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NEW CATALYSTS FOR COAL PROCESSING: METAL CARBIDES AND NITRIDES

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NEW CATALYSTS FOR COAL PROCESSING: METAL CARBIDES AND NITRIDES THIRD SEMIANNUAL REPORT

S. Ted Oyama & David F. Cox

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Abstract

Unsupported molybdenum nitride (Mo_2N) and molybdenum carbide supported on alumina (Mo_2C/Al_2O_3) were compared against commercial sulfided MoS_2/Al_2O_3 and Ni-Mo-S/Al_2O_3 for hydrotreating coal-derived gas oil at 633 K (360 °C) and 13.7 MPa (2000 psig). When the catalytic rates were compared on the basis of active sites measured by chemisorption, the nitrides and carbides were estimated to have activities as much as five times that of Ni-Mo-S/Al_2O_3 and MoS_2/Al_2O_3. The comparison was based on sites titrated by CO on the carbide and nitride and by O_2 on the sulfided catalysts. The gas oil product quality from the carbide and nitride catalysts was significantly better than the thermal blank, indicating that the materials were active under practical hydrotreating conditions. X-ray photoelectron spectroscopy analysis after reaction of the Mo_2N and Mo_2C/Al_2O_3 catalysts indicated that surface sulfiding was not extensive.

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Executive Summary

Catalytic hydroprocessing of oil derived from coal to remove heteroatoms and to saturate aromatic rings is a crucial first step in the refining of these hydrocarbon resources. As the quality of available feeds decreases with time there are increasing needs to develop better catalysts for hydrotreating [1,2]. This report describes hydrotreating of a low sulfur, coal derived liquid at industrial conditions, 633 K (360 °C) and 13.7 MPa (2000 psig) in a three-phase flow reactor with a new class of catalysts: supported and unsupported molybdenum carbide and nitride. The new catalysts have activity surpassing that of a commercial sulfided Ni-Mo/Al_2O_3 catalyst.

Introduction

Catalysts for hydrotreating reactions have traditionally been sulfides of molybdenum with cobalt and nickel promoters [3,4,5]. This report presents the performance of a new type of catalyst: carbides and nitrides of molybdenum. These materials differ substantially from previous molybdenum compounds in being metallic interstitial alloys of carbon and nitrogen and not insulating layered compounds. Interest in their catalytic properties is a result of their recent availability in very high surface area form [6,7].

The present study is motivated by a previous report that the carbides and nitrides are active for denitrogenation of quinoline under batch conditions [8,9]. This high activity in hydroprocessing reactions have been confirmed in a number of studies using model feeds [10,11,12,13]. Here, the performance of the compounds for hydroprocessing is reported using a real feedstock derived from coal liquids. Particular attention is placed on hydrodenitrogenation (HDN). Activities of the molybdenum carbide and nitride catalysts are compared with that of traditional sulfided catalysts, Mo/Al_2O_3 (Amocat™-1B) and Ni-Mo/Al_2O_3 (Shell 324), under identical conditions. A blank reactor packed with inert alundum chips served as a thermal control.

Results and Discussion

The molybdenum carbide and nitride catalysts were prepared as reported earlier [14]. The molybdenum carbide was supported on γ-Al_2O_3 by impregnating the support with an aqueous ammonium molybdate solution and carburizing the dried solid in a 20% CH_4/H_2 reactant stream. The molybdenum nitride was prepared by the temperature programmed reaction of molybdenum trioxide in a flowing ammonia stream. The carbide and nitride catalysts were passivated in 1 % O_2/He after preparation.

Reactivity was measured in stainless steel 7.9mm/14.3 mm (ID/OD) reactors with the catalysts (14/20 mesh) physically mixed with alundum chips (14/20 mesh) to a bed volume of 11 cm^3 and held by plugs of the same chips. The reactors were operated at 633 K and 13.7 MPa with cocurrent upward flow of oil (4 $cm^3\ h^{-1}$) and H_2 (106 $\mu mol\ s^{-1}$, 159 cm^3(STP) min^{-1}). Such upward flow ensures good catalyst contacting and operation in the kinetic regime with a liquid saturated in hydrogen. Temperatures were monitored by movable thermocouples mounted axially along the length of the reactor.

Catalysts were packed into the reactor to give the same number of active sites when possible. Active sites were counted by the static chemisorption of O_2 in the case of Ni-Mo-S/Al_2O_3 and MoS_2/Al_2O_3 and CO chemisorption in the case of molybdenum carbide and nitride

The coal-derived feed is referred to as a coal-derived gas oil because it has a similar boiling point range to the intermediate stream of the same name found in petroleum refining. The coal gas oil was obtained from the Wilsonville coal liquefaction facility (Run 257). The catalysts showed no signs of deactivation for the duration of the run of 260 hours.

Table 1 gives a comprehensive summary of the product qualities after 260 hours on oil. The molybdenum carbide and nitride catalysts yield products that are significantly better than those from the blank (thermal) reactor. The blank product characteristics are close to those of the feed. Furthermore, all the measurements indicate product qualities are higher than those from sulfided Ni-Mo-S/Al_2O_3 and MoS_2/Al_2O_3. Notable is that there was little aromatic saturation, as measured by C13 NMR, or change in the ratio of H/C achieved by all but Mo_2N at these process conditions.

Table 1
Analysis of the Product after 260 Hours on Coal Gas Oil

	Mo_2N	Mo_2C/Al_2O_3	$NiMoS/Al_2O_3$	MoS_2/Al_2O_3	Blank	Feed
C / wt%	88.76	88.64	88.68	88.64	88.35	88.54
H / wt%	11.05	10.83	10.79	10.77	10.73	10.73
H/C ratio	1.50	1.47	1.46	1.46	1.46	1.46
S / ppm	28	49	38	55	84	116
N / ppm	1730	2410	2890	2900	3480	3580
Aromatics / wt%	29.6	32.1	32.3	33.0	33.4	33.5

Table 2 compares *relative* pseudo first-order rate constants for desulfurization, denitrogenation, and aromatic saturation relative to Ni-Mo-S/Al_2O_3. The pseudo first-order rate constants (k) themselves are obtained by integrating the expression $V = F_o \int dx/kC$ where F_o is the molar flow rate, k is the rate constant and C is the concentration. This results in the expression, $k = (1/\tau)\ln(C_{feed}/C_{product})$, where $\tau = V/v_o = 11\ cm^3/159\ cm^3\ s^{-1} = 0.069$ s. The pseudo rate constants are further normalized by the amount of active sites in each of the reactors.

A concern with using molybdenum carbide and nitride for hydrotreating applications is that the formation of molybdenum sulfide is thermodynamically favored in the presence of sulfur [14,15]. Consequently, the catalysts were characterized after reaction by XRD and XPS analyses. XRD did not show the presence of crystalline MoS_2 at the detection limit concentration of 1 wt% on the molybdenum nitride (molybdenum carbide was not examined). The results from XPS are shown in Table 3.

Table 2
Estimated Relative First-Order Rate Constants[a] per "Active Site[b]"

Catalyst	Desulfurization	Denitrogenation	Aromatic saturation
Mo_2N	1.3	3.4	3.4
Mo_2C/Al_2O_3 [c]	2.1	5	3.1
MoS_2/Al_2O_3	0.67	0.98	0.41
$Ni\text{-}Mo\text{-}S/Al_2O_3$	1	1	1

[a] Calculated by $[\ln(co/c)_i]/[\ln(co/c)_{Ni\text{-}Mo}]$.

[b] As titrated by CO for the carbide and nitride and by O for the sulfides.

[c] Rate constant corrected by 718/268, the ratio of μmol O uptake by Ni-Mo to CO uptake by Mo_2C/Al_2O_3 in the reactors.

Table 3
Surface Composition Measured by XPS

Mo_2N / mol%								
	C	O	Mo	S	N	Na	Al	Si
fresh	24.4	29.2	21.3	--	25.0	--	--	--
used	46.8	28.6	12.5	3.2	7.9	--	--	0.9
reduced	12.8	42.9	26.2	--	18.1	--	--	--
Mo_2C/Al_2O_3 / mol%								
fresh	4.8	37.8	1.9	--	--	--	55.5	--
used	33.4	40.0	2.0	1.4	0.8	0.2	22.2	--
reduced	3.1	60.4	4.7	--	--	--	31.7	--

Fresh catalyst reduced with flowing H_2 at atmospheric pressure and 677 K (404°C).

The XPS data for molybdenum nitride catalyst withdrawn from the reactor reported in Table 3 indicates a sulfur-to-molybdenum ratio of 3.2/12.5 = 0.26, well below the expected ratio of 2 should MoS_2 have been formed within the sampling depth for XPS (roughly 1-2 nm). Consequently, it does not appear that extensive sulfiding of the molybdenum nitride occurred during its use. The same argument and conclusion applies to Mo_2C/Al_2O_3. It cannot be ruled out, however, that some MoS_2 was formed at the topmost atomic layers of the nitride (carbide) crystallite surface. An analysis of the oxidation states of molybdenum in the used molybdenum carbide and nitride catalysts indicates that not all the molybdenum was reduced to the Mo^{+4} state (only 63% in the case of Mo_2N) during the pretreatment.

It is clear from the results that molybdenum carbide and nitride are active for hydrotreating under practical industrial conditions. While the feedstocks were coal-derived liquids, it is very likely that molybdenum nitride and carbide will exhibit similar catalytic properties for hydrotreating petroleum-derived liquids.

Conclusions

It is significant that for a reasonable attempt at counting sites (CO adsorption on the nitrides and carbides and static O_2 adsorption on the sulfides) that Mo_2N and Mo_2C/Al_2O_3 compare very favorably with a commercial sulfided $Ni\text{-}Mo/Al_2O_3$ catalyst. It also noteworthy that the XPS data indicate that Mo_2N and Mo_2C are not detectably sulfided despite operation at high pressures, temperatures, and with real hydrocarbon feeds.

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