

Supporting information

Facile and Rapid Synthesis of Durable SSZ-13 Catalyst using Choline Chloride Template for Methanol-to-Olefins

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The XRD patterns of the resulting products are shown in Fig.S1(a). CHA-shaped structural characteristic diffraction peaks were identified in all samples. When CC was used as the template agent, all peaks of the product were completely corresponding to the diffraction characteristic peak of SSZ-13 synthesized with TMADaOH as template agent, and the product was pure phase SSZ-13 molecular sieve. Analcime (ANA) zeolite and small amount of CHA-type existed in the sample with BA template. Except for the CHA-type peak, structural characteristic diffraction peaks of mordenite (MOR) zeolite appear at positions of $2\theta=6.5, 13.5, 22.1$ and 25.7° , and MOR hybrid peaks are the main ones. It may be twisted side channels of MOR molecular sieves having same eight-membered ring channel structure as CHA topological structure. BH may be more inclined to be used as a structure-guiding agent for the synthesis of MOR molecular sieves.

The influence of Si/Al ratio on the SSZ-13 reactor was explored. With the same amount of other ingredients, the Si/Al ratio ($n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$) was adjusted in the range from 20 to 50. The XRD information of the resulting SSZ-13 samples is presented in Fig.S1(b). The relative crystallinity of pure phase crystalline could reach 87.13% until the ratio reached 20. When Si/Al ratio reached 40, the relative peak intensities increased to 107.8% (Table S1). However, as the Si/Al

ratio continued to rise, the peaks for minor phases began to appear. As it reached 45, ANA characteristic peaks were significantly enhanced at 15.8 and 26°, and the characteristic peaks of SSZ-13 also decreased. When the Si/Al ratio increased to 50, the main peaks were ZSM-4 and only few were SSZ-13. To sum up, high SiO₂ concentration, low alkali concentration and highly polymerized silicate ions inhibited the formation of regular crystal nucleus, which led to the gradual generation of hetero-crystals in the zeolite structure. Therefore, considering the hydrothermal stability, the most appropriate ratio of Si/Al is 40.

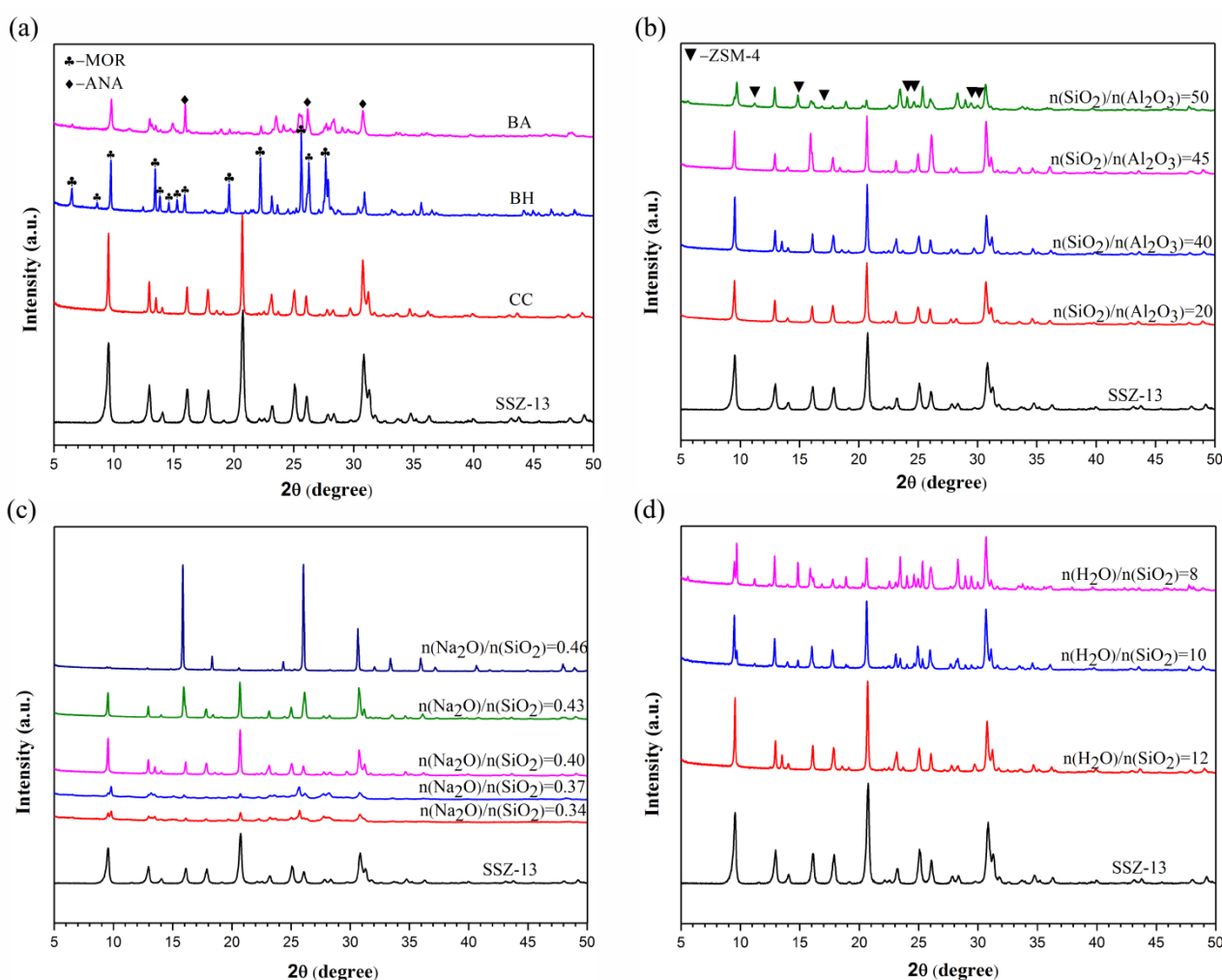


Fig.S1. The XRD information of the product by change different conditions (a) quaternary ammonium bases (b) ratio of the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ (c) $n(\text{Na}_2\text{O})/n(\text{SiO}_2)$ (d) $n(\text{H}_2\text{O})/n(\text{SiO}_2)$.

Molecular sieve materials were generally synthesized in an alkaline environment, and the alkalinity required is correlated with the Si/Al ratio. Fig.S1 (c) displays the XRD patterns of samples with $n(\text{Na}_2\text{O})/n(\text{SiO}_2)$ ranging from 0.34 to 0.46. There were weak SSZ-13 and MOR

peaks located at 13.5, 19.8 and 23.3° under ratios between 0.34 to 0.37. With the ratio reaching 0.40, the characteristic peak intensity of SSZ-13 was significantly enhanced, indicating that pure phase SSZ-13 was obtained with high crystallinity. When the alkali/silicon ratio reached 0.43, SSZ-13 peaks still existed, but the characteristic peaks of hetero-phase square zeolite gradually appeared. As the alkali-silicon ratio further increased to 0.46, due to the high alkalinity, most of the silicon species in the system existed in the gel in the form of free states, resulting in a decrease in the silicon content that could enter the molecular sieve skeleton. The characteristic peak of SSZ-13 gradually disappeared and pure phase ANA with a low Si/Al ratio was obtained. Therefore, the optimum alkali-silicon ratio for SSZ-13 synthesis is determined to be 0.4.

Table S1. The phase of synthetic products in different $n(\text{H}_2\text{O})/n(\text{SiO}_2)$

$n(\text{H}_2\text{O})/n(\text{SiO}_2)$	Crystallization temperature	Crystallization time	Phase composition	Relative crystallinity
8	140 °C	2d	CHA+ANA	35.35%
10	140 °C	2d	CHA	74.1%
12.31	140 °C	2d	CHA	97.1%

The wetting degree of the initial raw material (ratio of $n(\text{H}_2\text{O})/n(\text{SiO}_2)$) would affect the synthesis of the SSZ-13. Table S1 and Fig.S1 (d) presents the structure information. With the ratio of $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ being in the range from 10 to 12, notable SSZ-13 characteristic peaks appeared at the locations of $2\theta=9.51, 12.9, 14.0, 16.1, 17.7, 20.9$ and 30.8° . The peak locations were consistent with the standard pattern, i.e. pure phase SSZ-13 zeolite could be obtained with the relative crystallinity reaching 74.1% and 97.1%, respectively. The peak of SSZ-13 was significantly reduced and other peaks (mainly ANA peaks) showed up as the ratio decrease to 8. Considering resource utilization, crystallinity, and other factors, $n(\text{H}_2\text{O})/n(\text{SiO}_2)=12$ was identified as the desirable synthesis condition.

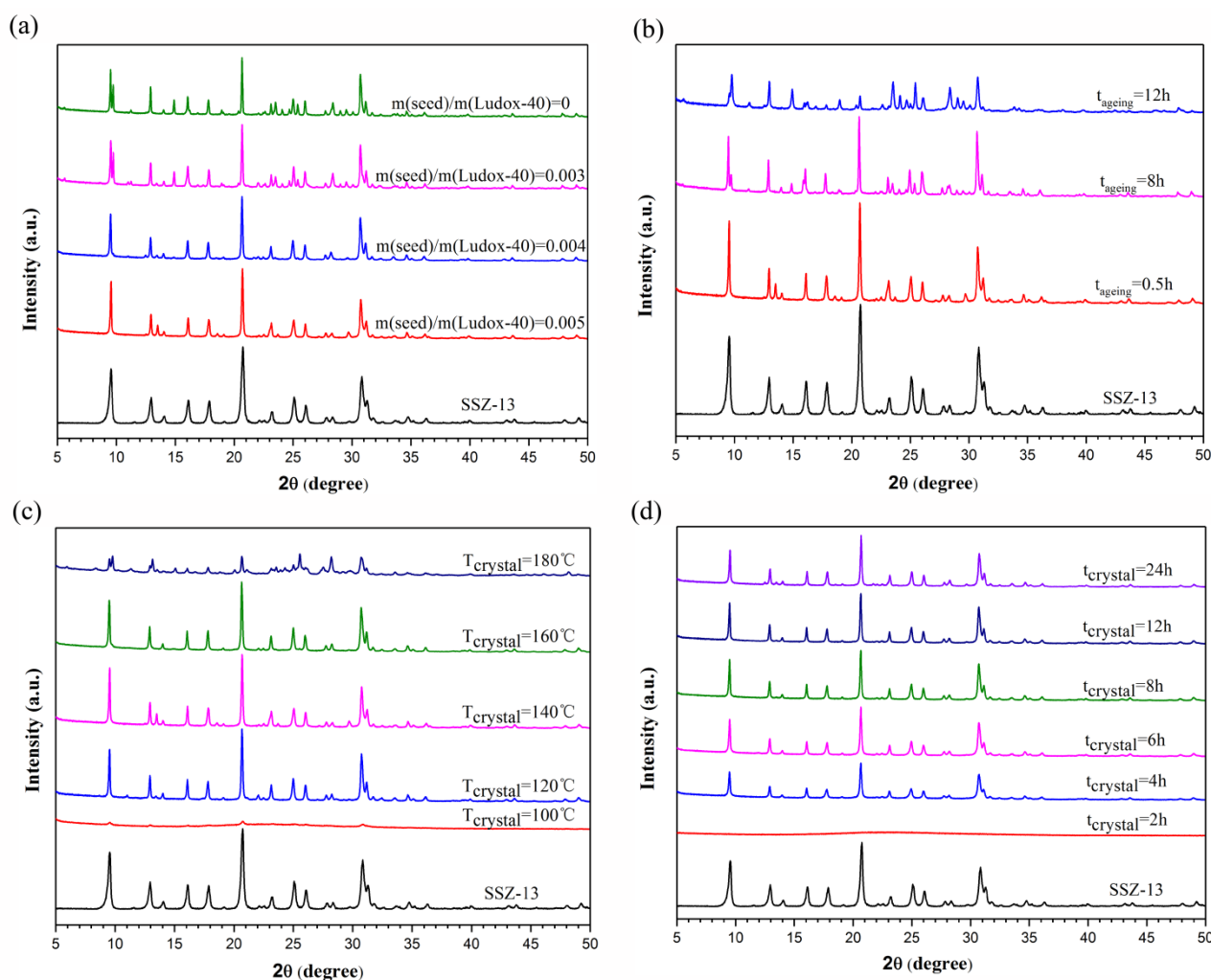


Fig. S2. The XRD information of the product by change different conditions (a) inoculating seed (b) t_{ageing} (c) crystallization temperature (T_{crystal}) (d) crystallization time (t_{crystal}).

Table S2. The phase of synthetic products in different aging time

Ageing time	Crystallization temperature	Crystallization time	Phase composition	Relative crystallinity
0.5h	140 °C	2d	CHA	107.8%
8h	140 °C	2d	CHA+few MOR	79.3%
12h	140 °C	2d	MOR+few CHA	27.0%

Fig. S2 (a) presents the impact of crystallization rate, which was reflected by the mass percentage of seed and silicon source (Ludox-40) ($m(\text{seed})/m(\text{Lodox-40})$). There was sharp peak of SSZ-13 without hybrid phase under the percentage 0.004. However, the hybrid MOR characteristic diffraction peak was generated at the characteristic peak of 9.5, 15 and 28°, when the crystal seed was further reduced to 0.003. If relying on template agent CC as crystallization promoter, MOR phase would inevitably form, though SSZ-13 could still be produced. Therefore, an appropriate

amount of seed addition (at least 0.004) can not only accelerate the crystallization process of SSZ-13, but also ensure that the molecular sieve is of pure phase and high crystallinity.

The aging process at room temperature may promote the formation of more silica-aluminic acid for the subsequent formation of Si-Al skeletons and lattices. As can be seen from Fig. S2 (b) and Table S2, the pure phase SSZ-13 molecular sieve can be produced when aging time was 0.5 h. With t_{ageing} increasing to 8 h, the MOR peaks were detected. In addition, the crystallinity of the product decreased from 107.8% to 79.3%. When t_{ageing} was extended to 12 h, the characteristic peaks of SSZ-13 decreased significantly at 9.5° and 30.84° , and almost disappeared at 20.8° , which means that the products were mainly MOR and amorphous phase.

T_{crystal} plays an important role in the size, structure and purity of molecular sieve. Fig. S2 (c) presents the XRD patterns of samples prepared at various temperatures ($T_{\text{crystal}}=100, 120, 140, 160$ and 180°C). It is clear that the material's crystallinity decreased obviously less than 120°C . With the temperature reaching 180°C , five-membered ring was more likely to form. In addition to the SSZ-13 characteristic peaks, MOR type heterocrystalline peak was also detected at $2\theta=25.5^\circ$. The crystal structure is usually composed of four-membered rings and six-membered rings in the temperature ranges from 120 to 160°C . It is beneficial to the synthesis of SSZ-13 and can obtain pure phase SSZ-13 molecular sieve. An appropriate crystallization temperature is very important to reduce the energy consumption and increase product purity. Therefore, 120°C is selected as the optimal crystallization temperature for the next step.

The crystallization time is another crucial parameter for the synthesis of molecular sieves. The XRD patterns of the materials prepared with t_{crystal} of 2, 4, 6, 8, 12 and 24 h were presented in Fig. S2 (d). Due to the increase of t_{crystal} , the peaks SSZ-13 were constantly enhanced. In the early stage of crystallization ($t_{\text{crystal}} < 2$ h), the peak intensity of the product was extremely weak, and it was difficult to detect the existence of grains by XRD. This indicates that the crystal just began to grow within 2 h and the crystallization was not sufficient, with only a small amount of crystalline molecular sieve. This stage can be considered as the initial stage of crystallization, namely the

induction period for the formation of SSZ-13 crystal nucleus. With the extension of t_{crystal} , the crystallization rate of SSZ-13 was greatly improved. When the t_{crystal} was 4 h, the relative crystallinity of the product could reach 71% (Table S3). In the middle and late stage of crystallization ($t_{\text{crystal}} > 8$ h), the synthesis rate of SSZ-13 slowed down significantly, and the relative crystallinity of the products tended to be stable. To shorten the SSZ-13 synthesis cycle as much as possible, the optimal crystallization time was determined to be 4 h. Based on the experimental results above, the optimal conditions for the synthesis of SSZ-13 using CC as structural guide agent were determined.

Table S3. The phase of synthetic products in different crystallization time

Crystallization temperature	Crystallization time	Phase composition	Relative crystallinity
140 °C	24h	CHA	96%
140 °C	12h	CHA	97%
140 °C	8h	CHA	96%
140 °C	6h	CHA	89%
140 °C	4h	CHA	71%
140 °C	2h	Amorphous	8%

According to the findings above, the optimal conditions for the synthesis of SSZ-13 are summarized below: $t_{\text{ageing}} = 0.5$ h, $m(\text{CC})/m(\text{SiO}_2) = 0.14$, $n(\text{H}_2\text{O})/n(\text{SiO}_2) = 12$, 0.004 inoculating crystal, $n(\text{Na}_2\text{O})/n(\text{SiO}_2) = 0.4$, $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3) = 40$, 120°C static crystallization for 4 h. The relative crystallinity can reach 103.41%.

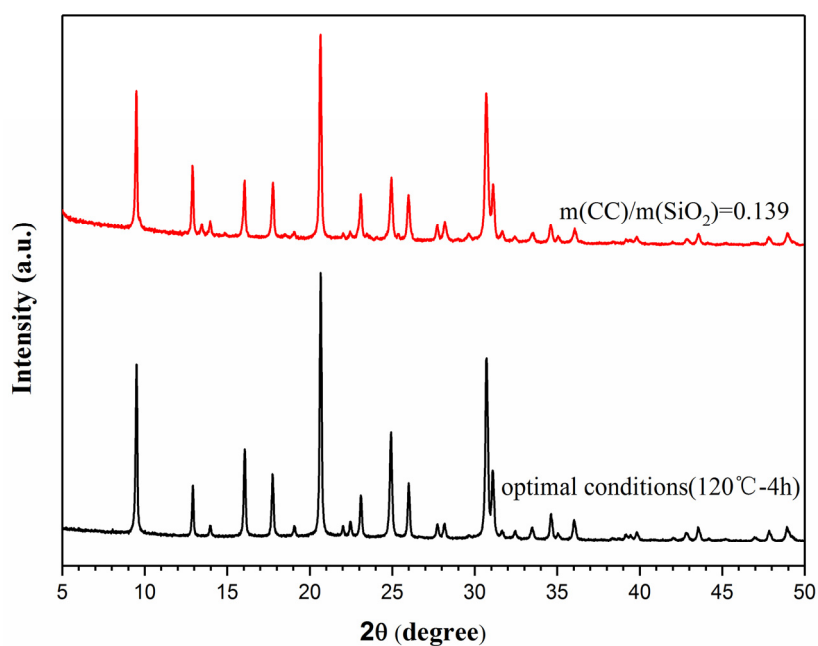


Fig. S3. XRD of SSZ-13 synthesized under optimal conditions

Table S4. The phase of synthetic products in different $m(\text{CC})/m(\text{SiO}_2)$

$m(\text{CC})/m(\text{SiO}_2)$	Crystallization temperature	Crystallization time	Phase composition	Relative crystallinity
0.32	140 °C	2d	CHA	107.8%
0.21	140 °C	2d	CHA	105%
0.14	140 °C	2d	CHA	101.2%
0.11	140 °C	2d	CHA+ANA	87%
0.07	140 °C	2d	CHA+ANA	73%
0	140 °C	2d	ANA	---
0.14	120 °C	4h	CHA	103.41%

Table S5. Different mass ratio of TPPS and Ludox-40

Sample	4-1	4-2	4-3	4-4	4-5	4-6
$m(\text{TPPS})/m(\text{Ludox-40})$	1/180	1/60	1/36	7/180	1/18	1/12

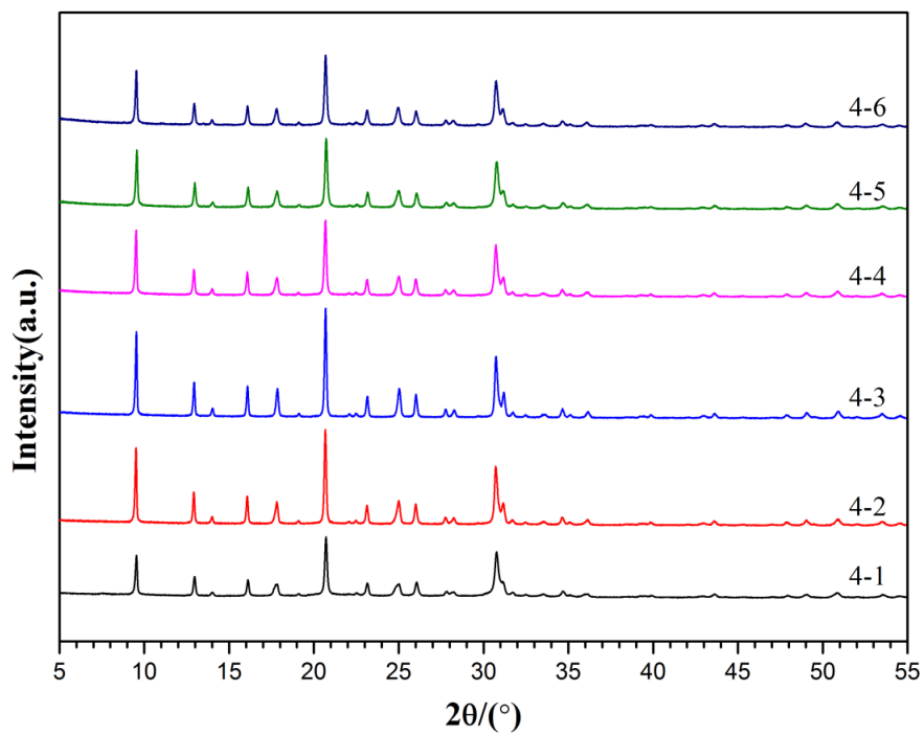


Fig. S4. XRD of products in different TPPS amount

Table S5. Mass ratio of KH550 to Ludox-40

Sample	5-1	5-2	5-3	5-4	5-5	5-6	5-7
m(Ludox-40)/ m(KH550)	$\frac{36}{1}$	$\frac{18}{1}$	$\frac{12}{1}$	$\frac{9}{1}$	$\frac{18}{3.38}$	$\frac{18}{6.77}$	$\frac{2}{1}$

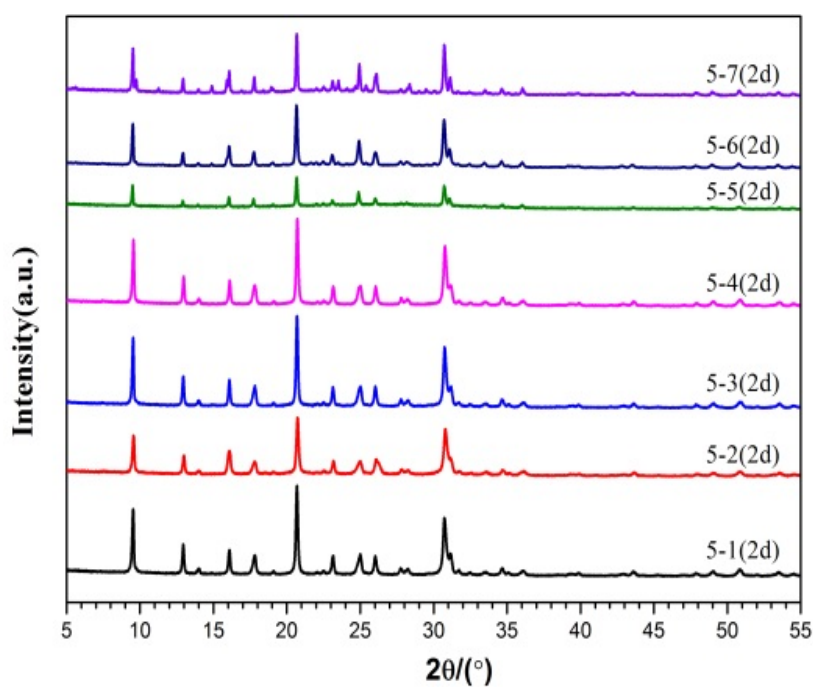


Fig. S5. XRD of products in different KH550 amount

Table S6. FWHM data of [101] crystal plane of samples after crystallization for 2 days

Sample	5-1	5-2	5-3	5-4	5-5	5-6	5-7
FWHM(101)/°	0.137	0.151	0.130	0.123	0.087	0.119	0.069

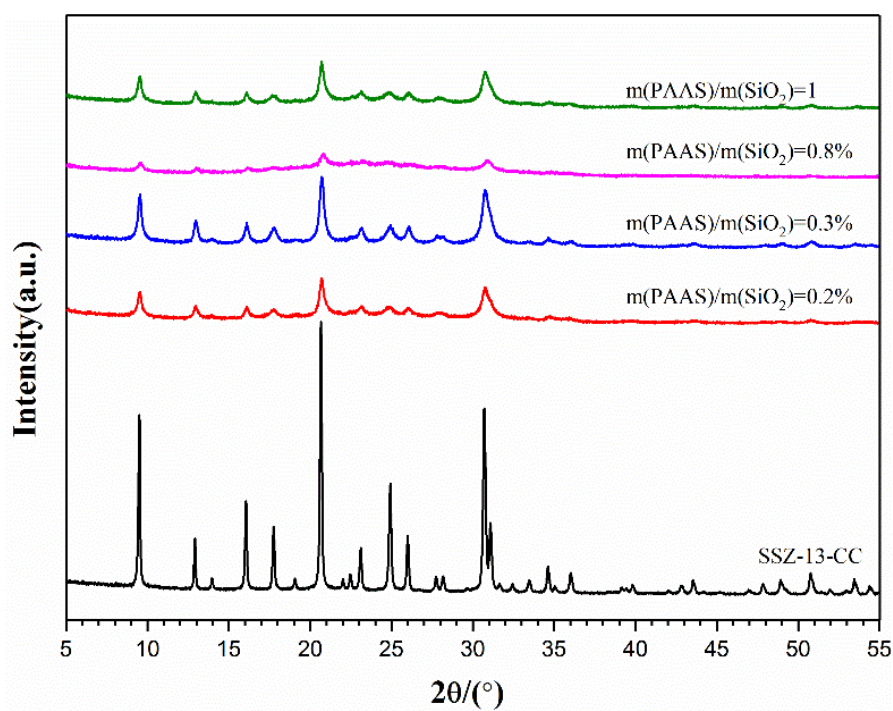


Fig. S6. XRD of products in different PAAS amount