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Hydrotreating of heavy vacuum gas oil (HVGO) on molybdenum and tungsten nitrides catalytic phases

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Abstract

A series of supported and unsupported Mo_2N and W_2N phases were synthesized by means of the treatment under ammonia atmosphere at 700°C of Mo and W oxides. The X-ray diffraction and electron microscopy techniques verified the formation of the Mo_2N and W_2N ceramic phases, while the N_2 adsorption (BET) was used to determine the surface areas, between 46–133 m^2/g for Mo_2N (unsupported) and 81–101 m^2/g for W_2N (unsupported). The supported phases had surface areas between 109–113 and 109–122 m^2/g, for Mo_2N/Al_2O_3 and W_2N/Al_2O_3, respectively. The catalytic hydrotreating of a heavy vacuum gas oil (HVGO) derived from Maya crude (i.e. 2.21 wt.% S, 0.184 wt.% N_2) was performed on both, supported and unsupported Mo nitrides and W nitrides, which promoted the HDN reaction preferentially, up to 26.6% on Mo_2N/Al_2O_3 and up to 22.3% on W_2N/Al_2O_3, against 3.26% on the reference catalyst, i.e. $CoMo/Al_2O_3$ at 350°C and 80 kg/cm^2. Also, the rates for HDN increased with the crystallite size in the unsupported W_2N series. Also, the pore volume and mean pore diameters of the Mo_2N/Al_2O_3 and W_2N/Al_2O_3 series improve substantially with respect to the pure ceramic phases.

Keywords: Metal transition nitrides; Molybdenum; Tungsten; Hydrotreating

1. Introduction

The increasing abundance of heavy oil fractions in the refinery, together with more strict environmental regulations comprising the emission of SO_x, NO_x, CO and the refractory polyaromatic compounds, have motivated an intensive research on new catalytic materials for upgrading the properties of gasoils [1]. Also, the general trends in refineries point towards the treatment of heavier crude fractions having a higher concentration of vacuum residuals and asphaltenes, as well as a higher proportion of heteroatoms like sulfur, nitrogen, oxygen and metals (Ni,V). Then, the catalytic hydrotreating process becomes a crucial step in the refining scheme, either for the sulfur removal or the saturation of aromatic rings, motivating further development of new catalytic systems. In this respect, the transition metal nitrides, like Mo_2N and W_2N, are being proposed as alternative systems for obtaining higher thermal resistance properties with respect to the conventional catalytic systems based on supported Ni–Mo and CoMo sulfides [2–4]. In this work, the textural and structural properties of the Mo and W nitrides were characterized by means of N_2 adsorption at 78 K (BET) and X-ray diffraction, respectively; then, their catalytic properties were tested for HDS and HDN of a heavy vacuum gasoil (HVGO) derived from Maya crude, with the aim of determining the potential usefulness of those materials for the treatment of real feeds having a high sulfur content, i.e. 2.21 wt.%.

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In a subsequent study, a series of experiments are performed separately, using model molecules like thiophene and pyridine, to understand better the mechanisms taking place in the HDT reactions occurring on the Mo_2N and W_2N ceramic phases.

2. Experimental

A series of transition metal nitrides including Mo_2N and W_2N were prepared in the unsupported and supported form by means of the programmed reduction of precursor metal oxides, like MoO_3 and WO_3, following the Volpe–Boudart method, i.e. the oxides were treated under ammonia atmosphere at 700°C. The main variable used in the preparation of the unsupported solids was the space velocity of the carrier gas, from 12 to 128 h^{-1}, while the supported materials were synthesized under constant gas flow, i.e. MHSV = 38.74 for alumina-supported W_2N and MHSV = 30.38 for alumina-supported Mo_2N materials, but their metal loadings varied from 5 to 20 wt.%. Also, a series of supported CoMo/catalysts were prepared by means of the incipient wetness technique, using γ-alumina as a carrier (citerion). The structural properties of the nitrides were characterized by means of X-ray diffraction using a Siemens D-500 diffractometer and a Jeol-100CX electron microscope. The textural properties were determined by means of the adsorption of N_2 at 78 K (BET method), using a Micromeritics ASAP-2000 instrument. The catalytic properties of these materials were tested in a batch type reactor for HDS/HDN activity in the conversion of an HVGO derived from Maya crude (2.21 wt.% S and 0.184 wt.% N_2), at 350°C, under 80 kg/cm^2 and stirring at 210 rpm for 3 and 5 h, respectively.

3. Results and discussion

Table 1 shows the initial synthesis conditions and the bulk final properties of the unsupported and supported catalysts, while Figs. 1 and 2 show the X-ray diffraction patterns (XRD) of the Mo and W series, respectively. The phases γ-Mo_2N and β-W_2N were identified clearly from these patterns and were verified at a microscopic scale by means of electron diffraction in the transmission electron microscope (TEM). The

Table 1
Effect of the molar space velocity (MHSV) on the textural properties of the unsupported and supported materials

Catalyst	Flow NH_3 (μmol/s)	MHSV (h^{-1})	Surface area (m^2/g)[a]	Average pore size (Å)[a]	Pore volume (cm^3/g)	Crystal size (1 1 1) (Å)[b]
MN-SA	50	12.66	12	104	0.032	145
MN-SB	70	17.76	28	133	0.010	142
MN-SC	90	22.90	30	69	0.052	151
MN-SD	100	25.32	54	73	0.098	102
MN-SE	120	30.38	72	46	0.084	96
WN-SA	100	32.28	46	84	0.010	62
WN-SB	120	38.74	44	99	0.010	68
WN-SC	180	59.04	48	81	0.010	66
WN-SD	70	22.63	41	101	0.104	65
WN-SE	50	16.14	41	98	0.109	65
WN-05/Al_2O_3	120	38.74	229	109	0.630	–
WN-10/Al_2O_3	120	38.74	229	109	0.632	–
WN-15/Al_2O_3	120	38.74	199	122	0.601	–
WN-20/Al_2O_3	120	38.74	196	110	0.553	–
MN-05/Al_2O_3	120	30.38	223	113	0.634	–
MN-10/Al_2O_3	120	30.38	214	111	0.604	–
MN-15/Al_2O_3	120	30.38	196	110	0.545	–
MN-20/Al_2O_3	120	30.38	195	109	0.532	–

[a] From BET analysis.
[b] From XRD analysis.

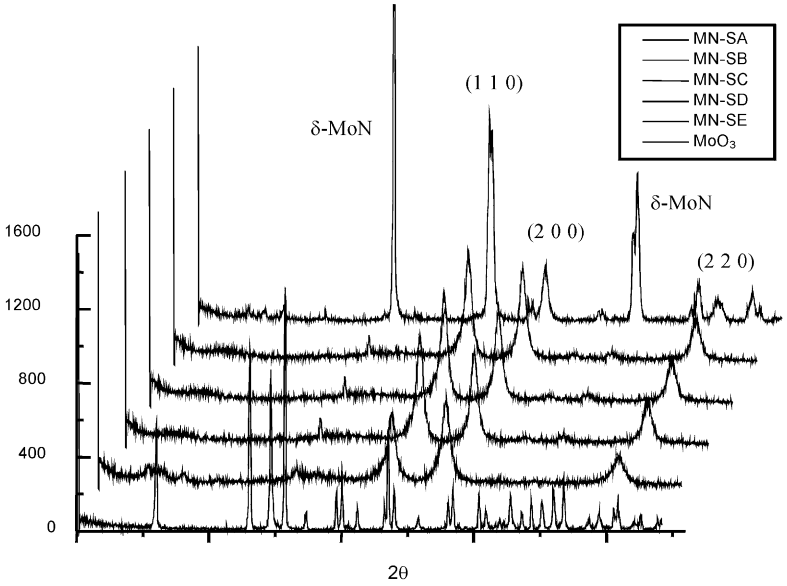

Fig. 1. X-ray diffraction patterns of the Mo nitrides.

unsupported solids show the typical X-ray diffraction peaks corresponding to the γ-Mo_2N phase, i.e. (1 1 1), (2 0 0) and (2 2 0), at 37.4, 43.5 and 63 (°2θ) and the typical series of β-W_2N phase at 37.8, 43.9 and 63.8 (°2θ), while the XRD patterns of the supported catalysts showed the presence of similar phases.

The HDS and HDN reactions were carried out in a batch type reactor for 3 h, after the activation

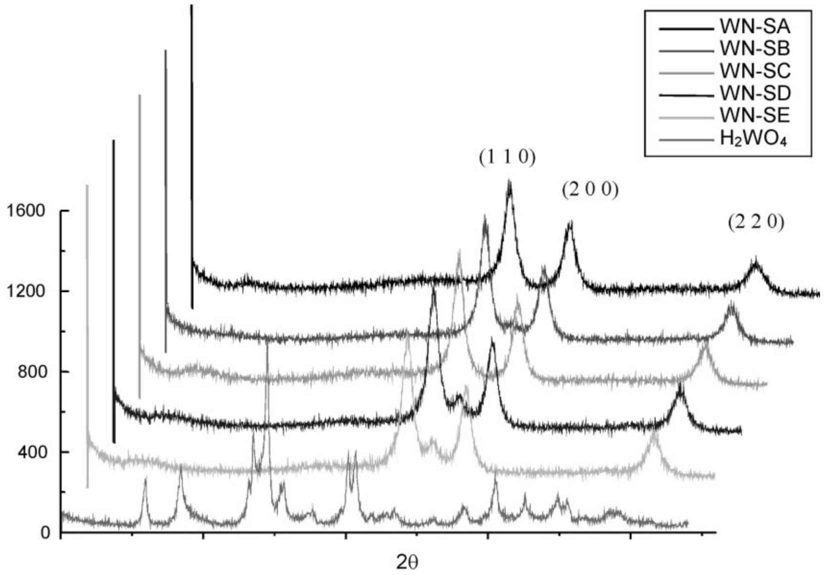

Fig. 2. X-ray diffraction patterns of the W nitrides.

Table 2
HDS/HDN activity (%) of unsupported and supported materials for HVGO conversion at 350°C, 80 kg/cm^2, 210 rpm (after 3 h)[a]

Catalysts	S (wt.%)	N (wt.%)	HDS (%)	HDN (%)	Ni (ppm)	V (ppm)
HVGO	2.21	0.184	–	–	0.1	0.80
Blank	2.18	0.183	1.35	0.54	0.098	0.80
$CoMo/Al_2O_3$	1.83	0.178	17.20	3.26	<0.05	0.27
MN-SA	2.13	0.099	3.62	46.19	<0.05	0.43
MN-SB	1.89	0.121	14.47	34.23	<0.05	0.52
MN-SC	1.99	0.126	9.95	31.52	<0.05	0.28
MN-SD	1.96	0.119	11.31	35.32	<0.05	0.27
MN-SE	1.90	0.138	14.02	25.00	<0.05	0.38
WN-SA	2.13	0.110	3.62	40.21	<0.05	0.15
WN-SB	2.07	0.105	6.33	42.93	<0.05	0.32
WN-SC	2.12	0.116	4.07	36.95	<0.05	0.52
WN-SD	2.02	0.101	8.59	45.10	<0.05	0.11
WN-SE	2.03	0.103	8.14	44.02	<0.05	0.10
$MoN-05/Al_2O_3$	2.05	0.180	7.23	2.22	<0.05	0.25
$MoN-10/Al_2O_3$	1.98	0.166	7.69	9.78	<0.05	0.16
$MoN-15/Al_2O_3$	1.97	0.138	10.85	25.00	<0.05	0.28
$MoN-20/Al_2O_3$	1.90	0.135	14.02	26.60	<0.05	0.21
$WN-05/Al_2O_3$	2.12	0.178	4.50	3.26	<0.05	0.37
$WN-10/Al_2O_3$	2.10	0.154	4.97	16.30	<0.05	0.24
$WN-15/Al_2O_3$	2.01	0.150	9.04	18.47	<0.05	0.42
$WN-20/Al_2O_3$	1.99	0.143	12.66	22.28	<0.05	0.36

[a] The percentage of S, N and Ni, V corresponds to the residual content.

of the solids under hydrogen flow (4 l/h) for 1 h. Only the unsupported catalysts having the proper textural properties were tested during 3–5 h. In the temperature interval used, the pressure increased up to 220 kg/cm^2. Table 2 contains the main conversion data in the HDS/HDN reactions for the unsupported and supported materials. These results show that the activity of the transition metal nitrides, in the HDN reaction, was superior to the blank runs and to the reference catalysts tested under similar conditions. The lower surface area of the Mo and W nitrides that were prepared under high MHSVconditions, seems related to a lower rate for HDN, but these materials showed also a higher activity with respect to the supported CoMo sulfides.

All the catalysts series were active for sulfur removal (HDS), but the Mo based nitrides showed the highest rates. Excepting the MN-SB materials, the relative activity of the catalysts increased with the diminution of the crystal size. In comparison, the behavior of the W nitrides was similar to the Mo nitrides series, both having an equivalent crystal size. All the unsupported catalysts were found active for the removal of metals (Ni,V), the final Ni content being about 20% with respect to the original content in the feed; i.e., the final Ni content was about 0.05 ppm. The W nitrides (WN series) showed HDM rates (hydrodemetallization) higher than the CoMo sulfides (i.e. from $CoMo/Al_2O_3$), especially for V removal, but the rest of the catalysts did not show any further improvement with respect to the reference catalyst.

Table 3 shows the concentration of asphaltenes and aromatics, as well as the physical properties of the products. One observes that the product quality improves significantly on the supported $CoMo/\gamma\text{-}Al_2O_3$ catalysts, and the Mo and W nitrides show a lower hydrogenation rate for aromatics. However, the asphaltenes proportion diminished more rapidly in the case of the Mo nitrides, with respect to the W nitrides and CoMo sulfides. In contrast to this behavior, the nitrides prepared under MHSV conditions seem very similar to the reference catalysts. Also, the

Table 3
Properties of the products derived from HVGO reaction at 350°C on unsupported and supported Mo,W nitrides

Catalysts	Specific gravity (20/4°C)	Gravity (°API)	Ramsbottom carbon (wt.%)	Asphaltenes (wt.%)	Aromatics (wt.%)
HVGO	0.9187	22.05	0.10	2.5	32.5
Blank	0.9172	22.27	0.37	2.3	32.2
$CoMo/Al_2O_3$	0.9167	22.07	0.22	2.1	27.9
MN-SA	0.9162	22.30	0.25	1.8	30.5
MN-SB	0.9161	21.57	0.20	2.0	29.4
MN-SC	0.9165	22.42	0.17	1.9	29.7
MN-SD	0.9181	22.15	0.16	1.7	29.7
MN-SE	0.9174	22.27	0.17	1.8	29.8
WN-SA	0.9180	22.17	0.23	2.1	31.0
WN-SB	0.9181	22.15	0.24	2.0	31.0
WN-SC	0.8935	26.35	0.25	1.8	31.4
WN-SD	0.9175	22.25	0.25	1.7	31.1
WN-SE	0.9089	22.14	0.23	1.8	31.6
$MoN-05/Al_2O_3$	0.9191	21.95	0.20	2.32	32.3
$MoN-10/Al_2O_3$	0.9169	22.32	0.23	2.31	32.1
$MoN-15/Al_2O_3$	0.9183	22.25	0.25	2.12	31.6
$MoN-20/Al_2O_3$	0.9182	22.10	0.39	2.09	30.5
$WN-05/Al_2O_3$	0.9176	22.20	0.26	2.10	32.5
$WN-10/Al_2O_3$	0.9152	22.59	0.23	2.37	32.4
$WN-15/Al_2O_3$	0.9156	22.60	0.25	2.20	32.0
$WN-20/Al_2O_3$	0.9153	22.37	0.27	2.18	32.1

Ramsbottom carbon content in the products increased as a consequence of the residual coke formation after the reaction. This effect was also observed in the rest of the catalysts.

Also, Table 2 contains the results of the catalytic activity of the supported nitrides, in function of the metal concentration (5, 10 15 and 20 wt.% Mo, W). The catalysts having 20 wt.% metal content (Mo,W) showed the highest activity in the whole series, which is probably due to a consequence of their higher concentration of the corresponding metals. However, their conversion was lower than the CoMo sulfided catalysts, possibly due to the promoting action of cobalt.

The main properties of the products are reported in Table 3. In all cases, only a slight diminution of the asphaltenes and the aromatics content occurs on the supported materials, which could be attributed to diffusion effects in the support. Also, those catalysts showed a similar behavior for the removal of V and Ni, with respect to the initial metal content in the feedstock, e.g., the final concentration of Ni and V was down to about 80 wt.% for the catalyst $Mo_2N/\gamma\text{-}Al_2O_3$ — 10.

4. Conclusions

The preparation of catalytic materials based on the transition metal nitrides was successfully achieved using high temperature (i.e. 700°C) nitration of Mo oxides and W oxides. The textural properties of the supported materials were developed for obtaining a surface area up to 229 m^2/g and a pore volume around 0.5 cm^3/g, which are adequate for carrying out the HDS and HDN catalytic reactions of HVGO derived from Maya crude (i.e. up to 2.21 wt.% S and 0.184 wt.% N_2). These catalysts showed less activity for the sulfur removal from HVGO, with respect to the reference catalyst (i.e. CoMo/alumina) under similar operation conditions. However, the ceramic materials were more active for HDN than their industrial counterparts [5]. The results are coincident with other reports [6], which indicated that Mo_2N is highly selective in the hydrodenitrogenation of quinoleine. Also, the hydrogenation properties and stability of these nitrides was superior [3] than sulfided $CoMo/Al_2O_3$ catalysts. Then, the present work extends those previous results to the HDN of real feedstock, for assessing the like the HVGO derived from Maya crude.

The influence of the surface area of the unsupported Mo_2N and W_2N materials, on their catalytic properties, was not significant, but the crystal size seemed to contribute to the catalytic activity of these solids. The activity for HDS and HDN observed in the transition metal nitrides studied here, is more probably linked to the metal character of those ceramic phases, which might play a role in the dehydrogenation–hydrogenation of the hydrocarbon molecules involved in those reactions, together with the subsequent removal of their heteroatoms. Further work is underway to study more specifically the active phases being present on the nitrides, as well as the influence of some reaction variables in the product distribution and yields. The pore size values reported in Table 2 are more probably arising from interparticle pores, rather than micropores, and that is why the values corresponding to the unsupported and supported materials are so similar.

Further Reading

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