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## Microwave-Hydrothermal Synthesis and Characterization of Zirconium Substituted SBA-15 Mesoporous Silica

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Zirconium substituted mesoporous SBA-15 molecular silica with Si/Zr ratios of 10, 20, 40, and 80 have been successfully synthesized at 373 K under microwave-hydrothermal conditions within about 2 h. The degree of framework substitution has been monitored by means of powder X-ray diffraction (XRD), nitrogen adsorption, and UV–vis diffuse reflectance (DRUV) spectroscopy techniques. Nitrogen adsorption data and XRD patterns confirmed that, the structure, high surface area, and uniform pore size distribution are maintained in the crystallized samples with Si/Zr ratio of 20. Further increase in zirconium loading (Si/Zr = 10) showed the loss of textural properties. The Zr–SBA-15 samples with Si/Zr = 20, 40, and 80 showed a characteristic oxygen to zirconium charge-transfer band at about 210 nm in DRUV–vis spectra consistent with monoatomic dispersion of zirconium in these samples, whereas the presence of a shoulder band at about 240 nm is observed for the sample having Si/Zr ratio of 10 which indicated the formation of zirconium oxide along with SBA-15. These results show that microwave-assisted synthesis is an ideal approach to prepare Zr-substituted SBA-15, which is expected to be useful as a selective oxidation catalyst for reactions involving large molecules.

### Introduction

Owing to the moderate acidity and oxidizing capabilities, zirconium-based catalysts have wide applications.<sup>1</sup> However, low surface areas of these materials restrict their industrial applications. Therefore, attempts are being made to perform isomorphic substitution of Si by Zr in zeolites and zeolite-like materials. This has led to the synthesis of microporous zirconium silicates with MFI, MEL, BEA, and AFI topology.<sup>2–5</sup> Such zeolitic frameworks are found to possess catalytic activities similar to titanium containing molecular sieves. The potential of Zr-substituted molecular sieves to catalyze the reactions with bulkier molecules has been further expanded by its successful incorporation in the recently reported mesoporous MCM-41 and -48 and HMS framework.<sup>6–12</sup> However, the suitability of these mesoporous frameworks to catalyze reactions involving large molecules is still not clear mainly because of their poor hydrothermal stability. Thus, attempts are being made to improve their hydrothermal stability using various synthesis and postsynthesis routes.

These efforts have resulted in a successful synthesis of hydrothermally stable SBA-15 mesoporous silica with uniform hexagonal channels ranging from 50 to 300 Å.<sup>13,14</sup> This mesoporous silica has been synthesized in a strongly acidic medium using a triblock organic copolymer as a template under hydrothermal conditions.<sup>14</sup> The isomorphous substitution of heteroelements in all silica mesoporous SBA-15 could lead to a useful catalyst for the reactions involving bulkier molecules. Thus, various synthesis and postsynthesis attempts have been made to prepare Al-, V-, and Ti-substituted SBA-15 frameworks.<sup>15–19</sup> Because of strong acidic media involved during the synthesis, the postsynthesis route is found to be more effective over direct synthesis. However, such an approach has been found to reduce the textural properties of the mesoporous framework.

Therefore, efforts need to be focused on nonconventional routes for the direct synthesis of heteroatom substituted SBA-mesoporous silica. Hence, to achieve this goal, we have been concentrating our research efforts on a nonconventional route, namely, microwave-assisted hydrothermal (M–H) synthesis. The term microwave-hydrothermal process was coined by Komarneni and colleagues<sup>20</sup> in 1992, and this process has been used for the rapid synthesis of numerous ceramic oxides, hydroxylated phases, porous materials, and metal powders.<sup>20–24</sup>

The microwave-assisted synthesis of molecular sieves is a relatively new area of research.<sup>25</sup> It offers many distinct advantages over conventional synthesis. They include rapid heating to crystallization temperature because of volumetric heating, resulting in homogeneous nucleation, fast supersaturation by the rapid dissolution of precipitated gels, and eventually a shorter crystallization time compared to conventional autoclave heating.<sup>25</sup> Furthermore, it is energy efficient and economical. This method has been successfully applied for the synthesis of several types of zeolites, namely, zeolite A, Y, ZSM-5, MCM-41, metal-substituted aluminophosphates, and gallophosphates.<sup>25</sup> It has also been successfully applied for the synthesis of mesostructured thiogermanates/germanium sulfides<sup>26</sup> and for titanium substituted MCM-41 molecular sieve.<sup>27</sup> Recently, we have successfully prepared Ti–SBA-15 (up to bulk Si/Ti = 20) without any loss in textural properties using the microwave assisted approach.<sup>28</sup>

In continuation of our efforts, we herein report a successful direct synthesis of zirconium substituted SBA-15 mesoporous silica up to a bulk Si/Zr ratio of 20, under microwave-hydrothermal conditions. The crystallized samples have been characterized with the help of X-ray diffraction, nitrogen adsorption, and DRUV–vis spectroscopy to distinguish the nature of zirconium species inside the SBA-15 channel. Because SBA-15 is hydrothermally stable, Zr–SBA-15 could serve as a potential selective oxidation catalyst for many large molecules.

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## Experimental Section

**Sample Preparation.** Zirconium substituted SBA-15 samples were prepared using tetraethyl orthosilicate, TEOS, (Aldrich) and zirconyl chloride octahydrate,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , (Aldrich) as a silica and zirconium source, respectively.

A triblock poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide), ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ; m.w. 5,800; Aldrich) referred to herein after as EO–PO–EO, was used as a structure directing agent. Typically, 2 g of triblock EO–PO–EO was dispersed in 15 g of double distilled water. The resultant solution was mixed with 60 g of a 2 M HCl (J. T. Baker) solution containing requisite amount of zirconyl chloride under stirring to obtain homogeneous solution. Finally, 4.25 g of tetraethylorthosilicate (TEOS, Aldrich) was added to homogeneous solution with stirring to form a reactive gel with a composition of 2 g of polymer/0.020 mol  $\text{SiO}_2$ / $x$  mol  $\text{ZrO}_2$ /0.12 mol HCl/3.92 mol  $\text{H}_2\text{O}$ ; ( $x = 0/0.002/0.001/0.0005/0.00025$ ; for Si/Zr =  $\infty$ , 10, 20, 40, and 80, respectively). The gel thus obtained was allowed to crystallize without stirring under microwave-hydrothermal conditions at 373 K for 2 h. Microwave-hydrothermal synthesis was performed using MARS5 (CEM Corp., Matthews, NC) microwave digestion system. This system operates at a maximum power of 1200 W, and power can be varied from 0 to 100% and is controlled by both pressure as well as temperature to a maximum of 350 psi and 513 K, respectively. A 2.45 GHz microwave frequency was used which is the same as that in domestic microwave ovens. The syntheses were carried out in double-walled digestion vessels, which have an inner liner and cover, made up of Teflon PFA and an outer vessel shell of Utem polyetherimide, a high strength material. The crystallized product was filtered, washed with warm distilled water, dried at 383 K, and finally calcined at 813 K in air for 6 h.

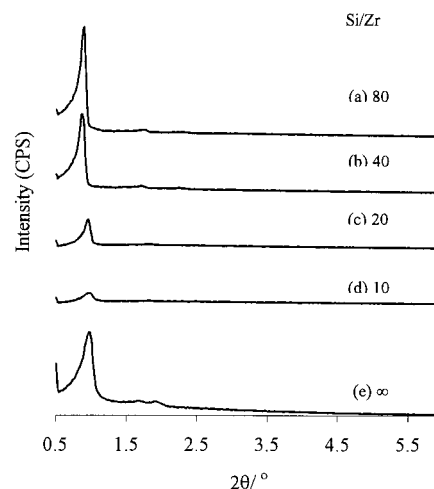
**Characterization.** X-ray diffraction patterns were recorded using a Philips X'pert powder diffractometer system with Cu K $\alpha$  radiation (40 kV, 40 mA) with a  $0.02^\circ$  step size and 1 s step time over the range  $0.5^\circ < 2\theta < 6^\circ$ . The samples were prepared as thin layers on an aluminum sample holder.

The textural properties of the samples were evaluated using nitrogen adsorption/desorption measurements with an Auto-sorb-1 (Quantachrome) unit. Nitrogen adsorption/desorption isotherms were measured at 77 K after degassing samples below  $10^{-3}$  Torr at 473 K for 4 h. The BET specific surface area ( $S_{\text{BET}}$ ) was estimated using adsorption data in a relative pressure range from 0.05 to 0.2. The external surface area,  $S_{\text{ex}}$  and primary mesopore volume,  $V_p$ , were estimated using the  $\alpha_s$ -plot method, as described elsewhere.<sup>30,31</sup> Amorphous nonporous silica ( $S_{\text{BET}} = 7.0 \text{ m}^2/\text{g}$ , Thiokol) was used as a reference adsorbent. The calculation of mesopore size distribution (PSD) was performed by analyzing the adsorption data of the  $\text{N}_2$  isotherm using recently developed KJS (Kruk, Jaroniec, Sayari) approach.<sup>32</sup> The pore diameter corresponding to the maximum of PSD is denoted as  $W_{\text{KJS}}$ . The total pore volume,  $V_t$ , was estimated from the amount adsorbed at a relative pressure of 0.95.

UV–vis diffuse reflectance spectra (DRUV) were measured with a Varian CARY 3E double beam spectrophotometer. Powders were loaded in a quartz cell, and spectra were collected in the wavelength range from 190 to 600 nm against a siliceous SBA-15 standard.

## Results and Discussion

An optimum crystallization time of 2 h has been reported previously for the preparation of highly ordered SBA-15 mesoporous silica under microwave-hydrothermal conditions.<sup>33</sup> Hence, all of the syntheses here were performed for 2 h, and



**Figure 1.** X-ray diffraction pattern for the calcined Zr–SBA-15 samples with bulk Si/Zr ratio of (a) 80, (b) 40, (c) 20, (d) 10, and (e)  $\infty$  obtained under M–H conditions.

crystallized samples were subjected to characterization. The results obtained are discussed in the following sections, and the Si/Zr ratio of the prepared samples are treated on bulk basis.

**X-ray Diffraction Analysis.** Calcined siliceous SBA-15 and Zr–SBA-15 samples with varying amounts of zirconium loading displayed a well-resolved pattern with a sharp peak at about  $0.8^\circ$  and two weak peaks at about  $1.6^\circ$  and  $1.7^\circ$  that matched well with the reported pattern<sup>14</sup> (Figure 1). However, the intensities of the peaks are found to decrease with an increase in zirconium loading.

The XRD peaks are indexed to a hexagonal lattice with  $d(100)$  spacing corresponding to a large unit cell parameter ( $a$ ). The estimated unit cell parameters for the calcined samples are given in Table 1. The unit cell parameters for the calcined Zr–SBA-15 samples are found to be higher compared to those of the siliceous SEA-15 sample. Interestingly, higher unit cell parameters are observed for samples having Si/Zr ratios of 80 and 40 compared to those obtained for samples having higher zirconium content. This may indicate that at low levels of loading zirconium acts as a framework stabilizing agent which can be judged from XRD patterns (Figure 1) wherein the sharpness as well as narrower peak width for samples having low zirconium content are noticed. Such expansion of unit cell parameter may indicate the successful incorporation of zirconium in the framework.

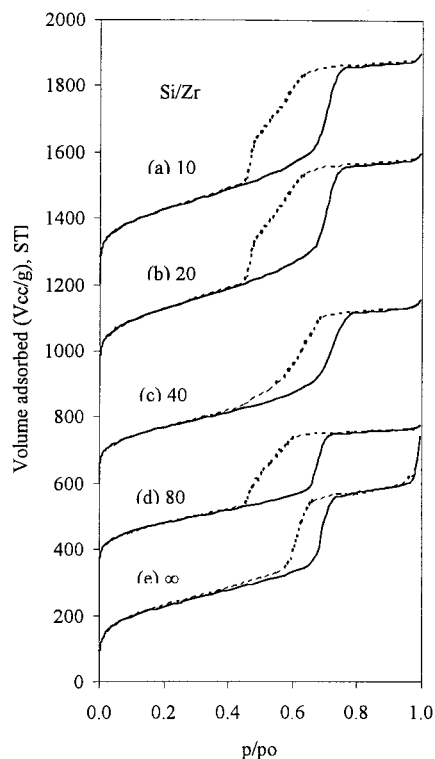
**Nitrogen Adsorption.** Figure 2 shows nitrogen adsorption/desorption isotherms for siliceous SBA-15 and various Zr–SBA-15 samples. The estimated textural parameters such as specific surface area,  $S_{\text{BET}}$ , external surface area,  $S_{\text{ex}}$ , primary mesopore volume,  $V_p$ , total pore volume  $V_t$ , and mesopore size,  $W_{\text{KJS}}$ , for various samples are compiled in Table 1. The calculated mesopore size distribution based on KJS approach for each sample is shown in Figure 3.

All of the nitrogen adsorption/desorption isotherms are found to be of Type IV in nature as per the IUPAC classification and exhibited a H1 hysteresis loop which is typical of mesoporous solids.<sup>34</sup> Furthermore, the adsorption branches of each isotherm showed a sharp inflection in the relative pressure range of about 0.62–0.68. This is a characteristic of capillary condensation within uniform pores.<sup>30</sup> The position of the inflection point is clearly related to a diameter in the mesopore range, and the sharpness of these steps indicates the uniformity of the mesopore size distribution.<sup>30,31</sup> The pore size distribution curves shown in Figure 3 show an average pore size of about 76 Å for samples

**TABLE 1: Structural Parameters for the Various Calcined Zr–SBA-15 Samples Prepared under Microwave-Hydrothermal Conditions<sup>a</sup>**

Si/Zr ratio	$d_{100}$ (Å)	$a^b$ (Å)	BET specific surface area, $S_{\text{BET}}$ , (m <sup>2</sup> /g)	external surface area, $S_{\text{ex}}$ , (m <sup>2</sup> /g)	primary mesopore volume, $V_p$ (cm <sup>3</sup> /g)	pore volume, $V_t$ (cm <sup>3</sup> /g)	primary mesopore size $W_{\text{KJS}}$ (Å)
10	89.96	103.7	651	20.2	0.65	0.72	76
20	89.89	103.7	830	15.8	0.85	0.90	76
40	90.92	104.8	847	16.8	0.90	1.01	77
80	90.92	104.8	860	17.6	0.95	1.05	76
∞	89.01	102.7	811	25.8	0.91	0.98	72

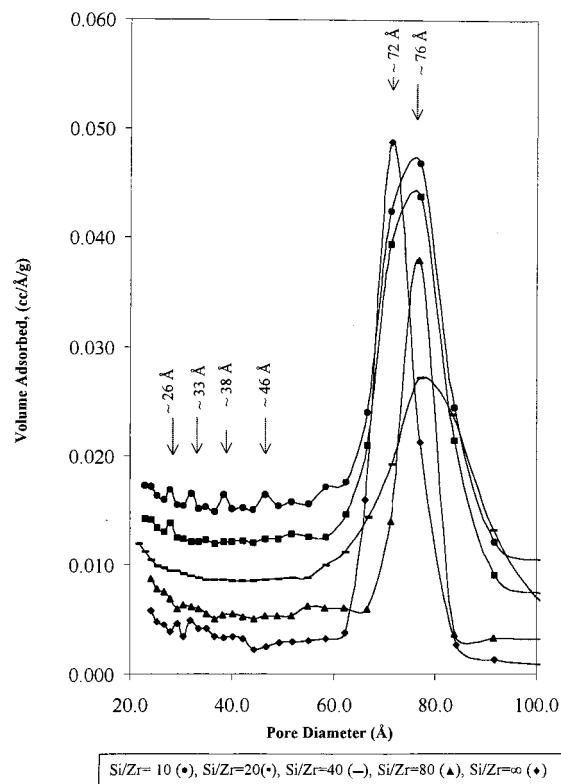
<sup>a</sup> Syntheses are performed at 373 K for 2h. <sup>b</sup>  $a = 2/(3)^{1/2}d_{100}$ .



**Figure 2.** Nitrogen adsorption (—)/desorption (···) isotherms for various Zr–SBA-15 samples obtained under M–H conditions at 77 K. The adsorption/desorption isotherms for samples with bulk Si/Zr ratio of (a) 10, (b) 20, (c) 40, (d) 80, and (e) ∞ are shifted by 1200, 900, 600, 300, and 0 cm<sup>3</sup> STP/g, respectively.

having Si/Zr ratio of 10, 20, 40, and 80, whereas an average pore size of about 72 Å is noticed for sample with Si/Zr ratio ∞. Furthermore, the presence of additional smaller pores of about 26, 33, 38, and 46 Å is noticed for the sample with the highest zirconium loading. These results indicate that, the Zr–SBA-15 could be crystallized without any decrease in mesopore size via the direct synthesis approach under microwave-hydrothermal conditions. Furthermore, the textural parameters (Table 1) for samples having low zirconium contents are found to be improved compared to those obtained for samples having Si/Zr ratios of 10, 20, and ∞ which in turn supports the framework stabilization role for zirconium at low levels of substitution. The specific surface area and total pore volume for the sample having Si/Zr ratio of 10 was found to be lower than the corresponding siliceous sample. This may be due to the formation of Zr–O–Zr linkages with in the mesoporous framework of SBA-15 with an increase in zirconium loading. An additional evidence for such an event is obtained from UV–vis spectroscopy and is discussed in the following section.

**Diffuse UV–vis Reflectance Spectroscopy (DRUV) Spectroscopy.** DRUV spectroscopy is extensively used and perhaps one of the best techniques to detect the framework and



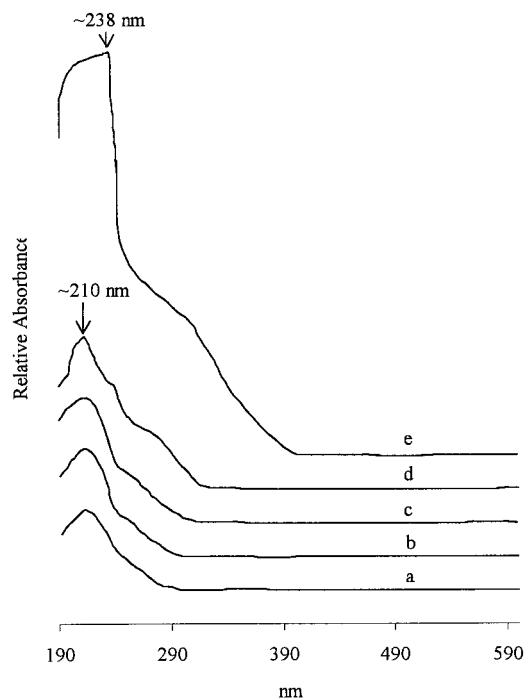
**Figure 3.** Pore size distribution for various Zr–SBA-15 samples with bulk Si/Zr ratios of (●) 10, (■) 20, (○) 40, (▲) 80, and (◆) ∞. The PSD curves for samples with bulk Si/Zr ratio of 10, 20, 40, 80, and ∞ are shifted by 0.01, 0.007, 0.005, 0.003, and 0 cc/Å/g, respectively.

extraframework zirconium species.<sup>10</sup> In addition to this, X-ray absorption spectroscopy is also a powerful technique to distinguish the state and coordination of zirconium ions present in micro- and mesoporous zirconium substituted molecular sieves.<sup>2,10</sup>

Zirconium-containing mesoporous silica, Zr-MS is found to have an absorption band at 205–215 nm.<sup>11</sup> In Zr–ZSM-5 (MFI), an absorption band is observed at 212 nm.<sup>2</sup> Both absorption bands are usually attributed to ligand-to-metal charge transfer (LMCT) from an O<sup>2-</sup> to an isolated Zr<sup>4+</sup> ion in a tetrahedral configuration. In ZrO<sub>2</sub> where there is full connectivity of Zr–O–Zr linkages, the LMCT shifts to lower energy of about 230 nm.<sup>3,9,10</sup>

The ultraviolet spectra of a series of Zr–SBA-15 samples and ZrO<sub>2</sub> phase are shown in Figure 4. The absorption band maximum is observed at about 210 nm for samples having Si/Zr ratio of 10, 20, 40, and 80, and its intensity is found to increase monotonically with an increase in Si/Zr ratio. This indicates the presence of isolated Zr<sup>4+</sup> ions in the SBA-15 mesoporous framework. Furthermore, a small shoulder at about 240 nm indicating nanoscopic regions of Zr–O–Zr linkages is found to accompany UV–vis spectrum for the sample having a Si/Zr ratio of 10. Therefore, an attempt was made to investigate





**Figure 4.** Diffuse reflectance UV-vis spectra of calcined Zr-SBA-15 samples with different zirconium loadings corresponding to bulk Si/Zr ratios of (a) 80, (b) 40, (c) 20, (d) 10, and zirconium oxide (e).

the structural form of such linkages with the help of high angle X-ray measurements. However, the characteristic peaks of  $\text{ZrO}_2$  could not be detected.

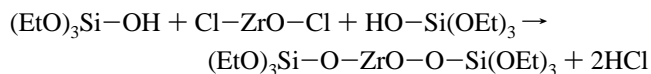
**Mechanism of Zirconium Substitution.** The above characterization results suggest a successful isomorphous substitution of zirconium inside the siliceous framework of SBA-15 under microwave-hydrothermal conditions. Hence, attempts are made to investigate the mechanism of formation of Zr-SBA-15 under microwave-hydrothermal conditions.

It has been proposed that the assembly of the mesoporous silica organized by triblock copolymer species in acid media occurs through a  $(\text{S}^\circ\text{H}^+)(\text{X}^\circ\text{I}^+)$  pathway.<sup>14</sup> Furthermore, the relative times required for silica mesophase precipitation to occur depend on the acid anion and are found to be the shortest in the presence of  $\text{Cl}^-$  anion when used in the form of hydrochloric acid.<sup>14</sup> The precipitation time was also found to decrease with an increase in  $\text{Cl}^-$  ion concentration.<sup>14</sup>

Because the SBA-15 framework is crystallized in a highly acidic condition, it is important to use a stable zirconium (organic/inorganic) source under such condition for its successful incorporation in SBA-15 framework. Hence, attempts were made to prepare a zirconium substituted SBA-15 framework using zirconium alkoxide, namely zirconium propoxide and zirconium oxychloride as an organic and inorganic zirconium sources, respectively. However, the use of zirconium propoxide led to the formation of the  $\text{ZrO}_2$  species because of rapid hydrolysis of the zirconium source owing to its high electrophilicity over the silica source under present synthesis conditions. On the other hand, the use of zirconium oxychloride in the present study led to the successful crystallization of the Zr-SBA-15 framework which in turn reflected the stability of the used inorganic source under acidic conditions. Such stability can be anticipated in terms of the common ion effect of  $\text{Cl}^-$  ions, which is likely to be absent for other halide sources of zirconium, namely, zirconium bromide and iodide, if employed, under present synthesis conditions. Thus, the role of the zirconium source is

found to be critical for a successful crystallization of the Zr-SBA-15 framework.

Thus, under microwave hydrothermal conditions, the hydrated zirconium oxychloride employed in the present investigation is expected to dehydrate rapidly to a stable dehydrated form under highly acidic conditions, which is expected to undergo heterocondensation polymerization reaction with partially hydrolyzed alkoxy silane (TEOS) to produce additional hydrochloric acid as per the reaction



Such heterocondensation polymerization reactions are reported to be fast with respect to homocondensation reaction between partially hydrolyzed silica species.<sup>35</sup> Under the influence of microwaves, the polymerization of these reactive species is believed to be fast because of rapid heating and fast supersaturation. This would lead to an increase in  $\text{Cl}^-$  anion concentration and would eventually decrease precipitation time for mesophase silica formation, which is expected to follow the proposed reaction mechanism.<sup>14</sup>

## Conclusions

Direct synthesis of zirconium substituted SBA-15 mesoporous silica, up to  $\text{Si/Zr} = 20$ , has been achieved using zirconium chloride as a zirconium source under microwave-hydrothermal conditions within 2 h at 373 K without any loss in textural properties. The role of the zirconium source is believed to be important for successful incorporation as well as rapid precipitation of Zr-SBA-15 under microwave-hydrothermal conditions. On the basis of the obtained results, the microwave-hydrothermal synthesis approach is believed to be an ideal way to prepare zirconium substituted SBA-15 mesoporous silica, which could be useful as a selective oxidation catalyst for large organic molecules.

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