Novel Supported Bimetallic Carbide Catalysts for Coprocessing of Coal with Waste Materials

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Table of Contents

Abstract

The effect of phosphorus on Mo_2C supported on γ-Al_2O_3 and activated carbon was studied. The catalysts were characterized by CO chemisorption, BET surface area measurements, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and tested for their reactivity for hydroprocessing reactions, particularly hydrogenation (HYD), 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 Mo_2C was synthesized on γ-Al_2O_3 previously treated with P than when the Mo component and P were added together on γ-Al_2O_3. Post reaction characterization indicates that the catalysts were tolerant of sulfur.

Introduction

It is well documented that sulfided catalysts with additives are used in hydrotreating reactions such as hydrogenation (HDN), hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodemetallization (HDM) [1,2,3]. Additives such as P have a promotional effect when added to the oxide forms of the catalyst 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 [4,5]. 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 [6,7,8,9]. There has also been some work on supported carbides and nitrides [10,11,12,13]. However, information available on the effect of additives on transition metal carbide catalysts and their reactivity for hydrotreating reactions is very limited [14]. In this report the synthesis and characterization of Mo_2C on γ-Al_2O_3 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 hydrogenation (HYD) of quinoline, hydrodenitrogenation (HDN) of quinoline and hydrodesulfurization (HDS) of dibenzothiophene are reported. In addition, post-reaction composition is also discussed.

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.

The XRD patterns of the synthesized catalysts show mostly the features of the support, but the presence of β-Mo_2C (hcp, P63/mmc) can also be clearly discerned. The intensity of the Mo_2C peaks in the Mo_2C/γ-Al_2O_3-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 γ-Al_2O_3-P likely due to the formation 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.* [15], who suggested that this was due to the formation of an $AlPO_4$ 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 1. Characteristics of supported Mo_2C

Catalyst	CO uptake	Dispersion	S_g
	µmol g^{-1}	%	m^2g^{-1}
40% Mo_2C-P/γ-Al_2O_3	40	2.9	237
40% Mo_2C/γ-Al_2O_3-P	39	2.8	271
40% Mo_2C/γ-Al_2O_3	72	5.2	223
20% Mo_2C/C	42	6.1	300
Mo_2C [22]	99	2.0	42
γ-Al_2O_3	-	-	260

Table 2 gives the atomic composition of fresh Mo_2C/γ-Al_2O_3 and Mo_2C/γ-Al_2O_3-P catalysts from XPS analysis without any pretreatment to remove the passivation layer.

Table 2. Atomic composition of supported Mo_2C

Catalyst	O	C	Mo	Al	P	S
fresh Mo_2C/γ-Al_2O_3	56	14	5.8	24	0	0
spent Mo_2C/γ-Al_2O_3	43	30	4.3	20	0	2.0
fresh Mo_2C/γ-Al_2O_3-P	58	15	5.4	20	1.5	0
spent Mo_2C/γ-Al_2O_3-P	43	30	4.3	18	2.7	2.0

In the case of Mo_2C/γ-Al_2O_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.

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/Al_2O_3 catalyst (Shell 324) and unsupported Mo_2C catalyst. Table 3 provides a summary of the steady state reactivities in terms of conversion and 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/Al_2O_3 used in the reaction was 140 μmol (based on O_2 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 Mo_2C catalyst. A similar positive effect of P additive for the HDN reaction was observed by Eijisbouts *et al.* [16] and Robinson *et al.* [17]. 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-Al_2O_3. The Mo_2C/C has a higher activity than the Mo_2C/γ-Al_2O_3 catalyst. The products from quinoline HDN were hydrogenated (HYD) quinoline compounds (1, 2, 3, 4-tetrahydroquinoline, 5, 6, 7, 8-tetrahydroquinoline and o-propylaniline) and hydrodenitrogenated hydrocarbons (propylcyclohexane and propylbenzene).

Table 3. Summary of reactivity of supported Mo_2C

Catalyst	HYD	HDN	HDS	HDN TOR	HDS TOR
	%	%	%	/ 10^{-3} s^{-1}	/ 10^{-3} s^{-1}
Mo_2C-P/γ-Al_2O_3	29	64	48	1.5	0.72
Mo_2C/γ-Al_2O_3-P	28	57	80	1.3	1.2
Mo_2C/γ-Al_2O_3	45	33	65	0.76	0.98
Mo_2C/C	29	49	65	1.1	0.98
$NiMoS/Al_2O_3$ [22]	47	38	79	0.46	0.62
Mo_2C [22]	39	47	43	1.1	0.65

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 Mo_2C catalysts are higher than the reference sulfide catalyst and unsupported Mo_2C. In addition, the TOR of Mo_2C/γ-Al_2O_3-P is the highest when compared to other catalyst, clearly indicating a positive effect of P pretreatment on the γ-Al_2O_3 support. A similar positive effect of P on the support for sulfided catalysts for HDS reactions was observed by Prada Silvy *et al.* [18] . Comparing the TOR for the two P containing catalysts indicates that the method of P inclusion is also important because the TOR of the Mo_2C-P/γ-Al_2O_3 is significantly lower than the Mo_2C/γ-Al_2O_3 and Mo_2C/C catalysts. In none of the catalysts was there an indication of phosphide formation.

Post-reaction Characterization

The catalysts were characterized by XRD after the hydroprocessing reactions. The bulk Mo_2C 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 indicate 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 tested for hydrogenation, hydrodenitrogenation and hydrodesulfurization reactions. The activity of the catalysts was higher when compared to Ni-Mo-S/Al_2O_3 (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.

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