

# Controlling the chemistry of the micropore volume in pillared clays and micas

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## Abstract

Pillared clays are microporous materials formed by propping apart clay layers with robust inorganic polyoxocations. The chemistry of the micropore space can be tailored by choosing suitable pillaring species, by adding various functionality to the pillar surfaces, and by incorporating small metal particles within the micropores. We have found that by using a commercially available zirconyl acetate solution as the zirconia polyoxocation precursor, zirconia-pillared micas with superior properties of crystallinity and microporosity can be produced. Catalytic tests have shown that treatment of a zirconia-pillared montmorillonite with sulfate increases the acid site strength and density of the zirconia pillars. In addition to materials with enhanced acidity, it is desirable to produce materials with little or no acidity for use as metal supports for catalysts in applications such as light alkane dehydrogenation, where support acidity leads to undesirable side reactions. Tetrasilicic fluoromica can be pillared by silsesquioxane oligomers derived from the in situ hydrolysis of an aminosiloxane reagent. After a two step calcination, the silica-pillared fluoromica produced has a high surface area and crystallinity, and the combination of the inert fluoromica layers with the non-acidic silica pillars makes this new material an interesting nonacidic support for noble metal catalysts.

*Keywords:* Micropore volume; Pillared clays; Micas; Zirconia

## 1. Introduction

Microporous materials containing pores less than 20 Å in dimension are interesting because the dimensions of micropores are in the same order as the dimensions of organic molecules. These materials offer the potential for selectivity based on molecular size in important processes involving adsorption and catalysis. Zeolites [1] are crystalline aluminosilicates with

micropores of well-defined size ranging from 4 to 7 Å and are commercially important as catalysts, adsorbents, and ion exchange materials. Materials with micropores in larger sizes than those of faujasite zeolites, and that also possess the stability necessary for catalytic applications, are less readily available. Several approaches to the synthesis of microporous materials with pore sizes greater than 7 Å have been explored. Aqueous metal–phosphate systems incorporating organic templates have produced large channel molecular sieves such as VPI-5 [2] and cloverite [3], and more recently semicrystalline

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aluminosilicate/silicate materials of the MCM-41 family with pore sizes ranging from 15 to greater than 100 Å have been prepared in systems using liquid crystal-like templates [4]. Pillared clays are microporous materials formed by propping apart clay layers with robust inorganic polyoxocations to create microporous galleries [5]. These galleries range in height from 5 to 15 Å, allowing access of large hydrocarbon molecules. The chemistry of the micropore space in pillared clays can be tailored by varying the composition of the clay layers, by choosing different pillaring species to control the pillar composition, by adding various functionality to the pillar surfaces, and by incorporating small metal particles within the micropores.

Alumina-pillared montmorillonites are the most conveniently prepared pillared clays and have been studied intensively as acidic catalysts for hydrocarbon transformations [6]. At high temperatures the acidity is mainly of a Lewis nature, resulting in catalysts with lower activity than is shown by typical acidic zeolites. In contrast, sulfate-treated zirconia contains strong acid sites [7], readily catalyzing the isomerization of n-butane at temperatures of 150°C or lower. Pillared clays with zirconium oxide pillars were among the first reported thermally stable oxide-pillared clays [8], and the prospect of modifying zirconia-pillared clays with sulfate

to form strongly acidic microporous materials is attractive. Previous work in this area has shown that montmorillonite clays pillared by zirconyl chloride solutions containing ammonium sulfate exhibited increased Brønsted acidities [9].

Almost all of the reported work on zirconia-pillared clays has employed zirconyl chloride solution as the pillaring agent. We have recently shown [10] that synthesis of zirconia-pillared clays using zirconyl acetate as the agent to pillar tetrasilicic fluoromica results in pillared micas with higher crystallinity, surface area, and stability than those prepared from zirconyl chloride. Typical X-ray diffraction patterns of zirconia-pillared tetrasilicic fluoromica (ZrTSM) prepared with zirconyl acetate and zirconyl chloride pillaring agents are shown in Fig. 1. The low angle line resulting from the layer repeat distance of ca. 21 Å is better defined in the sample prepared from zirconyl acetate and the BET surface area is higher. Simple application of the technique of sulfate modification, as is performed on bulk zirconia to enhance the acidity of zirconia-pillared clays, is not successful. In the case of bulk zirconia, the typical procedure is: precipitate amorphous zirconium hydroxide from zirconyl chloride solution; treat the dried, but uncalcined, precipitate with sulfuric acid; and follow with calcination. We have found that soaking zirconia-pillared clays with

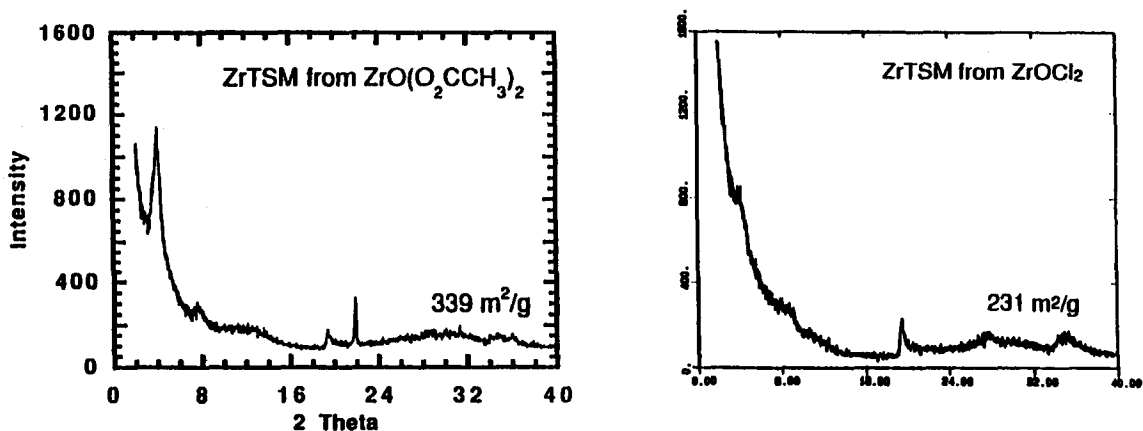


Fig. 1. X-ray powder diffraction patterns (Cu K  $\alpha$  radiation) of zirconia-pillared tetrasilicic mica prepared with zirconyl acetate and zirconyl chloride pillaring solutions.

sulfuric acid causes severe loss of crystallinity and surface area. This problem can be alleviated by using ammonium sulfate solutions instead of sulfuric acid, as is shown in Fig. 2. While the crystallinity and surface area of ammonium sulfate soaked ZrTSM are lower than for untreated ZrTSM, the 21 Å diffraction line corresponding to the layer repeat distance remains and significant surface area and micropore volume are retained.  $\text{SO}_4/\text{ZrTSM}$ 's affinity for ammonia was compared to those of  $\text{SO}_4/\text{ZrO}_2$  and untreated ZrTSM by temperature programmed decomposition (TPD) in order to estimate the number and strength of the acid sites. As shown in Fig. 3, the strongly acidic  $\text{SO}_4/\text{ZrO}_2$  adsorbed 427  $\mu\text{mole/g}$  of  $\text{NH}_3$ , retaining a portion until  $> 600^\circ\text{C}$  (i.e., its decomposition temperature) in the TPD analysis, while ZrTSM adsorbed 245  $\mu\text{mole/g}$  of  $\text{NH}_3$ , all of which desorbs at temperatures below  $500^\circ\text{C}$ . However, the sulfate-treated ZrTSM contains more acid sites, adsorbing 906  $\mu\text{mole/g}$  of  $\text{NH}_3$ , and these acid sites retain  $\text{NH}_3$  to  $> 600^\circ\text{C}$ , therefore showing comparable strength to those in  $\text{SO}_4/\text{ZrO}_2$ . Since both  $\text{SO}_4/\text{TSM}$  and

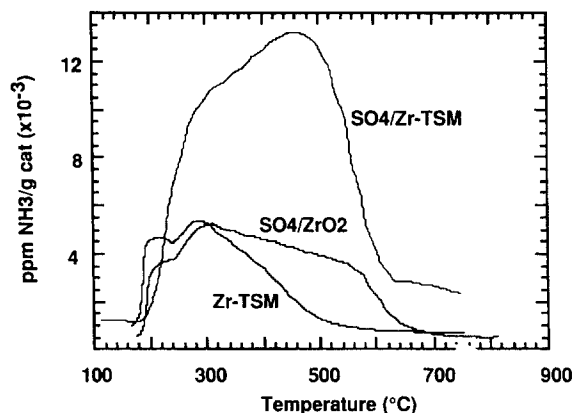


Fig. 3. Ammonia thermal programmed decomposition of bulk  $\text{SO}_4/\text{ZrO}_2$ , ZrTSM and ZrTSM treated with 1 M  $(\text{NH}_4)_2\text{SO}_4$ .

$\text{SO}_4/\text{ZrO}_2$  decompose with loss of sulfate at temperatures greater than  $600^\circ\text{C}$ , the strongest acid sites cannot be distinguished by the ammonia TPD technique.

Despite the indication of strong acidity in  $\text{SO}_4/\text{ZrTSM}$  by ammonia TPD, no activity for n-heptane isomerization was detected, even in samples loaded with small amounts of platinum. This is due to blockage of the micropore volume to alkane molecules. While  $\text{NH}_3$  can ac-

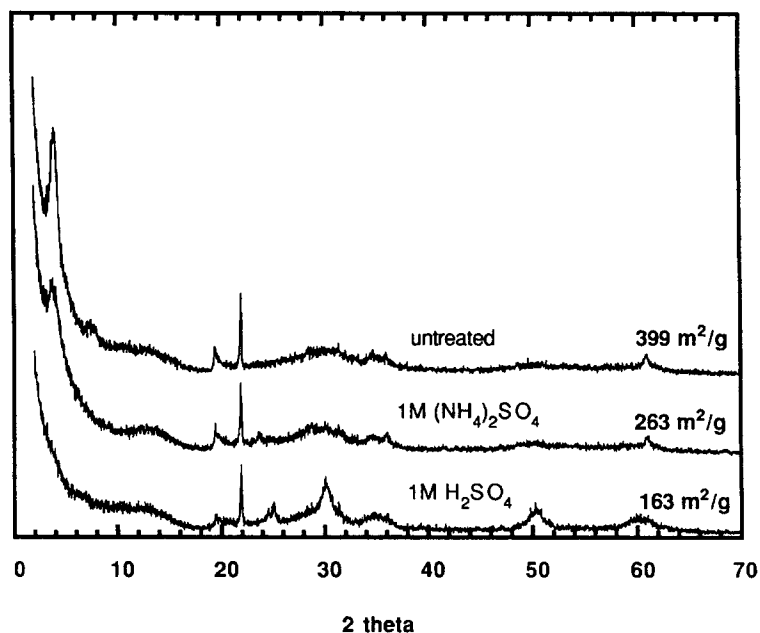


Fig. 2. X-ray powder diffraction patterns (Cu K  $\alpha$  radiation) of ZrTSM (top), ZrTSM treated with 1 M  $(\text{NH}_4)_2\text{SO}_4$  (middle), and ZrTSM treated with 1 M  $\text{H}_2\text{SO}_4$  (bottom).

cess the acid sites in  $\text{SO}_4/\text{ZrTSM}$ , hexane adsorption measurements showed little uptake. For example, the ZrTSM sample tested absorbed 9 wt% n-hexane and had a BET surface area of  $350 \text{ m}^2/\text{g}$ , while the  $\text{SO}_4/\text{ZrTSM}$  sample absorbed only 0.1 wt% n-hexane and had a surface area of  $101 \text{ m}^2/\text{g}$  at a loading of 4.1% sulfur. Samples with lower sulfur loadings had higher surface areas and hexane adsorptions, but still showed no heptane isomerization activity.

Among the 2:1 layered clay minerals, tetrasilicic fluoromica has a relatively high layer charge which results in a high pillar density in pillared TSM. By using a clay with less charge on the layers, such as montmorillonite, the pillar density will be lower and pore blockage by sulfate may be decreased. Zirconia-pillared montmorillonite was prepared by pillaring HPM-20 bentonite with zirconyl acetate [10], yielding ZrMont with a  $20 \text{ \AA}$  layer repeat distance and a surface area of  $320 \text{ m}^2/\text{g}$ . ZrMont was sulfated by soaking samples of uncalcined pillared clay in solutions of  $(\text{NH}_4)_2\text{SO}_4$  followed by calcination at  $500^\circ\text{C}$ . The surface areas and micropore volumes of  $\text{SO}_4/\text{ZrMont}$  samples were not much lower than those of the unsulfated ZrMont, as shown in Table 1. The samples were loaded with Pt and tested for n-heptane isomerization activity by flowing n-heptane in  $\text{H}_2$  over the catalysts in a fixed bed and increasing the temperature while monitoring the products. Bulk  $\text{Pt}/\text{SO}_4/\text{ZrO}_2$  was also tested as a reference. The conversion of heptane as a function of temperature is plotted in Fig. 4. The  $\text{SO}_4/\text{ZrMont}$  catalysts do show activity for heptane conversion above  $240^\circ\text{C}$ , while the unsulfated ZrMont was inactive (not shown). However, the activity of the pillared clay cata-

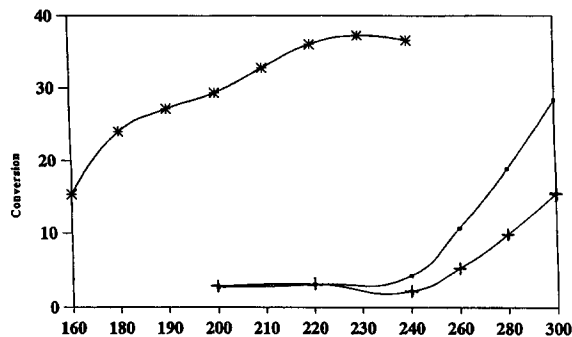


Fig. 4. Conversion of n-heptane vs. reaction temperature for bulk  $\text{SO}_4/\text{ZrO}_2$  (\*), ZrTSM treated with 0.2 M  $(\text{NH}_4)_2\text{SO}_4$  (+), and ZrTSM treated with 1 M  $(\text{NH}_4)_2\text{SO}_4$  (■). Conditions: 160 psi,  $\text{H}_2/\text{C}_7 = 6.5$ , WHSV = 11.

lysts is substantially lower than that of the bulk  $\text{SO}_4/\text{ZrO}_2$  strong acid, which isomerizes heptane at  $160^\circ\text{C}$ . The isomerization selectivity differs between the two types of catalysts, as shown in Fig. 5.  $\text{SO}_4/\text{ZrO}_2$  produces greater amounts of cracked products as conversion increases, lowering the  $\text{C}_7$  selectivity, while both  $\text{SO}_4/\text{ZrMont}$  catalysts show high selectivities for isomerization to branched heptanes. At 25%

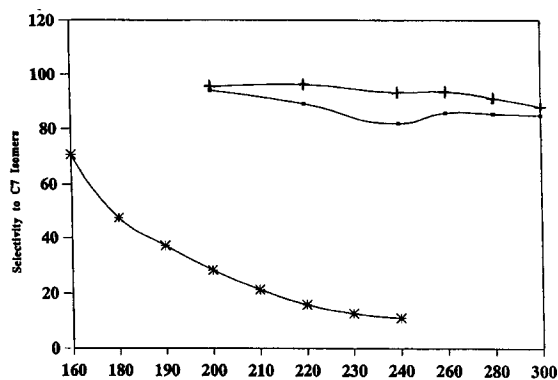


Fig. 5. Selectivity of n-heptane converted to heptane isomers vs. temperature for bulk  $\text{SO}_4/\text{ZrO}_2$  (\*), ZrTSM treated with 0.2 M  $(\text{NH}_4)_2\text{SO}_4$  (+), and ZrTSM treated with 1 M  $(\text{NH}_4)_2\text{SO}_4$  (■).

Table 1

Characterization of sulfated zirconia-pillared montmorillonite catalysts. Samples were loaded with 0.3 wt% Pt by incipient wetness impregnation with  $\text{H}_2\text{PtCl}_6$  before soaking in  $(\text{NH}_4)_2\text{SO}_4$  solution and calcining to  $500^\circ\text{C}$

Sample	$(\text{NH}_4)_2\text{SO}_4$ soak (M)	Surface area ( $\text{m}^2/\text{g}$ )	Micropore volume ( $\text{ml}/\text{g}$ )	Sulfur content (wt%)
ZrMont	none	320	0.112	—
$\text{SO}_4/\text{ZrMont}1.0$	1.0	300	0.103	3.78
$\text{SO}_4/\text{ZrMont}0.2$	0.2	332	0.115	1.89

C<sub>7</sub> conversion, the selectivity to C<sub>7</sub> isomers is 45% for the SO<sub>4</sub>/ZrO<sub>2</sub> catalyst, while at the same conversion SO<sub>4</sub>/ZrMont catalysts have an isomerization selectivity greater than 80%. The data suggest that the lifetimes of the carbocation intermediates on the bulk sulfated zirconia are longer than those on the pillared clay.

While increasing the acidity of microporous materials continues to be an important goal, materials with little or no acidity are useful as adsorbents and as catalyst supports for noble metal catalysts. Suppression of support acidity minimizes undesirable acid-catalyzed side reactions that occur during metal-catalyzed reactions such as paraffin dehydrogenation. By dispersing the noble metal in the micropore volume of a pillared clay, high dispersion of the metal phase is accomplished, and the shape selectivity provided by the confining micropore volume of the pillared clay can minimize the formation of undesirable higher molecular weight compounds and coke precursors. Varying the composition of both the oxide pillars and the clay layers offers the opportunity to control the pore geometry and surface chemistry of oxide-pillared clays to produce microporous materials with very low acidity. We have previously shown that adding Mg to Sn/Pt catalysts supported on alumina-pillared TSM increases their selectivity for propane and isobutane dehydrogenation [11].

Silica has low acidity as an adsorbent or as a catalyst support. Therefore, by pillaring a clay that has layers of inherently low acidity with silica pillars, a microporous pillared clay of low acidity should result. Sodium tetrasilicic mica (NaTSM) is a synthetic clay-like material of formula Na[Mg<sub>2.5</sub>Si<sub>4</sub>O<sub>10</sub>F<sub>2</sub>] which shows no acidity by ammonia adsorption techniques [12].

Cu-TSM catalyzes the dehydrogenation of methanol to form methyl formate selectively, while the Cu-exchanged forms of other silicate minerals catalyze the dehydration of methanol simultaneously, due to the acidity of the minerals [13]. Therefore, we expect that by propping open the layers of tetrasilicic mica with silica pillars, a microporous pillared clay of very low acidity will result. Dispersing a noble metal such as platinum in the microporous galleries should make a unique material that is useful as a catalyst for hydrocarbon reactions such as alkane dehydrogenation.

Silica-pillared clays formed from smectites such as montmorillonite, hectorite, and beidellite have been synthesized by exchanging the clays with solutions of organosilicon oligomers formed by hydrolysis of such precursor reagents as 2-(2-trichlorosilylethyl)pyridine (TCSEP) [14] or 3-aminopropyltrimethoxy-silane [15]. We found that aminopropyltriethoxysilane (APTES) was preferred over TCSEP as a silica precursor to prepare silica-pillared tetrasilicic mica [16]. In order to prepare SiTSM with high surface area and microporosity, a two step calcination procedure was necessary. When NaTSM is treated at reflux with an aqueous solution of APTES for 4 days, the TSM layers are expanded to 21.5 Å, but no microporosity exists, as shown in Table 2. When the APTES-treated NaTSM is calcined at 400°C, then washed with water to remove intermediate decomposition products and recalined at 600°C, microporous silica-pillared TSM with a layer repeat distance of 17.5 Å and high surface area is produced. If the intermediate calcination and wash procedure is omitted and the APTES-exchanged TSM is calcined directly to 600°C, the layers remain

Table 2  
Characterization of APTES-treated NaTSM

Thermal treatment	Layer repeat (Å)	Surface area (m <sup>2</sup> /g)	Micropore volume (ml/g)
120°C dried	21.5	17	0
600°C calcined	16.8	31	0
400°C calcined, washed, 600°C calcined	17.5	315	0.108

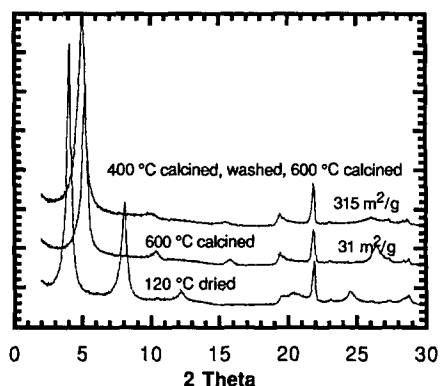


Fig. 6. X-ray powder diffraction patterns (Cu K $\alpha$  radiation) of APTES treated TSM dried at 120°C (bottom), calcined directly to 600°C (middle), and calcined at 400°C, washed with water, and recalined at 600°C (top).

expanded at a repeat distance of 16.8 Å, but there are no accessible micropores, as demonstrated by the low surface area. X-ray diffraction patterns of the APTES-treated TSM prior to calcination, and after both one- and two-step calcinations to 600°C are shown in Fig. 6.

In order to test the usefulness of SiTSM as a low acidity catalyst support for the dehydrogenation of isobutane to isobutene, 0.5 wt% Zn was loaded on a sample of high surface area

SiTSM via incipient wetness impregnation with aqueous Zn(NO<sub>3</sub>)<sub>2</sub>. After calcination at 400°C, 0.5 wt% Pt was added by impregnation with H<sub>2</sub>PtCl<sub>6</sub>. The catalyst was loaded into a down-flow microreactor and reduced in H<sub>2</sub> at 575°C, then exposed to pure flowing isobutane at the same temperature. Conversion of isobutane and selectivity to isobutene over a 24 h period are presented in Fig. 7. The isobutane conversion starts at 50%, and declines to ca. 20% over the 24 h period. The selectivity to isobutene remains above 90% after a brief induction period. The selectivity is equivalent to that of ZnPt catalysts supported on bulk silica, but although the initial activity is higher, the ZnPt/SiO<sub>2</sub> catalysts have a lower deactivation rate [17].

The chemistry of the micropore volume of pillared clays can be controlled to some degree by a variety of techniques. We have shown that the acidity of pillared clays can be enhanced by using zirconia in the pillars and adding sulfate. However, while the acidity of the sulfated zirconia-pillared clays is increased by sulfate, they are not as active as bulk SO<sub>4</sub>/ZrO<sub>2</sub> in heptane isomerization. Similarly, a pillared clay of very low acidity can be produced by using silica in

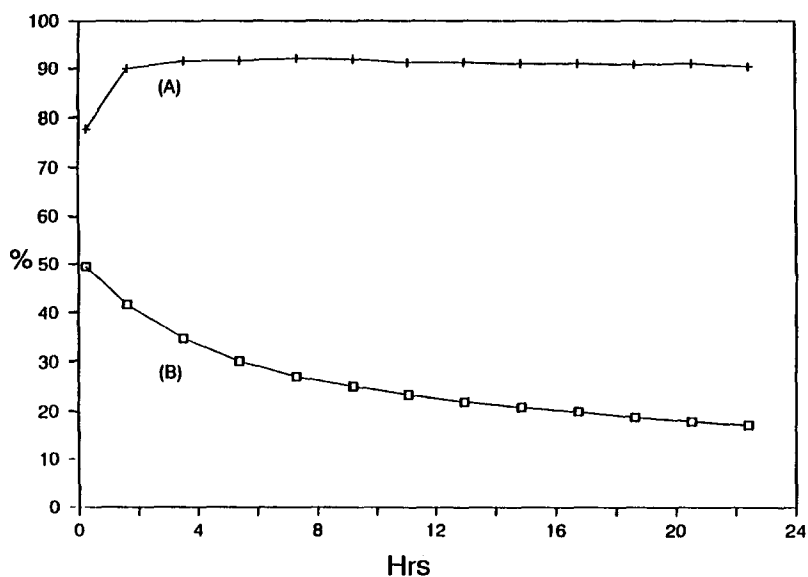


Fig. 7. Selectivity of isobutane converted to isobutene (A), and conversion of isobutane (B) over ZnPt/SiTSM catalyst. Conditions: 575°C, 1 atm pure i-C<sub>4</sub>, GHSV = 362.

the pillars and nonacidic tetrasilicic mica as the clay layers. Noble metal can be effectively dispersed on this support, but the resulting catalysts are not yet more effective in alkane dehydrogenation reactions than similar catalysts supported on bulk silica. It remains a challenge to design pillared clay catalysts in which the chemistry is sufficiently controlled to take advantage of the unique geometry of the pillared clay micropores in order to produce catalysts with superior properties.

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