

Synthesis, Characterization, and Reactivity Studies of Supported Mo₂C with Phosphorus Additive

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Received June 2, 1997; revised December 11, 1997; accepted January 20, 1998

The effect of phosphorus on Mo₂C supported on γ -Al₂O₃ and activated carbon was studied. The catalysts were characterized by CO chemisorption, BET surface area measurements, X-ray diffraction, X-ray photoelectron spectroscopy, and near-edge X-ray absorption fine structure, and tested for their reactivity for hydroprocessing reactions, particularly hydrogenation, hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), using model liquid compounds. The P-containing catalysts had higher reactivity for HDN than those without P. HDS was higher when the Mo₂C was synthesized on γ -Al₂O₃ previously treated with P than when the Mo component and P were added together on γ -Al₂O₃. Postreaction characterization indicates that the catalysts were tolerant of sulfur. © 1998

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INTRODUCTION

It is well documented that sulfided catalysts with additives are used in hydrotreating reactions such as hydrogenation (HYN), hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetallization (HDM) (1–6). Additives such as P have a promotional effect when added to the oxide forms of the catalyst (1–6) and this effect is typically explained in terms of dispersion of the metal salts on the support, modification of acid sites or formation of a new active phase (7–9). Clearly, little agreement exists in the literature on these effects. In recent years the application of transition metal carbides and nitrides for hydrotreating reactions has been studied in great detail (10–22). There has also been some work on supported carbides and nitrides (23–30). However, information available on the effect of additives on transition metal carbide catalysts and their reactivity for hydrotreating reactions is very limited (31). In this paper the synthesis and characterization of Mo₂C on γ -Al₂O₃ and an activated carbon support and the effect of phosphorus additive are reported. The catalysts were synthesized by a temperature-programmed reaction method and were characterized by CO chemisorption,

BET surface area measurements, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and near-edge X-ray absorption fine structure (NEXAFS). The reactivity of the catalysts for simultaneous HYD of quinoline, HDN of quinoline, and HDS of dibenzothiophene are reported. In addition, postreaction composition is also discussed.

EXPERIMENTAL

The supports used in this study were γ -Al₂O₃ (surface area 260 m² g⁻¹, Akzo Nobel) and activated carbon (500 m² g⁻¹, Aldrich Chemical Co.). The precursor for MoO₃ was (NH₄)₆Mo₇O₂₄ · 4H₂O (Aldrich Chemical Co., ACS grade) and for P was (NH₄)₂HPO₄ (Aldrich Chemical Co., 99%). The chemicals used in the reactivity study were dibenzothiophene (Aldrich, 99.5%), quinoline (Aldrich Chemical Co., 99.9%), benzofuran (Aldrich Chemical Co., 99.9%), tetralin (Aldrich Chemical Co., 99.5%), amylbenzene (Aldrich Chemical Co., 99.5%) and tetradecane (Jansen Chimica, 99%). The gases used were 20% CH₄/H₂ (Airco, UHP Grade), He (Airco, Grade 5.0), CO (Linde Research Grade, 99.97%), 0.5% O₂/He (Airco, UHP Grade), and H₂ (Airco, Grade 5.0). A Ni–Mo–S/Al₂O₃ sample (Shell 324) was sulfided *in situ* in a 10% H₂S/H₂ stream at 723 K for 3 h prior to reaction.

Synthesis

Supported carbide catalysts were synthesized from supported oxides by a temperature-programmed reaction method in which the sample reacts with a reducing gas stream while the temperature is raised progressively. The supported oxides were obtained from the precursors impregnated by the incipient wetness technique. The phosphorus additive was added to the catalyst by two methods: (i) the co-impregnation of the precursors on the support and (ii) the impregnation of ammonium molybdate on the P-treated support.

The synthesis of the supported carbides was carried out in two stages. The first stage involved the synthesis of the supported MoO₃ and the second stage involved temperature-

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programmed reaction of the MoO_3 to obtain the supported Mo_2C . Three types of supported MoO_3 samples were synthesized. The first had only MoO_3 impregnated on a support ($\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ or MoO_3/C). The second had both MoO_3 and the P additive co-impregnated on the support ($\text{MoO}_3\text{-P}/\gamma\text{-Al}_2\text{O}_3$). The third had MoO_3 deposited on a support which had been previously treated with the additive ($\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3\text{-P}$). The first type of supported MoO_3 was synthesized by impregnating a solution of ammonium molybdate in water on the support by the incipient wetness technique. The impregnated sample was air dried for 5 h and calcined in air at 723 K for 2 h, and then cooled to room temperature. Because of solubility limits of the precursors, the impregnation and calcination was done in two stages: in the first stage 55% and in the second stage 45% of the total loading was impregnated and then calcined. The second type of supported MoO_3 was synthesized by dissolving ammonium molybdate and ammonium phosphate in an amount of water calculated to give incipient wetness, and co-impregnated on the support. Again, the total loading was added in two stages, 55% in the first and 45% in the second. After each stage the sample was air dried for 5 h and calcined at 723 K for 2 h. The third type of supported MoO_3 was synthesized by first impregnating a solution of ammonium phosphate on the support, air drying for 5 h and calcining at 723 K for 2 h and cooling to room temperature. This was followed by impregnating a solution of ammonium molybdate on this P-treated support, air drying for 5 h, calcining at 723 K for 2 h, and finally cooling to room temperature.

The supported Mo_2C samples ($\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$, $\text{Mo}_2\text{C}/\text{C}$, $\text{Mo}_2\text{C-P}/\gamma\text{-Al}_2\text{O}_3$, $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3\text{-P}$) were synthesized by a temperature-programmed reaction between the supported MoO_3 (synthesized as described above) and a methane/hydrogen gas mixture in a flow reactor system. The supported oxide was transferred to a quartz reactor, which was heated by a clam shell furnace (Applied Test Systems, Inc. Series 3210) controlled by a temperature programmer (Omega, Model CN2000). A 20% CH_4/H_2 gas mixture was passed through the reactor and the temperature was increased in a linear manner from room temperature to 1000 K and held for 0.5 h. The sample was cooled in a He gas stream and passivated in a 0.5% O_2/He gas flow to form a protective oxide layer on the surface of the carbide. The outlet gas was monitored by a mass spectrometer (AMETEK Dycor, Model MA100). The passivation was performed until a steady state O_2 signal was obtained in the mass spectrometer, indicating O_2 was no longer being consumed in the passivation process.

Characterization

The synthesized catalysts were characterized by CO chemisorption, surface area measurements, XRD, XPS,

and NEXAFS. Before the adsorption measurements the passivated sample was reduced in a 10% H_2/He gas mixture at 723 K for 2 h and cooled in He gas to room temperature. Then CO chemisorption was followed by BET surface area determinations at 77 K. XRD analysis of the fresh and spent catalysts was carried out using a powder diffractometer (Scintag, Model ASC0007 with a $\text{CuK}\alpha$ monochromatized radiation source), operated at 45 kV and 40 mA. XPS (Perkin Elmer, Model 5600 ci XPS/Auger, Mg source) analysis of the fresh and spent $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3\text{-P}$ catalysts was performed to study the change in surface characteristics after the hydrotreating reaction. Measurements were carried out without any pretreatment except for washing of the spent samples with n-hexane. The C 1s peak at 285 eV was taken as the reference for the binding energy. NEXAFS measurements of supported Mo_2C catalysts were carried out at the U1 beamline of the National Synchrotron Light Source at the Brookhaven National Laboratory. Details regarding the experimental setup for studying powder materials have been described previously (32, 33). In the current study, NEXAFS spectra were recorded by measuring the electron-yield intensity by a channeltron electron multiplier located near the sample holder. To make the electron-yield method more surface sensitive, the entrance of the channeltron was biased by a negative voltage of 100 eV to repel low-energy, secondary electrons (32). Under these conditions the probing depth of the NEXAFS technique near the carbon region is generally in the range 1.0–1.5 nm (34). As described previously (32, 33), powder samples were pressed into a stainless steel sample holder of 6-mm diameter and 1-mm depth. The sample could be heated resistively using two tungsten wires spot-welded onto the back of the sample holder. The chemisorbed surface oxygen on the supported Mo_2C catalysts was removed by heating the samples to 723 K in a stream of H_2 at 8 kPa pressure, and maintaining the temperature and pressure for 0.5 h. The chamber was then evacuated to below 10^{-5} Pa for NEXAFS measurements.

Reactivity

The reactivity of the catalysts for HYD, HDN, and HDS was tested at 3.1 MPa and 643 K in a high pressure reactor system with a trickle-bed reactor using model liquid compounds. HYD refers to the conversion of quinoline to 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, and orthopropylaniline, HDN refers to conversion of quinoline to propylcyclohexane and propylbenzene, and HDS refers to conversion of dibenzothiophene to biphenyl. The liquid feed consisted of 3000 ppm sulfur (dibenzothiophene), 2000 ppm nitrogen (quinoline), 500 ppm oxygen (benzofuran), 5 wt% amylbenzene, 15 wt% tetralin, and the balance tetradecane. The catalysts were in the form of pellets (16/20 mesh) placed in a 316 SS reactor heated by

a fluidized sand bath (Techne, Model SBL-2). Prior to the reactivity study the catalyst was heated in H_2 gas flow at $100\text{ cm}^3/\text{min}$ ($67\text{ }\mu\text{mol s}^{-1}$) at 723 K for 2 h at atmospheric pressure. After the pretreatment, the temperature of the reactor was lowered to 643 K , and the pressure of the system was increased to 3.1 MPa . Liquid feed was introduced to the system at a rate of $5\text{ cm}^3/\text{h}$ with a liquid pump (LDC Analytical, Model NCI 11D5) giving a liquid hourly space velocity (LHSV) of 5 h^{-1} . The H_2 gas flow rate was maintained at $150\text{ cm}^3/\text{min}$ ($100\text{ }\mu\text{mol s}^{-1}$) with a mass flow controller (Brooks, Model 5850 E). An analysis of mass transfer in the system is reported in ref. (35). Liquid samples were collected at regular intervals for 60 h and analyzed by a gas chromatograph (HP, Model 5870) using a flame ionization detector (FID) and a capillary column (CPSIL-5CB, Chrompack Inc.). After the reaction the catalysts were washed in hexane to remove liquid compounds and were dried for postreaction characterization.

RESULTS AND DISCUSSION

Characterization

A summary of the surface properties of the catalysts are given in Table 1. The total surface area of the alumina supported systems is generally slightly smaller than that of the support itself. The exception is the P-treated alumina which shows complete retention of the original surface area. The P apparently stabilizes the support against sintering at the elevated temperatures of carbide formation. XRD patterns of the synthesized catalysts are shown in Fig. 1. Although the features of the support are seen to predominate, the presence of β - Mo_2C (hcp, P63/mmc) on the support can be clearly discerned. From Fig. 2, a change in the Mo_2C morphology can be seen with the addition of P to the support by comparing the intensities of the XRD patterns of different kinds of $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$. The intensity of the Mo_2C peaks in the $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3\text{-P}$ is higher than the catalyst without P, suggesting that the particle size is larger for the former catalyst, even though the support surface area is larger. This result is consistent with a decreased interaction between MoO_3 and $\gamma\text{-Al}_2\text{O}_3\text{-P}$ likely due to the for-

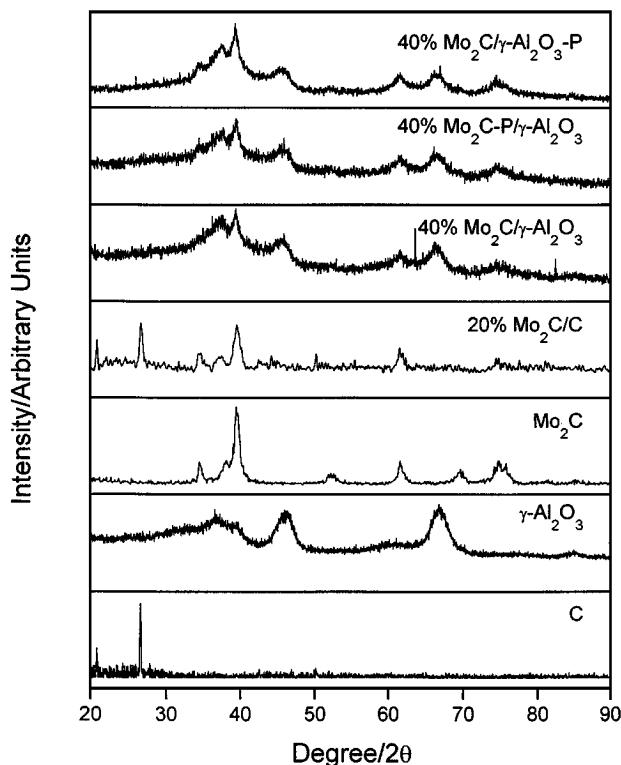


FIG. 1. XRD patterns of supported Mo_2C .

mation of a P layer on the support, causing the formation of larger MoO_3 grains and consequently larger particles of Mo_2C . This phenomenon of interaction was also observed by Zeuthen *et al.* (36), who suggested that this was due to the formation of an AlPO_4 phase. Although, our XRD patterns suggest no evidence for the formation of a phosphate (Al or Mo) on the catalysts, the phosphate may exist as a thin surface layer. Neither Raman nor infrared measurements gave any indication of the formation of a bulk phase. The dispersions of the Mo_2C catalysts are compared in Table 1. It can be seen that the dispersion of the Mo_2C catalysts with P is lower than the catalyst without any additives. This can again be attributed to the formation of a surface phosphate phase. Table 2 gives the atomic composition of fresh $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3\text{-P}$ catalysts from XPS analysis without any pretreatment to remove the passivation layer. In the case of $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$, the atomic concentration of C is 14%, of which 15% is carbidic carbon (BE of 282.5 eV) and 85% is graphitic carbon (by deconvolution). The atomic concentration of Mo is 5.8% which was deconvoluted to yield 25.2% Mo_2C and 74.8% MoO_3 and MoO_2 . For all the carbide catalysts, it was found that P is in a highly oxidized state (P^V). The atomic composition of the catalysts did not noticeably differ with the addition of P. The atomic concentration of C is 15% which was deconvoluted to yield 17.7% carbidic carbon and 83.3% graphitic carbon. The atomic concentration of Mo is 5.4% of which 22.7% is Mo_2C and 77.3% is MoO_3 and MoO_2 .

TABLE 1

Characteristics of Supported Mo_2C

Catalyst	CO uptake ($\mu\text{mol g}^{-1}$)	Dispersion (%)	S_g ($\text{m}^2\text{ g}^{-1}$)
40% $\text{Mo}_2\text{C-P}/\gamma\text{-Al}_2\text{O}_3$	40	2.9	237
40% $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3\text{-P}$	39	2.8	271
40% $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$	72	5.2	223
20% $\text{Mo}_2\text{C}/\text{C}$	42	6.1	300
Mo_2C (22)	99	2.0	42
$\gamma\text{-Al}_2\text{O}_3$	—	—	260

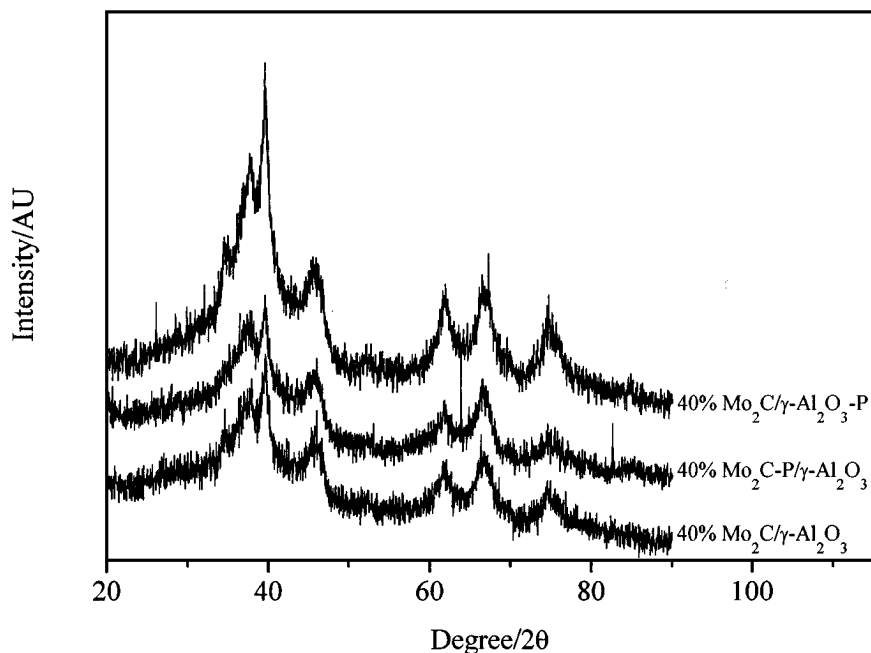


FIG. 2. XRD patterns of 40% $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3\text{-P}$, 40% $\text{Mo}_2\text{C-P}/\gamma\text{-Al}_2\text{O}_3$, and 40% $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$.

To further understand the nature of the various supported Mo_2C catalysts, it is very important to determine whether the carbon atoms remain carbidic or graphitic. As demonstrated in previous studies (33, 34, 37, 38), the NEXAFS technique is very sensitive for probing the local structural and electronic properties of transition metal carbides. In addition, due to their differences in electronic band structures, the C K-edge features of carbides are substantially different from those of other forms of carbon, such as graphite (33, 39) or carbonaceous species (33). Figure 3 shows a comparison of C K-edge features of two well-characterized carbide overlayers prepared on the single crystal surfaces of V(110) and Mo(110) (37). As typically observed for early transition metal carbides (34, 37–41), the C K-edge features of vanadium and molybdenum carbides in Fig. 3 are characterized by two low-energy features at ~ 285.5 and ~ 288 eV, and a broad peak at ~ 295 eV. The spectroscopic assignments of the C K-edge features of early transition metal carbides have been discussed in detail previously (34, 37–42). In brief, the two low-energy resonances at < 290 eV in Fig. 3 can be assigned to the transitions of

C 1s electrons to the p-d(t_{2g}) and p-d(e_g) hybridized orbitals, respectively. Similarly, the broad feature at ~ 295 eV can be assigned to the transition of C 1s electrons to an unoccupied orbital that involves contributions from 2p and 3p orbitals

TABLE 2

Atomic Composition of Supported Fresh and Spent Catalysts

Catalyst	O	C	Mo	Al	P	S
Fresh $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$	56	14	5.8	24	0	0
Spent $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$	43	30	4.3	20	0	2.0
Fresh $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3\text{-P}$	58	15	5.4	20	1.5	0
Spent $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3\text{-P}$	43	30	4.3	18	2.7	2.0

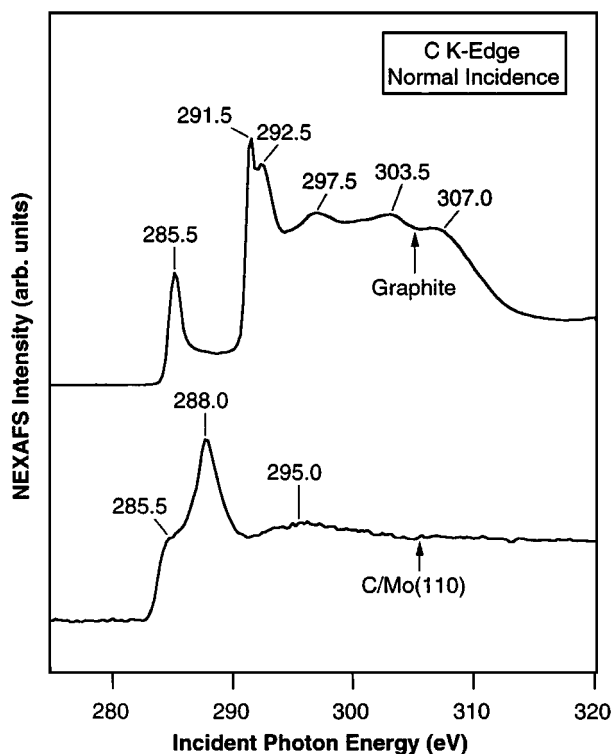


FIG. 3. Comparison of NEXAFS spectra of C K-edge features of graphite with carbide overlayers on Mo(110) single crystal surfaces (37).

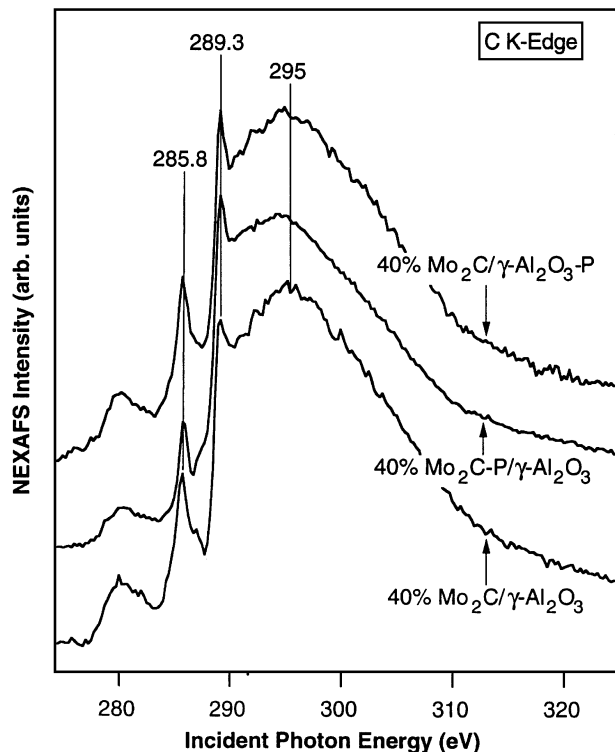


FIG. 4. Comparison of C K-edge features of 40% Mo₂C/γ-Al₂O₃-P, 40% Mo₂C-P/γ-Al₂O₃, and 40% Mo₂C/γ-Al₂O₃.

of carbon and the d and s states of metals (38, 42). Figure 3 also shows that the C K-edge features of a polycrystalline graphite sample are qualitatively different from those of transition metal carbides.

Figure 4 shows a comparison of the C K-edge features of supported catalysts, Mo₂C/γ-Al₂O₃-P, Mo₂C-P/γ-Al₂O₃, and Mo₂C/γ-Al₂O₃. All three samples are characterized by two relatively sharp resonances at 285.5 and 289.3 eV, and a relatively broad feature at 295 eV. The peak positions of these features are very similar to those previously observed for unsupported powder materials of Mo₂C (33) and Mo₂C-O (43). The identical peak positions of the C K-edge features in Fig. 4 suggests that the local electronic and structural environment of carbon is very similar in the three supported carbide catalysts. Furthermore, a comparison of Figs. 3 and 4 clearly reveals that the characteristic graphitic NEXAFS features are absent in Fig. 4, indicating that carbon atoms retain their carbidic nature on all three supported Mo₂C catalysts.

Reactivity

The hydrotreating reactions were carried out at 643 K and 3.1 MPa and the activity of the catalysts are compared to a commercial Ni-Mo-S/Al₂O₃ catalyst (Shell 324) and unsupported Mo₂C catalyst. Table 3 provides a summary of the steady state reactivities in terms of conversion and

TABLE 3
Summary of Reactivity of Supported Mo₂C

Catalyst	HYD (%)	HDN (%)	HDS (%)	HDN TOR/ 10 ⁻³ s ⁻¹	HDS TOR/ 10 ⁻³ s ⁻¹
Mo ₂ C-P/γ-Al ₂ O ₃	29	64	48	1.5	0.72
Mo ₂ C/γ-Al ₂ O ₃ -P	28	57	80	1.3	1.2
Mo ₂ C/γ-Al ₂ O ₃	45	33	65	0.76	0.98
Mo ₂ C/C	29	49	65	1.1	0.98
NiMoS/Al ₂ O ₃ (22)	47	38	79	0.46	0.62
Mo ₂ C (22)	39	47	43	1.1	0.65

turnover rates (TOR) for HDN and HDS, based on equal number of surface metal atoms (corresponding to 70 μmol) loaded in the reactor. The amount of reference catalyst Ni-Mo-S/Al₂O₃ used in the reaction was 140 μmol (based on O₂ chemisorption). The HDN TOR of the catalysts with P added to the support is higher than the reference sulfide catalyst, and both supported and unsupported Mo₂C catalyst. A similar positive effect of P additive for the HDN reaction was observed by Eijisbouts *et al.* (44) and Robinson *et al.* (45). In addition, the catalyst with P co-impregnated on the support has slightly higher HDN activity than the catalyst synthesized on a P treated γ-Al₂O₃. The Mo₂C/C has a higher activity than the Mo₂C/γ-Al₂O₃ catalyst. The products from quinoline HDN were HYD quinoline compounds (1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, and o-propylaniline) and hydrodenitrogenated hydrocarbons (propylcyclohexane and propylbenzene). The steady state product distribution of quinoline are given in Table 4. It can be seen that for the Mo₂C-P/γ-Al₂O₃ catalyst the amount of HYD products is lower and the HDN products is higher when compared to other catalysts in this study.

TABLE 4
Summary of Product Distribution of the Catalysts for Quinoline (QNL) Conversion at 3.1 MPa and 643 K

Catalyst	% Conversion of QNL	Products (mol%)					
		1-THQ	5-THQ	OPA	PCH	PBZ	Others ^a
40%Mo ₂ C-P/γ-Al ₂ O ₃	93	9	17	7	51	9	7
40%Mo ₂ C/γ-Al ₂ O ₃ -P	84	20	18	9	30	14	9
40%Mo ₂ C/γ-Al ₂ O ₃	76	17	33	11	23	10	6
40%Mo ₂ C/C	74	14	15	3	36	20	12
Ni-Mo-S/γ-Al ₂ O ₃ (22)	85	20	30	6	23	12	9
Mo ₂ C (22)	86	14	24	6	30	11	15

^a Includes light hydrocarbons and gaseous products.

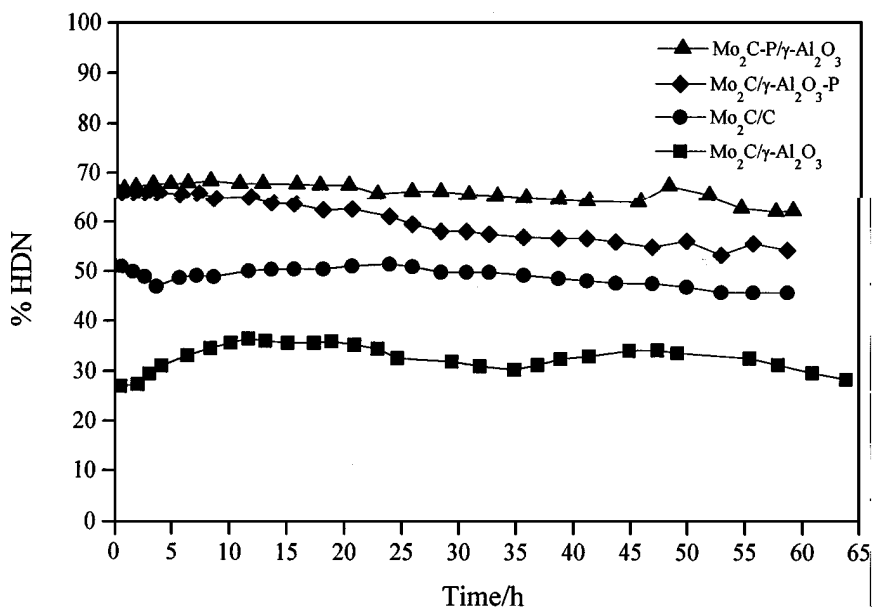


FIG. 5. Comparison of HDN performance on supported Mo₂C at 643 K and 3.1 MPa.

The steady-state conversion and TOR of the catalysts for HDS of dibenzothiophene are compared in Table 3. Biphenyl was the only product detected (product distribution at steady state is 100% biphenyl) from dibenzothiophene HDS. From Table 3 it can be seen that the HDS TOR of the supported Mo₂C catalysts are higher than the reference sulfide catalyst and unsupported Mo₂C. In addition, the TOR of Mo₂C/ γ -Al₂O₃-P is the highest when compared to other catalyst, clearly indicating a positive effect of P pretreatment on the γ -Al₂O₃ support. A similar positive effect of P on the support for sulfided catalysts for HDS reactions was observed by Prada Silvy *et al.* (46). Comparing the TOR for the two P containing catalysts indicates that the method of P inclusion is also important because the TOR of the Mo₂C-P/ γ -Al₂O₃ is significantly lower than the Mo₂C/ γ -Al₂O₃ and Mo₂C/C catalysts. In none of the catalysts was there an indication of phosphide formation.

Postreaction Characterization

The catalysts were characterized by XRD after the hydroprocessing reactions. The bulk Mo₂C structure did not change for any of the catalysts during reaction, indicating they are tolerant of sulfur. Table 2 gives the comparison of atomic composition of elements from XPS analysis of the fresh and spent catalysts. The results show that the total S content is only 2%, and this again clearly indicates that the catalysts are tolerant to sulfur for hydrotreating reactions.

CONCLUSIONS

New catalysts with P additive were synthesized by temperature programmed reaction, characterized by CO

chemisorption, surface area measurements, XRD, XPS, and NEXAFS, and tested for hydrogenation, hydrodenitrogenation and hydrodesulfurization reactions. The activity of the catalysts was higher when compared to Ni-Mo-S/Al₂O₃ (Shell 324), and the catalysts were tolerant of sulfur. The increase in the reactivity of the P treated catalyst can be explained on the basis of a reduced support-metal oxide interaction.

ACKNOWLEDGMENTS

This paper was written with support from Akzo Nobel and the U.S. Department of Energy under the Coal Research at U.S. Universities Program Grant DE-FG26-97FT97265.

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