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MoS_2 Promotion with Nickel in Organic Solvents: Hydrogenation of Aromatics

M. V. LANDAU,* L. I. NIKULINA,* B. K. NEFEDOV,* A. S. GOLUB,†
YU. N. NOVIKOV,† AND M. E. VOL'PIN†

*The All-Union Research Institute of Petroleum Refining and †Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, USSR

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The catalytic activity of sulfided $Ni_{1/3}MoS_2$ samples prepared by MoS_2 impregnation with nickel nitrate solutions in 14 organic solvents, water, and ammonia was examined in the hydrogenation of *o*-xylene containing some thiophene and compared with that of samples impregnated with the nickel salt melt. Promotion of MoS_2 was found to depend on the nature of the solvent affecting both surface area of catalysts and amount of nickel promoter, which can be chemically bound on the surface of molybdenum disulfide. © 1986 Academic Press, Inc.

INTRODUCTION

It is known that the catalytic activity of MoS_2 and WS_2 in reactions of hydrogenation and hydrodesulfurization can be improved by adding some nickel, cobalt, or iron (*1, 2*). Earlier studies showed that this effect was observed after impregnation of $MoS_2(WS_2)$ with an aqueous solution of nickel nitrate (*3*) or acetate (*4, 5*), or with a nickel or cobalt nitrate solution in liquid ammonia (*6–8*) followed by solvent removal and sulfiding.

Although comparative data on the performance of various solvents are not available, the nature of these solvents well may affect the activity of the catalysts. In this connection, it is noteworthy that (a) in an aqueous medium MoS_2 can be partially oxidized (*9*); (b) MoS_2 absorbs up to 0.5 mole of NH_3 per one Mo atom (*10*), which is supposed to indicate penetration of the solvent inside the lamellar MoS_2 structure; and (c) dixalcogenides of Group IV–V metals form intercalated lamellar compounds with organic solvents (*11–13*). In addition, the solvent may influence the character of the promoter:$MoS_2(WS_2)$ interaction by forming solvate complexes with the nickel or cobalt salt.

This paper reports comparative data on the activity in the hydrogenation of *o*-xylene containing some thiophene (3 mass% S) for catalysts prepared by impregnation of MoS_2 with $Ni(NO_3)_2$ (Ni/Mo = 0.33) using either various solvents or the salt melt.

EXPERIMENTAL

Sample preparation. Purified natural molybdenite DM-1 with 6 m^2/g surface area and 40.3 mass% sulfur content was used as the base MoS_2. Sixteen diverse solvents (water, ammonia, amides, amines, oxygen- and sulfur-containing compounds) of nickel nitrate were selected on the ground of preliminary solubility tests. Catalyst samples were prepared as follows. $Ni(NO_3)_2 \cdot 6H_2O$ (14.2 g) was dissolved in 150 cm^3 of solvent (sometimes with heating); then 30 g of MoS_2 was added to the resulting solution and the mixture was heated (except for the case with ammonia) at 323–353 K for 3 h with stirring. At the end of this period the solvent was removed in a rotary evaporator. The resulting air-dried product was heated in nitrogen at 433–453 K for 3 h and pelleted in a press (pellet diameter, 1.0–1.6 mm) before use in catalytic experiments. To impregnate MoS_2 with a nickel salt melt, the disulfide powder was mixed in a mortar

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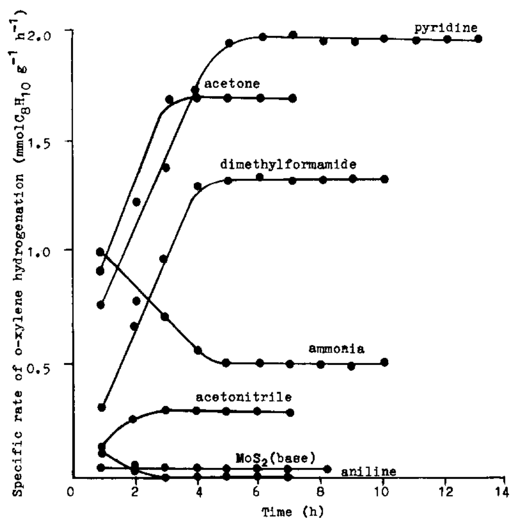

FIG. 1. Time dependence of reaction rate during sulfiding in *o*-xylene (3% S as thiophene): hydrogenation on the base MoS_2 and fresh $Ni_{1/3}MoS_2$ catalysts (T = 623 K, P = 4.0 MPa, $V_{sp} = 1\ h^{-1}$, $H_2/C_8H_{10} = 6$).

with $Ni(NO_3)_2 \cdot 6H_2O$ crystals in the same proportion, and heated under nitrogen at 453 K for 6 h.

The surface area of the crystals were determined by the BET method from the low-temperature nitrogen adsorption (volumetric procedure) after a catalytic test.

The catalytic activity in the hydrogenation of *o*-xylene with 3 mass% sulfur as thiophene was measured in a flow reactor process. Namely, the reaction rate was measured at a total pressure of 4.0 MPa, temperature of 623 K, liquid feed mixture space velocity of 1 h^{-1}, and molar ratio $H_2:C_8H_{10}$ of 6 after stabilization of the *o*-xylene hydrogenation rate (see Fig. 1), and normalized to the weight of the catalyst discharged, $W_g = U \cdot x/v$, or to its surface area, $W_s = W_g/S_{sp}$, where U = amount of *o*-xylene (mmol) charged to the reactor in 1 h, x = *o*-xylene conversion, v = catalyst weight after testing (g), and S_{sp} = surface area (m^2/g). The initial weight of the samples charged was 10.0 g. The content of the *o*-xylene hydrogenation products—dimethylcyclohexane and some dimethylcyclohexene—was determined by GLC.

RESULTS AND DISCUSSION

The hydrogenation rate stabilized at the end of 5 h in all cases, except for the base MoS_2 (Fig. 1). During this time the catalyst was sulfided and the residual solvent was removed. The weight loss after the activity test depended on the solvent and varied from 0.0 (ammonia) to 15.5 (DMFA), 17.7 (pyridine), and 18.2 (DMSO) mass%. The stationary rate was substantially affected by conditions of the catalyst activation. The common dependence was the same as demonstrated in Table 1 for the catalyst prepared in DMFA. The highest W_g value was obtained after heating in pure H_2S or sulfiding with the reaction mixture under the reaction conditions. Preheating in H_2, NH_3, or N_2 resulted in a sharp loss in the catalytic activity which suggested that treatment of the catalyst with a sulfiding agent is necessary after drying to ensure the best performance of the promoter. Later, relative catalyst activity was evaluated as the stationary rate of *o*-xylene hydrogenation on sulfiding catalyst with a feedstock mixture (C_8H_{10}–C_4H_4S) in the course of catalytic reaction.

Promotion of MoS_2 with $Ni(NO_3)_2$ increased its catalytic activity by a factor of 3 to 40 depending on the nature of the solvent (Table 2). The use of aniline led to a loss in catalytic activity of base MoS_2.

TABLE 1

Effect of Conditions for Catalyst Activation on the Stationary Hydrogenation Rate for $Ni_{1/3}MoS_2$ Prepared in DMFA (623 K, 4.0 MPa)

Conditions for activation of $Ni_{1/3}MoS_2$ catalyst	W_g (mmol $C_8H_{10} \cdot g^{-1}\ h^{-1}$)
H_2S, 623 K, 6 h	1.42
(*o*-Xylene–thiophene) catalytic reaction (H_2S/H_2), 623 K, 6 h	1.33
H_2, 623 K, 6 h	0.77
NH_3, 673 K, 6 h	0.32
N_2, 623 K, 6 h	0.18

TABLE 2

Effect of Solvent on the Activity of $Ni_{1/3}MoS_2$ and MoS_2 in the Hydrogenation of *o*-Xylene (623 K, 4.0 MPa)

Solvent	$Ni_{1/3}MoS_2$			MoS_2		
	S_{sp} (m^2/g)	W_g (mmol $C_8H_{10}/g \cdot h$)	$W_s \cdot 10^2$ (mmol $C_8H_{10}/m^2 \cdot h$)	S_{sp} (m^2/g)	W_g (mmol $C_8H_{10}/g \cdot h$)	$W_s \cdot 10^2$ (mmol $C_8H_{10}/m^2 \cdot h$)
—[a]	5	1.00	20.00	6	0.05	0.8
Aniline	9	0.00	0.00	—	—	—
Diglyme	—	0.14	—	—	—	—
Formamide	—	0.21	—	5	0.67	13.4
Acetonitrile	11	0.28	2.5	—	—	—
DMSO	—	0.45	—	—	—	—
Hexamethapol	—	0.47	—	—	—	—
Ammonia	—	0.50	—	—	—	—
Piperidine	—	0.63	—	—	—	—
Dimethylacetamide	11	0.70	6.4	—	0.55	—
THF	—	0.90	—	—	—	—
N-Methylformamide	14	1.00	7.1	—	0.38	—
Butanol	—	1.05	—	—	—	—
Water	6	1.15	19.2	6	—	—
DMFA	7	1.33	19.0	8	0.67	8.4
Acetone	9	1.68	18.7	9	0.52	5.8
Pyridine	10	1.96	19.6	8	0.50	6.2

[a] Impregnation with a nickel salt melt.

The solvents studied can be divided into two groups according to their influence on the promotion: (I) solvents ensuring the highest activating effect, and (II) solvents producing catalysts of much lower activity. Group I includes water, DMFA, acetone, and pyridine. Also, a similar effect was observed when catalysts were prepared by impregnating MoS_2 with the $Ni(NO_3)_2 \cdot 6H_2O$ salt melt). All other solvents in Table 2 belong to Group II. The W_g values of catalysts prepared using Group I solvents increased in the order shown in Table 2, while the specific activity value, W_s, remained constant throughout the series due to increasing surface area.

The effect of solvent on catalyst activity can be attributed both to the modification of MoS_2 itself and to the contribution of the solvent to the interaction of MoS_2 with the nickel salt. The treatment of MoS_2 with solvents lacking nickel salt (Table 2) resulted in an increase in W_g and W_s by one order of magnitude regardless of the nature of the solvent, which may be due to some change in the morphology of secondary agglomerates of MoS_2 crystals and improved access to active sites. On the other hand MoS_2 treated with Group I solvents was one-half to one-quarter as effective as the corresponding catalysts which contained nickel, suggesting that the nature of the solvent affects mainly the interaction of MoS_2 with nickel nitrate. This is also evident from comparative data on the activity of catalysts prepared by applying nickel nitrate from a Group I (acetone) or Group II (formamide) solvent to MoS_2 pretreated with formamide or acetone, respectively. As shown in Table 3, pretreatment of MoS_2

TABLE 3

Effect of Pretreatment of MoS_2 with Solvents on the Activity of $Ni_{1/3}MoS_2$ in *o*-Xylene Hydrogenation (623 K, 4.0 MPa)[a]

Catalyst	W_g (mmol $C_8H_{10}/g \cdot h$)
$Ni(NO_3)_2$–formamide/MoS_2	0.21
$Ni(NO_3)_2$–formamide/MoS_2–acetone[b]	0.22
$Ni(NO_3)_2$–acetone/MoS_2	1.68
$Ni(NO_3)_2$–acetone/MoS_2–formamide[b]	1.65

[a] For an explanation, see the text.

[b] With intermediate 10-h exposure of MoS_2 pretreated with solvent under the conditions of catalytic runs.

with diverse solvents essentially had no effect on the performance of $Ni_{1/3}MoS_2$ catalysts, and it was only the nature of the solvent used for the application of nickel that was responsible for the catalytic activity.

These results suggest that the solvent affects the state of nickel, probably by forming solvate complexes whose stability characteristics may determine both the ability of nickel ions to interact with MoS_2 at the sulfiding stage and the state of the promoter in the catalyst. The nature of the solvent may have a dual effect on the state of the metal (nickel) promoter in sulfided catalysts:

(a) the state of the promoter, and thus the catalytic activity, may vary depending on the solvent, and

(b) the same promoter species capable of activating MoS_2 may be formed in any solvent, but its relative amount may vary, which may cause a difference in the catalytic activity.

To solve this problem gamma resonance spectroscopy was used. Catalyst samples were synthesized by impregnation of MoS_2 with $^{57}Fe(NO_3)_3$ solutions in formamide and acetone via a procedure similar to that used to prepare $Ni_{1/3}MoS_2$. The results of catalytic tests showed (*14*) that although the activating effect of Fe was one-third to one-fifth as high as that of Ni, its variation with the nature of the solvent followed the relationships found for the latter metal. It was also demonstrated that sulfided catalysts treated with hydrochloric acid held their activity in repeated tests, although most of the iron had been removed by the treatment. Gamma resonance spectra obtained for the catalysts after repeated tests showed that the same iron species, Fe^{3+}, was present in each catalyst, but the content of that species was about eight times higher in the case of acetone than in the case of formamide. These results agree with previous data (*4, 5*) which demonstrated that the activating effect on MoS_2 exhibited by nickel was proportional to the content of certain Ni^{2+} cations which differ from those present in bulk nickel sulfides (as determined by magnetic measurements) and cannot be removed from sulfided catalysts by hydrochloric acid.

Since the content of Fe^{+3} cations bound to the MoS_2 surface in catalysts synthesized in formamide is by far lower than that in the case of acetone solvent one can suggest that Group II solvents prevent Fe^{3+} or Ni^{2+} promoter cations from anchoring on the MoS_2 surface. This would result in a lower activating effect on MoS_2 and may even deactivate the base disulfide, probably by blocking the active sites with products of the sulfiding solvate. Group I solvents have a much weaker tendency, if any, to impede the interaction of Fe(Ni) with MoS_2; therefore they give the most active catalysts.

Thus these studies provide a new way of controlling the effect of the promoter on the hydrogenating activity of MoS_2-based catalysts by selecting the type of solvent to be used at the stage at which the promoter is introduced (metal of Group VIII). The nature of the solvent has been found to influence the amount of promoter chemically bound on the MoS_2 surface.

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