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**CHARACTERIZATION OF SILICA-SUPPORTED MOLYBDENUM CATALYSTS
BY ESR, XPS AND THIOPHENE HYDRODESULFURIZATION**

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Two Mo/SiO₂ samples have been prepared by impregnation of silica gel with aqueous solution of molybdophosphoric heteropoly acid or ammonium heptamolybdate. The catalysts were studied by ESR and IR spectroscopy, X-ray diffraction, and XPS. Their activity was measured in the reaction of thiophene hydrodesulfurization. The silica-supported P-Mo heteropoly acid, with a preserved Keggin structure of the heteropoly anion and sulfided by H₂S, exhibited two times higher steady conversion in comparison with ammonium heptamolybdate supported on silica at pH=11 and calcined and sulfided at 500°C.

INTRODUCTION

In spite of numerous investigations on molybdenum containing hydrodesulfurization (HDS) catalysts, the nature of their catalytic performance is still unclear. The activity of those catalysts is determined from their chemical and phase composition, the preparation mode and activation procedure [1-3]. We have shown in a series of studies that heteropoly compounds supported on Al₂O₃ [4], TiO₂ [5] or SiO₂ [6-8] manifest high HDS activity which may exceed those of conventional catalysts [5].

In continuation of previous publications [6-10] the present work deals with the effect of preparation and subsequent treatment of Mo/SiO₂ on the state of molybdenum and the catalytic activity in thiophene hydrodesulfurization.

EXPERIMENTAL

Silica gel (Aerosil A-175, BET area=175 m²g⁻¹) was used as a carrier for the investigated catalysts. Sample 1 was prepared by impregnation of the support with an aqueous solution of molybdophosphoric heteropoly acid (H₃PM₁₂O₄₀ x H₂O, research grade). The catalyst was dried in air at 70°C for 4 h and calcined for 2 h at 250°C. Sample 2 was prepared by impregnation with a solution of ammonium heptamolybdate at pH=11. The catalyst was dried at 110°C for 4 h and calcined at 500°C for 2 h. Molybdenum content was 17 wt. %.

The samples were pretreated in a flow of hydrogen sulfide for 30 min at the temperature of calcination. The physically adsorbed hydrogen sulfide was removed by purging with argon at room temperature. After that the catalysts were heated (or cooled down) in argon flow to the reaction temperature. The catalytic activity of the samples was measured at 350°C in a flow system at atmospheric pressure and space velocity of 0.5-1 h⁻¹. The activity was evaluated from the conversion of thiophene into hydrocarbons.

Infrared (IR) spectra of the samples in the 400-1200 cm⁻¹ range were recorded on a SPECORD 75 IR spectrometer in KBr discs or on a Bruker 113V IR instrument in the 200-400 cm⁻¹ interval in CsI pellets.

The electron spin resonance (ESR) spectra were acquired on a Bruker 200 D spectrometer at room temperature. Prior to recording, the samples were treated in a quartz reactor with flow of air, hydrogen sulfide or hydrogen-thiophene mixture.

X-ray diffraction patterns were registered on a DRON-3 powder X-ray diffraction spectrometer using CoK_α radiation.

X-ray photoelectron spectra were measured by an ESCALAB 3 instrument with AlK_α radiation. The state of molybdenum was

monitored in the calcined samples. Also, spectra of presulfided samples, subsequently having operated under reaction conditions for 200 min were recorded. The binding energy values were calibrated by means of the C 1s line as an external standard (BE= 285 eV). The position of the peaks is reported within 0.2 eV accuracy.

RESULTS AND DISCUSSION

The oxidation state of the samples was examined by means of infrared spectroscopy. The IR spectrum of sample 1, calcined at 250°C, demonstrated bands at 1060, 957, 860, and 790 cm^{-1} . The results indicate that the selected conditions of air treatment preserved the Keggin structure of the initial molybdophosphoric heteropoly acid in this sample. The selected synthesis conditions for sample 2, pH=11 and calcination at 500°C, gave rise only to the formation of MoO_3 , as concluded from the appearance of IR bands at 990, 860, 820, and 620 cm^{-1} [11]. After sulfiding at 500°C, the IR spectrum of that sample exhibited the bands of the support and a band at 373 cm^{-1} due to the Mo-S vibrations in MoS_2 [12]. Weak and broad lines of 2θ at about 13.5-15 and 33-35° in the X-ray diffraction diagram of pre-sulfided sample 2 confirmed the formation of molybdenum sulfide of low crystallinity [13].

As shown in a previous work [8], simultaneous reduction of molybdenum and partial sulfur substitution for oxygen in the heteropoly anion of the P-Mo heteropoly acid take place in sample 1 when treated with hydrogen sulfide at 250°C. Complementary experiments by X-ray diffraction and IR spectroscopy showed that MoS_2 was not formed in the sample pretreated in this way.

Figure 1 presents the time dependence of thiophene conversion over pre-sulfided samples. Sample 1 exhibited high initial conversion, which rapidly decreased with time and attained a permanent level after about 2 h of operation. Changes of selectivity with time were also observed. Butane was the major product with sample 1 at the beginning of the

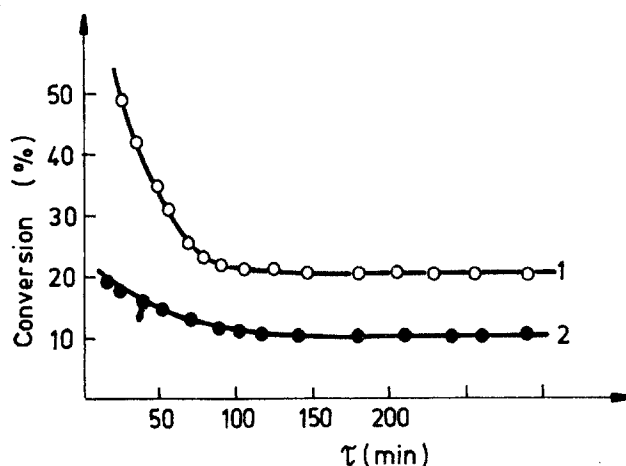


Fig. 1. Thiophene conversion into hydrocarbons at 350°C and space velocity of 0.6 h⁻¹: 1 - sample 1, 2 - sample 2

experiment. After about 60 min the amount of butane drastically decreased to a value which was twice lower than the initial one and retained this value till the end of the run. The initial high content of butane in the reaction products is related to the high hydrogenating activity of the catalyst.

Sample 2 manifested a much lower initial thiophene conversion than sample 1 and after about 2 h reached a steady conversion of thiophene which was two times lower than that on sample 1 (Fig. 1). The results of catalytic activity measurements enabled us to suggest that the state of molybdenum in the two samples was different, both at the beginning of catalyst operation and after attaining a steady thiophene conversion.

By means of X-ray photoelectron spectroscopy (XPS) and ESR spectroscopy, the catalysts were investigated in the state which corresponded to their working state after attaining a steady thiophene conversion. The binding energy of the Mo 3d_{5/2} and Mo 3d_{3/2} electrons in calcined sample 1 (Fig. 2-1) was 232.4 and 235.5 eV, respectively, which conforms to 316

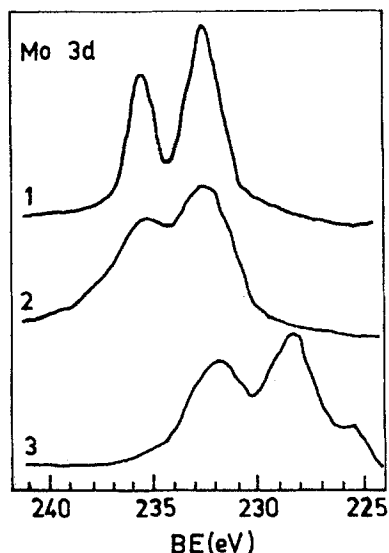


Fig. 2. X-ray photoelectron spectra of differently treated samples: 1 - sample 1 calcined at 250°C,
 2 - sample 1 after attaining a steady HDS activity,
 3 - sample 2 after attaining a steady HDS activity

Mo(VI) in an oxygen environment [14-17]. Hydrogen sulfide treatment of this sample gave rise to a slight deformation and broadening of the Mo 3d doublet (Fig. 2-2). This is consistent with the presence of an additional doublet of Mo(V) (231.3 and 234.4 eV) which is superimposed on the basic Mo(VI) doublet [16]. A small shoulder on curve 2 (Fig.2) at low BE values could be an indication that some traces of Mo(IV) species are present in the presulfided sample after attaining a steady state conversion.

The photoelectron spectrum of sample 2 in the range of Mo 3d contained a doublet at 232.0 and 229.1 eV. These values correspond to energies of S 2s electrons [19]. Besides, a peak at 161.8 eV has also been reported, which is evidence for Mo(IV) surrounded by sulfur ions in bulk molybdenum sulfide

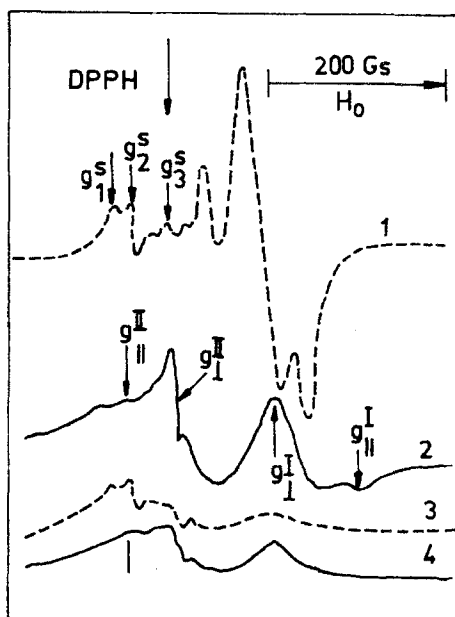


Fig. 3. ESR spectra of: 1 - sample 1 treated with hydrogen sulfide at 250°C, 2 - the same sample after attaining a steady thiophene conversion, 3 - sample 2 treated with hydrogen sulfide at 500°C, and 4 - the same sample after attaining a steady thiophene conversion

[14,18,19]. A low intensity peak was observed in the range of low sulfidic sulfur [20]. The S:Mo ratio determined from the XPS data was equal to 2.

Signals due to Mo(V) ions in octahedral oxygen- or mixed oxygen-sulfur environment in partially dehydrated molybdophosphoric heteropoly acid (Fig.3-1) [8] were present in the ESR spectrum of sample 1 calcined and treated with hydrogen sulfide at 250°C. An intense signal, denoted by S, with parameters $g_1 = 2.042$, $g_2 = 2.029$ and $g_3 = 1.999$ was attributed to the occurrence of paramagnetic sulfur radicals stabilized by Mo(V) ions [8,21]. Treatment of the sample with a hydrogen-thiophene mixture caused this signal to disappear

(Fig. 3-2). Signals I and II were observed in the spectrum registered after attaining a steady conversion over sample 1. Signal I with parameters $g_{\perp} = 1.938$ and $g_{\parallel} = 1.894$ (Fig. 3-2) is associated with Mo(V) ions in an oxygen environment [22], whereas the anisotropic signal II with parameters $g_{\perp} = 1.998$ and $g_{\parallel} = 2.04$ is attributed to Mo(V) ions in an oxygen-sulfur environment [8,23].

A very weak signal S was recorded in the spectrum of sample 2 pretreated with hydrogen sulfide at 500°C. Signals I and II were registered with this sample after attaining a steady thiophene conversion. However, in this case the intensity was lower than that of sample 1.

The variable state of molybdenum in the precursor state of the samples determines their behavior during reduction and sulfiding. Sample 2 could not be reduced and sulfided at 250°C while octahedrally coordinated molybdenum in a supported molybdophosphoric heteropoly acid (sample 1) was partially reduced and sulfided at 100°C [10]. The state of sulfur in the investigated samples is different. In presulfided sample 1 the sulfur is present in three forms: i) reversibly chemisorbed hydrogen sulfide, ii) sulfur atoms replacing oxygen in the molybdenum surrounding of the heteropoly compound and iii) sulfur radicals [10]. A decrease in intensity of signal S in the ESR spectra after attaining steady state conversion shows that the sulfur radicals can interact with hydrogen during the reaction. Additional hydrogen sulfide can be formed. Only strongly bound sulfidic sulfur was detected with the slightly active but stable sample 2.

Usually the HDS activity is associated with the presence of sulfur vacancies along the edges of the MoS_2 structure [24]. Silbernagel [23] related the activity in the HDS to the presence of thio-Mo(V) defects in MoS_2 . It was suggested that the higher initial HDS activity of $\text{CoMo}/\text{Al}_2\text{O}_3$ catalysts can be attributed to oxosulfides [25,26]. In full accordance with Korányi et al. [17,25,26], our results show that the lower degree of sulfidation under mild reaction conditions leads to

higher activity. The high initial activity of presulfided sample 1 is mainly associated with the presence of paramagnetic Mo(V) species in O- and O,S-surroundings. Removal of weakly bonded sulfur and accumulation of strongly held sulfur in molybdenum surrounding during catalysis is the reason for the observed initial deactivation [27].

Our results, obtained by several methods, indicate that the sample containing only molybdenum sulfide exhibits about 2 times lower initial and steady thiophene conversion in comparison with partially sulfided P-Mo heteropoly acids containing Mo(V) species in an O,S-environment.

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