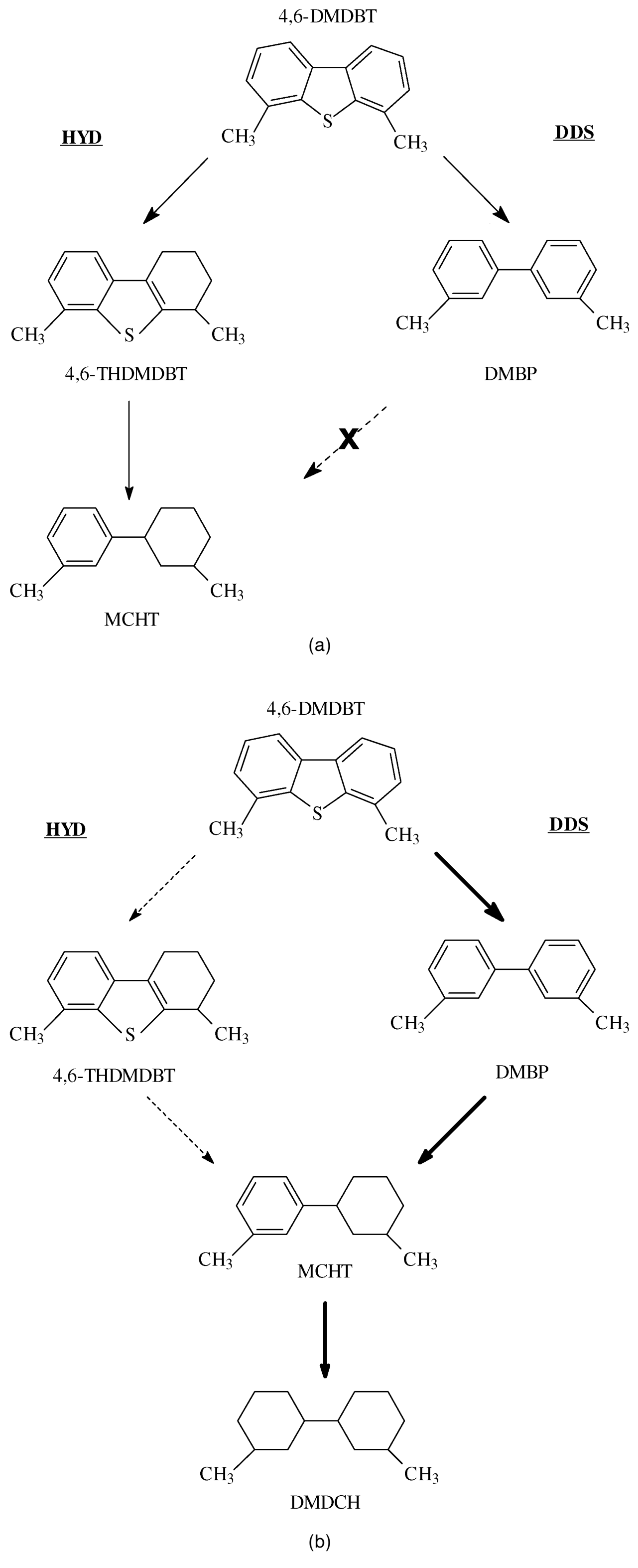

Figure 2. Simplified scheme for HDS of 4,6-DMDBT: (a) alumina-supported carbide or alumina-supported sulfide, (b) silica-supported platinum, the pathway going through 4,6-THDMDBT (minor) is dotted.

1(a) the number of moles of 4,6-DMDBT and of the two major products are linearly correlated for short contact times (<0.4 s). The intermediate in the desulfurization route with primary hydrogenation (HYD) (4,6-THDMDBT) is almost constant, given the experimental uncertainty, but not negligible at short contact time, when a zeroth-order reaction is observed. The HYD rate can therefore be expressed as the sum of the 4,6-THDMDBT and MCHT formation rates. The straight lines at low conversion are plotted for contact times less than 0.4 s (conversion of 60 mol%) and the results are presented in table 1 ($r_{\mathrm{HYD}}/r_{\mathrm{DDS}} = 0.69$). These linear plots for 4,6-DMDBT transformation and for DMBP and MCHT + 4,6-THDMDBT formation are characteristic of zeroth-order reactions. Furthermore, alumina-supported molybdenum carbide catalysts favor the direct desulfurization (DDS) route (table 1). Indeed, MCHT is formed more slowly than DMBP, which is not expected over good hydrogenation catalysts such as supported molybdenum carbides [22,23]. Aegerter *et al.* [24] used CO adsorption followed by FTIR spectrometry to characterize the oxidation state of molybdenum; they found molybdenum in a high oxidation state. Recently, we characterized Mo_2C/Al_2O_3 catalysts by X-ray photoelectron spectroscopy (XPS); we also found that a larger fraction of the molybdenum is in the Mo(IV) (binding energy 230.0 eV, surface concentration 23%) and Mo(VI) (binding energy 232.0 eV, surface concentration 35%) states, although part is in an oxidation state close to Mo(0) (binding energy 228.2 eV, surface concentration 42%). These results are consistent with high acidity for the Mo_2C/Al_2O_3 catalysts [24]. Molybdenum in the Mo(IV) and Mo(VI) states appears to favor the DDS instead of the HYD route for HDS of 4,6-DMDBT. Indeed, acidity is needed for C–S bond cleavage through an E_2 elimination [3].

3.2. Comparison with alumina-supported sulfided catalysts

The catalytic activities of supported molybdenum sulfided catalysts are presented in figure 1(b). The conversion of 4,6-DMDBT per gram of catalyst differs from the results for supported carbide catalyst. However, MoS_2/Al_2O_3 is as stable as Mo_2C/Al_2O_3 on stream, as shown in figure 3. Both catalysts could be used for HDS at these levels of sulfur in the feed. The reaction is again zeroth order if the initial point is omitted. The overall rate is $1.48 \times 10^{-6}\,\mathrm{mol\,g^{-1}\,s^{-1}}$ (table 1), which is lower than that found for Mo_2C/Al_2O_3. Furthermore, the rate of HYD ($r_{\mathrm{HYD}} = 0.71$) is higher than that of DDS ($r_{\mathrm{DDS}} = 0.59$), which is expected from the literature [4,25,26].

It was previously found that Mo_2C/Al_2O_3 catalysts are more active than MoS_2/Al_2O_3 for high-pressure hydrogenation in the absence or in the presence of sulfur [22]. However, in the HDS reaction, the MoS_2/Al_2O_3 and Mo_2C/Al_2O_3 catalysts show similar activities for HYD ($r_{\mathrm{HYD,MoS_2/Al_2O_3}} = 0.71$, $r_{\mathrm{HYD,Mo_2C/Al_2O_3}} = 0.76$), but the sulfided catalyst (MoS_2/Al_2O_3) favors HYD ($r_{\mathrm{HYD}}/$

Table 1

Rates estimated for the zeroth-order HDS reaction of 4,6-DMDBT (250 ppm S) at 613 K and 4 MPa total pressure (r_{HDS}, total rate; r_{HYD}, hydrogenation rate; r_{DDS}, direct desulfurization rate)

	Mo_2C/Al_2O_3 ($\times 10^6$ mol $g_{catalyst}^{-1}$ s^{-1})	MoS_2/Al_2O_3 ($\times 10^6$ mol $g_{catalyst}^{-1}$ s^{-1})	Pt/SiO_2 ($\times 10^6$ mol $g_{catalyst}^{-1}$ s^{-1})
r_{HDS}	1.87	1.48	7.41
r_{HYD}	0.76	0.71	5.01 [a]
r_{DDS}	1.10	0.59	1.28 [b]
r_{HYD}/r_{DDS}	0.69	1.20	3.91

[a] Calculated from the rate of formation of MCHT at short contact time (<0.18 s).

[b] Calculated from the rate of formation of DMBP at short contact time (<0.18 s).

$r_{DDS} = 1.20$). Indeed, C–S bond cleavage is disfavored with respect to MoS_2/Al_2O_3, as already reported [3,27]. In conclusion, Mo_2C/Al_2O_3 catalysts are more active than MoS_2/Al_2O_3 in the overall HDS reaction and favor the DDS route for 4,6-DMDBT.

3.3. Comparison with supported metallic catalysts

The catalytic activities of Pt/SiO_2 catalysts are presented in figure 1(c). The 4,6-DMDBT conversion per gram of catalyst is again linear, but reactant and product concentrations do not correlate. Furthermore, the kinetic behavior of the supported noble metal catalyst is completely different from that of the supported sulfided or carbide catalysts. The scheme presented in figure 2(a) is not valid, as can be seen from figure 1(c). Indeed, MCHT and DMBP are not major products of the reaction. These products are in fact intermediates of the reaction, conversion per gram of catalyst increasing up to contact times of 0.09 and 0.17 s for DMBP and MCHT, respectively, then decreasing. The major product of the reaction over this catalyst is DMDCH, the completely hydrogenated product of the reaction. The DDS and HYD routes are linked and not independent. A scheme corresponding to HDS of 4,6-DMDBT at 250 wt ppm S over noble metal catalysts can then be proposed (figure 2(b)). DDS rates and HYD rates can be extracted from short contact times (<0.18 s) (table 1); HDS rates are higher than those for supported carbide or sulfide catalysts. However, the noble metal catalyst is not stable on stream, which suggests that it is not sulfur resistant. Indeed, the HDS conversion is halved after 20 h of use and has not yet reached the steady state. In spite of a high initial activity and good hydrogenation properties, supported noble metal-based catalysts are not stable in the presence of 250 wt ppm S.

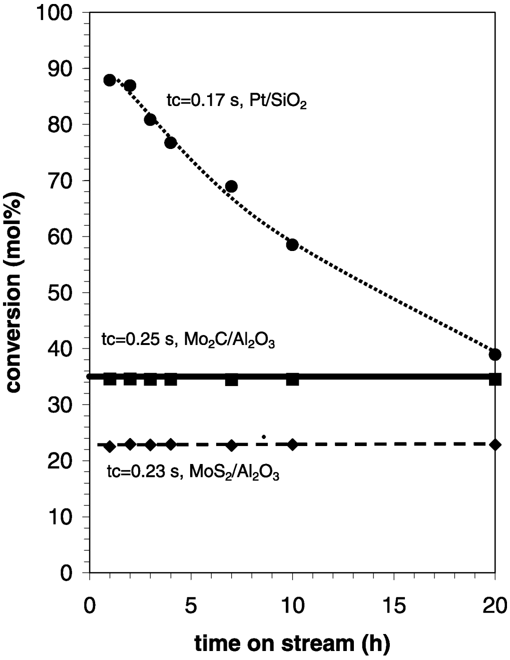

Figure 3. Deactivation of catalysts during HDS of 4,6-DMDBT. Conversion of 4,6-DMDBT versus time on stream.

4. Conclusions

Mo_2C/Al_2O_3 catalysts show a catalytic behavior in HDS completely different from that of MoS_2/Al_2O_3 and Pt/SiO_2. Mo_2C/Al_2O_3 favors the DDS pathway for the HDS of 4,6-DMDBT, which is not expected, because molybdenum carbides are good hydrogenation catalysts. Mo_2C/Al_2O_3 is more active than MoS_2/Al_2O_3 with regard to overall HDS, HYD and DDS rates. Both catalysts are stable in HDS runs. Mo_2C/Al_2O_3 could replace alumina-supported molybdenum sulfide at low sulfur levels for deep HDS of refractory compounds. On the contrary, supported noble metal-based catalysts are active but not stable at these levels of sulfur.

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