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Synthesis of mesoporous ZSM-5 using different saccharide meso templates and directing agents

C Wan Nur Izati C Wan Ahmad and Zainab Ramli

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
Corresponding Author: zainab@kimia.fs.utm.my

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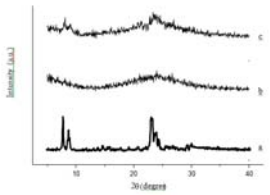
GRAPHICAL ABSTRACT



X-ray diffractogram of a) ZSM-5-SUC b) ZSM-5-GLU and c) ZSM-5 without template

ABSTRACT

The mesoporosity of microporous ZSM-5 was synthesised by investigating the effect of different structure directing agents, and mesotemplates. In this study, tetrapropylammonium hydroxide (TPAOH) and tetrabutylammonium hydroxide (TPABr) were used as directing agents that could direct the formation of microporous ZSM-5 structure while saccharides (glucose and sucrose) were chosen as mesotemplates reagents. ZSM-5 zeolite was synthesized by hydrothermal method at 100oC with initial molar composition of Al_2O_3: $50SiO_2$: $8TPA^+$: $1500H_2O$: 20 saccharides. ZSM-5 was synthesized without using mesotemplate was also synthesized to make comparison with the templated samples. All synthesized samples were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) and nitrogen adsorption analysis. XRD results showed that only sample prepared by TPAOH as directing agent and sucrose as meso template (ZSM-5-SUC) formed ZSM-5 crystal phase while the rest of the samples showed dominantly amorphous material. Nitrogen adsorption analysis revealed all samples show high surface area (> 500 m^2/g) with isotherm of the Type IV ie mesoporous characteristics. However analysis of the t-plot of all samples indicated that only ZSM-5-SUC sample a mixture of microporous and mesoporous characteristics with the mesoporous pore size distribution centred at 4.7 nm. Study showed that the present OH^- for the TPA ion is important in order to direct the formation of ZSM-5 microporous structure while sucrose facilitate the formation of mesoporosity of the ZSM-5 due to its mineralizing property. As compared to TPABr, the use of TPAOH as the directing agent is a good template because OH ion is able to transform Al^{3+} into tetrahedral aluminate ion which accounted for the formation of tetrahedral aluminosilicate framework of mesoporous ZSM-5 structure.

Keywords: *ZSM-5 zeolite, saccharide mesotemplate, structure directing agent*

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1. INTRODUCTION

Zeolite is a crystalline, microporousaluminosilicate material with well-defined pore structures and have crystalline networks of AlO4- and SiO4 tetrahedra. It has a topological network of uniformly linked cavities and pores of molecular dimensions that gives rise to their molecular sieving properties. Zeolites are extremely useful as catalysts for several important due to its high hydrothermal stability, strong acidity, well defined microporosity and shape selectivity [1]. Many applications of zeolites as catalyst rely on their acidity and on the pore structure. Zeolite Socony Mobil-5 (ZSM-5) is a high silica zeolite. It has unique shape of selectivity, solid acidity, ion exchangeability, pore size, thermal stability and structural network [2]. Basically, porous materials are divided into three classes depending on their pore size. Microporous has pore size smaller than 2 nm, mesoporous has pore size between 2 nm and 50 nm, while macroporous has pore size larger than 50 nm. The microporous zeolites have high specific surface area, excellent stability and unique shape selectivity. However, in selectivity of the reaction, large reactant molecules that yield large transition products could not succeed inside the micropores of conventional zeolites. This is due to their pore size range and desirable features that able for diffusion limitations that restrict substrate accessibility to the surfaces of the active sites. The active sites are located inside framework channel which play an important role in the shape selective catalytic reaction. Ion exchange properties of traditional aluminosilicate zeolites arise from the isomorphous positioning of aluminium in tetrahedral coordination within their Si/Al frameworks [3]. Ion exchange properties of traditional aluminosilicate zeolites arise from the isomorphous positioning of aluminium in tetrahedral coordination within their Si/Al frameworks [1].

Here, we report the hydrothermal synthesis of mesoporous ZSM-5 using different saccharide meso templates, glucose and sucrose. The samples were also synthesized under same hydrothermal condition by using different directing agents, tetrapropylammonium hydroxide (TPAOH) and tetrapropyl ammonium bromide (TPABr). The aim of this study is to provide some information about the effect of saccharide meso templates and structure directing agents on the formation of mesoporous ZSM-5 in terms of their framework structure, crystallinity, pore size, pore volume and surface area. The properties on the formation of mesoporous ZSM-5 were investigated by using X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR) and nitrogen adsorption analysis. ZSM-5 with glucose and sucrose template were compared with conventional ZSM-5 to study the influence on different saccharide meso templates. While, ZSM-5 with sucrose templated was used to study the effect on the different structure directing agent, tetrapropylammonium hydroxide (TPAOH) and tetrapropyl ammonium bromide (TPABr).

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2. EXPERIMENTAL

2.1. Materials

The reactant materials used for the synthesis were tetraethyl orthosilicate (TEOS) as silica source, aluminium sulphate octadecahydrate, $Al_2(SO_4)_3$.18H2O as alumina source, 40 % tetrapropyl ammonium hydroxide solution (TPAOH) and tetrapropyl ammonium bromide (TPABr) as the structure directing agents. Anhydrous glucose, $C_6H_{12}O_6.H_2O$ and sucrose, $C_{12}H_{22}O_{11}$ were used as saccharide meso templates in the reaction. Distilled water was used throughout the experiment as washing liquid.

2.2. Synthesis

The mesoporous ZSM-5 was prepared with the molar composition of 1 Al_2O_3: 50 SiO_2: 8 TPAOH: 1500 H_2O. 0.28g aluminium sulphate octadecahydrate $Al_2(SO_4)_3.18H_2O$ and 6.25 mL tetrapropyl ammonium hydroxide (TPAOH,40%) were dissolved in 3.75 mL of distilled water under stirring to form a clear solution. Then, 5 mL tetraethyl orthosilicate (TEOS) was added dropwisely into the homogenous solution under vigorous stirring and leave stirring for 6 hours. The homogenous solution was aged at 100°C for 16 hours. The obtained precursor of ZSM-5 was mixed with glucose aqueous solution. After stirring for another 30 minutes, the resulted suspension was transferred into Teflon bottle and keep at 100°C for 48 hours. The resulting solid was then filtered through vacuum filtration, wash with distilled water and dry at 60°C overnight. Finally, the resulted powder was calcined in air at 550°C for 6 hours.

2.3. Characterization

X-Ray diffraction (XRD) patterns were obtained by a Bruker Advance D8 using Siemens 5000 diffractometer and filtered using filtered Cu Kβ radiation. The diffractogram on XRD patterns were analysed at 2θ angles in the range of 5° to 40° with step interval of 1 degree and 1 second per step of step time at room temperature. Measurements were done by using a bracket sample holder with a continuous mode of scanning rate.

Fourier Transform Infrared (FTIR) spectrum were analysed by using Perkin Elmer Model 1600 Fourier Transform Infrared Spectrometer. The spectrum range recorded was from 4000 cm-1 to 400 cm-1. KBr pellet method was used in this method. The sample was mixed with KBr pellet with ratio 1:100 and grounded until fine mixture was formed. The sample mixture was then transferred to the pellet making die. The mixtures were tamped down on the anvil and 10 tonnes was applied for 3 minutes. The sample was then placed into a sample holder and analyzed. The spectrum was recorded.

Nitrogen adsorption and desorption isotherms of the ZSM-5 samples were measured using nitrogen as adsorbate at 77 K by a Micromeritics 3 Flex Surface Characterization analyzer. This analysis was carried out in order to determine the BET surface area, type of pore, micropores area and pore volume of the sample. About 0.2 g zeolite sample which was previously calcined at 550 °C for 6 hours was utilized as the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Effect of Different Saccharide Meso Template

3.1.1. X-Ray Diffractogram

From the XRD pattern, the very sharp reflections of ZSM-5-SUC pattern confirmed the formation of crystalline phase. The peaks at 2θ 8.05°, 8.95°, 23.25°, 24.05° and 24.6° observed are indexed to the MFI topology. As for ZSM5-GLU, no diffraction peaks were observed. The lower intensity peaks of ZSM-5-GLU and ZSM-5 without template indicates that the pore walls were not completely converted into crystalline structure and they formed amorphous structure. This indicates that the conventional ZSM-5 almost to form crystal structure but the percentage of crystal structure is very low. Thus, this indicates that the present of sucrose as saccharide meso template could facilitate the formation of ZSM-5 crystal phase.

3.1.2. Fourier Transform Infrared

From the FTIR result, all samples have broad hydrogen bond (OH bond) absorption peak at wavenumber 3458.19 cm^{-1} for ZSM-5-GLU, 3462.35 cm^{-1} for ZSM-5-SUC and 3438.24 cm^{-1} for ZSM-5 without template due to the present of water molecule (OH bond). ZSM-5-GLU has sensitive asymmetric of T-O-T stretching (T=Si, Al) at 1645.57 cm^{-1} and insensitive

asymmetric T-O-T stretching at 1087.48 cm^{-1}. ZSM-5-SUC has sensitive asymmetric of T-O-T stretching (T=Si, Al) at 1645.76 cm^{-1} and insensitive asymmetric T-O-T stretching at 1097.52 cm^{-1}. ZSM-5 without template has sensitive asymmetric of T-O-T stretching (T=Si, Al) at 1647.12 cm^{-1} and insensitive asymmetric T-O-T stretching at 1089.04 cm^{-1}. ZSM-5-GLU, ZSM-5-SUC and ZSM-5 without template have sensitive symmetric of T-O-T stretching (T=Si, Al) at 802.29 cm^{-1}, 802.67 cm^{-1} and 791.09 cm^{-1} respectively. Double ring absorption peak was indicated to double 5-ring secondary building unit which is the characteristics belongs to the framework of mesoporous ZSM-5. ZSM-5-SUC shows strong double 5-ring peak with higher intensity at 557.54 cm-1 as compared to ZSM-5-GLU and ZSM-5 without template.

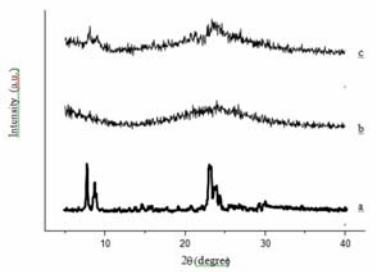

Figure 1 X-ray diffractogram of a) ZSM-5-SUC b) ZSM-5-GLU and c) ZSM-5 without template [5].

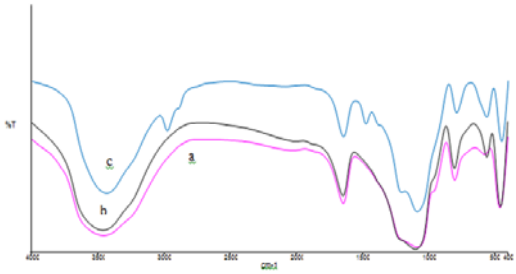

Figure 2 Infrared spectra a) ZSM-5-GLU b) ZSM-5-SUC and c) ZSM-5 without template

3.1.3. Nitrogen Adsorption Analysis

From the isotherm plot, it can be shown that all as-synthesised ZSM-5 with different saccharide meso templates were identified as Type IV physisorption isotherm with obvious hysteresis loop at a high relative pressure, reflecting the existence of mesopores structure. The synthesized sample using sucrose as saccharide meso template showed H1 hysteresis loop which associated with capillary in an open ended cylindrical channel at uniform size and shape. On the other hand, the synthesized sample without template and using glucose as saccharide meso templates showed Type IV with H2-type hysteresis loop which associated with a capillary condensation in bottle pores shape. Compared with ZSM-5 without template, the ZSM-5-SUC and ZSM-5-GLU samples exhibited a broader hysteresis loop from P/Po= 0.5 to 1, which was due to the existence of both micropores and mesopores. From t-plot obtained, it can be seen that all saccharide meso templates of ZSM-5 has line crossing nearly to zero. ZSM-5-GLU shows the highest BET surface area which was 709.3 m^2/g. While, BET surface area of ZSM-5-SUC and ZSM-5 without template were 590.2 m^2/g and 655.4 m^2/g respectively. This shows that ZSM-5-GLU exhibits mesopores material because it has small micropores surface area. While, ZSM-5-SUC exhibits both mesopores and micropores material. From BJH desorption pore volume, it can be seen that ZSM-5-SUC has broad pore size distribution at 4.71 nm with pore volume of 0.0472 cm3/g followed by ZSM-5-GLU and ZSM-5 without template which have very narrow pore size distribution. From the result obtained, ZSM-5-SUC saccharide meso template has larger pore volume than ZSM-5-GLU and ZSM-5 without template.

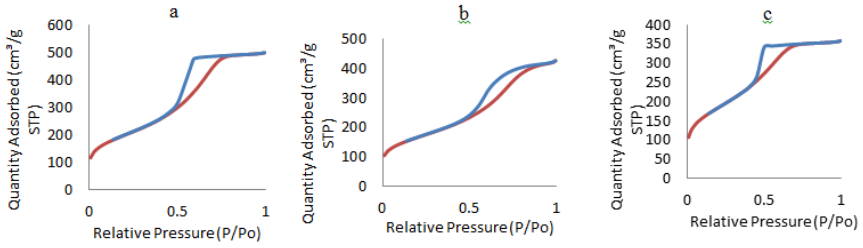

Figure 3 Isotherm plot of a) ZSM-5-GLU, b) ZSM-5-SUC and c) ZSM-5 without template

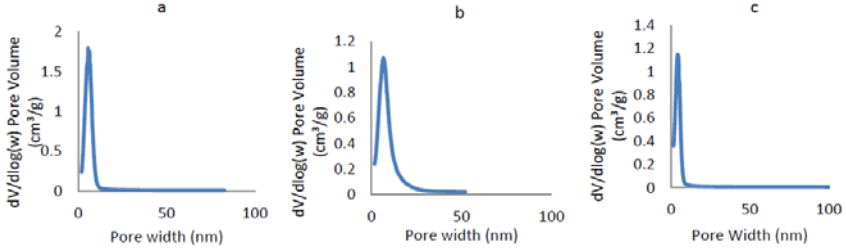

Figure 4 BJH pore distribution of a) ZSM-5-GLU, b) ZSM-5-SUC and c) ZSM-5 without template

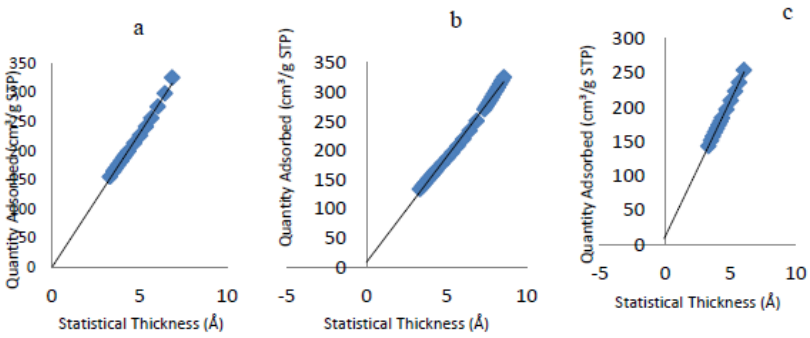

Figure 5 t-plot of a) ZSM-5-GLU, b) ZSM-5-SUC and c) conventional ZSM-5 without template

3.2. Effect of Different Directing Agents

3.2.1. X-Ray Diffractogram

From XRD patterns, ZSM-5-SUC-TPAOH exhibit diffraction peaks at 2θ = 7.85°, 22°, 22.9°, 23.2° and 23.9°. The very sharp diffraction peaks of the ZSM-5 sample with TPAOH as directing agent confirm that the formation of a highly crystalline ZSM-5 phase. While ZSM-5-SUC with TPABr as directing agent shows low intensity peaks at 2θ 8°, 23°, 23.6° and 24.3 24,6°. ZSM-5-TPABr showed dominant amorphous but it only shows small intensity and was not entirely converted into crystalline structure of the formation of ZSM-5 structure. This result obtained indicates that TPAOH plays important role in the formation of ZSM-5 crystal phase. This is due to the present of OH^- that would dissolve with aluminium ion to form tetrahedral framework structure.

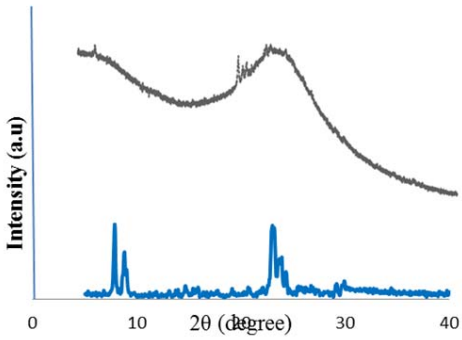

Figure 6 X-Ray diffractogram of a) ZSM-5-SUC-TPAOH and b) ZSM-5-SUC-TPABr

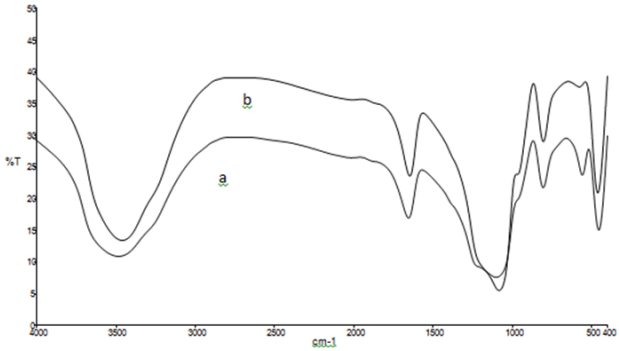

Figure 7 Infrared spectra a) ZSM-5-SUC-TPAOH and c) ZSM-5-SUC-TPABr

3.2.2. Fourier Transform Infrared

From the FTIR result, both samples have broad hydrogen bond (OH bond) absorption peak at wavenumber 3462.35 cm^{-1} for ZSM-5-SUC-TPAOH and 3460.73 cm^{-1} for ZSM-5-SUC-TPABr. This broad peak shown was due to the present of water molecule (OH bond). ZSM-5-SUC-TPAOH has sensitive asymmetric of T-O-T stretching (T=Si, Al) at 1645.76 cm^{-1} and insensitive asymmetric T-O-T stretching at 1097.52 cm^{-1}. While, ZSM-5-SUC has sensitive asymmetric of T-O-T stretching (T=Si, Al) at 1646.91 cm^{-1} and insensitive asymmetric T-O-T stretching at 1083.72 cm^{-1}. ZSM-5-SUC-TPAOH and ZSM-5-SUC-TPABr have sensitive symmetric of T-O-T stretching (T=Si, Al) at 802.67 cm^{-1} and 804.43 cm^{-1} respectively. Double ring absorption peak was indicated to double 5-ring secondary building unit which is the characteristics belongs to the framework of ZSM-5. ZSM-5-SUC-TPAOH shows strong double 5-ring peak with higher intensity at 557.54 cm^{-1} as compared to ZSM-5-SUC-TPABr which shows low intensity at 577.20 cm^{-1}.

3.2.3. Nitrogen Adsorption Analysis

From the isotherm plot, it can be shown that ZSM-5-SUC with tetrapropylammonium hydroxide and tetrapropylammonium bromide are identified as Type IV physisorption isotherm with obvious hysteresis loop at a high relative pressure, reflecting the existence of mesopores structure. Compared with ZSM-5-SUC TPABr, the ZSM-5-SUC TPAOH sample exhibited a broader hysteresis loop from P/Po= 0.5 to 1, which was due to the existence of both micropores and mesopores. From t-plot obtained, it can be seen that both directing agents of ZSM-5-SUC has line crossing nearly to zero. The BET surface area of ZSM-5-SUC with TPAOH and TPABr directing agents are 590.2 m^2/g and 709.4 m^2/g respectively. This shows that ZSM-5-SUC with TPABr directing agent exhibits mesopores material because it has small micropores surface area. From BJH desorption pore volume, it can be seen that ZSM-5-SUC with TPAOH directing agent has broad pore size distribution at 47.19Å with pore volume of 0.0472 cm^3/g. While ZSM-5-SUC with TPABr directing agent has very narrow pore size distribution with the maximum pore width distribution at 33.19 Å and with pore volume of -0.001437 cm^3/g.

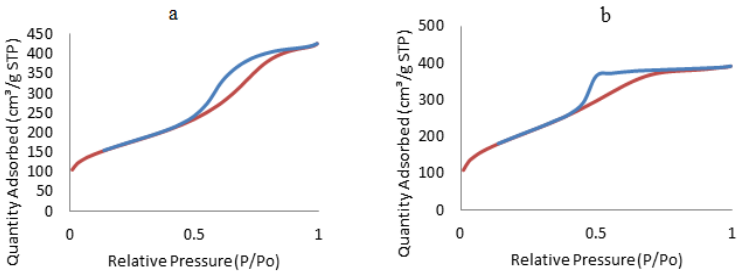

Figure 8 Isotherm plot of a) ZSM-5-SUC with TPOH and b) ZSM-5-SUC with TPABr

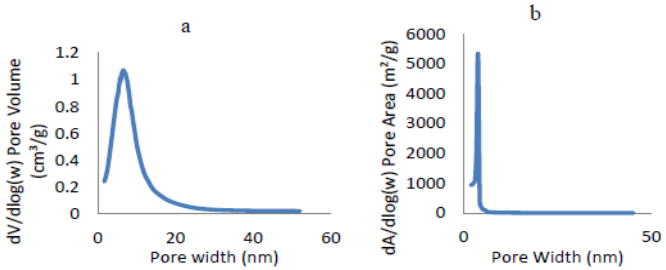

Figure 9 BJH pore distribution of a) ZSM-5-SUC with TPOH and b) ZSM-5-SUC with TPABr

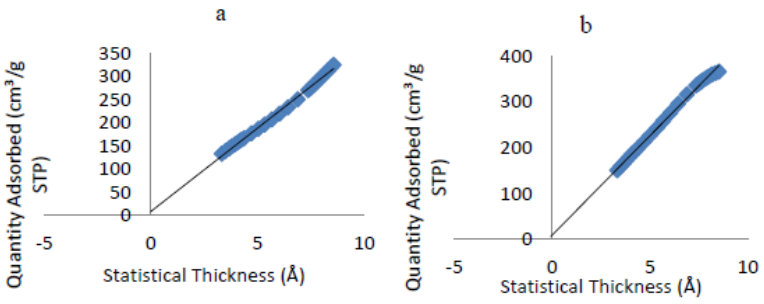

Figure 10 t-plot of a) ZSM-5-SUC with TPOH and b) ZSM-5-SUC with TPABr

4. CONCLUSION

Hydrothermal synthesis of mesoporous ZSM-5 was studied using various saccharide meso templates and directing agents. The mesoporosity was created in the synthesis by using sucrose and glucose as saccharide meso templates. Tetrapropylammonium bromide and tetrapropylammonium hydroxide as directing agents. XRD results demonstrated that the present of sucrose as saccharide meso template could facilitate the formation of ZSM-5 crystalline phase with sharp diffraction peaks. FTIR results also confirmed that ZSM-5-SUC shows the framework of mesoporous ZSM-5 with strong double 5-ring peak with higher intensity at 557.54 cm-1 as compared to ZSM-5-GLU and ZSM-5 without template.

For the effect of structure directing agents, XRD patterns show that ZSM-5-SU-TPAOH has very sharp diffraction peak and it indicates that the sample exhibit crystalline properties. While, ZSM-5-TPABr was almost to form crystalline structure

with high intensity but narrow diffraction peaks. From nitrogen adsorption analysis, it shows that ZSM-5-SUC-TPAOH has larger pore volume with small BET surface area compared to ZSM-5-SUC-TPABr. In conclusion, TPAOH able to dissolve the Al^{3+} during synthesis time and the hydroxide ion was transformed into aluminate.

It is recommended to increase the synthesis time in the formation of mesoporous ZSM-5 in order to improve in crystallinity of high-silica zeolite. This is because, time is significantly has a best influence on the formation of crystal phase. As long as time is concerned, zeolite synthesis may perform successive crystal phase transformation. Other than that, this study can be extended for the application of mesoporous ZSM-5 using Friedel craft alkylation reaction.

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