

EFFECT OF HETEROATOM ON PROPERTIES OF SiO₂-SUPPORTED HETEROPOLYMOLYBDATESAlla SPOJAKINA^a, Nina KOSTOVA^a and Kveta JIRATOVA^b^a *Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria;**e-mail: cheminfo@ipchp.ipc.bas.bg*^b *Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Czech Republic; e-mail: jiratova@icpf.cas.cz*

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SiO₂-supported trihydrogen phosphododecamolybdate acid H₃PMo₁₂O₄₀ (denoted as H₃PMo) and tetrahydrogen silicododecamolybdate acid H₄SiMo₁₂O₄₀ (denoted as H₄SiMo) and their lithium salts have been studied using IR spectroscopy, temperature programmed reduction and measurement of the thiophene conversion. Lacunar anions of H₃PMo and, under some conditions, of H₄SiMo are formed if lithium is present in the catalyst. Unlike the supported hetero polyacids, lithium combined with the analogues of defect Keggin anions formed during calcination enhances hydrodesulfurization of thiophene.

Key words: Silica-supported heteropolymolybdates; Hydrodesulfurization of thiophene; IR spectroscopy; Temperature programmed reduction; Phosphomolybdates; Silicomolybdates; Heterogeneous catalysis.

In recent years considerable interest in silica-supported molybdenum catalysts based on heteropoly compounds has been marked. Although heteropoly compounds have been known for over 160 years, attempts to use them as catalysts started in the early sixties and during the last twenty years, studies on synthesis, characterisation and catalytic properties of heteropoly acids and their salts have been very intensive. Results of the research have been summarised in various review articles¹⁻⁵. Heteropoly compounds are interesting due to their unique acidic properties and oxidizing ability which can be systematically controllable by the change of countercation and the constituent elements in the anion. Polyanions exist in the form of oxide clusters of well-defined structure, and hence, catalyst design on molecular level and development of model systems in scientific research is possible. From that reason, heteropoly compounds are utilised in many catalytic reactions¹⁻¹⁰. In 1980s, several new large-scale industrial processes (*e.g.* the oxidation of methacrolein, the hydration of isobutene, and the polymerization of tetrahydrofuran) were initiated by using heteropoly compounds¹.

In heterogeneous catalysis, heteropoly compounds are used either as active components of supported catalysts or starting (initial) material for preparation of metal-oxide catalysts. Studies on supported heteropoly compounds are especially important, since

the surface area of heteropoly compounds is usually low. Moreover, interaction of a support and heteropoly compound can change properties of heteropoly compounds used. It seems to be probable that strength of interaction is determined by constituent elements of heteropoly compounds and acid-base properties of the support. However, in literature there is not uniform opinion on the stability of heteropoly compounds formed on the support surface^{3,11-13}. Formation of heteropoly compounds was also observed in the supported catalysts prepared by impregnation of a support with a solution of ammonium heptamolybdate as a result of interaction between the molybdenum compound and the support cation^{14,15}. Due to substitution of molybdenum with support ions^{13,16,17} mixed compounds of the supported heteropoly compound can be formed.

Heteropoly compounds serve^{1,7} as catalysts or precursors of catalysts acting in various acid-type and oxidation reactions including hydrodesulfurization (HDS). As the main component of HDS catalysts is molybdenum, study of the properties of supported Mo-heteropoly acids and of their behaviour in the HDS reaction is very interesting. The catalysts obtained by deposition of P-Mo, Si-Mo or Ti-Mo heteropolyacids on anatase have shown¹⁷ high HDS activity as a result of favourable ionic state of molybdenum. Different effect of alkali cations in the SiO₂-loaded salts of H₃PMo on the thiophene conversion were also shown¹⁸. In the present paper, we explore the effect of heteroatom in the silica-supported H₃PMo and H₄SiMo heteropolyacids, and of their lithium salts on formation of molybdenum phases, their physical properties and activities of sulfided catalysts in hydrodesulfurization of thiophene.

EXPERIMENTAL

Starting heteropolyacids H₃PMo and H₄SiMo were commercial products (Merck, Germany) and parent lithium salts Li₃PMo₁₂O₄₀ and Li₄SiMo₁₂O₄₀ were synthesized according to Tsigdinos¹⁹ by addition of lithium carbonate (Merck, Germany) in stoichiometric ratios to hot solutions of H₃PMo or H₄SiMo. The catalysts have been prepared by incipient-wetness impregnation of silica (Aerosil, $S_{\text{BET}} = 175 \text{ m}^2 \text{ g}^{-1}$) using aqueous solutions of the H₃PMo and H₄SiMo and of their lithium salts. pH of the suspensions containing SiO₂ and the acids were about 1-1.5, pH of the suspensions containing the support and lithium salts of heteropolymolybdc acids was about 1.8-2. The catalyst samples are denoted HPMo, HSiMo, LiPMo, and LiSiMo. A sample with the same amount of lithium, as LiPMo sample, (denoted HLiSiMo) was prepared by impregnation of silica with a solution made²⁰ by dissolving MoO₃ and lithium carbonate in a very dilute ammonia solution (pH 9-10). All catalyst samples (Table I) containing about 12 wt.% of Mo were dried at 70 °C for 4 h and calcined in air at 350 °C for 2 h.

IR spectra (650-1100 cm⁻¹) were recorded at room temperature with a Specord IR-75 spectrometer. The samples were pressed with KBr in the ratio 1 : 150. The spectrum of the support was eliminated by the use of a compensation method¹⁴.

The temperature programmed reduction (TPR) measurements were carried out in an apparatus described earlier²¹. A hydrogen-nitrogen mixture (10 mole % of H₂) was used to reduce samples at a flow rate of 17 ml 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 and atmospheric pressure. Every experiment was made with a fresh catalyst sample (0.2 g) which was

standardized by heating in argon (flow rate 40 ml min⁻¹) at 350 °C for 1.5 h. The calcined catalyst was activated by sulfidation with H₂S (350 °C, flow rate 65 ml min⁻¹, 0.5 h). After the activation was completed, the catalyst was flushed with argon at the same temperature for 0.5 h, then feeding of the reaction mixture (6 mole % of thiophene in hydrogen, 25 ml min⁻¹) was started and the activity of the catalyst was measured during 4 h. The HDS activity of the catalyst sample was evaluated as thiophene conversion to C₄ hydrocarbons (butane, but-1-ene and *cis/trans* but-2-enes) as well as to hydrogen sulfide. Gas chromatography analysis of the reaction products (a Cvet 104 gas chromatograph, Russia, equipped with TCD detector, hydrogen as a carrier gas) was carried out with two consequently connected columns. In the first one (2 m, 10 % Carbowax 1500 supported on Chromosorb W, 110 °C) non-converted thiophene was separated from other reaction products (butane, but-1-ene, *cis/trans* but-2-enes, hydrogen sulfide) which were further separated in the second column (6 m, diatomite treated with 20 wt.% of β,β'-oxidipropionitril, 20 °C).

RESULTS AND DISCUSSION

IR Spectra

IR spectra of all samples are shown in Fig. 1 and the frequencies of particular bands of the samples are listed in Table II. In the spectrum of dried HPMo catalyst (Fig. 1 – 1), the bands at 1 060, 957, 860, and 790 cm⁻¹ characteristic of Keggin structure of the initial H₃PMo acid anion can be seen^{14,22,23}. On the other hand, in the spectra of dried HSiMo and LiSiMo catalyst samples (Fig. 1 – 2, 4), the bands at 957, 910, 860, and 780 cm⁻¹ characteristic of the H₄SiMo acid anion appear. The 860 cm⁻¹ band appearing as a shoulder in the spectrum of the HSiMo catalyst (Fig. 1 – 2) indicates a deformation of the SiMo⁴⁺ anion, probably as a result of the anion–support interactions.

In literature, there is no uniform opinion on the state of the H₄SiMo acid in the SiO₂-supported catalysts. Banares *et al.*²⁴ have shown that the silicomolybdic acid species are destroyed during calcination at temperatures around 300 °C. In contrast, Goncharova *et al.*²⁵ have proved preservation of the H₄SiMo and H₃PMo acids after

TABLE I
Some characteristics and thiophene hydrodesulphurization activity of the SiO₂-supported heteropolymolybdates

| Catalyst | Li, wt. % | S _{BET} , m ² g ⁻¹ | Thiophene conversion ^a |
|----------|-----------|---|-----------------------------------|
| HPMo | 0 | 160 | 20 |
| HSiMo | 0 | 125 | 5 |
| LiPMo | 0.29 | 130 | 44 |
| LiSiMo | 0.22 | 130 | 15 |
| HLiSiMo | 0.22 | 135 | 26 |

^a After 10-h time-on stream.

Splitting of the 957 and 1 060 cm⁻¹ bands, two new bands (830 and 845 cm⁻¹) instead of the 860 cm⁻¹ band and other new bands (910 and 980 cm⁻¹) appearing in the spectrum of the dried LiPMo sample (Fig. 1 – 3) prove an interaction of the PMo₁₂O₄₀³⁻ anion with silica. Contrary to this, the same sample, when calcined at 350 °C, shows neither the bands at 830 and 845 cm⁻¹, nor the bands at 910 and 980 cm⁻¹. Splitting bands at 957 and 1 060 cm⁻¹ (Fig. 1 – 8) prove^{14,22} the presence of lacunar [PMo₁₁O₃₉]⁷⁻ anion with defect Keggin structure. Since H₃PMo acid is stable only in the pH range 0.8–1.5 and pH of the impregnation solution used was about 2, formation of lacunar heteropolyanion in the LiPMo sample could be a result of the lithium salt hydrolysis during the impregnation procedure. IR spectrum of the dried LiSiMo sample (Fig. 1 – 4) shows intensive band at 910 cm⁻¹, characteristic of the SiMo₁₂O₄₀⁴⁻ anion of the initial

TABLE II
Characteristic IR bands (cm⁻¹) of the studied samples and model compounds

| Sample | $\nu_{as}(\text{P-O})$ | $\nu_{as}(\text{Mo=O})_l$ | $\nu_{as}(\text{Si-O})$ | $\nu_{as}(\text{Mo-O}_b\text{-Mo})$ | $\nu_{as}(\text{Mo-O}_c\text{-Mo})$ | δ |
|---|------------------------|---------------------------|-------------------------|-------------------------------------|-------------------------------------|------------------|
| Dried catalyst | | | | | | |
| HPMo | 1 090 | 957 | – | 860 | 790 | – |
| HSiMo | – | 957 | 910 | 860 | 780 | – |
| LiPMo | 1 045 | 980, 957 | 910 | 845, 830 | 780 | – |
| LiSiMo | – | 957 | 910 | 860 | 780 | – |
| HLSiMo | – | 980, 935 | 910, 900 | – | 780 | – |
| Calcined catalyst | | | | | | |
| HPMo | 1 060 | 990, 957 | 910 | 860, 820 | 780 | 650 |
| HSiMo | – | 957 | 910 | 860, 820 | 780 | 650 |
| LiPMo | 1 060 1 045 | 990, 957 935 | 910 | – | 780 | – |
| LiSiMo | – | 990, 957 | 910 | 805 | 780 | – |
| HLSiMo | – | 970, 955 935 | 910 | 805 | 860, 805 | 725 |
| Model compounds (refs ^{14,22,23,28,32}) | | | | | | |
| H ₃ PMO | 1 060 | 957 | – | 860 | 780 | – |
| H ₂ SiMo | – | 957 | 910 | 860 | 780 | – |
| [PMo ₁₇ O ₃₉] ⁷⁻ | 1 060 1 010 | – | 930, 910 | 860 | 790, 742 | 600 ^a |
| [SiMo ₁₁ O ₃₉] ⁸⁻ | – | 975 | 930, 910 | 870, 830 | 740 | 535 ^b |
| MoO ₃ | – | 990 | – | 860, 820 | – | 650 ^c |
| MoO ₄ ²⁻ | – | 935 | – | 895 | – | – |

^a (O–P–O); ^b (O–Si–O); ^c (Mo–O–Mo).

Li salt. The band could also show a formation of new Si–O–Mo bonds on the silica-surface. Preservation of the band in the IR spectrum of the calcined LiSiMo sample (Fig. 1 – 9) documents higher thermal stability of the acid freshly formed on the silica-surface.

In the spectrum of dried HLiSiMo catalyst sample (Fig. 1 – 5), low intensive bands at 980 and 935 cm^{-1} and more intensive band at 900 cm^{-1} with shoulder at 905 cm^{-1} , characteristic of the $[\text{MoO}_4]^{2-}$ ion in tetrahedral coordination³¹ can be seen. After calcination at 350 °C, the bands at 955, 935, 910, 895, 860, 805, and 725 cm^{-1} are observed in the IR spectrum (Fig.1 – 10) These bands are characteristic of the H_4SiMo anion and the lacunar $[\text{SiMo}_{11}\text{O}_{39}]^{8-}$ anion exhibiting defect Keggin structure^{14,22}. In the HLiSiMo catalyst preparation, relatively high pH value of the suspension (about 8–9) causes formation of Li_2MoO_4 and $(\text{NH}_4)_2\text{MoO}_4$ salts in the liquid phase and on the surface of the HLiSiMo sample. Hydrolysis of the HLiSiMo salt and ammonia evolution in the course of catalyst calcination suggest a possible solid phase reaction between molybdate ion and the support to occur, which results in formation of the H_4SiMo acid. Probable formation of H_4SiMo acid on the surface of our catalyst can be also confirmed by the finding²⁴ that H_4SiMo acid was formed in the silica-supported molybdenum catalyst (0.4 to 20 wt.% Mo) prepared by impregnation with a $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ solution.

A complex of lithium with an analogue of suitable lacunar heteropolyanion $[\text{SiMo}_{11}\text{O}_{39}]^{8-}$ of H_4SiMo acid is formed on the surface of calcined HLiSiMo sample (Fig. 1 – 10). Most probably, a phase of distorted H_4SiMo acid along with the anion is present on the catalyst surface. The results are in good agreement with the information that alkali cations stabilize polymolybdate structure³³.

TPR Measurements

Reduction profiles of all samples (Fig. 2) indicate heterogeneity of the molybdenum species present on the silica support. The TPR profiles of the heteropoly acids and of

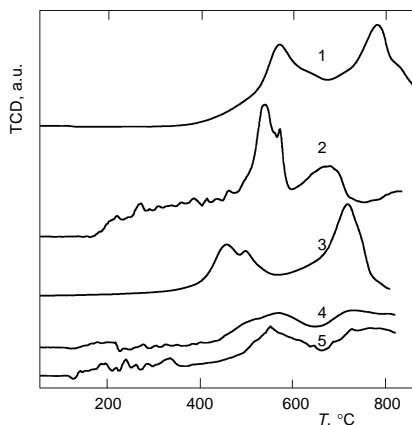


FIG. 2
TPR patterns of silica-supported heteropolymolybdates: 1 HPMo, 2 HSiMo, 3 LiPMo, 4 LiSiMo, and 5 HLiSiMo

their lithium salts can be divided into two parts, low- and high-temperature peaks, roughly separated by the temperature of 650 °C. Low-temperature peaks of the lithium salts, especially of the LiPMo sample, appear at lower temperatures than those of the supported acids. The shift to lower temperatures could be associated with different catalyst phases discussed above. Molybdenum phases difficult to reduce can be revealed in the second part of the TPR profiles.

Variation in the ease of active phase reduction is also accompanied by differences in reducibility (Table III). With the exception of the LiPMo sample, reduction of all other samples is not finished at 800 °C. The calculation of the degree of the active phase reduction from 25 to 800 °C shows that the highest amount of hydrogen consumed in reduction was observed with the HSiMo sample, while the lowest with the LiSiMo sample. As the catalysts were prepared with equal amounts of reducible phases, the data in Table III prove worse reducibility of the catalyst samples containing lithium.

In the TPR spectrum of the HSiMo sample (Fig. 2, curve 2), an indication of the beginning of reduction process can be seen at relatively low temperature – about 200 °C. Such low temperature of reduction is probably associated with the phases within the HSiMo sample, formed during calcination and not connected with the support surface, which are highly dispersed and thus, more easily reduced.

Thiophene Conversion

Catalytic activities of the catalyst samples observed shortly after the reaction beginning can be seen from Fig. 3 (Fig. 3a shows conversions of thiophene to C4 hydrocarbons, Fig. 3b thiophene conversion to H₂S) and Fig. 4 (thiophene conversion to butane). Theoretically, thiophene conversions to hydrocarbons and to H₂S should be the same but various effects, for example different rates of H₂S adsorption and desorption or its

TABLE III
Temperature programmed reduction patterns of the catalysts

| Catalyst | T_{\max} , °C | | | mmol H ₂ g _{cat} ⁻¹ (25–800 °C) |
|----------|-----------------|-------|-----|---|
| | 1 | 2 | 3 | |
| HPMo | 569 | (620) | 780 | 0.44 |
| HSiMo | 536 | 569 | 669 | 0.64 |
| LiPMo | 448 | 498 | 718 | 0.34 |
| LiSiMo | (495) | ~580 | 724 | 0.20 |
| HLSiMo | 515 | 658 | 748 | 0.27 |

surface reaction with active phases, can play a role and affect the results of hydrotreating activity. Over the HPMo, LiPMo and partly HLiSiMo samples, both values of thiophene conversion are roughly equivalent. The course of activities with time-on-stream is approximately the same – the initial thiophene conversion to hydrocarbons changes with time only slightly and reaches its steady-state value after 2 h. However, quite different behaviour can be seen with the HSiMo and LiSiMo samples showing low initial hydrotreating activities. Over the HSiMo sample, the thiophene conversion to hydrocarbons being low in the beginning starts to increase reaching its maximum after *ca* 70 min. Then the conversion quickly decreases (Fig. 3a) reaching 5% after 10 h (not shown in the Fig. 3a). Similarly, over the LiSiMo sample, the thiophene conversion after reaching the maximum activity after *ca* 40 min begins slowly to decrease approaching the steady-state value of 15%.

The amount of hydrogen sulfide evolved during the reaction is almost constant over the HSiMo sample (Fig. 3b) and indicates that reorganization of active sites or adsorption of H₂S on the catalyst surface proceeds in the course of catalytic reaction, which could decrease the initial activity of the sample³⁴. Most probably, phase transformation of the H₄SiMo acid to molybdenum oxide (revealed in the IR spectrum; see Fig. 1,

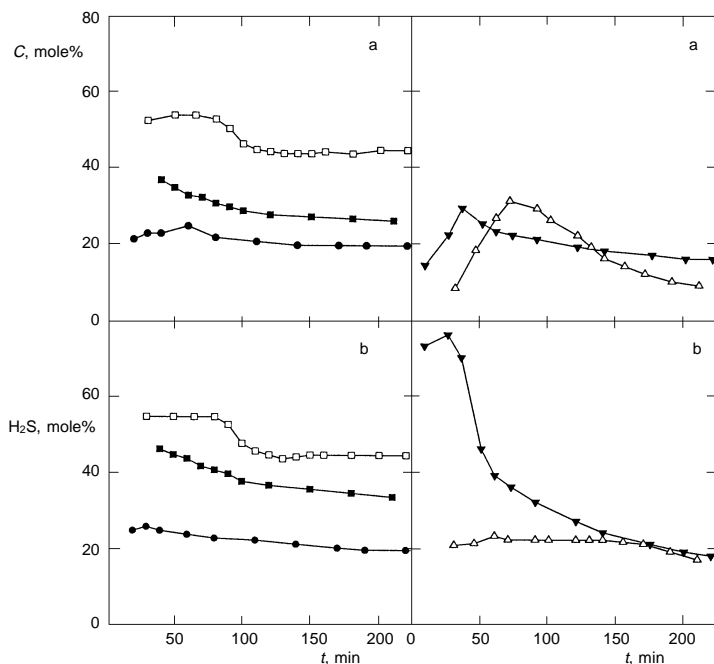


FIG. 3

Thiophene conversion (*C*) to hydrocarbons (a) and to hydrogen sulfide (b) in the presence of catalysts: HPMo (●), HLiSiMo (■), LiPMo (□), HSiMo (Δ), and LiSiMo (▼) vs time-on-stream (*t*)

curve 2) proceeds during the thiophene decomposition and the process is accompanied by both enlargement of molybdenum species and a decrease in the thiophene conversion.

A large amount of H₂S evolving from the LiSiMo sample shortly after the reaction beginning seems to confirm the idea of the active sites reorganization – a quick decrease in the high initial thiophene conversion to hydrogen sulfide is observed over this sample. Hydrogen sulfide adsorbed during presulfidation quickly desorbs (Fig. 3b) and increases the conversion of thiophene to hydrocarbons in a shorter time after the reaction beginning (Fig. 3b) than that observed with the HSiMo sample (Fig. 3a). A sharp decrease in the thiophene conversion to hydrogen sulfide decelerated shortly after the reaction beginning (≈50 min) and approached its steady-state value (practically identical with the value obtained over the HSiMo sample) after 3-h time-on-stream.

Steady-state thiophene conversions (determined after 10-h time-on-stream) of all catalysts are presented in Table I. The highest steady-state hydrotreating activity (thiophene conversion 45%) was observed with the LiPMo sample, whereas the lowest (5%) with the HSiMo sample. The HPMo and LiSiMo samples showed approximately the same hydrotreating activities (20 and 15%, respectively). Steady-state activity of the HLiSiMo sample is not as high as that of the LiPMo sample but higher (26%) than those of the HSiMo and LiSiMo samples.

Comparing the thiophene conversions obtained over the catalysts with their IR spectra it seems to be evident that the LiPMo and HLiSiMo samples containing lacunar

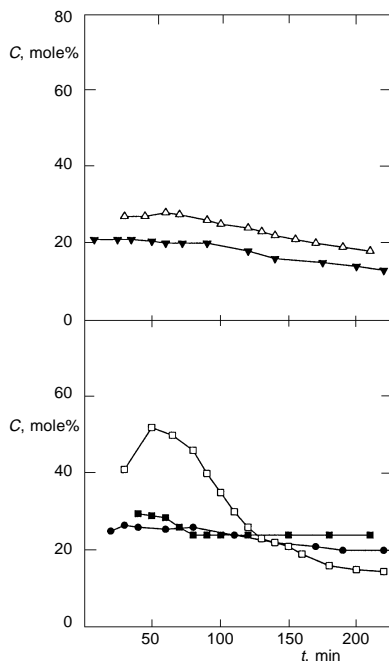


FIG. 4

Thiophene conversion (*C*) to butane in the presence of presulfidized catalysts: HPMo (●), HLiSiMo (■), LiPMo (□), HSiMo (Δ), and LiSiMo (▼) vs time-on-stream (*t*)

compounds $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ and $[\text{SiMo}_{11}\text{O}_{39}]^{8-}$, respectively, exhibit higher thiophene conversions than the samples without them. The vacancy of molybdenum in lacunar compounds increases its coordinative unsaturation and thus, the thiophene interaction with the coordinatively unsaturated molybdenum compounds also increases, which manifests in higher thiophene conversion³⁵.

Hydrogenation activity of the samples (the butane/C4 hydrocarbons ratio) does not show large differences in all, except the LiPMo samples (Fig. 4). With the LiPMo sample, formation of butane quickly decreased after reaching its maximum at *ca* 70-min time-on-stream. Over the HLiSiMo sample, a not fully distinct maximum in the hydrogenation activity appeared at the same time-on-stream, which indicates rapid stabilization of the catalyst surface properties.

In spite of high pH value of the suspension (8–9) used during preparation of the HLiSiMo sample, polymolybdates are formed in the course of the catalyst sample calcination. The arisen polymolybdates or those supported on silica can be stabilized by lithium, as no MoO_3 phase was detected in all catalyst samples containing lithium. Lacunar $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ or $[\text{SiMo}_{11}\text{O}_{39}]^{8-}$ compounds are formed on silica surface when lithium salts of H_3PMo or H_4SiMo are supported. Nature of the heteroatom seems to affect the lacunar anion formation. The results of catalytic activity measurements confirm that lithium combined with the newly formed $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ or $[\text{SiMo}_{11}\text{O}_{39}]^{8-}$ analogues with defect anions enhances, contrary to the supported heteropoly acids, the thiophene conversion.

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