

## TPS and TPR study of HDS catalysts and process mechanism

I. Shtereva<sup>1\*</sup>, D. Vladov<sup>2</sup>, S. Rakovsky<sup>1</sup>, B. Iliencko<sup>3</sup>

<sup>1</sup> Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria

<sup>2</sup> University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd., 1756 Sofia, Bulgaria

<sup>3</sup> The Gas Institute, National Academy of Sciences of Ukraine, 39 Degtyarivska St., 03113 Kyiv, Ukraine

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Ni(Co)-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrodesulphurisation (HDS) process have been studied by means of kinetic, temperature-programmed reduction (TPR), and temperature-programmed sulphidation (TPS) methods. It has been established that on increasing the amount of MoO<sub>3</sub> active phase, and that of NiO promoter, both catalyst activity in the reaction of HDS and selectivity to butane are growing up. Correlations have been established between catalyst activity and TPR peak temperature so as between catalyst activity and TPS peak area. An approach is proposed to predict catalyst activity based on TPR and TPS characteristics. There is experimental evidence confirming a supposition that the active species in the reaction are oxysulphides that are being formed on the surface of the catalyst during activation. At least two types of active sites were found to be present on the surface: hydrogenation and hydrodesulphurization entities, their activity being dependent in a different way on temperature of the TPR peak maximum on activating the catalyst.

**Keywords:** HDS, Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, TPR, TPS

### INTRODUCTION

Supported Ni(Co)-MoO<sub>3</sub> catalysts are extensively used in hydrotreatment that is one of the most important processes in oil refining. Crude oil fractions treatment in the refineries impose the primary purpose of organic sulphur removal from the stream prior to use as various fuels [1–5]. It is so, as on the one hand, the quality of oil is constantly deteriorating, while on the other hand, the requirements for fuel quality are constantly growing up in view of environmental protection. Since 2005, European Community fuel regulations require sulphur levels less than 10 ppm after 1st January 2009 [6]. It should be noted that 10% of the global market for catalysts are hydrotreating catalysts [7]. The major segment of these catalysts is used for hydrodesulphurization (HDS).

Thomas *et al.* [8] arbitrarily characterize catalyst reducibility by the temperature at which 50% of the transition metal species are reduced. The authors have found that the HDS activity increases on decreasing this temperature. This feature suggests that reduction of the transition metal compounds is a crucial step in the transformation of the oxidic precursor into the sulphided catalyst.

Temperature-programmed reduction (TPR) has been shown to be a sensitive technique to study reducibility and it has been applied successfully for

characterization of CoO/Al<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and Co(Ni)-MoO<sub>3</sub> catalysts [9]. A series of temperature-programmed desorption and reduction experiments have been performed over *in-situ* sulphided bare  $\gamma$ -alumina support, alumina-supported monometallic Ni, Mo, and bimetallic NiMo catalysts. Temperature-programmed desorption (TPD) and TPR results were related to active site assignment of nickel- and molybdenum-associated centres in hydrodenitrogenation (HDN) and HDS reactions [10]. The influence of catalyst sulphidability on HDS activity has been studied in detail by Scheffer *et al.* [11]. They proved that active Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts are well sulphidable at low temperatures.

Since hydrodesulphurization reactions are carried out in a hydrogen atmosphere, it is tempting to investigate whether a direct correlation exists between the reactivity of various sulphur species registered by TPR and HDS activity [12]. During hydrodesulphurization extra hydrogen is always consumed due to the hydrogenation of unsaturated hydrocarbons. This is often undesirable, because it leads to loss of expensive hydrogen. On the other hand, hydrogenation and hydrocracking will become more important processes in the future as the need for clean fossil fuels has been extended to heavy petroleum fractions and coal [8]. Therefore, in addition to the HDS activities of the catalysts, it is also important to determine their hydrogenation activity.

Many studies have investigated the nature of the active phase in these catalysts [13] and the most

\* To whom all correspondence should be sent  
E-mail: stereva@ic.bas.bg

widely accepted model is that of Co(Ni)-Mo-S proposed by Topsøe *et al.* [14]. In this model, Ni or Co promoters of the active phase are enhancing the activity of sites located at the edges of molybdenum sulphide. Recently, Topsøe has also reported the existence of new sites of metallic character. These sites, located adjacent to the edges in the basal planes of the MoS<sub>2</sub> crystallites, have the ability to perform hydrogenation reactions [15], the latter being a favoured route in hydrodesulphurization. It has been suggested that the more active sites exist in MoS<sub>2</sub> crystallites of more than one slab. However, they can also exist in one slab crystallites having only weak interaction with the support [16]. The existence of these active sites and prevention of inactive species formation can be achieved by carefully controlling the metal-sulphur interaction during catalyst activation. Therefore, it is important to determine precisely the temperature of sulphidation of the catalyst during activation. The easiest way to do this is by using temperature-programmed sulphidation (TPS) data on the catalyst samples.

## EXPERIMENTAL

### Catalysts preparation

A series of alumina-supported NiO-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts (12, 15, 18 wt.% MoO<sub>3</sub>, and 2, 3, 4 wt.% NiO) were prepared by consecutive impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Cherok, surface area of 128 m<sup>2</sup> g<sup>-1</sup>) with an aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Merck), followed by impregnation with an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Acros Organics). In each impregnation step, the suspensions were stirred continuously at ambient temperature for 6 h, dried at 70°C under constant stirring for 2 h, further drying at 120°C, and finally calcined 4 h at 500°C. The amounts of ammonium heptamolybdate and nickel nitrate were so calculated as to obtain compositions of desired formulation.

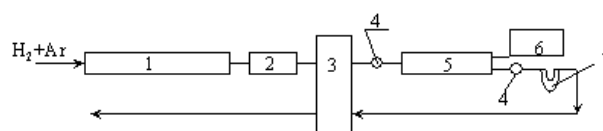
### Catalytic activity measurements

The model reaction of thiophene hydrodesulphurization was carried out in a continuous flow reactor. Catalyst amount was 0.5 g and a sieve fraction of 0.25–0.50-mm size was used. A measure of HDS activity of the catalyst was accepted to be the rate of thiophene decomposition, while the rate of *n*-butane (b) formation was taken as a measure for hydrogenation activity. HDS and hydrogenation activities in the reaction were determined after *in situ* preliminary activation of each catalyst sample in a flow mixture of 10% H<sub>2</sub>S in H<sub>2</sub> at 400°C for 2 h. The reaction was carried out in a continuous flow reactor at ambient pressure and excess of hydrogen.

The liquid reactant was fed into the reactor by means of a Gilson 302 piston pump. Gas feed rates were regulated and controlled by a Matheson flow regulator. The catalytic activity of the samples was measured at 300, 350, and 400°C. The reactor was directly connected by means of a 6-way valve to a gas chromatograph equipped with a thermal conductivity detector. Separation of the reaction products was performed on two GC columns. One of them had a length of 2 m and was filled with 10% Carbowax 1500 on Chromosorb to separate unreacted thiophene from the reaction products. The second column had a length of 8 m and was filled with 20%  $\beta\beta'$ -oxydipropionitrile on Diatomite, which separated the products of the reaction. GC-identified compounds were: unconverted thiophene, *n*-butane, 1-butene, *cis*-2-butene, *trans*-2-butene, and hydrogen sulphide. Thiophene conversion rate was selected to be a criterion for evaluating HDS activity, while the rate of *n*-butane formation was a measure of hydrogenation (HYD) activity. Before measurements, steady state conditions were attained at each reaction temperature for 2 h. Experimental confirmation that the reaction is proceeding in the kinetic region was obtained by calculating Weisz's criterion, which was less than unity.

### TPR and TPS measurements

The specific temperature of reduction of the various phases in the oxide form of the catalyst samples was determined by the method of temperature-programmed reduction. The reducing mixture containing 10% H<sub>2</sub> in argon was deoxygenated over a Pt/asbestos filter at 130°C, dried in a molecular sieve 5A filter and then fed into a tubular quartz reactor at a flow rate of 25 cm<sup>3</sup>.min<sup>-1</sup>. The TPR started from room temperature and the temperature was increased linearly at a ramp of 10 grad.min<sup>-1</sup> up to 600°C. The amount of catalyst sample charged in the reactor was 0.1 g. The TPR setup was equipped with a thermal conductivity detector. A scheme of the experimental setup is presented in figure 1.

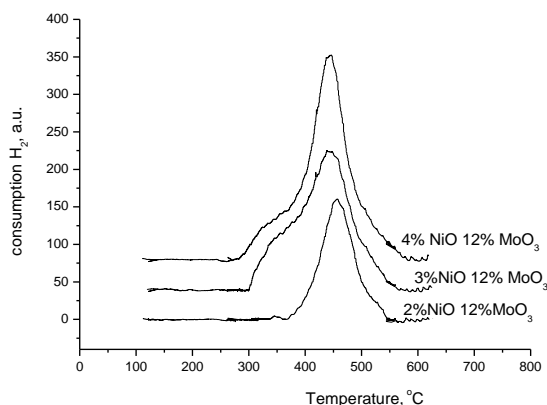


**Fig. 1.** Experimental set-up for temperature-programmed reduction: 1 – Matheson electronic mass flow regulator, 2 – Pt/asbestos catalyst and molecular sieve (0.5 nm), 3 – thermal conductivity detector; 4 – six-way valve, 5 – catalytic reactor placed in an oven, 6 – micro-processor-controlled thermal regulator, 7 – water trapping unit for evolved vapour during reduction.

In TPS experiments, reduced catalyst samples were cooled down to room temperature and TPS was carried out with similar equipment. 10% H<sub>2</sub>S were added to the reaction mixture and the heating procedure followed the conditions at which the TPR run had been conducted.

## RESULTS AND DISCUSSION

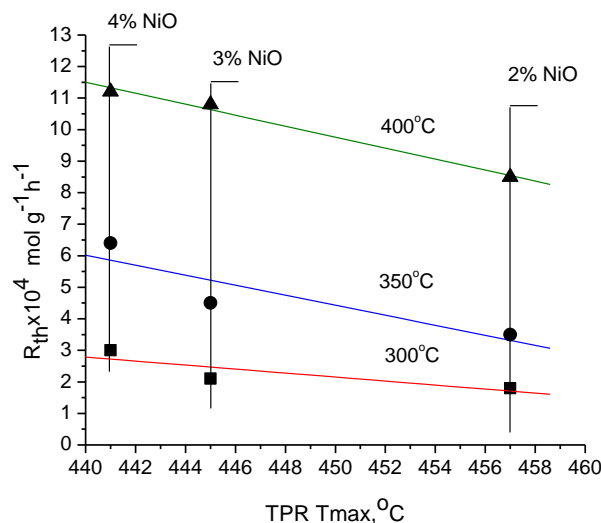
TPR measurements were conducted to determine catalyst reducibility. Figure 2 displays patterns of 12% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> samples promoted by 2, 3, and 4% NiO. All the runs were carried out up to the temperature, which is actually used in the HDS process (600°C). TPR profiles of samples having 15% and 18% MoO<sub>3</sub> had the same appearance with peak maxima shifted to lower temperatures by increasing NiO content but also on increasing MoO<sub>3</sub> content.



**Fig. 2.** TPR patterns of 12% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> promoted by 2, 3, and 4% NiO.

It is seen that by increasing NiO content the reduction occurred at lower temperatures, while the peak area was growing up. It should be noted here that in our previous studies with the same catalyst samples [17, 18] it was found that the rate of thiophene decomposition and the selectivity to butane formation increased with the increase in nickel content. An enhanced catalyst activity on increasing promoter amount has also been observed in the case of Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalysts [11]. Brito and Laine have assigned a TPR peak at 457°C in Ni-Mo-Al<sub>2</sub>O<sub>3</sub> to reduction of octahedrally coordinated Mo<sup>6+</sup> ions of a Ni-Mo-O phase [19]. Accordingly, the peaks observed in this study at 441, 445, and 457°C of the 12% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst samples promoted by 2, 3, and 4% NiO, respectively, we assign to reduction of this species. TPR patterns of 15 and 18% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst samples, also promoted by 2, 3, and 4% NiO, demonstrated a peak in the same temperature interval, but it was shifted to lower temperatures with the increase of MoO<sub>3</sub> content.

Figure 3 represents dependences of sample HDS activity on the TPR peak maximum attributed to reduction of octahedrally coordinated Mo<sup>6+</sup> ions of a Ni-Mo-O phase in 2, 3, and 4% NiO-promoted 18% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst samples at reaction temperatures of 300, 350, and 400°C. The dependences have similar appearance at the three temperatures of HDS reaction. It is seen that activities of samples of greater nickel content, i.e. lower temperatures of the TPR maxima, are higher.

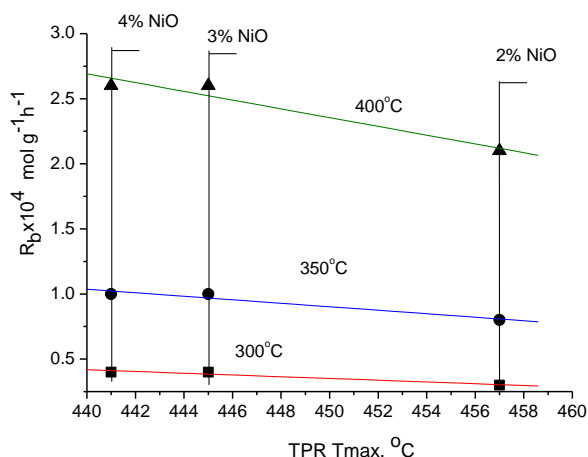


**Fig. 3.** Dependence of thiophene decomposition rate at various reaction temperatures on peak maximum in TPR patterns of NiO-promoted 18% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.

At selected reaction temperatures, the rate of thiophene decomposition is increased on decreasing the temperature of reduction of the active phase. This is experimental evidence for suggested mechanism of reduction of these catalysts put forward on the basis of quantum chemical calculations [20]. According to the proposed mechanism, during the first step of catalyst activation, i.e. reduction, hydrogen is bonded to the oxygen entities of the MoO<sub>3</sub> phase to liberate H<sub>2</sub>O and thus an oxygen vacancy is formed on the surface. Sulphur is chemisorbed on the so formed vacancy during the second step of the activation process, namely sulphidation. Certainly, a lower temperature of reduction will contribute to the formation of more vacancies thus increasing catalyst activity. This result is also in agreement with an established higher activity of catalysts, for which 50% reduction is occurring at a lower temperature [8]. In our case, for the samples of different composition, this dependence had the same character as that of active samples having a higher content of Ni and Mo.

Another important for the industry characteristics of these catalysts is their hydrogenation activity. Figure 4 illustrates dependence of the butane

formation rate on the temperature of peak maximum in the TPR pattern of the same catalyst samples.



**Fig. 4.** Dependence of butane formation rate at various reaction temperatures on the temperature of peak maximum in TPR patterns of NiO-promoted 18% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.

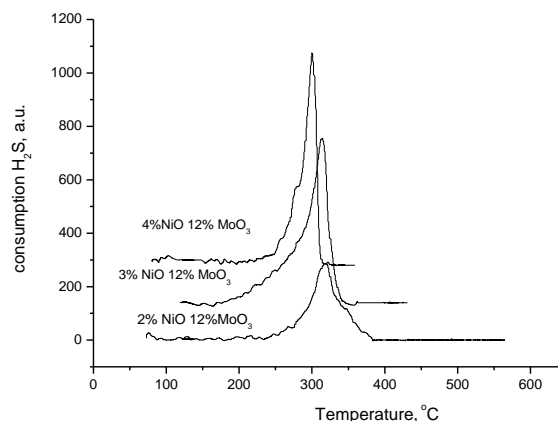
Comparing the tendencies shown in figures 3 and 4 it is seen that both the HDS and hydrogenation activities are decreasing with the increase in temperature of the peak maxima during TPR analysis of the catalyst samples, but the slopes are different. It is evident that the two processes take place on two types of active sites on the catalyst surface in agreement with a supposition of Radomyski [21]. According to this author, thiophene is adsorbed on one type of active sites and then it decomposes into butenes and H<sub>2</sub>S, but if it is adsorbed on another type of active sites, at first, it is hydrogenated into tetrahydrothiophene and the latter is decomposed into the products of the reaction.

The effect of sulphidation during catalyst activation was also studied with respect to changes of properties. Figure 5 represents TPS patterns of 12% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> samples promoted by 2, 3, and 4% nickel oxide.

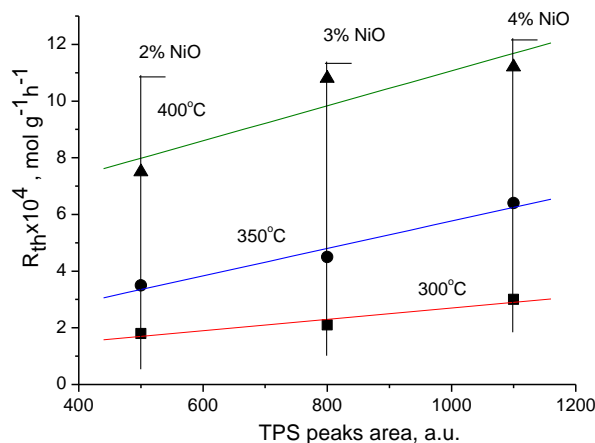
The increase in NiO content gives rise to an increase of the TPS peak area and a shift of the peak maximum to a lower temperature. The same kind of dependence was also observed with samples of higher MoO<sub>3</sub> content (15 and 18%). The increase in MoO<sub>3</sub> quantity led also to peak shifts to lower temperatures if samples of the same NiO content were compared.

Figure 6 illustrates dependences of thiophene decomposition rate at a reaction temperature of 300, 350, and 400°C on TPS peak area of 12% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst samples promoted by various quantities of NiO (2, 3, 4%). It is seen that an increase in the TPS peak area resulting from the increase of nickel amount in the catalyst sample

leads to a higher HDS activity. Similar dependences were observed with other promoted MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> samples containing 15 and 18% MoO<sub>3</sub>.



**Fig. 5.** TPS patterns of 12% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst samples promoted by 2, 3, and 4% NiO.

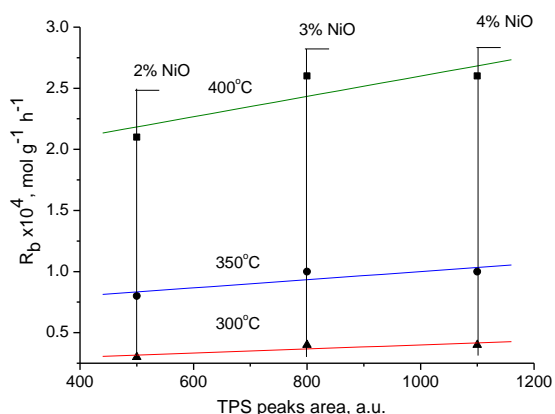


**Fig. 6.** Dependences of thiophene decomposition rate at various reaction temperatures on peak area of TPS profiles of NiO-promoted 12% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst samples.

The increase in TPS peak area comes as a result of an increase in sulphur quantity chemisorbed on the surface of these catalysts. This dependence was observed with all reaction temperatures studied. Our results are a new experimental evidence supporting the reaction mechanism of thiophene hydrodesulphurization over a Mo catalyst proposed on the basis of molecular orbital calculations [22]. According to this mechanism, the thiophene molecule is adsorbed *via* the sulphur atom on a vacancy between two Mo atoms of the oxysulphide, which is being formed on the catalyst surface during activation. The C–S bond in the adsorbed thiophene is weakened and after an attack by hydrogen molecule this bond is broken. Butane and butenes are liberated as well as hydrogen sulphide. It is evident that according to this reaction mechanism the increase in sulphur amount

(in the oxysulphide) on the catalyst surface would lead to enhanced activity.

For all the studied catalyst samples an increase in the hydrogenating activity (expressed as the rate of butane formation) was also observed on increasing sulphur content in the catalyst. This correlation has a similar character but a lower slope if compared to the changes in HDS activity (Fig. 7).



**Fig. 7.** Dependence of the butane formation rate at various reaction temperatures on the peak area in TPS patterns of NiO-promoted 12% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts samples.

Thus, the effect of sulphur on catalyst activity for hydrogenation and HDS once again suggests that at least two types of sites occur on the surface of the activated catalysts, which are responsible for hydrogenation and hydrodesulphurization reactions. These results are further confirmation of earlier formulated suggestion during a study of the effect of catalyst pretreatment on catalyst activity and selectivity [23].

## CONCLUSIONS

The first step in HDS of sulphur-containing organic compounds on Ni-Mo catalysts involves adsorption *via* the sulphur atom on a vacancy at the catalyst surface. During catalyst activation at least two types of active sites are being formed on the surface responsible for hydrogenation and hydrodesulphurization reactions. The activity and selectivity of these catalysts can be predicted based on TPR and TPS data.

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## ИЗСЛЕДВАНЕ С ТПР И ТПС НА КАТАЛИЗАТОРИ ЗА ХДС И МЕХАНИЗЪМ НА ПРОЦЕСА

Ис. Щерева<sup>1\*</sup>, Д. Владов<sup>2</sup>, Сл. Раковски<sup>1</sup>, Б. Илъенко<sup>3</sup>

<sup>1</sup> *Институт по катализ, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*

<sup>2</sup> *Химикотехнологичен и металургичен университет, бул. „Климент Охридски“ 8, 1756 София, България*  
*Институт за газ, Национална академия на науките, Киев, Украйна*

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(Резюме)

Чрез кинетични изследвания, температурно програмирана редукция (ТПР) и температурно програмирано сулфидиране (ТПС) са изследвани Ni(Co)-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> катализатори за хидродесулфуриране (ХДС). Установено е, че при увеличаване на количеството на активната фаза (MoO<sub>3</sub>) и на промотора (NiO) активността на катализатора в реакциите на ХДС и хидриране на бутан се увеличават. Установена е зависимост между температурата на максимума на ТПР пика, площта на ТПС пика и активността на катализаторите. Предложен е начин за предсказване на активността на катализаторите по техните ТПР и ТПС характеристики. Експериментално е потвърдено предположението, че активни в реакцията са оксисулфиди, образувани на повърхността на катализатора при неговото активизиране. Установено е наличието на поне два типа активни центрове на каталитичната повърхност – хидриращи и хидродесулфуриращи, чиято активност корелира по различен начин с температурата на максимума на ТПР пика.