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Thiophene conversion and ethanol oxidation on SiO_2-supported 12-PMoV-mixed heteropoly compounds

A.A. Spojakina [a,*], N.G. Kostova [a], B. Sow [b], M.W. Stamenova [a], K. Jiratova [b]

[a] Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

[b] Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic

Abstract

Surface properties of supported MoV heteropoly compounds and their activities in hydrodesulfurization of thiophene and oxidation of ethanol were studied. Vanadium incorporated into the phosphomolybdic acid anion increased extent of oxidative dehydrogenation of ethanol to acetaldehyde, whereas the catalyst with $(VO)^{2+}$ increased complete ethanol oxidation to CO_2. The catalysts with $(VO)^{2+}$ or one V atom in the anion showed an increase in HDS activity. Vanadium in anion of phosphomolybdic acid also increased hydrogenation ability. Acidic sites of medium strength were proved to be the most suitable for ethanol oxidation. Such explicit dependence of thiophene hydrodesulfurization on any type of acidic sites was not confirmed. Activity order of supported MoV heteropoly compounds in HDS of thiophene correlated well with the amount of hydrogen consumed during TPR.

Keywords: Heteropoly compounds; Thiophene hydrodesulfurization; Ethanol oxidation

1. Introduction

Molybdenum Keggin heteropoly compounds have been extensively studied either as active components of supported catalysts or as starting material for the preparation of oxidic catalysts [1,2]. Properties of heteropoly compounds (acid strength and oxidizing ability) can be easily controlled by their composition.

Heteropoly compounds with mixed addenda exhibit especially interesting catalytic features. Various properties of the compounds are significantly affected [3,4] by the substitution degree of molybdenum for vanadium. Though the MoV-mixed heteropoly compounds have been widely studied, their oxidizing ability remains controversial [2,5]. Polymolybdates can be interesting precursors of the hydrodesulfurization (HDS) catalysts [6], especially the polymolybdates with vanadium in their molecules, because vanadium can act not only as a poison of the HDS catalysts [7] but also act as their promoter [8]. For example, addition of 0.25–1.0 wt.% of vanadia promoted hydrodesulfurization and hydrogenation activity of $NiMo/Al_2O_3$ catalyst [8]. Vanadium sulfides were catalytically active in both hydrogenation and hydrodesulfurization reactions [9,10]. It seems that the effect of V on hydrotreating activity could depend on the vanadium origin.

In this paper the effect of V placed in the countercation position and of V substituting molybdenum atom in the anion of 12-phosphomolybdic acid on the acidity and catalytic properties have been examined. Polyfunctionality of the catalysts has been

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[*] Corresponding author. Fax: +3592-756-116.

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studied by the comparison of activities and selectivities in ethanol oxidation and thiophene hydrodesulfurization reactions.

2. Experimental

Preparation of initial compounds and catalysts. 12-Phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot H_2O$, Fluka) was used as parent compound. Phosphovanadomolybdic acid with one or two substituted Mo atoms (denoted as $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$) was prepared according to Tsigdinos and Hallada [11]. Phosphomolybdic acid with $(VO)^{2+}$ countercation (denoted as $(VO)_{1/5}PMo_{12}O_{40}$) was prepared according to Casarini et al. [4]. All catalysts were prepared by impregnation of silica (Cab–O–Sil, $S_{BET} = 290\,m^2\,g^{-1}$) with 1.25 mmol heteropoly acid per 1 g of the support. In dependence on the extent of Mo substitution for V, the amounts of Mo and V changed from 12 to ca. 10 wt.% and from 0 to ca. 1 wt.%, respectively. The amounts of Mo and $(VO)^{2+}$ in the $(VO)PMo_{12}$ catalyst were taken to be equal to those in the $HPMo_{11}V_1$ catalyst. The samples are denoted as $HPMo_{12}$, $HPMo_{11}V_1$, $HPMo_{10}V_2$, $(VO)PMo_{12}$. The catalysts were dried at 70°C for 4 h and calcined in the air at 350°C for 2 h.

Temperature-programmed desorption (TPD) of NH_3 was carried out with 0.05 g of a catalyst and helium as carrier gas (flow rate $15\,cm^3\,h^{-1}$). Prior to NH_3 desorption, all catalysts were calcined to 350°C. Then, 30 doses (840 μl each) of NH_3 were injected into the helium stream at 30°C. Desorption of NH_3 was started ($20°C\,min^{-1}$) and finished when temperature 350°C was reached. PFM Module of Origin program (Microcal Software, MA, USA) was applied to analyze the overall desorption peaks.

IR spectra ($400–1200\,cm^{-1}$) were recorded at the room temperature on a Bruker IFS-25 Fourier transform IR spectrometer. The samples were pressed with KBr in the ratio 1:150. A compensation method was used to eliminate the support spectrum.*Temperature-programmed reduction (TPR)* was carried out in an apparatus described earlier [12]. A H_2–N_2 mixture (10 mol.% of H_2) was used to reduce samples at a flow rate of $135\,cm^3\,min^{-1}$. The temperature was linearly raised at a rate of $20°C\,min^{-1}$ up to 850°C.

Hydrodesulfurization of thiophene was measured in a continuous flow reactor at 350°C, atmospheric pressure and with a fresh catalyst sample (0.2 g). The catalyst was heated up to 350°C (1.5 h, in argon) and activated by sulfidation with H_2S (350°C, $40\,cm^3\,min^{-1}$, 0.5 h). After activation, feeding of the reaction mixture (6 mol.% of thiophene in H_2, $25\,cm^3\,min^{-1}$) was started. Thiophene feeding lasted 4–5 h. The HDS activity was evaluated as thiophene conversion to hydrocarbons (ΣC_4) by the use of gas chromatography (GC) and selectivity as the thiophene conversion to butane.

Oxidation of ethanol (1000 ppm in the air) was measured within the temperature range of 120–210°C using GC as an analytical tool. Activity of a catalyst was determined as both conversion of ethanol obtained at 130°C and the T_{50} temperature at which 50% conversion of ethanol was observed. Selectivity of the oxidation reaction was determined as conversion to individual reaction products when total conversion of ethanol reached 50%.

Accuracy of catalytic activity determination in both thiophene hydrodesulfurization and ethanol oxidation reactions was better than 10 rel.%.

3. Results

3.1. IR spectra

IR spectra of the initial $H_3PMo_{12}O_{40}$ and its vanadium substituted compounds are presented in Fig. 1a. Characteristic bands of Keggin anion are shifted to lower frequencies proportionally to the number of introduced vanadium atoms. At the same time, shoulders at about 1085 and $990\,cm^{-1}$ appear. In contrast to V-substituted $HPMo_{12}O_{40}$ acids, vanadium in the cation position did not show any effect on the IR bands positions.

The IR bands positions substantially changed when the prepared heteropoly compounds are supported on silica and the catalysts calcined at 350°C. An interaction of the heteropoly compounds with the support caused enlargement of the main bands and a shift of their maxima to lower frequencies (Fig. 1b). The band at $1110\,cm^{-1}$, very intensive in the Cab–O–Sil spectrum, assigned to Si–O–(Si) vibrations in $[SiO_4]$-tetrahedra [13], appeared in the spectra of all silica-supported catalysts.

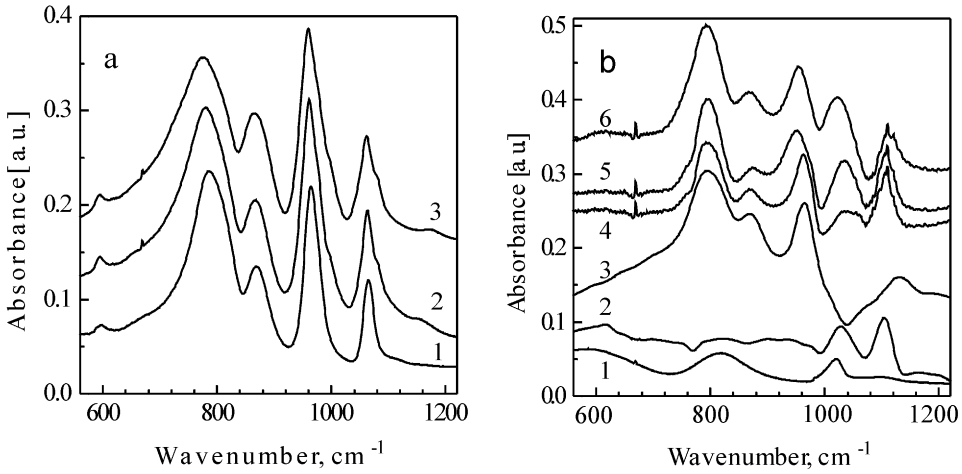

Fig. 1. (a) IR spectra of initial heteropoly acids: (1) $H_3PMo_{12}O_{40}$, (2) $H_4PMo_{11}VO_{40}$, (3) $H_5PMo_{10}V_2O_{40}$. (b) IR spectra of V_2O_5 (1) and the silica-supported catalysts: (2) V_2O_5, (3) $HPMo_{12}$, (4) $HPMo_{11}V_1$, (5) $HPMo_{10}V_2$, (6) $(VO)PMo_{12}$.

In the spectrum of the $HPMo_{11}V_1$ catalyst, a band at $1060\,cm^{-1}$ (also observed in the spectrum of the parent acid) was shifted to lower frequency and a shoulder at $1038\,cm^{-1}$ appeared. In the spectrum of the $HPMo_{11}V_1$ catalyst, a band at $1060\,cm^{-1}$ observed in the spectrum of the parent acid was shifted to lower frequency. A shoulder at $1038\,cm^{-1}$ appeared. In accordance with [14], occurrence of the latter can be explained by the splitting of the P–O bond, the result of deformation of the V containing heteropoly anion after the calcination. The IR spectrum seems to indicate fragmentation of the $H_4PMo_{11}V_1O_{40}$ molecules through interaction with silica which results in the formation of lacunar heteropoly anion.

$$[PMo_{11}V_1O_{40}]^{4+} \rightarrow [PMo_{11}O_{39}]^{7-} + [VO]^{2+}$$

A large band of around $1030\,cm^{-1}$ appeared in the spectra of both $(VO)HPMo_{12}$ and $HPMo_{10}V_2$ catalysts. The band was shifted to lower frequency in the spectrum of $HPMo_{10}V_2$. In case of $(VO)HPMo_{12}$, the shape of the $1030\,cm^{-1}$ band indicates the overlapping of P–O and V–O bands which arise at about 1060 and $1022\,cm^{-1}$, respectively (Fig. 1b-2, b-3, b-6). The $(VO)^{2+}$ cation in this catalyst can be bonded to the support as well. After the mixing of 1 wt.% of vanadia with SiO_2, IR spectrum showed large band at $1105\,cm^{-1}$, though pure V_2O_5 revealed bands at 600, 825 and $1022\,cm^{-1}$. Thus, appearance of the $1022\,cm^{-1}$ band in the spectrum of the SiO_2-supported system could indicate presence of the V–O bond. Since the amount of vanadia in the catalyst was very low, the $1030\,cm^{-1}$ band could prove highly dispersed vanadia either on the SiO_2 surface or over the heteropolyanion clusters. Probably, when $HPMo_{10}V_2$ catalyst is calcined, a part of vanadium is released out of the heteropoly anion and a mixture of the lacunar $H_3Mo_{12}O_{40}$ heteropolyanion and dispersed vanadia are formed on the silica surface.

3.2. *TPR of the catalysts*

TPR data of the catalysts calcined at 350°C are shown in Table 1and Fig. 2. TPR patterns of all catalysts are similar, since they consist of the two main reduction peaks observed at temperatures around 530 and 720°C. Detailed analysis of the TPR patterns indicates that the first reduction peak of the $HPMo_{12}$ and $HPMo_{11}V_1$ catalysts includes two overlapping peaks with maxima at 525 and 545°C. The low-temperature reduction peak (525°C) in the TPR patterns of the two remaining catalysts, $HPMo_{10}V_2$ and $(VO)PMo_{12}$, is missing. Reduction of the $(VO)PMo_{12}$ catalyst starts slowly at 300°C and quickly increases at 500°C to reach T_{max} at 542°C. With the $HPMo_{11}V_1$ sample, the peak at 545°C is hidden as a shoulder of the

Table 1
Results of TPR, TPD of ammonia, oxidation of ethanol and HDS of thiophene obtained over various SiO_2-supported 12-PMoV-mixed heteropoly compounds

Catalyst	$HPMo_{12}$	$HPMo_{11}V_1$	$HPMo_{10}V_2$	$(VO)PMo_{12}$
TPR				
mmol H_2 g^{-1} (20–800°C)	0.26	0.31	0.25	0.32
Reduction peak maximum (°C)				
T_1	522	525	–	–
T_2	543	540[a]	545	542
T_3	721	733	714	717
TPD				
mmol NH_3 g^{-1}	0.28	0.28	0.41	0.31
Desorption peak maximum (°C)				
T_1	70	85	84	80
T_2	96	122	121	115
T_3	164	161	174	178
T_4	312	227	236	273
Desorption peak area (rel.%)				
A_1	8	24	19	14
A_2	11	9	26	18
A_3	45	27	29	47
A_4	36	40	26	24
Oxidation of ethanol				
Conversion (%) at 130°C	49	39	44	65
Selectivity[b] (%)				
Ethylene	16.3	15	14	5.5
Diethyl ether	12.2	13	13	16
Acetaldehyde	8.5	15	14.5	9
CO_2	12	8	10	19
HDS of thiophene				
Conversion (%) after				
50 min	37	35	39	42
75 min	42	40	40	48
120 min	39	42	39	42
150 min	36	41	34	43
200 min	34	38	29	43
250 min	33	39	28	39
Selectivity (%) after				
75 min	36	35	35	32
120 min	35	33	32	28
200 min	29	33	27	25
250 min	24	33	24	25

[a] Shoulder.
[b] Expressed as conversions to individual products, %, observed at identical (50%) total conversion of ethanol.

first one. The TPR results show that vanadium in anion or in countercation position of heteropoly molybdates makes reduction of molybdenum species easier. The reduction up to 530°C could also include reduction of vanadium containing species. The second main peak (at about 720°C) is probably connected with a deeper reduction of Mo species ($HPMo_{12}$) and/or with reduction of a new phase containing V and P (Fig. 1b).

Reducibility of the catalysts, given by the amount of hydrogen consumed during reduction, is as follows: $(VO)PMo_{12} > HPMo_{11}V_1 \geq HPMo_{12} > HPMo_{10}V_2$.

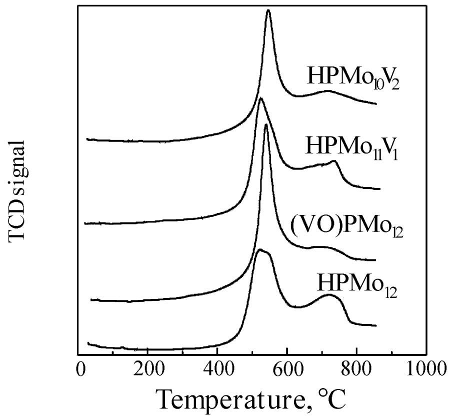

Fig. 2. TPR profiles of the catalysts.

3.3. *TPD of ammonia*

Data on TPD of NH_3 obtained with all catalysts (Table 1) showed slight differences in their acidic properties. Four peaks with maxima 70, 96, 164, and 312°C on the TPD pattern of $HPMo_{12}$ reveal acidic sites of different strength, medium strength being the most numerous. Introduction of one or two V atoms into the anion of $H_3PMo_{12}O_{40}$ caused a slight variation in acidity of the catalysts: Strength of the strongest acidic sites decreased, but that of the weaker sites increased. Portion of the stronger acidic sites decreased. Results agree with pyridine adsorption data [15] that prove lower ability of the V-containing acids to retain pyridine at an elevated temperature. Neutralization of $H_3PMo_{12}O_{40}$ with $(VO)^{2+}$ cation led to a decrease in the strength of the strongest acidic sites and to a slight increase in the strength of weaker sites. With the catalyst, the amount of the strongest sites decreased and that of the weaker sites increased. The data obtained show that the effect of $(VO)^{2+}$ cation on acidic properties of the $HPMo_{12}$ catalyst is lower than the effect of V substituted Mo in heteropoly anion.

3.4. *Catalytic activity*

Activities of the catalysts in ethanol oxidation in dependence on temperature were obtained [16] and data expressing activities at 130°C are given in Table 1. Compared with $HPMo_{12}$, the $(VO)PMoO_{12}$ catalyst showed higher catalytic activity. Contrary to it, the replacement of Mo in the anion for V led to a slight decrease in oxidation activities (the T_{50} temperatures (in °C), at which 50% conversion of ethanol was observed, are given in brackets):

$$
\begin{aligned}
&(VO)PMo_{12}(121) > HPMo_{12}(131)\\
&\quad > PMo_{11}V_1(136) \geq HPMo_{10}V_2(135)
\end{aligned}
$$

Activities of the catalysts with one or two vanadium atoms were similar and varied within an experimental error. Ethylene and acetaldehyde were main reaction products observed with all catalysts, and for that reason, simultaneous ethanol dehydration and oxidative dehydrogenation had to proceed. Diethyl ether in amount up to 10% was also observed with all catalysts. The catalysts with vanadium in the anion gave the increased extent of oxidative dehydrogenation of ethanol to acetaldehyde, whereas the $(VO)PMo_{12}$ catalyst showed higher conversion to CO_2.

Activity data obtained with HDS of thiophene are shown in Table 1. With all catalysts, thiophene conversion changed with increasing time-on-stream. Maximum non steady-state conversion was observed 1–2 h after the reaction beginning. The $(VO)PMo_{12}$ catalyst showed the highest catalytic activity, whereas the $HPMo_{10}V_2$ catalyst manifested the lowest activity of all. When the activity of the catalysts reached their steady-state values, activity order remained approximately the same as that obtained under non steady-state:

$$
\begin{aligned}
&(VO)PMo_{12}(39\%) \geq HPMo_{11}V_1(39\%)\\
&\quad > HPMo_{12}(33\%) > HPMo_{10}V_2(28\%)
\end{aligned}
$$

Steady-state hydrogenation activity of the catalysts (Table 1) changed with the introduction of vanadium into the $H_3PMo_{12}O_{40}$ anion: The $HPMo_{11}V_1$ catalyst showed high and stable hydrogenation activity contrary to the $(VO)PMo_{12}$ catalyst, whose hydrogenation activity was the lowest.

4. Discussion

Analysis of literature data show that information on the effect of vanadium on the activity of HDS catalysts could depend on the catalyst preparation, vanadium origin and a feed used during catalyst testing. In spite of reported HDS activity of vanadium sulfides [9,10] and published considerations that vanadium in low concentration could be a promoter of hydrotreating catalysts [8], Dejonghe et al. [17] did not find any increase in hydrogenation activity of a Mo/Al_2O_3 catalyst containing up to 2 wt.% V. They observed only a slight increase in hydrogenation activity of a $NiMo/Al_2O_3$ catalyst. Promotional effect of V on the oxidation activity was also not high [18], but its effect on reaction selectivity was more pronounced. Our results obtained from IR, TPR, TPD experiments and catalytic activity studies confirm that the MoV mixed heteropoly compounds can serve as interesting precursors of active sites in ethanol and thiophene conversions. Vanadium incorporated into the heteropoly compounds in amount of about 0.5 wt.% increases thiophene conversion (Table 1, $HPMo_{11}V_1$ and $(VO)PMo_{12}$). Initial catalytic activity of the $HPMo_{10}V_2$ catalyst with about 1 wt.% V is also high, but not very stable.

Close relation between the acidity and the activity in ethanol oxidation was proved in the paper: The activity correlates well ($R = 0.85$) with the amount of medium acidic sites (denoted as A_3 in Table 1). Cooperation of acidic sites of heteropoly molybdates in the oxidation of various organic compounds was proposed by Misono [18] and confirmed by Busca et al. [19].

Thiophene conversion over the studied catalysts did not show such a clear relationship with their acidic properties, though a decrease in acidity correlated well with a decrease in HDS activity of the silica-supported $HPMo_{12}$ catalysts [20]. Reaction mechanism can vary with a catalyst composition and reaction conditions. Assumption of different mechanisms is justified with respect to variety of surface structures of adsorbed thiophene [21].

Vanadium present in the $HPMo_{11}V_1$ and $(VO)PMo_{12}$ catalysts caused an increase in the reducibility of both the catalysts (Table 1) and, at the same time, an increase in thiophene conversion. The activity order correlates well ($R = 0.93$) with the amount of hydrogen consumed during TPR. The data thus obtained are in accordance with the findings [22,23] confirming good correlation of the HDS catalytic activity with the ease of reduction of molybdenum species. With both catalysts, the portions of more easily reducible species are higher than those observed with remaining catalysts. Without vanadium a deeper reduction of Mo species is observed (Fig. 2, $HPMo_{12}$).

In the $HPMo_{10}V_2$ catalyst, a part of vanadium is released during calcination and a mixture of the $H_3PMo_{12}O_{40}$, lacunar anion and very dispersed analog of V_2O_5 was formed. The latter can consequently form vanadophosphate [14] responsible for a decrease in the catalyst reducibility and the HDS activity.

Amount of butane in the reaction products informs us about hydrogenation ability of the HDS catalysts. From all catalysts studied, the $HPMo_{11}V_1$ catalyst shows the highest hydrogenation and HDS activities. The $HPMo_{10}V_2$ catalyst also manifested high initial HDS and hydrogenation activities that could be connected with its high initial acidity (Table 1). However, the HDS activity decreased fast owing, probably, to either a decrease in catalyst acidity or continuing vanadium release from anion detected by IR spectra (Fig. 1b).

Acetaldehyde detected in reaction products of ethanol oxidation (Table 1) proves that the reaction proceeds by both acid–base and reduction–oxidation mechanism. It was proposed earlier that oxygen atom in the oxidized product comes from water molecules [24] which are formed by ethanol dehydration on acidic sites. Water molecules, similarly as H_2S formed during thiophene conversion [20], can increase thermostability of V–Mo heteropoly compound structure [14]. It was shown that the V^{4+}/V^{5+} ratio in the V-containing heteropoly molybdate also affected oxidation activity [24]. In case of thiophene hydrodesulfurization running over supported heteropoly compounds we propose a variant of reaction mechanism taking into account participation of the acidic SH^- and OH^- groups, as well as coordinatively unsaturated sites linked with Mo^{5+} [20,25]. In the HDS reaction, the Mo^{5+} ions surrounded by oxysulfides [25,26] seem to be the most active species of molybdenum obtained from heteropoly compounds. Initial high hydrodesulfurization activity and amount of Mo^{5+} ions decreased until steady-state activity is obtained [25]. It is probable that optimal V^{4+}/V^{5+} ratio in the catalyst makes reduction of Mo^{6+} to Mo^{5+} easier and keeps the degree of reduction of the molybdenum species more stable. Facile reduction and reoxidation of $(VO)^{2+}$ species occurring near heteropoly anion was already mentioned [27]. It follows from our experiments that such species in the (VO)PMo_{12} sample as well as those released from anion of the $HPMo_{11}V_1$ catalyst during its partial fragmentation (see IR spectrum 4 in Fig. 1b) and anchored to the support near the newly formed lacunar anion could be the best vanadium species promoting and stabilizing thiophene hydrodesulfurization and butenes hydrogenation.

5. Conclusion

Vanadium incorporated into the anion of phosphomolybdic acid caused a decrease in the strength of strong acidic sites, but portion of acidic sites of medium strength is increased. The $(VO)^{2+}$ cation affected acidity of phosphomolybdic acid to a lesser extent. Vanadium placed in the anion of the acid increased extent of oxidative dehydrogenation of ethanol to acetaldehyde, whereas vanadium in the countercation increased complete ethanol oxidation to CO_2. Incorporation of the $(VO)^{2+}$ cation or replacement of one Mo atom in anion of phosphomolybdic acid for V caused an increase in hydrodesulfurization activity. Vanadium in anion increased hydrogenation function of HPMo acid. Acidic sites of medium strength seem to be the most suitable for ethanol oxidation to CO_2 and acetaldehyde. Such explicit dependence of thiophene hydrodesulfurization on any types of acidic sites was not confirmed. The activity order of MoV heteropoly compounds in HDS of thiophene correlated well with the amount of hydrogen consumed during TPR.

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