

Synthesis and Characterization of Zeolites by Conventional and Microwave-Assisted Methods Using (2-Hydroxyethyl)-trimethylammonium Hydroxide as a Template

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Different types of zeolites were synthesized using two different techniques: conventional hydrothermal synthesis (CHS) and microwave-assisted hydrothermal synthesis (MAHS) using (2-hydroxyethyl)trimethylammonium hydroxide (2-HETMAOH) as a template. The influence of the chemical composition of the starting sol and hydrothermal synthesis parameters, i.e., MW power, heating time, number of synthesis steps, conditions on the formation of zeolite by MAHS and CHS methods were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and IR spectroscopy. Zeolites obtained by conventional heating had irregular shapes, while these form microwave irradiation had regular rounded shapes. In both cases, in the presence of template, samples contained particles with sizes between 12 and 15 μm, and the samples without a template had spherical morphology with average particle size of 6 μm.

Zeolites are crystalline, microporous aluminosilicates with well-defined pores of molecular dimensions. They occur in nature and have been known for almost 250 years as aluminosilicate minerals. Examples are faujasite, mordenite, offretite, ferrierite, and chabazite.

Zeolites having both acidic and basic sites act as a catalyst for many reactions,[1] including side chain alkylation of toluene,[2] condensation reactions,[3] and selective alkylation of aromatic compounds containing oxygen and nitrogen.[4]

It is generally accepted that, in the hydrothermal synthesis of microporous materials, a so-called mineralizer is required to transfer the framework constituent elements from the amorphous gel phase via the solution phase to the surface of the growing crystals.[5–7] The homogeneity of the starting system and simultaneity of the events leading to the formation of precursor gel particles and their transformation into crystalline zeolitic material are of primary importance. Microwave heating techniques are now widely used in many applications of chemical research including organic/inorganic synthesis because they are fast and energy efficient techniques to avoid competitive reactions in many known processes.[8] The microwave-assisted hydrothermal process is also effective for zeolite synthesis from a silica–alumina gel precursor.[9] By combining hydrothermal crystallization with microwave heating, a new synthetic method has been developed, giving smaller and more uniform particles in a shorter time.[10] Zeolites are usually synthesized by hydrothermal treatment of the raw gels using autoclaves heated within convection ovens.[11] However, in recent years, several reports have been published on the microwave-assisted synthesis of different zeolitic materials, such as zeolites A, Y and ZSM-5, AlPO-5 and VPI-5, and mesoporous materials, such as MCM-41 and SBA-15.[12–19]

The advantage of microwave-assisted hydrothermal have prompted researchers to further explore the potential of MW-assisted synthesis for accelerating the synthesis of zeolites.[17–19] The action of microwave heating is still under debate.

In this work, zeolite was synthesize using (2-hydroxyethyl)-trimethylammonium hydroxide (2-HETMAOH) as a template by conventional hydrothermal (CH) method and by microwave-assisted hydrothermal (MAH)) before CH heating. Using ^{29}Si and ^{27}Al NMR spectroscopy, we have reported that 2-HETMAOH can direct the structure on the basis of the distribution of silicate and aluminosilicate species.[20,21] The crystallization of the zeolite by microwave heating has been also investigated and compared with its synthesis in a conventional oven using different aluminum source, i.e., aluminum powder and sodium aluminate. Several zeolites were synthesized with different conventional heating times and microwave radiation of exposure times the gel. Zeolites were characterized by XRD, IR, and SEM techniques. Highly crystalline samples were obtained by microwave heating with a significant reduction in the synthesis time.

Experimental

Materials. Sodium hydroxide (Merck), aluminum powder, $Al_2(SO_4)_3$ and sodium aluminate (Fluka Co.), SiO_2 (synthesized in our laboratory), silicon tetrachloride (99.8%; Janssen chemical Co.), (2-hydroxyethyl)trimethylammonium chloride (Fluka Co.) and amberlite resin IRA-400 (OH) (Aldrich Co.) were used. Double distilled water was used throughout.

Preparation of Solutions. Preparation of Silicate Solutions: Pure silica was produced by hydrolysis of silicon tetrachloride using doubly distilled water. The precipitate was filtered off and washed many times with water to remove all acid (at least five times using 1 L of water for each 5 g of the sample). It was then dried at ca. 110 °C for 48 h. The chemical reaction is:

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl. \quad (1)$$

Aqueous silicate solutions were prepared in a plastic bottle by

Published on the web April 13, 2007; doi:10.1246/bcsj.80.789

Table 1. Composition for the Synthesis of the Zeolites by Conventional Heating

Sample No.	Si /mol	Al /mol	Na /mol	2-HETMA /mol	H_2O /mol	Heating time /h
1	20	2	28	0	2200	60
2	20	2[a)]	28	0	2200	60
3	20	2	28	12	2200	60
4	20	2[a)]	28	12	2200	60

a) $Al_2(SO_4)_3$ was used as aluminium source for preparation of samples 2 and 4.

Table 2. Composition for the Synthesis of the Zeolites by Microwave-Assisted Hydrothermal and Conventional Hydrothermal Methods

Sample No.	Si /mol	Al /mol	Na /mol	2-HETMA /mol	H_2O /mol	MAH time /min	CH time /h
5	20	2	28	12	2200	45	2.0
6	20	2	28	12	2200	45	4.0
7	20	2	28	12	2200	45	8.0
8	20	2	28	12	2200	45	12.0

dissolving 9.0 g of SiO_2 in 100 mL of sodium hydroxide solution (1.2 M). Other silicate solutions were prepared by dissolving of 9.0 g of SiO_2 in 100 mL of (2-hydroxyethyl)trimethylammonium hydroxide (2-HETMAOH). (2-Hydroxyethyl)trimethylammonium chloride was converted to hydroxide form by dissolving it in minimum amount of water and passing down a column of Aldrich amberlite resin IRA-400 (OH). The dissolution of the silica was very slow at room temperature, so it was heated in an oven at 70 °C.

Preparation of Aluminate Solutions: Aqueous sodium aluminate solution was prepared by dissolving aluminum powder (1.35 g, 50 mmol) in 0.6 M 2-HETMAOH, aluminum powder (1.35 g, 50 mmol) in 0.6 M NaOH, and $Al_2(SO_4)_3$ (13.7 g, 40 mmol) in 100 mL of 10% H_2SO_4.

Preparation of Aluminosilicate Solutions: Aluminosilicate solutions were obtained by mixing sodium aluminate/2-HETMA aluminate (other aluminate solutions were prepared by dissolving aluminum sulfate in H_2SO_4 or dissolving of aluminum powder in NaOH) and sodium/2-HETMA silicate solutions. Compositions of the aluminosilicate solutions are summarized in Tables 1 and 2.

Synthesis of Zeolites. To prepare zeolites using conventional hydrothermal synthesis (sample numbers 1–4), the aluminosilicate gel was added to Teflon bottle, and then, the bottle was covered with a cap. The synthesis mixture was heated at temperature of 175 °C for 72 h.

In microwave-assisted hydrothermal synthesis (sample numbers 5–10), the aluminosilicate gel was exposed to low-power microwave radiation (100 W, operating at frequency of 2450 MHz) for 45 min at ca. 100 °C, and then, it was transferred to a hydrothermal vessel and placed in oven. Crystallization was carried out in a conventional oven between 2 and 18 h at a constant temperature of 175 °C.

The solid products obtained by both synthetic methods were filtered off and washed several times with distilled water. Subsequently, they were dried overnight at 110 °C and calcinated in static air at ca. 550 °C for 5 h.

Characterization. XRD pattern was recorded on an X-ray diffractometer (XRD, GBC MMA Instrument) with Be-filtered Cu Kα radiation (1.5406 Å) operating at 35.4 kV and 28 mA. The scanning range of 2θ was set between 5 and 55° with a step size of 0.05, and a scan rate of 3° min^{-1}.

The morphology of the zeolite was examined by using SEM. The SEM photographs were obtained on a JEOL JXA-840 SEM. The IR spectra for the framework vibration were recorded on a FT-IR spectrometer (Vector 22-Bruker) at room temperature as KBr pellets.

Results and Discussion

Conventional Hydrothermal Synthesis. The Influence of Aluminum Source: The effect of aluminum source was examined using the following mixture compositions: $20SiO_2$:Al_2O_3:$14Na_2O$:$2200H_2O$ (sample 1) and $20SiO_2$:$Al_2(SO_4)_3$:$14Na_2O$:$2200H_2O$ (sample No. 2) using aluminum powder (dissolved in NaOH) and $Al_2(SO_4)_3$, respectively. Figure 1 shows the XRD patterns of the corresponding samples, and although both samples have almost the same structure, for sample No. 2, the intensity of the reflection peak corresponding to the 32° (2θ) is grater.

IR spectra of the samples obtained using different aluminum sources were basically the same. SEM images of samples prepared by using different aluminum sources also showed no significant differences in the crystal morphology in relation to both size and shapes of the particles.

The Influence of Template: To determine the influence of the template, zeolite was synthesized in the presence of 2-HETMA using the following compositions: $20SiO_2$:Al_2O_3:$14Na_2O$:12(2-HETMA):$2200H_2O$ (sample No. 3). The crystalline phases were identified by XRD and are presented in Fig. 1. Although the spectral features between sample Nos. 1 and 3 are nearly the same, the intensity of the peaks at ca. 17, 26, and 27° (2θ) were greater for sample No. 3. The same results were obtained for sample No. 4 ($20SiO_2$:$Al_2(SO_4)_3$:$14Na_2O$:12(2-HETMA):$2200H_2O$) and sample No. 2, for which $Al_2(SO_4)_3$ was the source of aluminum. The samples synthesized in the presence of template contained large size (particles 10–12 μm), and the samples without template had a spherical morphology with an average particle size of 8 μm. Figure 2 shows the SEM images of sample Nos. 3 and 4. Table 1 lists the chemical composition of sample Nos. 1–4.

Microwave-Assisted Hydrothermal Synthesis. Influence of Conventional Heating Time: Conventional and micro-

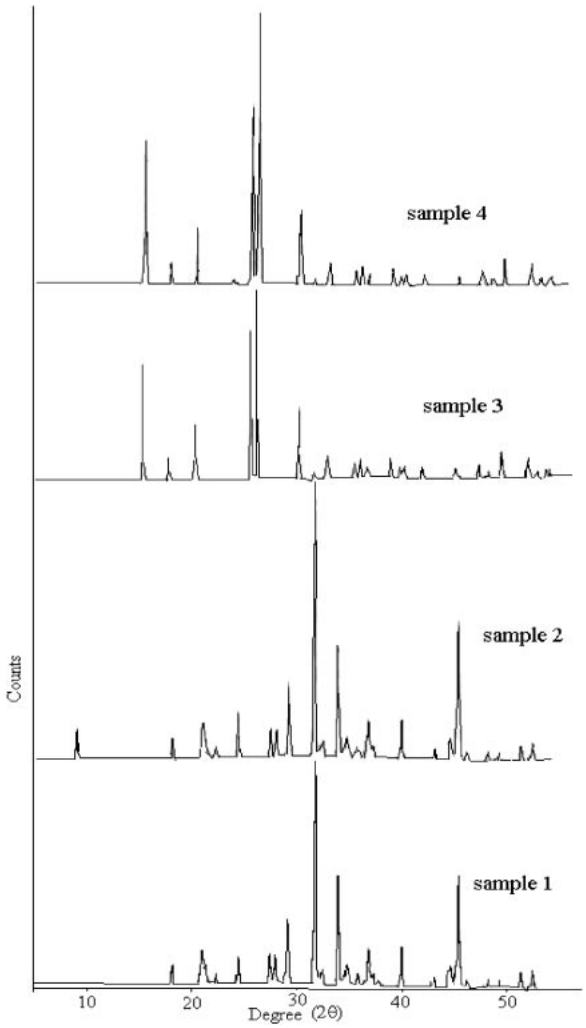

Fig. 1. XRD patterns for sample Nos. 1–4 by using CHS.

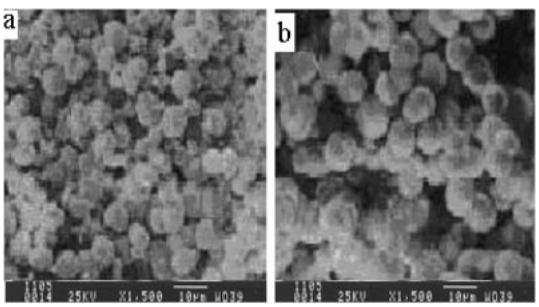

Fig. 2. SEM images of sample Nos. 3 and 4.

wave heating processes were combined in this study. The microwave heating process was performed using a household microwave oven (2.45 GHz, 100 W). The solution was stirred for 20 min before microwave heating. The solution was continuously irradiated with microwave, and boiling indicated the temperature was 100 °C or above.

In order to clarify the effect of microwave irradiation on the formation of the zeolites, the reaction suspension was partially irradiated during conventional heating. The microwave heating time was 30–45 min, and the conventional heating time was varied from 2 to 12 h (sample Nos. 5–8). Table 2 lists the

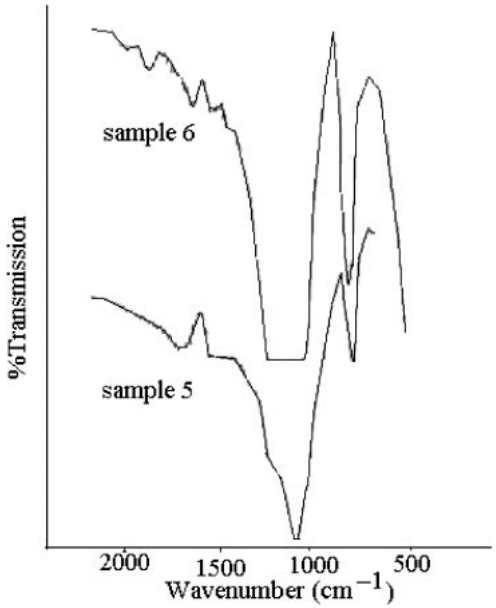

Fig. 3. FT-IR spectra of zeolite samples under microwave heating in gel for 45 min with conventional heating times 2 h (sample No. 5) and 4 h (sample No. 6).

chemical composition of the zeolites sample Nos. 5–8. IR spectra of the microwave-irradiated samples with varied conventional heating times were recorded in the frequency range 500–2000 cm^{-1}. Figure 3 shows the IR spectra of the sample Nos. 5 and 6 (conventional heating time 2 and 4 h, respectively). The band at ca. 635 cm^{-1} observed in the spectra was assigned to six-membered rings (D_6R) in the three-dimensional zeolite structure.[22] The intensity of the band at 635 cm^{-1} appeared to increase with an increase in the heating time. However, it does not change for the samples heated by conventional heating more than 4 h, indicating 100% crystallinity was obtained. The broad and strong peak that located at 1000 cm^{-1} corresponded to the Si(Al)–O group.[23] This peak was not affected by the aluminum concentration, because this group is located mainly in the zeolite structure and Al concentration can not change of Si(Al)–O intensity in IR spectrum. The XRD patterns of sample Nos. 5–8 are shown in Fig. 4. As can be seen, the intensity of peaks at $2\theta = 21$ and 27° do not change after 4 h (sample No. 6), indicating almost 100% crystallinity of the zeolite is obtained at 175 °C after 4 h.

SEM images of the zeolite after microwave heating in gel for 45 min with different conventional heating times (2, 4, 8, and 12 h) are shown in Fig. 5. Influence of the conventional heating time on the particle size, shape and aggregation is clearly observed from the SEM image. The SEM images confirm that the zeolite is completely crystalline after 4 h. The particles were uniform with a spherical morphology; however, as can be expected the sizes of particles increased with an increase in conventional heating times, i.e., the size of particles are 5, 7, and 8 μm for sample Nos. 6, 7, and 8, respectively.

The Effect of Template: The effect of the template, i.e., 2-HETMA was examined using same procedure as mentioned above, i.e., conventional and microwave heating possessing. Figure 6 shows SEM micrographs of sample Nos. 11 and 12 (see Table 3) synthesized by microwave irradiation (45 min)

and conventional heating time (4 h) with and without template, respectively. As can be seen, the size of the particles is clearly difference. The materials obtained in the presence of the template were spherical macroparticles with sizes between 12 and 15 μm, whereas the sample without template had a spherical morphology with sizes around 5–7 μm. Therefore, the presence of template can affect the size and morphology of the zeolite.

The Effect of Si/Al Ratio: An important variable that affects on the structure of zeolite is silicon/aluminum mole ratio. Sample Nos. 9–15 with Si/Al mole ratios of 7.5, 10, 15, 17.5, 25, and 30, respectively were synthesized by conventional and microwave-assisted heating method. The gel compositions of samples with different Si/Al mole ratios are listed in Table 3.

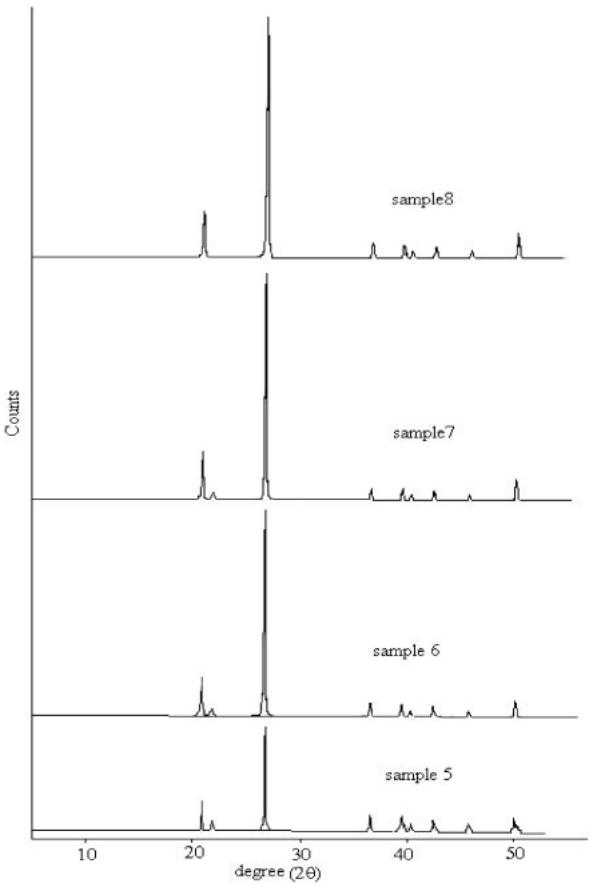

Fig. 4. XDR patterns of the zeolites with varying conventional heating times: 2.0 h (sample No. 5), 4 h (sample No. 6), 8 h (sample No. 7), and 12 h (sample No. 8).

Figure 7 shows XRD patterns of samples with different Si/Al mole ratios, and the XRD patterns for the zeolites are clearly different. Results showed that Si/Al mole ratio also has a considerable effect on the crystal structure of the zeolite. All zeolites were synthesized under the same experimental con-

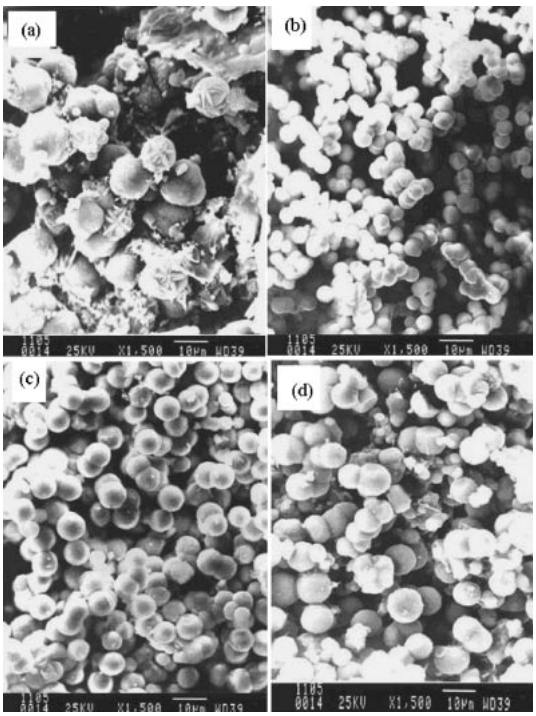

Fig. 5. SEM micrographs of sample Nos. 5–8.

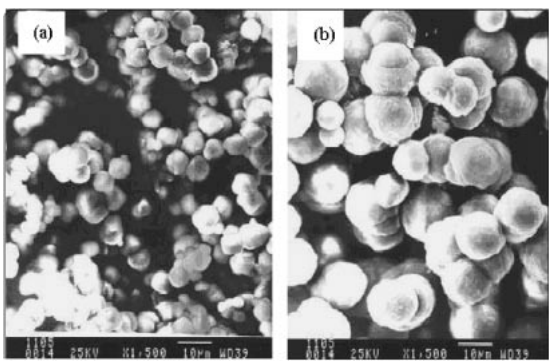

Fig. 6. SEM micrographs of the zeolites synthesized with microwave heating (45 min) and conventional heating (4 h) (a) without and (b) with template (2-HETMA).

Table 3. Composition for the Synthesis of the Zeolite with Different Si/Al Mole Ratios by MAHS

Sample No.	Si /mol	Al /mol	Na /mol	2-HETMA /mol	H_2O /mol	MAH time /min	CH time /h
9	15	2	28	12	2200	45	4.0
10	25	2	28	12	2200	45	4.0
11	30	2	28	0	2200	45	4.0
12	30	2	28	12	2200	45	4.0
13	35	2	28	12	2200	45	4.0
14	50	2	28	12	2200	45	4.0
15	60	2	14	12	2200	45	4.0

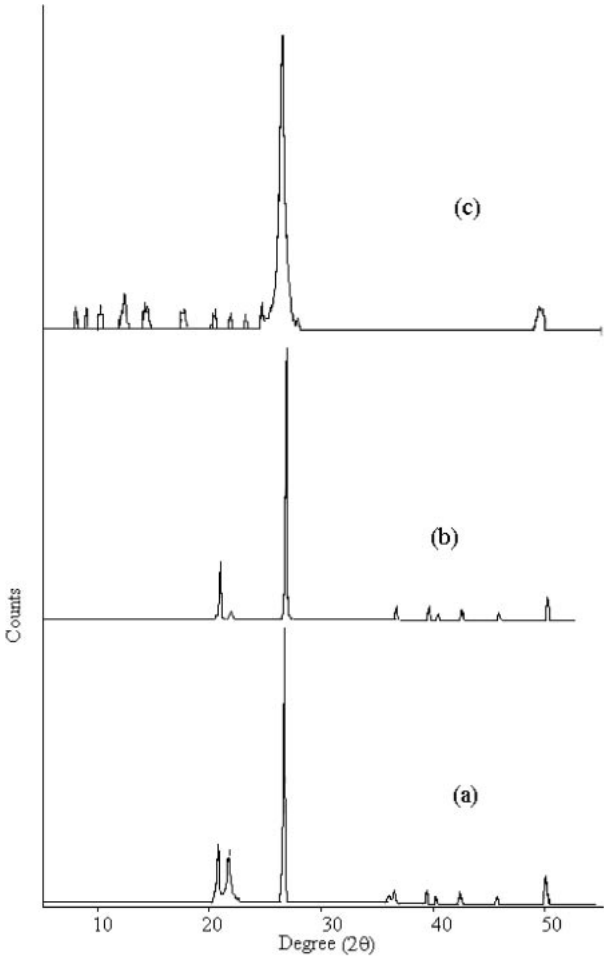

Fig. 7. XRD patterns of sample No. 9 (a), 10 (b), and 13 (c).

ditions, i.e., 45 min microwave irradiation and 4 h hydrothermal heating.

Thus, in order to obtain zeolites with large particle sizes and spherical shapes, several parameters, such as Si/Al mole ratio, template, and microwave-assisted hydrothermal synthesis, are important. It should be mentioned that zeolites with large particle size, uniform and spherical shape are useful in the industrial applications, for example, solid-phase extraction and heterogenic catalysis.

Conclusion

Results obtained from a series of experiments indicated that, in comparison with CHS, MAHS of zeolites has the advantages of short synthesis times, broad synthesis composition, small zeolite particle size, narrow particle size distribution, and high purity. The presence of a template had a strong effect on the size and morphology of obtained zeolite. Results revealed that zeolite synthesized using template 2-HETMAOH were spherical macroparticles with larger sizes than those produced without the template. In summary, zeolites with large sizes as well as particles with uniform and spherical shape can be obtained by controlling several parameters, such as Si/Al mole ratio, template, and MAHS.

We are very grateful to Mr. Farhadi (Department of Physics, University of Mazandarn) for his expert assistance in obtaining the X-ray spectra.

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