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Studies on the growth of ice crystal templates during the synthesis of a monolithic silica microhoneycomb using the ice templating method

S.R. Mukai · K. Onodera · I. Yamada

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Abstract Porous materials with a wide variety of functions can be obtained through sol-gel synthesis. Recently, we found that sol-gel based materials can be molded into a monolithic microhoneycomb structure by simply freezing their parent hydrogels unidirectionally. The main feature of the monoliths obtained through this method, which we named the Ice Templating Method, is that they have straight and aligned macropores, the sizes of which are in the micrometer range. As these macropores are the traces of the ice crystals which are formed during freezing and which practically act as the template, the sizes as well as the shape of them depend on how the template ice crystals are formed and how they grow. Therefore in this work, the growth behavior of the ice crystals formed during the unidirectional freezing of a silica hydrogel was examined and the influences of this growth behavior on the properties of the resulting monoliths were verified.

Keywords Ice templating · Freezing · Sol-gel process · Silica gel · Monolith · Microhoneycomb

1 Introduction

Porous materials are widely used as catalysts and adsorbents, and they support our daily lives in many different ways. Generally, the basic functions of such materials are provided by the active sites which are usually distributed on the surfaces of the micro/mesopores which form a 3-dimensional network in the materials. In order to utilize such sites and receive benefits from them, the accessibility of the sites must be kept as high as possible.

Generally, the accessibility of the inner parts of porous materials depends on the length of the diffusion paths within them. Porous materials are usually synthesized in the form of particles, so an effective way to increase accessibility is to reduce the size of the particles. However, such reduction brings about a different problem, a severe resistance to fluid flows. This means that a high inner accessibility and a low hydraulic resistance are not compatible. Indeed, there are many cases in which the accessibility is sacrificed just to keep the hydraulic resistance the material causes to acceptable levels.

This situation can be avoided by changing the morphology of the material, for example, from particles to fibers with small diameters (Cooke 1990; Matatov-Meytal and Sheintuch 2002). The lengths of the diffusion paths within fibrous porous materials are short, as they depend on the diameter of the fibers, and the hydraulic resistance the material causes can be minimized by properly aligning the axis of the fibers to the direction of fluid flow. Another example is a monolith having channels large enough to permit a hydrodynamic flow (Hjerten et al. 1989; Nijhuis et al. 2001; Vergunst et al. 2001; Svec et al. 2003; Siouffi 2003; Svec 2004; Roy et al. 2004). Among such monoliths, honeycombs, monoliths with straight and aligned macropores, the walls of which are thin and porous, are preferable, as the hydraulic resistance can be minimized. Porous honeycombs with mm-sized macropores (channels) and fairly thin walls have been developed and are widely used (Roy et al. 2004). The functions of such honeycombs can be further improved if the sizes of the macropores, as well as the thickness of the walls which form them, can be reduced. However when conventional methods are used for synthesis, there is a limit in reducing such sizes. Therefore, the development of a new

S.R. Mukai (✉) · K. Onodera · I. Yamada
Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Japan
e-mail: smukai@eng.hokudai.ac.jp

method to obtain honeycombs with smaller dimensions is desired.

The sol-gel process is a popular method to obtain porous materials. Recently, we found that materials which can be obtained through sol-gel processing can be molded to have a monolithic microhoneycomb structure by simply freezing their parent hydrogels unidirectionally (Mukai et al. 2003, 2004, 2008; Nishihara et al. 2005). As ice crystals which are generated within the hydrogel and which elongate during freezing act as the template, we named this new micromolding technique the "Ice Templating Method." Monoliths obtained through this method have straight and aligned macropores which are the traces of the ice crystal templates, the sizes of which are in the micrometer range. Moreover, the walls which form the macropores are thin and have developed micro/mesopores within them. Therefore, this material can be regarded as a material with a hierarchical pore system in which micro/mesopores are directly connected to macropores. As the macropores are straight and aligned, the pressure drop which occurs when fluids are passed through them is extremely low, and as the thickness of the walls is only a few micrometers at most, the diffusion paths within this material are also extremely short. Therefore, this material is a unique porous material in which a low resistance to fluid flows and short diffusion paths are compatible.

As the macropores of such monoliths are the traces of the ice crystal templates which are formed during freezing, the size as well as the shape of them depends on how the template ice crystals are formed and how they grow. Therefore in this work, the growth behavior of the template ice crystals in the ice templating method was examined, and how this behavior affects the properties of the resulting monolith was verified.

2 Experimental

First, a commercial sodium silicate solution (Wako Pure Chemical Industries, Ltd.) was diluted with distilled and deionized water and its SiO_2 concentration (C_S) was adjusted to 1.9 mol/L. Next, the pH of the solution was adjusted using an ion-exchange resin (Amberlite® IR120B HAG, Organo Corporation). The resulting solution was poured into a polypropylene tube (*i.d.*: 10 mm, *L*: 120 mm) up to a height of 100 mm. The tube was sealed and was maintained at 303 K. After the solution transformed to a hydrogel, the hydrogel was further aged to adjust its firmness (Mukai et al. 2008). Then the tube including the hydrogel was dipped into a liquid bath at a constant rate set in the range of 2.5 cm/h to 30 cm/h, and the hydrogel was frozen unidirectionally. The temperature of the bath was maintained at either 77 K or 193 K, and the surface level of the refrigerant in the bath was kept at a constant height. After the hydrogel was completely frozen, it was removed from the tube and was thawed. The water included in the hydrogel was exchanged with *t*-butanol, and then the hydrogel was freeze-dried at 263 K. The dried samples were divided into 5 or 10 equal parts in the axial direction for characterization.

The morphology of the samples was directly observed using a scanning electron microscope (SEM, JSM-5410, JEOL Ltd.). Nitrogen adsorption-desorption isotherms of the samples were measured at 77 K using a surface area and pore size analyzer (BELSORP-mini, BEL Japan Inc.), and the porous properties of the samples were evaluated by analyzing the obtained isotherms. The compression strength of the samples was measured using a load cell (FW-12K, A & D Company Ltd.).

3 Results and discussion

In the Ice Templating Method, the freezing process starts by dipping the tube including the precursor hydrogel into a cold bath at a constant rate. During this process, the hydrogel starts to freeze from its bottom, and the freezing front advances upward. Unless the temperature of the cold bath is high and/or the dipping rate is extremely high, the position of the freezing front is usually higher than the surface level of the refrigerant in the cold bath, so the ascending freezing front can be clearly observed, as shown in Fig. 1. In order to measure the actual freezing rate, the position of the freezing front was constantly monitored during freezing. Figure 2 shows a typical result, where the freezing rates are plotted as a function of the distance between the freezing front and the bottom of the hydrogel. The dipping rate and cold bath temperature were respectively fixed to 2.5 cm/h and 77 K in this experiment. It was confirmed that the hydrogel starts to freeze before the bottom of the tube including it touches the surface of the refrigerant, as the air between the refrigerant and the tube is cooled to extremely low temperatures. The actual freezing rate jumps up to a high value when the tube makes contact with the refrigerant and then decreases and finally reaches a fairly constant value. It can be noticed that the actual freezing rate is much higher than the dipping rate

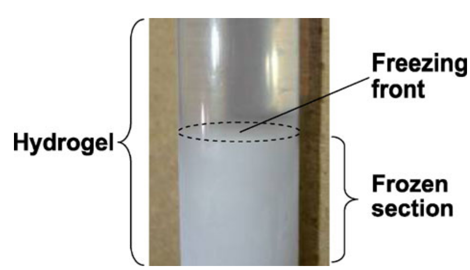


Fig. 1 Photograph of the freezing front of a silica hydrogel during unidirectional freezing

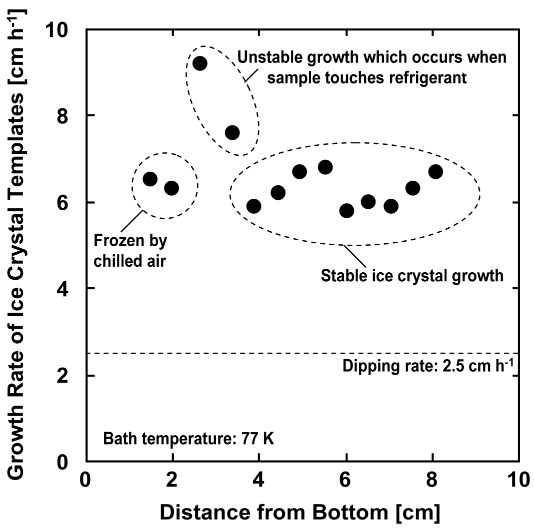


Fig. 2 Growth rate of ice crystal templates

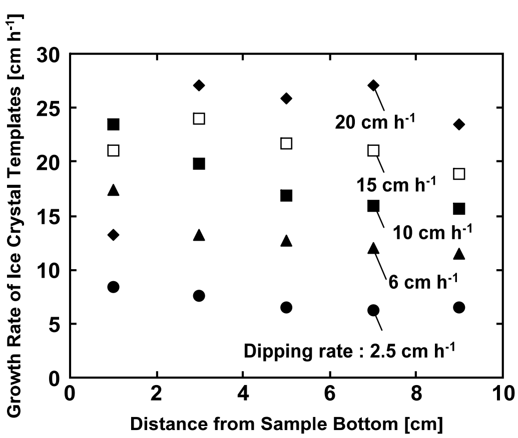


Fig. 3 Growth rate of ice crystal templates (bath temperature: 77 K)

throughout the whole freezing process as the dipping rate is low.

Figure 3 shows the results of experiments conducted at different dipping rates. The temperature of the cold bath was maintained to 77 K in this series. Note that the rapid increase followed by a rapid decrease in the freezing rate which occurs just before and right after the tube makes contact with the refrigerant is not included in the figure. At low dipping rates, the freezing rate decreases at the initial stage of freezing, and then levels off, whereas at high dipping rates, the freezing rate increases first. The same trend was observed at the initial stage of freezing when a cold bath maintained at 193 K was used (Fig. 4), but in this case the freezing rate tended to decrease as freezing proceeded. Actual freezing rates lower than the dipping rate were observed, but due to the higher freezing rates achieved at the initial stage of freezing, the level of the freezing front was always maintained above the level of the refrigerant.

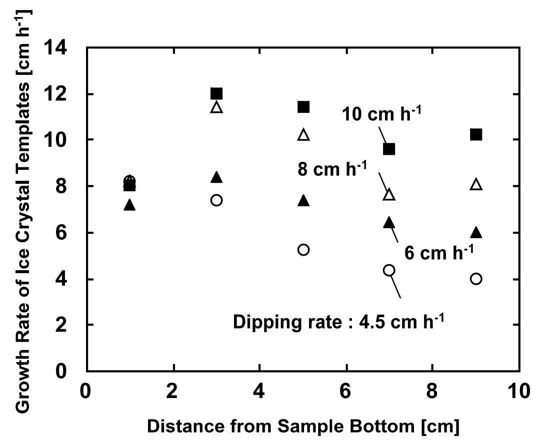


Fig. 4 Growth rate of ice crystal templates (bath temperature: 193 K)

Figure 5 shows typical cross sectional micrographs which represent each portion of a typical microhoneycomb divided in the axial direction. It can be noticed that the sizes of the channels of the bottom part of the microhoneycomb are not so uniform, which is thought to be due to the fact that the freezing rate significantly fluctuated when this portion was frozen. In the middle part of the microhoneycomb, which is thought to be frozen under a fairly stable freezing rate, the sizes of the channels were found to be quite uniform. At the upper part of the microhoneycomb, the sizes of the channels seem to be slightly larger than those of the middle part.

The upper part of a typical microhoneycomb was divided into smaller portions in the axial direction to verify how the sizes of the channels change in this region. The results are also shown in Fig. 5. It can be noticed that the size of the channels gradually increases. One explanation of why this increase occurs is that the freezing rate tends to decrease in this region, as the position of the freezing front is quite far from the level of the refrigerant when this region is frozen. The fact that the hydrogel is discontinuous at its top, and that there is a space filled with air between the hydrogel and the cap of the tube, is also thought to lead to a decrease in the heat removal rate, which leads to a decrease in freezing rate.

The height of the precursor of the microhoneycomb is usually adjusted to be 10 cm, but after freezing, the height slightly increases which is caused by the volume expansion of water during phase transition. As the flat top of the hydrogel becomes slightly uneven after freezing due to this expansion, this part is usually cut off and discarded, but in this work, we carefully recovered this part and observed the structure of it. As shown in Fig. 6, the topmost part of the microhoneycomb showed a different texture. No macropores could be found and it seems like a ridged "lid" which blocks the macropores was formed at the top of the microhoneycomb. During freezing, water migrates from the unfrozen upper part of the hydrogel to the freezing front of the ice crystal templates, and these templates elongate. When

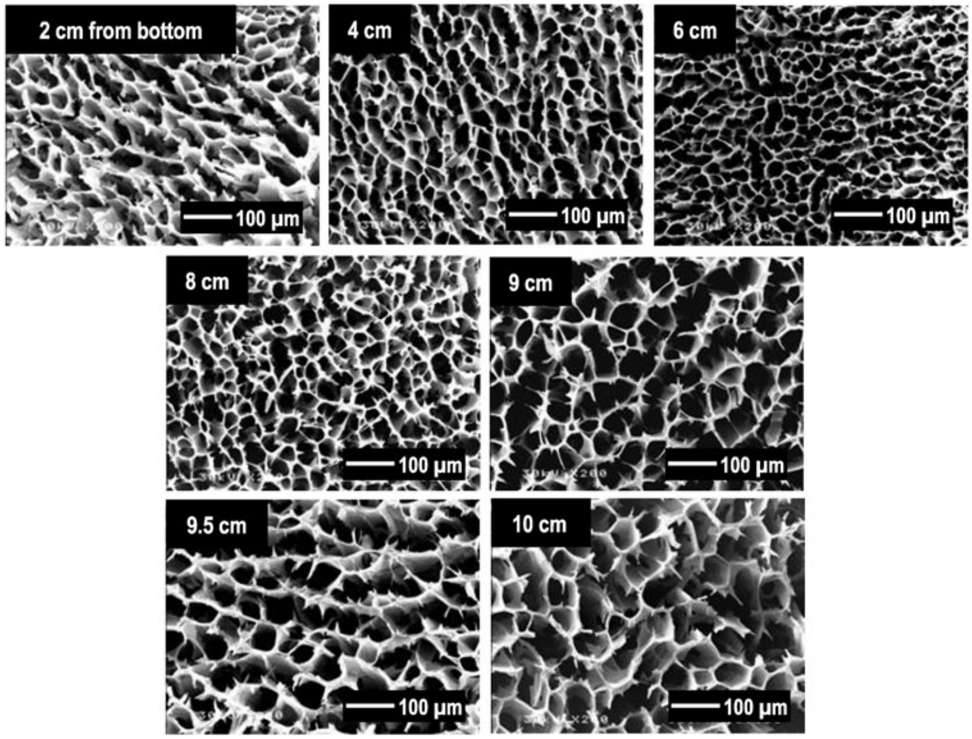


Fig. 5 Cross sectional SEM micrographs of a typical silica microhoneycomb obtained through the Ice Templating method (Bath temperature: 77 K, dipping rate: 2.5 cm h^{-1})

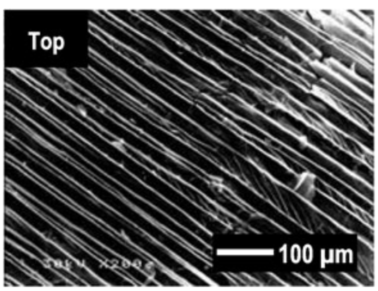


Fig. 6 SEM micrograph of the top of a typical silica microhoneycomb obtained through the Ice Templating Method (bath temperature: 77 K, dipping rate: 2.5 cm h^{-1})

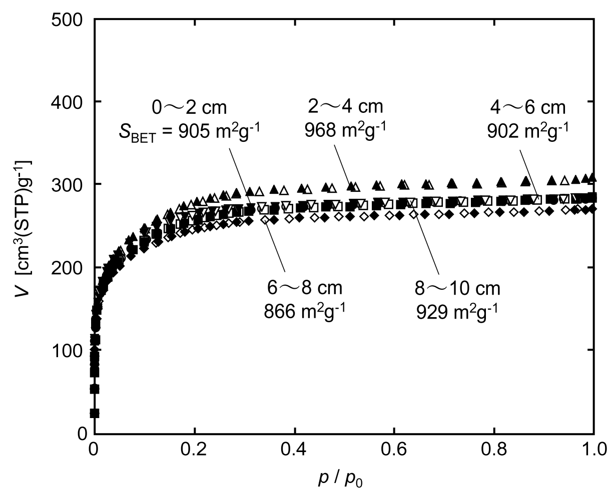


Fig. 7 Nitrogen adsorption isotherms (77 K) of a typical silica microhoneycomb obtained through the ice templating method (closed keys: adsorption branch, open keys: desorption branch)

the freezing front is about to reach the top of the hydrogel, a zone which lacks water is formed at the top part, as there is no water supply from above. This means that the ice crystal templates can no longer elongate, so macropores cannot be formed at the top, and a rigid lid is thought to be left behind.

As shown above, it was found that the growth behavior of the ice crystals significantly affects the morphology of the resulting microhoneycombs. Therefore, next we verified whether the growth behavior affects the nanostructure of the microhoneycombs. Figure 7 compares the nitrogen adsorption isotherms of the portions of a typical microhoneycomb equally divided into 5 parts in the axial direction. It can be noticed that the isotherms are quite identical, indicating that the growth behavior of the ice crystal templates hardly affects the nanostructure of the resulting microhoneycomb.

As the freezing rate affects the sizes as well as the uniformity of the channels of the resulting microhoneycomb, it is also likely to affect the structural strength of the monolith itself. Therefore, we also measured the compression strength of portions of a typical microhoneycomb obtained by equally dividing it into 10 parts in the axial direction. Representative results are shown in Fig. 8. The strength of the portions of the middle section of the microhoneycomb was found to be relatively high when compared with the top and bottom sections of the same microhoneycomb. This result indicates that a constant and stable freezing rate is required to maximize the strength of the microhoneycomb.

From the results shown above, it can be concluded that in the Ice Templating Method, the template ice crystals must be grown under a constant and stable freezing rate to obtain a microhoneycomb with a uniform structure and moderate strength. As the stability of the freezing rate depends on freezing conditions, *i.e.* cold bath temperature and dipping rate, finally we investigated how these conditions affect the value and stability of the actual freezing rate.

Maintaining the position of the freezing front above the surface level of the refrigerant of the cold bath used for freezing is thought to be one prerequisite to obtain a microhoneycomb with a uniform structure. If the position of the freezing front is located below the surface level of the refrigerant, the structure of the resulting microhoneycomb is likely to be disordered as it will be difficult for the ice crystal templates to grow vertically as significant heat removal occurs from the side walls of the vessel used for freezing. This means that a practical maximum dipping rate exists which depends on the cold bath temperature. Such maximum values were found to be about 12 $\mathrm{cm\,h^{-1}}$ and 25 $\mathrm{cm\,h^{-1}}$ for cold baths with temperatures 193 K and 77 K, respectively.

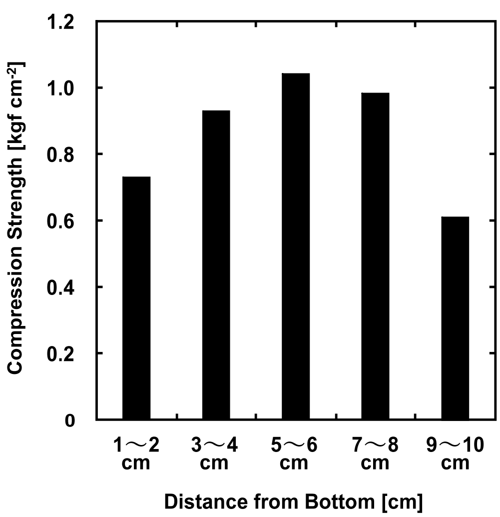
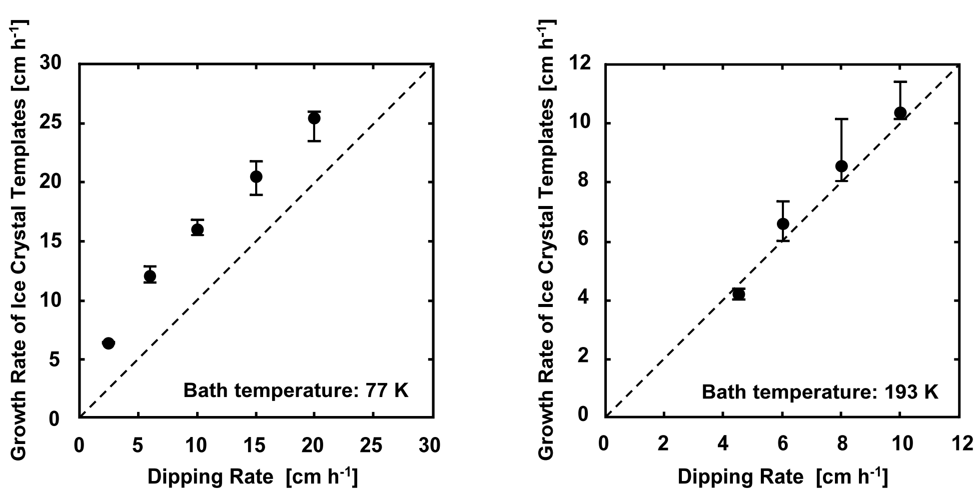


Fig. 8 Compression strength of a typical silica microhoneycomb obtained through the ice templating method

The cold bath temperature is also likely to affect the relationship between the dipping rate and the actual growth rate of the ice crystal templates. The driving force of heat removal increases with the decrease in the temperature of the cold bath, so it is assumed that the difference between the dipping rate and the actual growth rate of the ice crystal templates will increase with the decrease in the temperature of the cold bath. In order to confirm this, the average growth rates of the ice crystal templates grown under various freezing conditions were calculated and were compared with the dipping rates used to achieve them. Note that the growth rates obtained at the initial stage of freezing were omitted in calculations. The results are summarized in Fig. 9 where the growth rate of the ice crystal templates is plotted as a function of the dipping rate. The actual maximum and minimum growth rates observed at each dipping rate are also shown in the figure. The growth rates and dipping rates were found to be quite similar when a cold bath with a temperature of 193 K was used, and as expected, the difference between the dipping rate and the actual growth rate became larger when a cold bath with a temperature of 77 K was used. However, the stability of the growth rate was found to be higher when a cold bath with a lower temperature was used. Considering this result along with the fact that the controllable range of the growth rate of the ice crystal templates becomes wider when a cold bath with a lower temperature is used, it can be concluded that a cold bath with a lower temperature is favorable to obtain a microhoneycomb with a uniform structure and moderate strength using the Ice Templating Method.

From the results obtained in this work, the freezing mechanism in the Ice Templating method can be summarized as follows: As the heat of solidification of water is fairly high,

Fig. 9 Relationship between dipping rate and actual growth rate of ice crystal templates



and heat removal occurs mostly through conduction, a cold bath with a fairly low temperature is required to increase the driving force for the freezing of the precursor hydrogel at moderate rates. However, due to this low temperature the hydrogel starts to freeze before it makes contact with the refrigerant in the cold bath, and the freezing rate rapidly increases when the hydrogel touches the refrigerant. This high freezing rate pushes the level of the freezing front away from the surface level of the refrigerant. Due to this level gap, a larger amount of heat is allowed to flow into the hydrogel from its side, and this leads to the decrease in the rate of heat removal at the freezing front or in other words a decrease in the freezing rate. This heat flow increases with the increase in the level gap, therefore the freezing rate rapidly decreases and a quasi-steady state in which the hydrogel is frozen at a fairly constant freezing rate is achieved quite quickly.

4 Conclusions

In this work, the growth behavior of the ice crystals formed during the synthesis of a monolithic silica microhoneycomb using the Ice Templating Method was examined, and how it affects the properties of the resulting monoliths was verified. It was found that although the growth behavior hardly affects the nanostructure of the resulting monolith, the growth rate of the ice crystal templates must be kept stable in order to obtain a monolith with a uniform structure and moderate strength. Moreover, although the growth rate fluctuation at the initial stage of freezing is large, and the difference between the dipping rate and the actual growth rate of the ice crystal templates is larger, the usage of a cold bath with a lower temperature was found to be favorable, as the stability of the growth rate of the ice crystal templates was higher at the latter stage of freezing, and the controllable range of the growth rate, or in other words the controllable range of the size of the channels of the resulting microhoneycomb, is much wider.

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