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THERMO-PROGRAMMED REDUCTION STUDY OF $Pt/WO_x–ZrO_2$ MATERIALS BY THERMOGRAVIMETRY

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The thermo-programmed reduction study of $Pt/WO_x–ZrO_2$ materials prepared with different tungsten loading were performed by thermogravimetry. The samples were synthesized by impregnation method and calcined at 600, 700 and 800°C. The characterizations of both un-calcined and calcined materials were carried out using different techniques: thermal analysis (TG and DTA), X-ray diffraction (XRD) and thermo-programmed reduction (TPR). TG and DTA analysis of un-calcined were used to determination of calcination temperatures of the samples. XRD diffractograms were useful to help us in the determination of phase presents. TPR profiles showed between three and four events at different temperatures attributed to platinum reduction and the different stages of tungsten specie reduction.

Keywords: *TG and DTA analysis, thermo-programmed reduction, $Pt/WO_x–ZrO_2$ materials*

Introduction

Solid acid catalysts based on platinum supported on zircon oxide (ZrO_2) modified by tungsten oxide (WO_x) are widely studied as promising catalysts for isomerization and alkylation of hydrocarbons [1–4]. The use of these catalysts in such reactions depends on an accurate understanding of their reduction profile and their acidic properties because the main properties of the bifunctional catalysts, the activity and the selectivity are intimately related with these features [5, 6].

The reduction profile of materials normally has been studied in the literature for variations in the composition of gas mixture of hydrogen and some inert gas flowing through reactor which are monitored by a thermal conductivity detector (TCD) [7, 8]. The disadvantages this method is the small sensibility of TCD which many times not shown the reduction profile of the components that are in small content in the sample. Compared to that analytical technique of reduction profile study, the thermogravimetry can provide information about the metallic sites more accurate. In the TG experiments, the reduction rate of the several compounds contained in the sample is continuously measured by heating linearly of the material in a reductor gas stream (such as hydrogen). Due to reduction of the different compounds in the sample occurs a variation in the mass of the sample which is monitored by a thermal balance. Different events are relationed with the species supported and its interaction with the support [9, 10].

In this work was studied the thermo-programmed reduction profile of several $Pt/WO_x–ZrO_2$ materials synthesized with different tungsten loading and calcination temperatures. The effect of the tungsten loading and of calcination temperatures on the reduction properties were evaluated by TPR experiments. XRD technique was used to investigate the crystalline structures of the materials and TG/DTA technique were used for study the thermal stability of the samples, where TG/DTA analysis of un-calcined were used to determination of calcination temperatures of the samples.

Experimental

$Pt/WO_x–ZrO_2$ materials were synthesized by success impregnation of the tungsten and platinum precursors on source of support with basis on the method proposed by Hino *et al.* [11, 12]. The materials were synthesized using the following chemicals as starting materials: ammonium paratungstate – APT (Aldrich, 99.99 %), zirconium hydroxide (Aldrich, 97%) and platinum(II) chloride (Aldrich, 99.9%). These reactants were combined to obtain samples contain 1 mass% of platinum and 10, 15 and 20 mass% of tungsten after calcination treatments. After impregnations the samples were dried at 70–80°C for 4 h resulting in solids which were denominated of PWZ10, PWZ15 and PWZ20. These materials were calcined at 600, 700 and 800°C for 1 h. The characterization of both un-calcined and calcined materials was carried out using different techniques.

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The identification of the crystalline phases formed after calcination process were performed by X-ray diffraction in an equipment Shimadzu (XRD-6000) using Ni-filtered, CuK_α radiation, with diffraction angle (2θ) at range of 10–80°. TG/DTA analyses were used to determine the calcinations temperatures of the un-calcined samples. The thermal stability of the samples were studied by thermal analysis. The experiments were carried out on a Perkin Elmer TGA-7 instrument and on a Perkin Elmer DTA-1700 instrument at a heating rate of 10°C min^{-1} and under air flowing at a rate of 50 cm^3 min^{-1}.

The materials were characterized by temperature programmed reduction (TPR). The procedure consisted in activate the sample at 100°C for 30 min in nitrogen flow. After this treatment, the TPR profile was performed by heating of about 30 mg of sample from 100 to 900°C in a Mettler TGA-851 instrument at a heating rate of 20°C min^{-1} and under hydrogen flowing at a rate of 25 cm^3 min^{-1} on alumina crucible. The hydrogen consumption was evaluated by thermobalance.

Results and discussion

The thermal decomposition of APT and solid acid based on zircon oxide modified by tungsten oxide has been studied in the literature [13–15]. These compounds decompose at moderate temperatures, usually giving metallic oxides, pure metal particles and/or inorganic salts as final product. The composition of the final product depends on several variables such as the atmosphere (oxidizing, reducing or inert), temperature range of study, heating rate and active species-support interactions. In this work, TG and DTA analyses were useful to provide information about the decomposition of the samples as also about the determination of calcination temperatures of the un-calcined samples. Typical TG/DTG and DTA curves of $Pt/WO_x–ZrO_2$ materials as synthesized (un-calcinated) are shown in Figs 1–3 and the Table 1 summarizes TG and DTA data. TG/DTG curves of all samples showed basically two events of mass loss. The first event is attributed to release water molecules resulting of the synthesis as also the beginning of APT decomposition. The second event has been assigned to APT decomposition. APT decompositions occur in the several consecutive reactions liberating several products. Fouad and collaborators [15] studied and identify the decomposition products of APT and concluded that the thermal decomposition process occurs in four steps liberating nitrogen and dinitrogen oxides and ammonium ions. The decomposition of solid acid based on zircon oxide modified by tungsten oxide showed similar decomposition in relation to APT decomposition, except by temperatures range of decomposition. In this case, the thermodecomposition depends on active species-support interactions and of tungsten loading. In the samples un-calcined, the complete decomposition of precursors occurs between 30–550°C where the sample lost about 20% its initial mass. The residue at ca. 550°C corresponds essentially to $Pt/WO_x–ZrO_2$ oxides. The thermal treatment of precursor materials cause several changes in the support and in the active species dispersed: the support losses water, its surface shrinks and it crystallizes. For the other hand, the tung-

Table 1 Temperature range (Δ*T*) and mass loss of $Pt/WO_x–ZrO_2$ samples (un-calcined)

Sample	TG analysis		DTA analysis
	Δ*T*/°C	Mass loss/%	Δ*T*/°C
PWZ10	30–331	16.8	117–162 and 334–380
	331–550	3.2	426–468
PWZ15	30–386	16.5	132–185 and 375–403
	386–544	1.5	445–478
PWZ20	30–331	16.9	129–177 and 370–399
	331–550	1.1	447–481

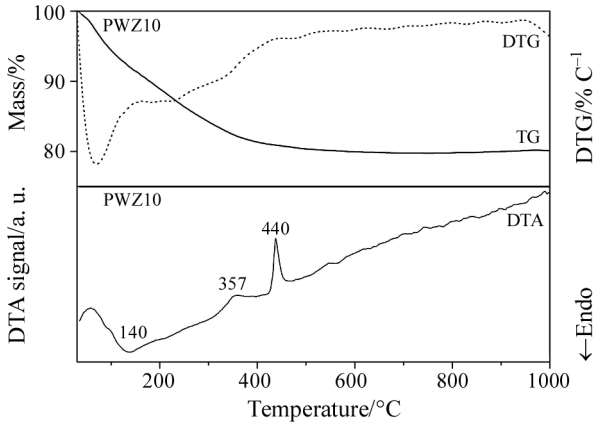

Fig. 1 TG/DTG and DTA curves of $Pt/WO_x–ZrO_2$ (PWZ10) sample (un-calcined)

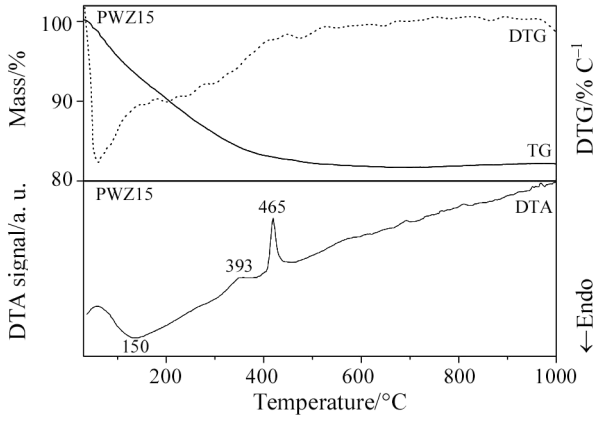

Fig. 2 TG/DTG and DTA curves of $Pt/WO_x–ZrO_2$ (PWZ15) sample (un-calcined)

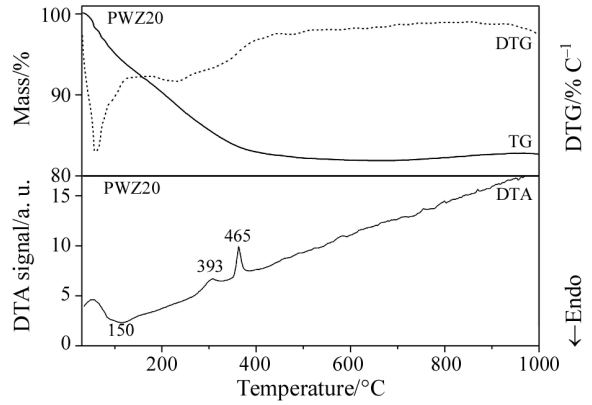

Fig. 3 TG/DTG and DTA curves of Pt/WO_x–ZrO_2 (PWZ20) sample (un-calcined)

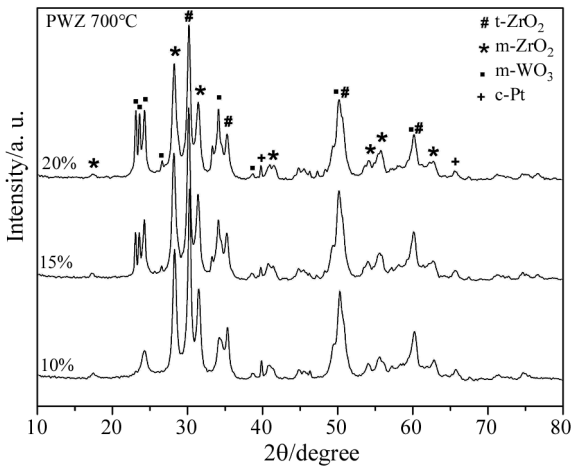

Fig. 4 XRD of Pt/WO_x–ZrO_2 (PWZ) samples with several tungsten loading (10, 15 and 20%) and calcined at 700°C

sten species diffuse and it is disperse on the support as WO_x species. The decomposition events of all samples are characterized in DTA curves (Figs 1–3) by endothermic and exothermic peaks between 115–185 and 330–403°C, respectively. The exothermic peak showed between 426–490°C in all DTA curves was attributed the crystallization of these samples.

The calcinations at 600, 700 and 800°C lead to removal of physically adsorbed water, decomposition of precursor, as well as condensation of tungstate species on zircon surface. In the case of Pt/WO_x–ZrO_2, the calcination process can also lead to the formation of acid sites as a result of adsorption of tungstate species on support creating sites acids of Bronsted-type. TG/DTG curves of samples calcined (not shown) revealed a mass loss of 0.5–1.5%, in the temperature range of 30–600°C probably related to the decomposition of the hydroxyl groups. DTA curves (not shown) of calcined samples not shown any peaks in the temperature range studied.

The XRD pattern of the un-calcined samples (not shown) revealed an amorphous phase. Although the diffractograms have not shown peaks referring to zirconium oxide and tungsten oxide phases one diffraction peak regarding platinum metallic phase was detected to 2θ=39.8°, what is an indicative that during the synthesis process is already obtained the metallic platinum. Crystalline phases were obtained by heat-treating at temperatures between 600, 700 and 800°C as suggested by the presence of strong peaks. X-ray diffractograms of the Pt/WO_x–ZrO_2 materials calcined at 700°C are shown in Fig. 4. All the diffractograms showed the main peaks of monoclinic (*m*) and tetragonal (*t*) phases of zircon oxide (ZrO_2) with 2θ=28.2° (*m*); 30.2° (*t*) and 31.3° (*m*) and monoclinic phase of tungsten oxide (WO_3). Other peaks relative to zircon oxide also were observed but they are overlap with the WO_3 oxide. WO_3 oxide only was observed in the samples contain more than 10% of tungsten (PWZ15 and PWZ20). This structure was characterized in the samples by peaks with 2θ=23.1, 23.6 and 24.3°. The presence of platinum on tungsten-zircon oxide (WO_x–ZrO_2) phase was observed even platinum is in small contents on surface of the solid acid. In these samples the platinum crystalline phase was identified by two main peaks at 2θ equal to 39.8 and 65.6°. The presence of platinum metallic species also was previously found in other works when the platinum was added before calcination [2]. Comeli *et al*. [16] studied and concluded that the tungsten induces electronic and/or steric modifications upon Pt particles in materials of type Pt/WO_x–ZrO_2.

Figure 5 shows the profiles of reduction of bulk WO_3 crystallites calcined at 700°C. TPR-TG curve exhibited a shoulder and two reduction peaks with maxima to 650, 748 and 870°C. These reduction peaks are related with the reduction of WO_3 and of its species formed. The first reduction peak begins to 630°C with the partial reduction of WO_3 forming an oxide of tungsten intermediate non-stoichiometric ($WO_{2.9}$). At approximately 685°C it happens the simultaneous reduction of this non-stoichiometric oxide and of WO_3. Soon after occurs the reduction of these oxides resulting in the WO_2 species. The reduction of WO_2 begins to 791°C forming metallic tungsten (W^0). This last reduction peak was not completed due to experimental conditions. Similar results were also observed by Vaudagna and collaborators [2].

DTG curves obtained during the hydrogen consumption of Pt/WO_x–ZrO_2 materials with different tungsten loading and calcined at different temperatures are shown in Figs 6–8. These curves were denominated of temperature-programmed reduction by thermogravimetric analysis (TPR-DTG). In accordance with the derivative curves (Figs 6–8) were identified between three to four main events of mass loss. TPR-DTG profile showed a reduction peak not well defined at low

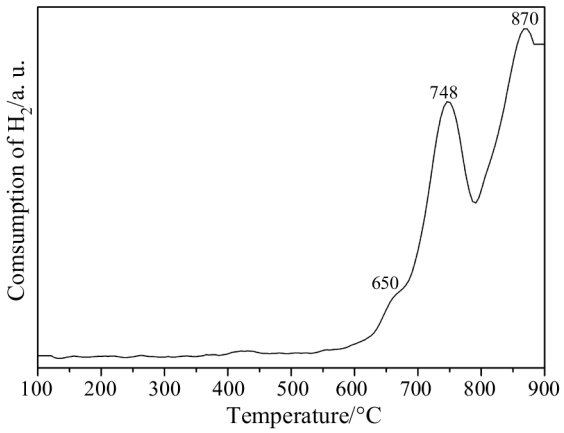

Fig. 5 TPR-DTG profiles of WO_3 crystallites calcined at 700°C

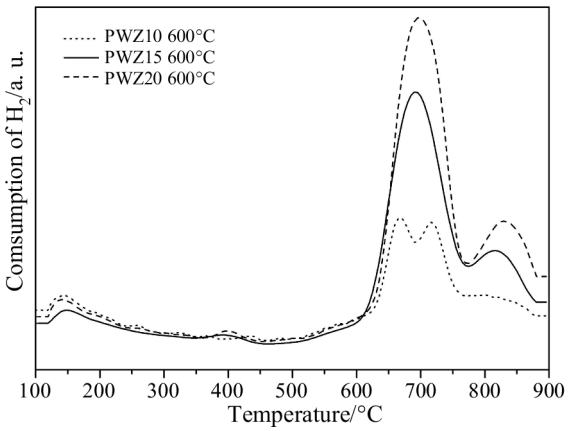

Fig. 6 TPR-DTG profiles of Pt/WO_x–ZrO_2 (PWZ) samples with several tungsten loading (10, 15 and 20%) and calcined at 600°C

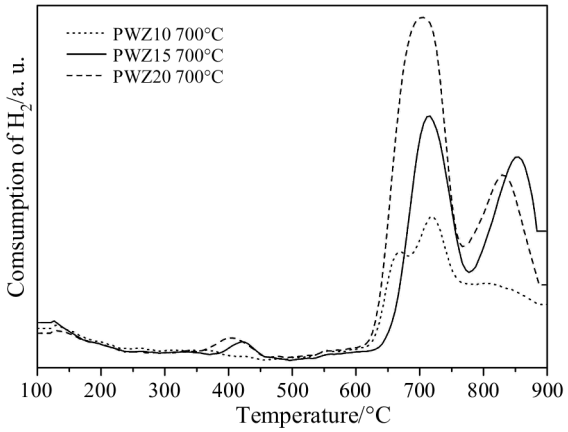

Fig. 7 TPR-DTG profiles of Pt/WO_x–ZrO_2 (PWZ) samples with several tungsten loading (10, 15 and 20%) and calcined at 700°C

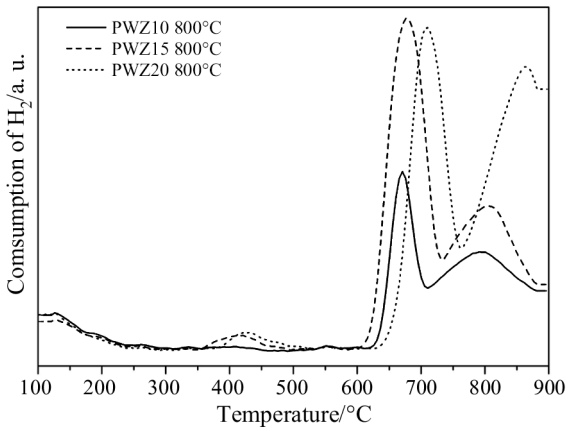

Fig. 8 TPR-DTG profiles of Pt/WO_x–ZrO_2 (PWZ) samples with several tungsten loading (10, 15 and 20%) and calcined at 800°C

temperatures (~150°C) which can be related with the platinum oxide reduction [2]. The low temperature for platinum reduction can be correlated with a low interaction between platinum oxide species and the support. In accordance with XRD results a part of platinum deposited in the support during the synthesis was reduced and after calcinations was obtained platinum metallic deposited on the support. The same behavior also was observed in other works when the platinum was added before calcination [2]. Therefore we are attributing that the peak showed at ~150°C is due the reduction of platinum oxide species remainder the synthesis process. TPR-DTG curves (Figs 6–8) indicated a mass loss for this event of about 1.6% what suggest that the platinum initially deposited are in the oxide shape. TPR-DTG profile also showed three to four overlapping reduction peaks which are related with WO_x reduction. In the samples contain 10% of tungsten (PWZ10) and calcined at different temperatures, XRD results not indicated the presence of WO_3 crystalline structure. With basis in these results, we assumed that the two peaks showed at 670 and 720°C in these samples can be attributed to reduction of WO_x species (oxides amorphous and non-stoichiometric). In this case the tungsten is in octahedral and tetrahedral coordination and the two peaks showed correspond the reduction of non-stoichiometric oxides to tungsten metallic which occurs in two steps where the total reaction can be written as: $WO_x+H_2 \rightarrow W+H_2O$. The samples containing 15 and 20% of tungsten (PWZ15 and PWZ20) calcined at 600°C exhibited similar behavior. In these samples, XRD results showed the presence of WO_3 crystalline structure. TPR-DTG profile for this samples showed two broad peaks which correspond to several reduction steps overlap.

The effect of calcination temperature in the profile of reduction of several Pt/WO_x–ZrO_2 materials also can be seen in Figs 6–8. In relationship the platinum species we detected that with the increase of calcination temperature the peak relationship the platinum reduction practically disappears. This can be related with an extensive platinum sinterization, or with the formation of mixed metal or yet with the forma-

tion of metal oxide clusters [17]. For the other hand, with the increase of calcination temperature we also have observed the appearance of a peak between 350–450°C in the samples contain 15 and 20% of tungsten (PWZ15 and PWZ20). The appearance of this peak can be related with the WO_3 crystallites which only was detected in the samples contain 15 and 20% of tungsten. In this case we can attribute this peak at catalytic action of the platinum on tungsten specie reduction [18]. These results are similar to those found by Benson *et al*. [19] in TPR studies of materials contain platinum species in which Pt catalyzed the partial reduction of tungsten via hydrogen spillover. Therefore, we can conclude that in the samples PWZ15 and PWZ20 calcined at 700 and 800°C the peak showed at 350–450°C is attributed at first step of WO_3 reduction ($WO_3 \rightarrow WO_{2.9}$). The broad and intense peak showed at 700°C is attributed to the second reduction step of WO_3 crystallites ($WO_{2.9} \rightarrow WO_2$) and to the beginning of the reduction of WO_x species. The third reduction peak which is showed at approximately 830°C can be attributed to third reduction step of WO_3 crystallites ($WO_2 \rightarrow W$) and to second step of WO_x species resulting in tungsten metallic species.

Conclusions

The thermal decomposition of all PWZ un-calcined materials occurs in the range of 30–550°C and result $Pt/WO_x–ZrO_2$ as final residue. Therefore, $Pt/WO_x–ZrO_2$ materials can be obtained after calcinations at temperatures above 550°C. The decomposition steps of all PWZ un-calcined materials were evidenced in DTA curves by endothermic and exothermic peaks. The crystallization of the $Pt/WO_x–ZrO_2$ materials started upon calcinations. All $Pt/WO_x–ZrO_2$ materials showed peaks in the XRD diffractograms due ZrO_2 (tetragonal and monoclinic) and platinum metallic phases upon calcinations at 600, 700 and 800°C. The WO_3 (monoclinic) phase only was observed in the samples with 15 and 20% of tungsten. The calcination treatments and the tungsten loading had influence in the reduction profile of $Pt/WO_x–ZrO_2$ materials. TPR profiles showed between three and four events at different temperatures which are attributed to platinum reduction and the different stages of tungsten oxide reduction.

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References

1 T. Onfroy, G. Clet and M. Houalla, J. Phys. Chem. B, 109 (2005) 3345.
2 S. R. Vaudagna, R. A. Comeli and N. S. Figoli, Appl. Catal. A Gen., 164 (1997) 265.
3 D. G. Barton, S. L. Soled, G. D. Meitzner, G. A. Fuentes and E. Iglesia, J. Catal., 181 (1999) 57.
4 R. A. Boyse and E. I. Ko, J. Catal., 171 (1997) 191.
5 F. D. Gregorio and V. Keller, J. Catal., 225 (2004) 45.
6 M. Valigi, D. Gazzoli, I. Pettiti, G. Maattei, S. Colonna, S. Rossi and G. Ferraris, Appl. Catal. A Gen., 231 (2002) 159.
7 G. C. Bond and S. P. Sarsam, Appl. Catal., 38 (1988) 365.
8 M. Afzal, G. Yasmeen, M. Saleem and J. Afzal, J. Therm. Anal. Cal., 62 (2000) 277.
9 A. M. Garrido Pedrosa, M. J. B. Souza, D. M. A. Melo, A. G. Souza and A. S. Araujo, J. Therm. Anal. Cal., 79 (2005) 439.
10 M. J. B. Souza, A. O. S. Silva, L. A. M. Pontes and A. S. Araujo, Studies Surf. Science Catal., 156 (2005) 829.
11 K. Arata and M. Hino, Mater. Chem. Phys., 26 (1990) 213.
12 M. Hino and K. J. Arata, J. Chem. Soc., Chem. Commun., 18 (1988) 1259.
13 J. Madarász, I. M. Szilágyi, F. Hange and G. Pokol, J. Anal. Appl. Pyrol., 72 (2004) 197
14 I. M. Szilágyi, J. Madarász, F. Hange and G. Pokol, Solid State Ionics, 172 (2004) 583.
15 N. E. Fouad, A. K. H. Nohman and M. I. Zaki, Thermochim. Acta, 343 (2000) 139.
16 R. A. Comelli, Z. R. Finelli, S. R. Vaudagna and N. S. Figoli, Catal. Lett., 45 (1997) 222.
17 D. L. L. Mercera, J. G. Van Ommem, E. B. M. Doesburg, A. J. Buggraaf and R. H. Ross, Appl. Catal., 78 (1991) 79.
18 D. G. Barton, S. L. Soled, G. D. Meitzner, G. A. Fuentes and E. Iglesia, J. Catal., 181 (1999) 57.
19 J. E. Benson, H. W. Kohn and M. Boudart, J. Catal., 5 (1966) 307.

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