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Effect of synthesis conditions on the molybdenum nitride catalytic activity

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Abstract

Properties of the molybdenum nitrides supported on alumina as well as on active carbon has been investigated in the reactions of thiophene and vacuum gas oil (VGO) hydrodesulfurization (HDS) as well as in the reaction of cyclohexene with hydrogen. Supported molybdenum nitride was more active in thiophene hydrogenolysis than sulfided Mo/Al_2O_3. Also in the reaction of VGO HDS alumina supported molybdenum nitride was more active than sulfided counterpart, however Mo_2N supported on active carbon exhibit low activity. In the products of the cyclohexene reaction over supported Mo_2N methyl-cyclopentanes and benzene has been found. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum nitride; Hydrodesulfurization; Isomerization

1. Introduction

Typical catalysts most frequently used for HDS and hydrodenitrogenation (HDN) of crude oils consist of a sulfided combination of either Co or Ni with either Mo or W, supported on alumina oxide. These catalysts posses high hydrogenation activities and are typically not sufficiently efficient in removing sulfur, nitrogen and oxygen from heavy oil fractions. Therefore, new hydrotreatment catalysts are being developed that can efficiently remove unwanted heteroatoms.

Transition metals nitrides and carbides has been extensively studied because of their unique catalytic properties since analogies with noble metals catalysts were observed. Nitrides and carbides are now well recognized as substitutes for noble metals, one of their main properties being strong hydrogenating function [1]. It is known that such strong hydrogenating function is necessary for deeper HDS/HDN treatment of fuels.

The introduction of nitrogen (carbon) atoms into the lattice of an early transition metal leads to an increase of the d electron density of this metal at the Fermi level and properties of Mo_2N (Mo_2C) shift towards those of noble metals [2]. Furthermore, during passivation step following nitride (carbide) preparation and before exposure to air, oxygen is incorporated into their lattice and as a consequence acidic function can appear.

It has been shown in many reports that molybdenum nitrides exhibit catalytic activity for HDS and HDN reactions and might offer an interesting alternative to existing catalysts. Thompson and co-workers [3] has shown that molybdenum nitrides and carbides are more hydrogen efficient for quinoline HDN and dibenzothiophene HDS than commercial sulfide catalyst. A nitrided Mo/Al_2O_3 catalyst was reported to be about three times more active in the HDN of carbazole than the sulfided and reduced Mo/Al_2O_3 [4]. Nagai et al. [5] have stated that alumina-supported nitride catalyst was more active for HDS of dibenzothiophene

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with significantly less consumption of hydrogen, than corresponding sulfide.

The purpose of the research described in this paper was to screen for the influence of some of the synthesis parameters on the catalytic properties of molybdenum nitride.

2. Experimental

Supported molybdenum nitrides were prepared by temperature programmed reduction of oxidic precursor with ammonia. Oxidic catalyst precursor containing 16% of MoO_3 were prepared on the γ-Al_2O_3 (supplied by HYDROMET Ltd., $S_{BET} = 234\,m^2/g$, medium pore diameter = 4.2 nm) or on the active carbon (type A supplied by CIECH, $S_{BET} = 815\,m^2/g$) by the wet impregnation method. After drying 24 h at 383 K catalyst supported on the alumina was heated for 4 h at 823 K in the air; the active carbon supported catalyst was heated under nitrogen flow. Oxidic catalyst precursors prepared in this way were used for nitridation or sulfidation.

The nitridation was performed in the stainless steel reactor according to the Volpe–Boudart [6]. Oxidic precursor charged into reactor was treated with flowing air for 4 h at 723 K. Then sample was linearly heated from room temperature to 773 or 973 K with heating rate 150 K/h in the NH_3 stream. Sample was maintained at the final temperature for 2 h then cooled down to room temperature and passivated by allowing to contact air through open ends of the tube. Conditions of the catalysts preparation are summarized in Table 1.

Catalytic properties of the prepared catalysts were determined in the HDS reactions of thiophene and of vacuum gas oil (VGO) as well as in the reaction of cyclohexene transformations.

Hydrodesulfurization (HDS) of thiophene over investigated catalysts was carried out in the gradientless stainless steel micro-reactor with internal recycle flow system. Conditions of the thiophene HDS test: temperature 673 K; catalyst weight 1 g (0.25–0.43 mm fraction), hydrogen flow $12\,dm^3/h$, pressure 0.1 MPa, thiophene concentration 4.5 vol.%.

Table 1
Conditions of molybdenum nitride synthesis

Procedure	Heating rate (K/h)	Final temperature of nitriding (K)	$GHSV_{NH_3}$ (h^{-1})
P1	150	773	1000
P2	150	773	15000
P3	150	973	15000

To compare the catalytic activity of the nitrided and the sulfided catalysts, sulfidation of the oxidic precursors was performed as well by 4 h exposure of the oxidic catalyst precursor in the stream of 4.5 vol.% thiophene in hydrogen at 673 K.

HDS of VGO containing 0.705 wt.% of sulfur over investigated catalysts was carried in a high-pressure stainless steel flow fixed bed reactor. Catalyst particles of $3\,cm^3$ of 0.60–0.80 mm in size diluted with $3\,cm^3$ of inert alumina, were introduced into the reactor. The reactor was operated at a pressure of 4.1 MPa, a temperature 613 and 633 K, an $LHSV = 1.5\,h^{-1}$ and a ratio $H_2/feed = 500\,Nm^3/m^3$. The activities reported were obtained after a period of 8 h operation. Sulfidation of catalyst was performed before a reaction run using a VGO at $p = 4.1$ MPa, $T = 653$ K for 8 h.

Measurements of the activity of the prepared catalysts for skeletal isomerization of cyclohexene (test reaction for acidic function) were carried out in the pulse micro-reactor connected with GC. Conditions of the cyclohexene test: $T = 593$–653 K, hydrogen flow = $4.8\,dm^3/h$, catalyst volume = $1\,cm^3$ (0.16–0.3 mm).

The BET surface areas were measured using nitrogen thermodesorption method. SEM studies were performed using ISM 5800 LV (JEOL) scanning microscope.

3. Results and discussion

Results of the investigation of the catalytic properties of the prepared molybdenum nitride catalysts are shown in Tables 2–4 and Figs. 1–3.

Table 2 shows some properties of the supported molybdenum nitride catalysts in relation with properties of the alumina supported sulfided molybdenum catalyst. Nitrided molybdenum is more active in the thiophene HDS than its sulfided form. Just like it in the case of unsupported catalysts [7], ammonia space velocity during nitridation, strongly affects the thiophene conversion over resulted catalyst. Nitridation of Mo/Al_2O_3 under low ammonia GHSV (procedure P1)

Table 2
Properties of supported oxynitrides and sulfides

Support/activation procedure	Surface area of pores with radius 1.5–100 nm (m^2/g)	Thiophene conversion (%)	Specific rate of thiophene HDS × 10^8 (mol/m^2 s)
Al_2O_3/S[a]	208	54	0.21
Al_2O_3/P1	212	42	0.16
Al_2O_3/P2	206	68	0.27
Al_2O_3/P3	196	71	0.30
C/P1	86	49	0.47
C/P2	86	75	0.72
C/P3	84	76	0.74

[a] Four hours of sulfidation in the stream of 4.5 vol.% thiophene in hydrogen at 673 K.

Table 3
Results of cyclohexene test

Catalyst support/activation procedure	Temperature (K)	Conversion (%)	Selectivity to (%)			
			Me–C_5[a]	Cracking	Hexenes	Benzene
Al_2O_3	593	32.0	96	0	4	0
	623	53.4	93	0	7	0
	653	66.2	84	0	16	0
Al_2O_3/P2	593	27.8	92	5	3	0
	623	38.2	86	7	6	1
	653	51.5	79	10	7	4
C/P2	593	6.5	100	0	0	0
	623	13.5	100	0	0	0
	653	20.7	95	2	0	3

[a] Methyl-cyclopentenes + methyl-cyclopentane.

leads to catalyst with lower HDS activity than its sulfidation. Specific rates of thiophene HDS over alumina supported catalysts are similar to each other and they are distinctly smaller than those ones obtained over active carbon supported ones. It suggests that interaction between support and molybdenum is one of the main factors influencing catalytic activity of the investigated catalysts.

Table 4
Results of the HDS of VGO tests on the investigated molybdenum catalysts

Temperature (K)	Catalyst support/activation	Desulfurization (%)
593	Al_2O_3/S	39
	Al_2O_3/P2	44
	C/P2	28
613	Al_2O_3/S	60
	Al_2O_3/P2	65
	C/P2	38
633	Al_2O_3/S	73
	Al_2O_3/P2	79
	C/P2	47

Active carbon supported molybdenum nitride catalyst provide higher conversion of thiophene than alumina supported one. The difference in activity can be explained by a different degree of Mo dispersion, however large part of carbon carrier surface area is generated by narrow pores ($r < 1.5$ nm) which can be inaccessible for thiophene molecules (as well as for active phase precursor). It seems that rather strong interaction alumina–molybdenum oxide decreases amount of MoO_3 accessible for nitridation. Active carbon posses more inert than alumina chemical character of the surface so MoO_3 supported on it is more easily transformed into nitride than it goes on alumina. This conclusion is confirmed by fact that catalyst C/P2 exhibits nearly the same

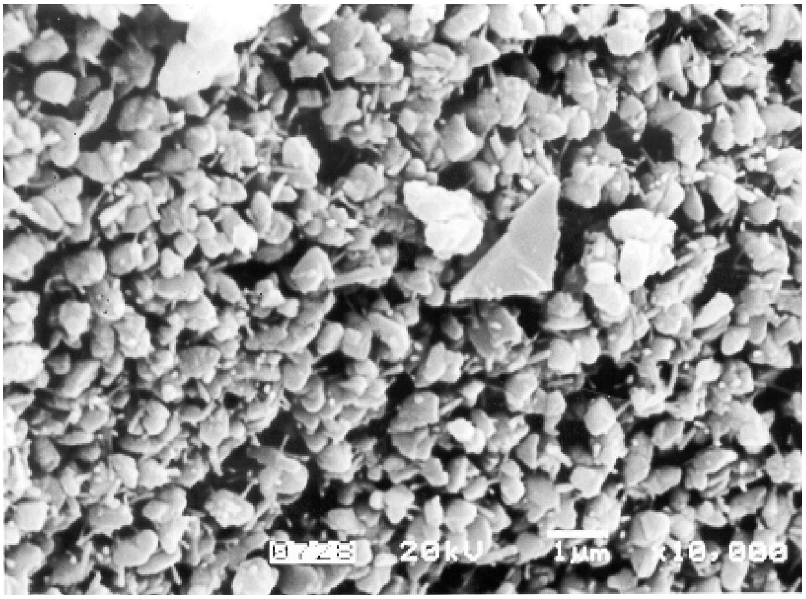

Fig. 1. Representative SEM image of the nitrided MoO_3 [7].

activity like catalyst C/P3 which was nitrided at higher temperature. Differences in catalytic activity between Al_2O_3/P2 and Al_2O_3/P3 are more pronounced (Table 2) what means that alumina supported catalyst needs higher temperature of nitridation than the active carbon supported counterparts. It seems that higher thiophene HDS activity of the carbon supported Mo_2N catalyst can be explained by the weak

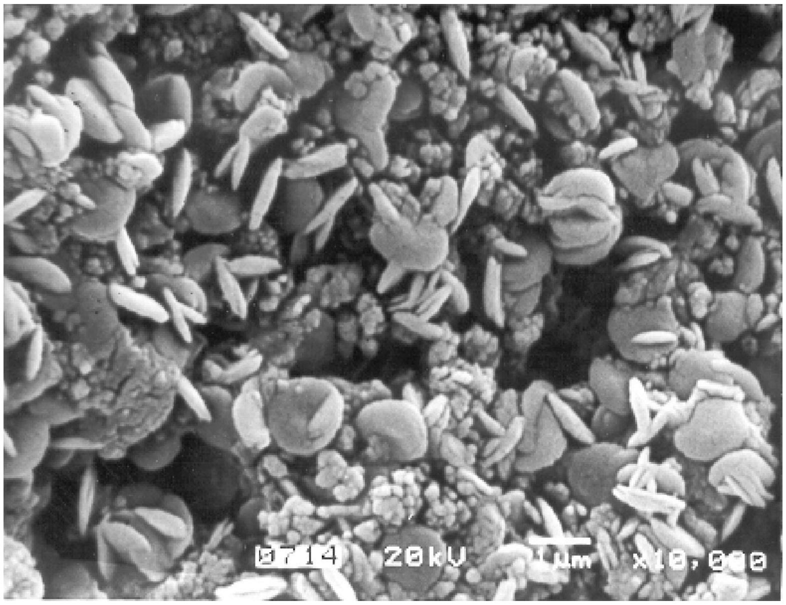

Fig. 2. Representative SEM image of the nitrided Mo/C/P2 sample.

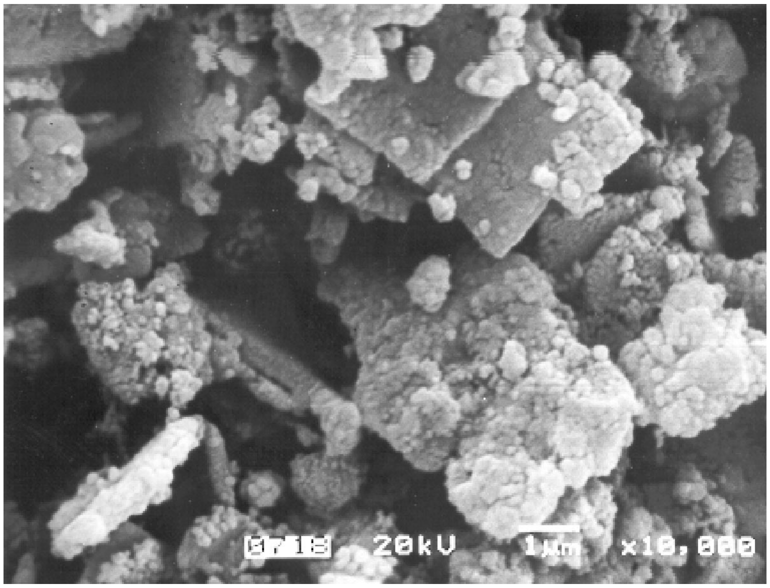

Fig. 3. Representative SEM image of the nitrided Mo/Al_2O_3/P2 sample.

interaction of oxidic molybdenum precursor with carbon surface. Similar effect was observed in the case of carbon supported sulfided Mo catalysts [8].

SEM images of the surface of Mo_2N, Mo/C/P2 and Mo/Al_2O_3/P2 catalysts are shown, respectively, in Figs. 1–3. In Fig. 1 well-ordered particles representing Mo_2N are seen [7]. The molybdenum nitride sample seen on this picture was prepared from unsupported MoO_3 at ammonia GHSV $= 10000\,h^{-1}$, heating rate 150 K/h (Fig. 1) and final temperature of nitriding 973 K [7]. Well dispersed particles with the shape similar to the shape of the unsupported Mo_2N particles, though smaller in size, are seen on the surface of Mo/C/P2 catalyst (Fig. 2). In the case of alumina supported catalyst small particles of Mo_2N seem to be more agglomerated (Fig. 3).

Results of the reaction of cyclohexene with hydrogen over investigated catalysts are shown in Table 3. Skeletal isomerization of cyclohexene proceeds only on catalysts having strong acid centers [9]. Composition of the products of this reaction indicate that three types of reaction proceed simultaneously: isomerization to five-membered ring, opening of the cyclohexene ring to *n*-hexene and cracking. Small amounts (∼1–2%) of benzene as well as of methyl-cyclopentane were also registered in the products of reaction carried over Mo_2N at the highest temperature of the test. No cyclohexane was registered in the products (probably due to low pressure). Yield of methyl-cyclopentane was added the yield of methyl-cyclopentene. The results given in Table 3 show that alumina support is the most active sample in the cyclohexene transformation (active carbon was inactive in this reaction). Alumina supported molybdenum nitride is somewhat less active. It can be concluded that alumina posses the largest number of strong acid centres.

Composition of the reaction products obtained over alumina differ from the composition of the products obtained over supported Mo_2N. The main product of the cyclohexene reaction over Al_2O_3 were methyl-cyclopentenes and hexenes. In the case of Mo_2N/Al_2O_3 composition of the reaction products was more complicated, the main products were: methyl-cyclopentenes, methyl-cyclopentanes, lower hydrocarbons (cracking products) and small amounts of hexenes. Small amounts of benzene which were found in the products of the reaction over nitrided catalysts indicate that the dehydrogenation of cyclohexene takes place over Mo_2N. This reaction is characteristic for catalysts with metallic character. Mo_2N supported on the active carbon exhibits the lowest activity in cyclohexene transformation and only small amounts of methyl-cyclopentenes and methyl-cyclopentanes were registered in the reaction products. Results of the cyclohexene test confirm that catalytic properties of molybdenum nitride are similar to the properties of noble metals based catalysts. Additionally it should be pointed out that nitrides are sulfur resistant. Acid function of the supported molybdenum nitride is determined mainly by the type of support.

Activity of the catalysts nitrided according to procedure P2 was tested in the reaction of VGO HDS and compared with activity of the sulfided Mo/Al_2O_3. As it is seen in Table 4, nitrided Mo/Al_2O_3 appears to be more active in the HDS of VGO than its sulfided form. Nitrided molybdenum catalyst supported on active carbon is distinctly less active in the HDS of VGO than the rest of the investigated catalysts. Although active carbon used in this investigation posses surface area S_{BET} 815 m^2/g however total area of mesopores was only 94 m^2/g. So this material is characterized by narrow pore structure. It seems that low activity of C/P2 in VGO HDS can be explained in part by narrow pore structure of the carrier and diffusion limitations. The active phase sintering cannot be excluded on the active carbon surface.

4. Conclusions

1. Catalytic activity of the molybdenum nitride is affected by the ammonia space velocity during nitridation and by the type of support.
2. Active carbon as a support of Mo_2N ensure higher than alumina catalytic activity in the reaction of thiophene HDS. Specific rate of thiophene HDS over the supported molybdenum nitride is lower than over alumina supported MoS_2.
3. Acidity of the supported nitrided molybdenum catalyst is determined mainly by the properties of the carrier. In the cyclohexene test Mo_2N exhibits metallic character.
4. The nitrided Mo/Al_2O_3 is more active than its sulfided form in the reaction of VGO HDS.

Acknowledgements

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