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**TITANIA-SUPPORTED MIXED HPMoV POLYOXOMETALLATES AS
PRECURSORS OF HYDRODESULFURIZATION CATALYSTS**

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Abstract

HDS catalysts were prepared by loading $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ or $\text{H}_4\text{PMo}_{11}\text{V}_1\text{O}_{40}$ polyoxometallates on TiO_2 (0.5 and 1.0 mmol (Mo+V)). Activity of the catalysts was tested in the HDS of thiophene. The activity of catalysts of low concentration was 2-3 times higher than the activity of those of high concentration. Temperature programmed reduction (TPR) and IR spectroscopy were used to determine the properties of the catalyst. TPR measurements proved that vanadium promotes and stabilizes HDS activity due to an increase in the $\text{Mo}^{5+}/\text{Mo}^{4+}$ ratio.

Keywords: TiO_2 , $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{PMo}_{11}\text{V}_1\text{O}_{40}$, thiophene, IR, TPR

INTRODUCTION

Recently, molybdenum catalysts containing polyoxometallates (heteropolycompounds) with the Keggin structure [1], as such, or supported on

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suitable carriers, have been studied very intensively. The use of polyoxometallates is of particular interest, because they have a well defined structure and composition. Their simultaneously present redox and acidic properties provide the possibility to control the specific activity and selectivity of catalysts. Even the limited possibilities of their modification, a change in the anion composition, heteroatom and counteraction, permit the construction of a catalytic system on the molecular level [1-5]. When the heteropolycompounds are loaded on supports, new heteropolyanions can be formed as a result of their interaction. The heteropolycompounds can include the support atom, and in this way, change their properties [6-9].

The mixed polyoxometallates in which one or more molybdenum atoms are substituted by another transition metal [2-4] are especially interesting from both scientific and practical point of view. For example, a mixed $H_4PMo_{11}V_1O_{40}$ acid is formed when one molybdenum atom in $H_3PMo_{12}O_{40}$ acid (HPMo) is substituted for a vanadium atom. Properties of the arising acid differ from the initial one although the Keggin structure is preserved. However, the negative anion charge increases, and its interaction with cations changes very intensively [10].

Polyoxometallates containing vanadium ion in their molecule are extensively studied as catalysts for oxidation [3, 11, 12]. The compounds could be also precursors of the catalytic sites in hydrodesulfurization [13]. It is known that vanadium in small amounts (0.25-1.0 wt.%) affects the catalytic activity of NiMo/Al₂O₃ catalysts [14] in hydrogenation and hydrodesulfurization reactions.

In this paper, the effect of vanadium on the properties of TiO₂-supported catalysts was studied. The catalysts were synthesized using both $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}V_1O_{40}$ heteropolyacids as initial compounds.

EXPERIMENTAL

Catalysts were prepared according to [15] by incipient wetness impregnation of TiO₂ (anatase, 75 m²/g) either with the aqueous solution of $H_3PMo_{12}O_{40}$ heteropolyacid (HPMo) or $H_4PMo_{11}V_1O_{40}$ acid (HPMoV). The catalysts are denoted as HPMo-6; HPMo-12 and HPMoV-6; HPMoV-12, where the numbers denote the molybdenum content in wt.%. All catalysts were dried for 4 h at 378 K, and calcined for 2 h at 623 K.

The surface area of the catalysts was determined by measuring the adsorption-desorption isotherms of nitrogen at -78 K (BET method).

HDS of thiophene was performed in a continuous flow reactor at 623 K and 0.1 MPa. Each experiment was carried out with a fresh catalyst (0.1 g) which was standardized by in-situ calcination (30 min) in argon at 623 K. The calcined catalyst was activated by sulfidation with a mixture of H₂S+H₂ during 1 h at a

temperature of 623 K and flow rate of 40 cm³ min⁻¹. We had found in our preliminary experiments that such sulfidation treatment leads to maximum activity of the catalysts. After the activation of the catalyst was completed, the catalyst was flushed (30 min) with argon at the same temperature, and subsequently with the reaction mixture (6 mol % of thiophene in hydrogen) with a WHSV of thiophene of 2 h⁻¹ being fed into the reactor. The activity of the catalyst was measured for 5 h. It was expressed as the conversion of thiophene to C₄ hydrocarbons. The hydrogenation selectivity of the catalysts was evaluated as the ratio of concentrations of normal butane and the sum of C₄ compounds found in the reaction products (n-C₄/ΣC₄).

TPR measurements were carried out in an apparatus described earlier [16]. Hydrogen/nitrogen mixture (10 mol% H₂) was used to reduce the catalysts at a flow rate of 17 cm³ min⁻¹. The temperature was increased linearly at a rate of 20 K min⁻¹ from 293 K up to 1123 K.

IR spectra (400-1200 cm⁻¹) were recorded at room temperature on a Bruker IFS-25 Fourier transform IR spectrometer. The catalysts were pressed with KBr in the ratio of 1:150. The alumina and titania absorption in the 400-1200 cm⁻¹ range was compensated by subtraction of the normalized spectrum of the equivalent amount of support from the spectra of the catalysts [17].

RESULTS AND DISCUSSION

The catalysts and some of their properties are shown in Table 1. No significant decrease in the surface after loading the acids is observed. The finding is in accordance with the result obtained earlier [18], showing that the TiO₂ surface area decreases only slightly up to 21 wt.% of molybdenum in the catalyst. Molybdenum is thoroughly dispersed on the support surface forming a monolayer when a low concentration of heteropolyacid is introduced onto the support. On the other hand, very likely a polylayer is formed when the content of molybdenum in the catalyst is high.

The heteropolyanion interacts with terminal OH groups of the TiO₂ thus increasing the number of the Ti-O-Mo bonds in the surface layer [19]. The IR spectra confirm the presence of different phases in the catalysts indicating the interaction between the support and the acids. In the spectrum of the initial HPMo acid (Fig. 1), bands at about 965 cm⁻¹ (M=O), 785 and 870 cm⁻¹ (Mo-O-Mo) and a band at 1065 cm⁻¹ (P-O) characteristic of the Keggin structure [20] are observed. The bands shift slightly to lower frequencies when one molybdenum atom is substituted by vanadium. Shoulders appear at about 1085 and 990 cm⁻¹.

Table 1
Composition (wt.%), specific surface area and TPR data of the catalysts

№	Catalyst	Composition		S_{BET} m^2/g	TPR data		
		Mo	V		$\text{mmol H}_2/\text{g}^{\text{a}}$	$\text{mmol H}_2/\text{g}^{\text{b}}$	$T_{\text{max}}, ^\circ\text{C}$
1.	HPMo-12	11.95	-	67	2.60	4.56	488; 760
2.	HPMo-6	6.01	-	68	1.62	2.42	453; 749
3.	HPMoV-6	5.50	0.26	70	0.98	1.56	463; 749
4.	HPMoV-12	11.03	0.50	68	1.96	2.70	514; 839
5.	TiO ₂	-	-	75	0.26	0.37	603

^a20-650°C, ^b20-800°C

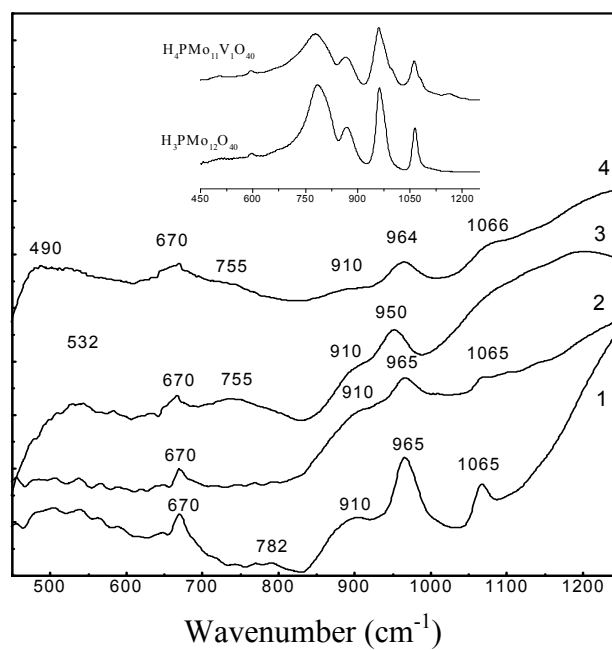


Fig. 1. IR spectra of the initial acids ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$) and the titania-supported catalysts: (1. HPMo-12; 2. HPMo-6; 3. HPMoV-6; 4. HPMoV-12)

More changes in the IR spectra are observed when the acids are supported on titania. The ratio of the bands in the spectra of the catalysts with different molybdenum content (HPMo-6 and HPMo-12) and the initial HPMo acid is constant. This result confirms that the Keggin structure of the calcined catalysts is preserved [13, 21] although some deformation is visible. The bands at about 1065 and 965 cm^{-1} are not changed, but the band characteristic of the Mo-O-Mo bond did not appear. Instead, a large plateau in the 850-920 cm^{-1} region and a band at about 910 cm^{-1} , characteristic of the titania-molybdenum heteropolyacid (TiMoHPA) [22], appear as a result of the interaction of the initial acid and the support. Neither can we exclude the presence of oxomolybdates. Their Mo=O bonds appear at 916 and 920 cm^{-1} [12, 23, 24]. We can state that in our catalysts a mixture of different Mo-containing phases is formed. The bands in the catalyst with low molybdenum content are of low intensity although their positions in the spectrum are similar to those appearing in the spectrum of the high-concentrated catalyst. No MoO_3 phase is formed in the low-concentrated catalysts (no bands at about 475; 610; 820; 860 and 995 cm^{-1} [21] were observed).

When the molybdenum atom in HPMo is substituted by the vanadium atom, the Keggin structure is disordered and the IR spectrum exhibits a change in the position of bands (Fig. 2): the V^{5+} ion disturbs the symmetry of the P-O_a bond in the HPMoV molecule due to changes in the Mo-O_d bond [25].

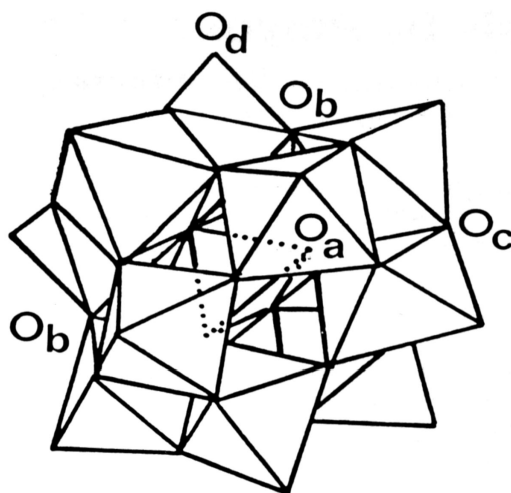


Fig. 2. Possibilities of position changes in a molecule of the Keggin structure
 $\text{P-O}_a \rightarrow \text{V-O}_a$; $\text{Mo-O}_d \rightarrow \text{V-O}_d$

The band, characteristic of the Mo-O_d bond, shifts to 990 cm⁻¹, whereas the band of the P-O bond is shifted to 1085 cm⁻¹ (Fig. 1). In the spectra of the catalysts with loaded HPMoV acid, this band is overlapped with a large band in the region of 1030-1100 cm⁻¹. An enlargement of the band to lower frequencies indicates a deformation of the V-O bond in the anion with the preserved Keggin structure [25]. Simultaneous increase of the spectrum line at higher frequencies demonstrates the overlapping of both the P-O and V-O bonds as a result of the vanadium-phosphate bond formation [25]. A strong absorption in the 1100-1200 cm⁻¹ region absorption observed in the spectra of the HPMo catalysts (Fig.1 - 1, 2) manifests the formation of phosphates [26] due to a stronger interaction of the HPMoV acid with the support (the anion is to a greater extent disordered).

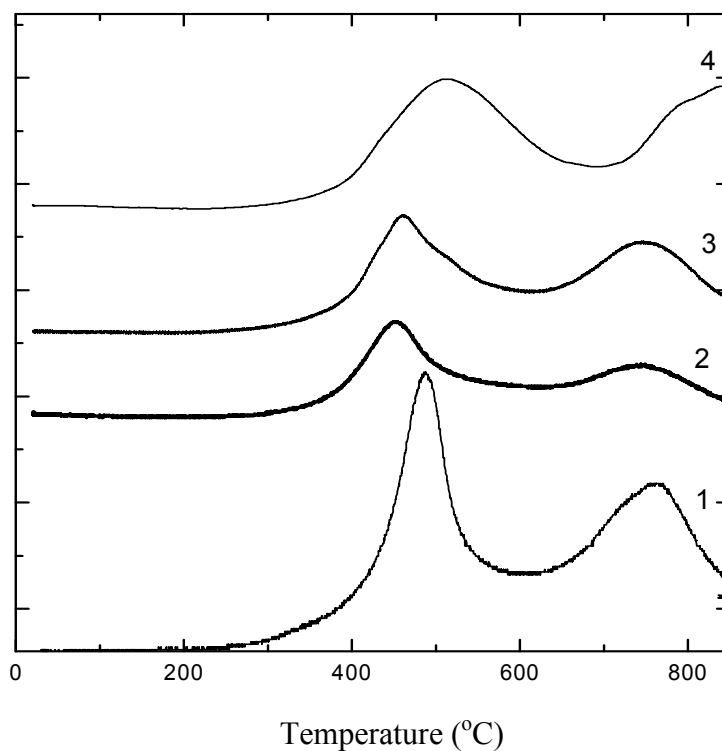


Fig. 3. TPR patterns of the catalysts: 1. HPMo-12; 2. HPMo-6; 3. HPMoV-6; 4. HPMoV-12

The IR spectra also show the presence of different phases in the catalysts appearing in dependence on their composition: a part of the initial acids with disordered structure, oxomolybdates, newly formed TiMoHPA and/or vanadium-phosphates.

The existence of a relation between the hydrodesulfurization activity of Mo-containing catalysts and their reducibility is known. Therefore, temperature programmed reduction (TPR) can help to reveal such properties of the catalyst as the shape and position of the TPR peaks depending on the phase composition of the catalysts. Two intense peaks appeared in the TPR patterns of our catalysts (Fig. 3).

In the TPR patterns of both HPMo catalysts, the first peak appears in the temperature region of 350-550°C, with its temperature maximum T_{\max} shifting to lower values when the concentration of molybdenum increases (Fig. 3). In the case of HPMoV catalysts, T_{\max} in the TPR patterns shifts to higher temperatures. It should be emphasised that a significant enlargement of the peak for the high-concentrated HPMoV catalyst occurs. Such enlargement could be explained with the heterogeneity of the reduced particles. The first peak is related likely to the reduction of polymolybdate phases formed in the catalyst. Both the initial HPMo and HPMoV acids and the new acids originating during the catalysts synthesis could be observed in the IR spectra (Fig. 1). Molybdenum present in the octahedral position (Mo_{oh}) of the phases is reduced more easily [27]. The process of MoO_3 phase reduction to MoO_2 phase [28] could explain the second peak in the TPR patterns. It should be noted that the catalysts containing vanadium (Table 1) consume much less hydrogen than the catalysts containing only molybdenum. The vanadium is likely to decrease the reducibility of the molybdenum phase (with the hydrogen consumption decreasing and the $\text{Mo}^{5+}/\text{Mo}^{4+}$ ratio increasing). The phase containing only molybdenum is reduced at a lower temperature.

Dependence of the observed hydrodesulfurization activity of the catalysts on time-on-stream value is presented in Fig. 4. The low-concentrated catalysts (6 wt.% Mo) exhibit a higher catalytic activity. This finding could be explained both by the promoting effect of the support and the formation of the active phase precursor (analogously to the TiMo heteropolyacid). Such a strong effect of the support on the catalytic activity was not observed when alumina and silica supports were used [23]. A high dispersion of Mo is achieved in the low-concentrated catalysts, whereas polylayer coverage is formed in the high-concentrated catalysts.

Substitution of molybdenum for vanadium increases and stabilizes the catalytic activity (Fig. 4). In contrast to the HPMoV catalyst, the initial high activity of the HPMo-12 catalyst decreases during the whole time of the catalysts' examination. We have shown earlier that a decrease in the concentration of Mo^{5+} active species is one of the reasons for catalyst

deactivation in a HDS reaction. Substitution of molybdenum by vanadium retards the process of the reduction of molybdenum ions to lower valence (Mo^{4+}) (see TPR data), and in this way, vanadium promotes the molybdenum active sites and stabilizes the hydrodesulfurization activity.

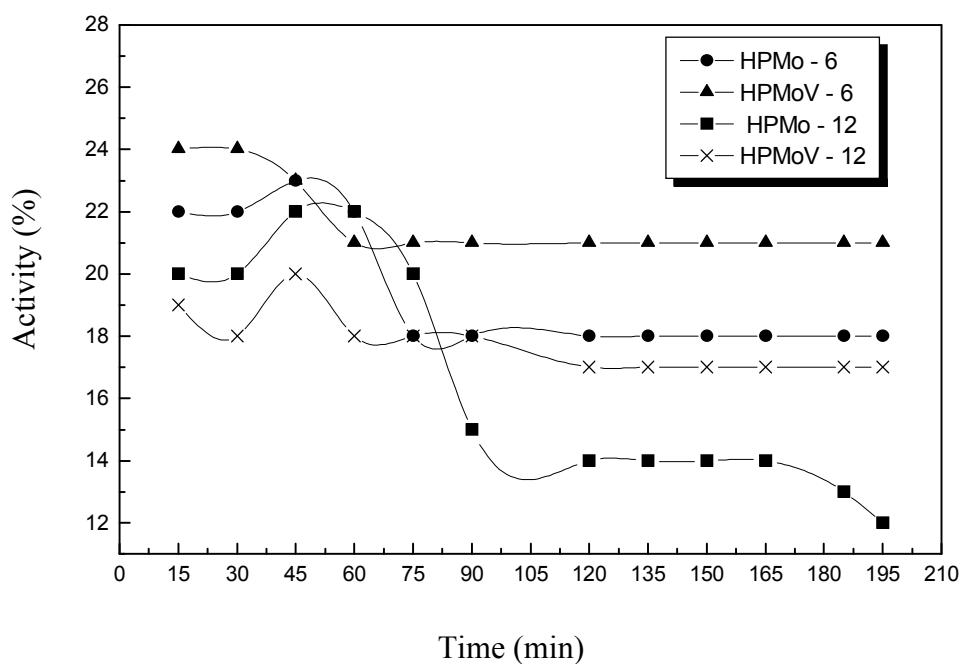


Fig. 4. HDS activity of the catalysts vs time on stream

Our experimental results also confirm the preservation of the initial Keggin structure in both HPMo and HPMoV acids supported over TiO_2 , although the IR spectra exhibit some disorder in their structure and prove the formation of the new TiMo heteropolyacid after the calcination of samples. The bands of the heteropolyacids (HPMo, HPMoV), vanadiumphosphate species and oxomolybdates appear in the IR spectra. Substitution of the molybdenum atom in the HPMo molecule by vanadium atom decreases the catalysts' reducibility and hydrogen consumption. Vanadium containing catalysts exhibit a higher and more stable hydrodesulfurization activity in comparison with the catalysts containing only molybdenum.

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