

Electronic Supplementary Information for  
**High-throughput synthesis of AlPO and SAPO zeolites by ink jet  
printing**

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### **C2Fast-III ink-jet printer**

For zeolite printing synthesis, a drop-on-demand (DOD) piezoelectric ink-jet printer (C2FAST-III) is used. The printer is commercially available from *Hangzhou Nanonov Co., Ltd.*. This printer has a holder for print head with 8 ink channels moving in X direction and a platform of 400mm\*500mm that moves in Y and Z directions. The printer head consists of eight separated nozzles which contains Si and P ink. The nozzles all have a micro valve to control the ink suction and dispensing according to the constructions from C2Fast-III software. During printing, the printer head and platform would move together to send the printer head into the designed area, proper amount of inks would be sucked and pressed out into the Teflon mold, after several runs of printing, the gradient formulations of zeolite precursors are formed.



Fig S1. C2Fast-III ink-jet printer

## C2Fast-III software

The composition variations design of zeolite precursors are drafted in a color picture with corresponding CMYK (cyan, magenta, yellow, black) parameters by C2Fast-III software. The software is used for data transfer between picture and printer, which establishes a one to one correspondence between the percent value of each color in an image and the printing volume of ink in relevant nozzle.

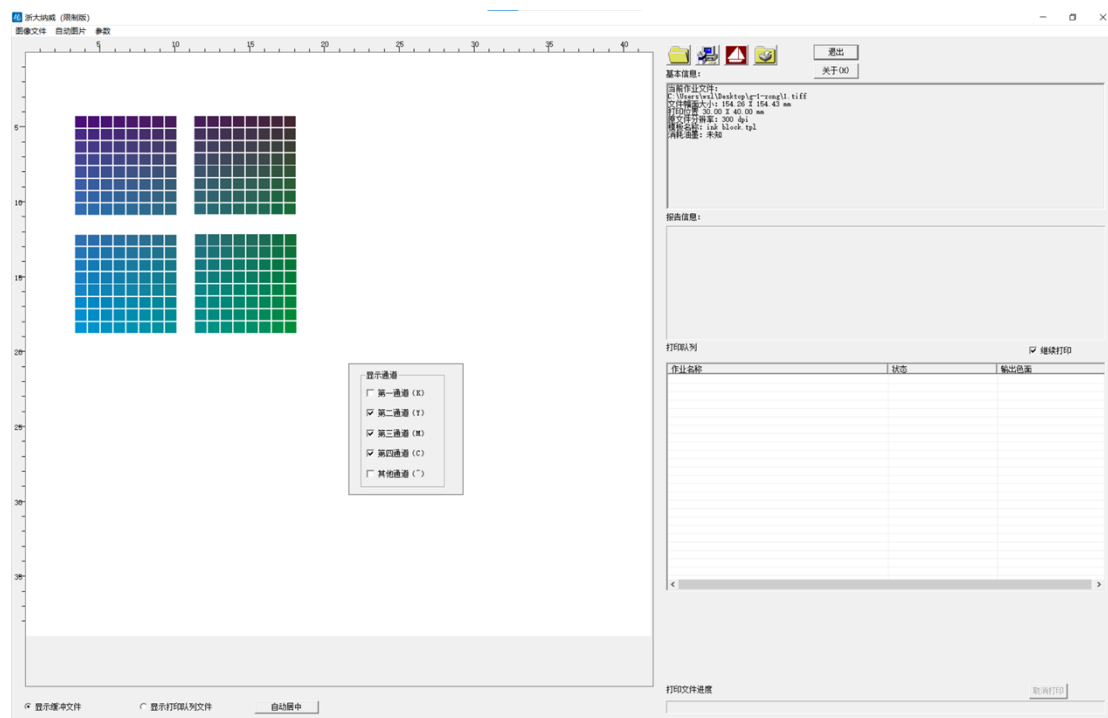


Fig S2. C2Fast-III ink-jet printing software

## Ink formulations

The fluid rheological requirements for printable inks are determined by the physics and the fluid mechanics of the drop generation process. Critical parameters of the ink are pH, particle size, viscosity, and surface tension. Any suppression of these parameters leads to a failure of printing process (printer head broken, printer head blocked, uneven distribution of ink on the substrates). The proper range of those parameters and the corresponding data of the inks used in this work are listed in table S1. The particle size of Al ink was much higher than the requirement for an appropriate ink (3000 nm > 1000 nm) so it's not suitable for printing, the strategy we applied is shown by Fig. S4. Three inks used in this work is aluminum isopropoxide/ isopropyl alcohol solution, phosphoric acid/aqueous solution and tetraethylorthosilicate (TEOS)/ethanol solution. For Al ink, 1.428 g aluminum isopropoxide is dissolved in 100 mL isopropyl alcohol and stirred under 60 °C for 2 h. For P ink, 1.428 mL phosphoric acid is added into 100 mL deionized water. For Si ink, 1.456 g TEOS is dissolved in 100 mL ethanol.

Table S1. Requirements for the ink and corresponding data of inks used in this work.

Parameters	pH	Particle size (nm)	Viscosity (mPa·s)	Surface tension (dyn/cm)
Range of requirements	2-12	<1000	5-30	20-55
Si ink	~6	1.0	5-10	21-22
P ink	~3	0.5	5-10	21-22
Al ink	~9	~3000	5-10	21-22

### **Experiment conditions**

After the inks were prepared, the multiwall Teflon reactors was fixed onto the certain area of the printing platform. The place of this area was calculated according to the location of printing picture in order to match them well. Teflon membrane was cut into small pieces and put into each small square (in case the samples get stick to the wall and cannot take it off). The printing cycles repeated for 20 times and then the multiwall reactors were dried under 60 °C for 12 h in an oven. After that, the multiwall reactors with dry gel was placed into a 2 L Teflon-lined autoclave above the 40 mL liquid phase of organic structure directing agent (Tetraethyl ammonium hydroxide 25% in aqueous solution) (Fig. S5). The autoclave was crystallized under 200 °C for 48 h. After it was cooled down, the samples were characterized by X-ray diffraction and scanning electron microscopy.

### **Ink jet printing**

The ink jet printing process was conducted using C2Fast-III printing system. The printing was started by filling the ink into the corresponding channels of the printer head (Magenta for P ink, Yellow for Si ink). The amount of Al ink (the value of cyan colour) is fixed for all small squares and it was regulated by manual adding (total amount for Al ink was 25.2 mL). A shrinkage step for the printer head was necessary in order to get rid of any air bubbles within the printer head and ink pipeline. After that, the printer would execute a clean step to further remove the bubbles. The next step was to upload the printing picture (Fig. S4d) and carry on one printing attempt, the aim of this step was to confirm the relative place between the picture and those multiwall reactors. We fixed the reactors onto the places we marked and then started the printing process. The printing cycles were repeated for 20 times (total amount was 17.7 mL for P ink and 20.5 mL for Si ink) before all was done. The printer head was disassembled and washed from the printer.

### **Dry gel conversion**

After the printing step was finished, the multiwall reactors were put into an oven which

has been pre-heated to 60 °C. The crystallization step was conducted through a dry-gel conversion method (DGC). The DGC is a widely approved crystallization method for zeolite synthesis<sup>1, 2</sup>, first reported by Xu and co-workers<sup>3</sup>, it is classified into steam-assisted crystallization and vapor-phase transport. The main difference between these two methods is whether or not to add the organic template into the dry gel. Template is added on the bottom of the autoclave for vapor phase transport while in the steam assisted crystallization method, the template is added into the dry gel. We used vapor phase transport in this work, the multi-wall reactor with dry gel was placed into a big autoclave above the 40 mL liquid phase of organic template (Fig S2). The vapor created during the crystallization step (200 °C) would get contact with the dry gel and help with the zeolite structure formation. As a result of that, we don't have to pay attention to the sealing conditions among each small squares of the multiwall reactor since the whole reactor was placed in a totally sealed environment.

### **Characterizations**

Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (EDX) analyses were taken on a Hitachi S-4800 microscope with a field-emission electron gun operating at 25 KV. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer operated at 30 mA and 40 kV with Cu Ka radiation with a scan rate of 20°/min. Ideally, XRD characterization should be done in a high-throughput model. But the high-throughput XRD instrument is currently unavailable in our lab. Fortunately, the manual XRD characterization takes only two minutes per sample, making the characterization of all samples time-comparable to the high-throughput synthesis method. As a proof-of-concept study, the manual XRD characterization is acceptable. In our following works, we will integrate the commercially available high-throughput XRD characterization with the high-throughput synthesis method to speed up the screening.

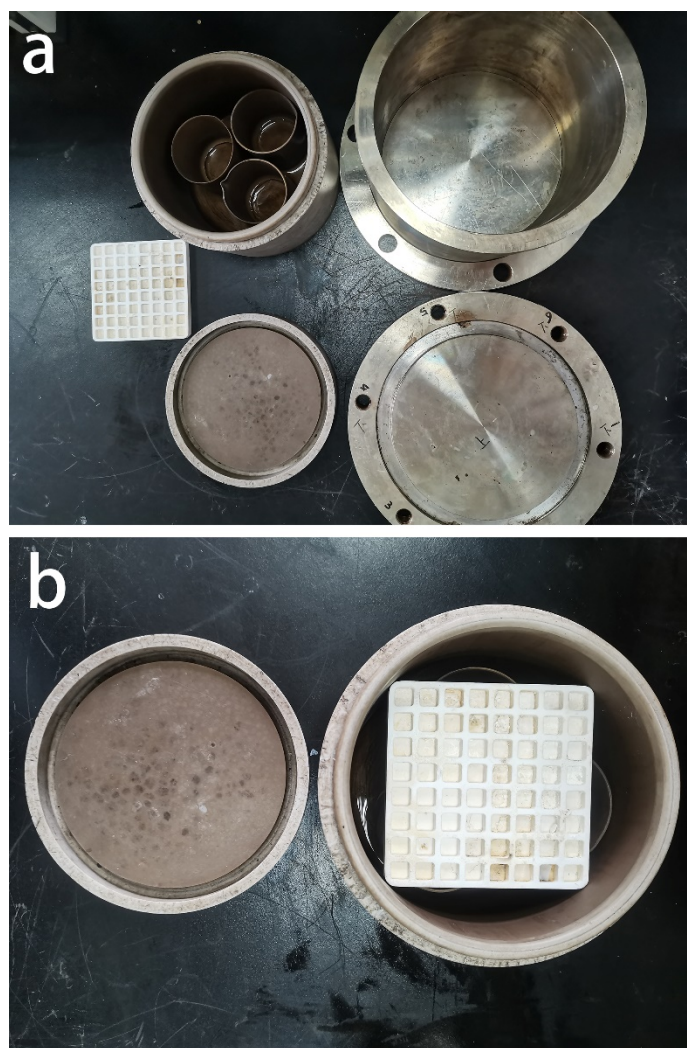


Fig. S3. a) Multiwall reactor (left), 2 L autoclave (middle, with 40 mL organic template) and stain-less steel autoclave (right). b) The multiwall reactor is placed into a 2 L autoclave above the 40 mL liquid phase of organic template.

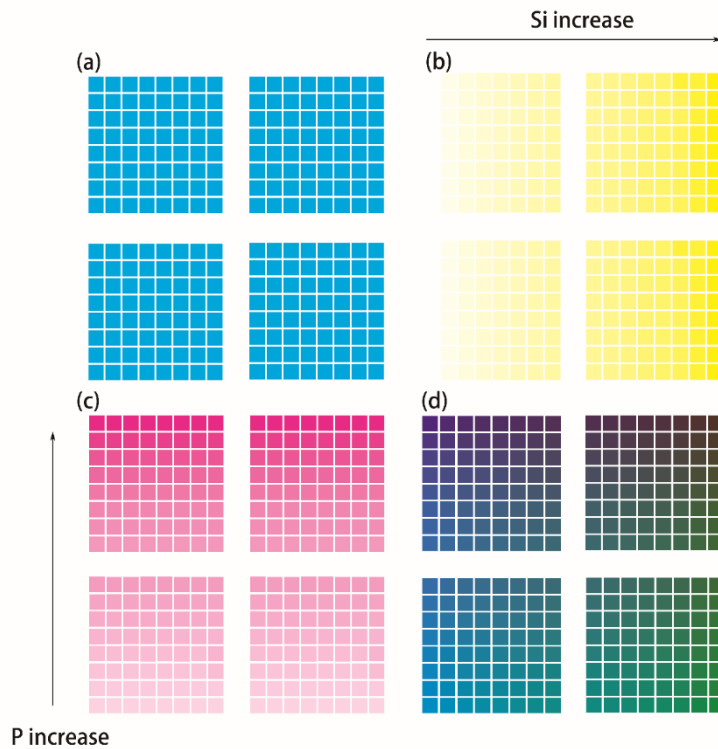


Fig. S4. Designed pictures for the Ink-jet printing.  $4 \times 8 \times 8$  small squares, each small square represents a specific formulation of zeolite precursor. a) Picture for Al. Since Al ink is unable to be printed, the amount of Al ink for every square is set to be equal, a fixed amount of Al ink is added in advance. b) Picture for Si. The content of Si ink is increasing from the left to the right. c) Picture for P. The content of P ink is increasing from the bottom to the top. d) The overall picture used in C2Fast-III software, a summary of Al, Si and P pictures.





Fig. S5. Multiwall Teflon reactor, contains 8\*8 holes (1 cm\*1 cm, 0.8 cm depth), corresponding to each small square respectively.

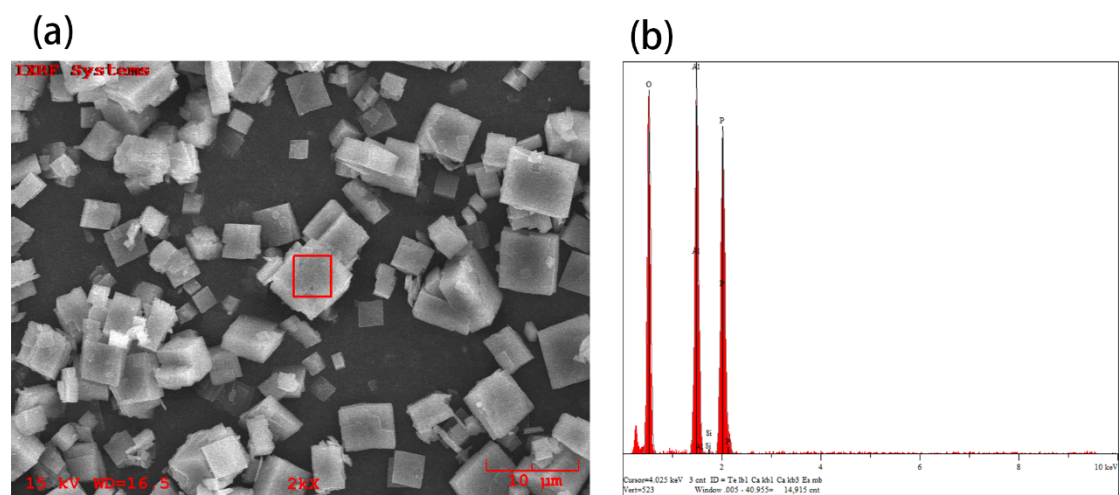


Fig. S6. Energy dispersive spectroscopy (EDS) of AlPO-18 product, no Si was detected.

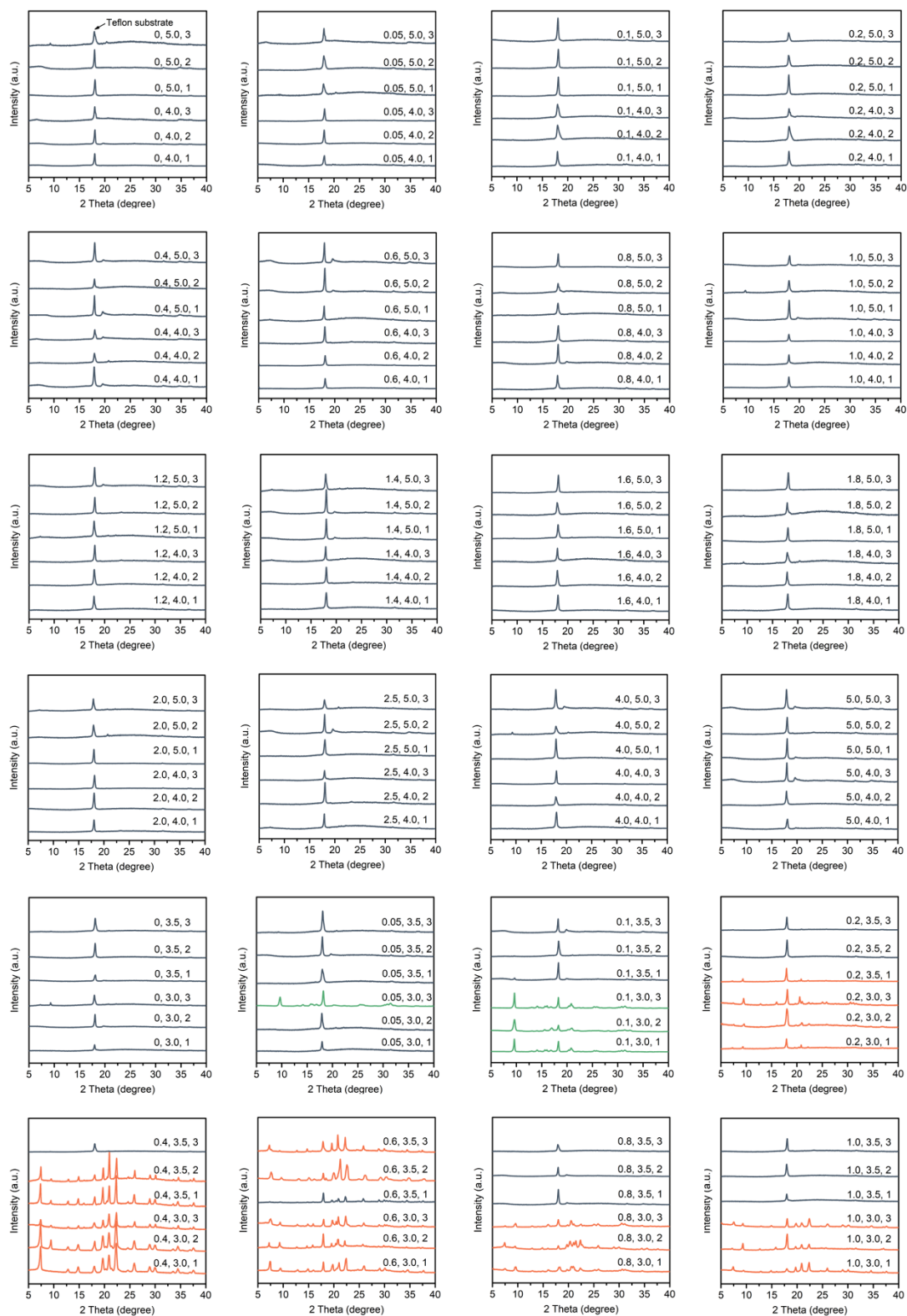


Fig. S7. XRD patterns for printed samples for every run (part 1, (0, 5.0 represents the Si/Al=0 and P/Al=5.0, 1, 2 and 3 means 1<sup>st</sup> run, 2<sup>nd</sup> run and 3<sup>rd</sup> run, Teflon substrate was put into each small square for more convenient characterization).

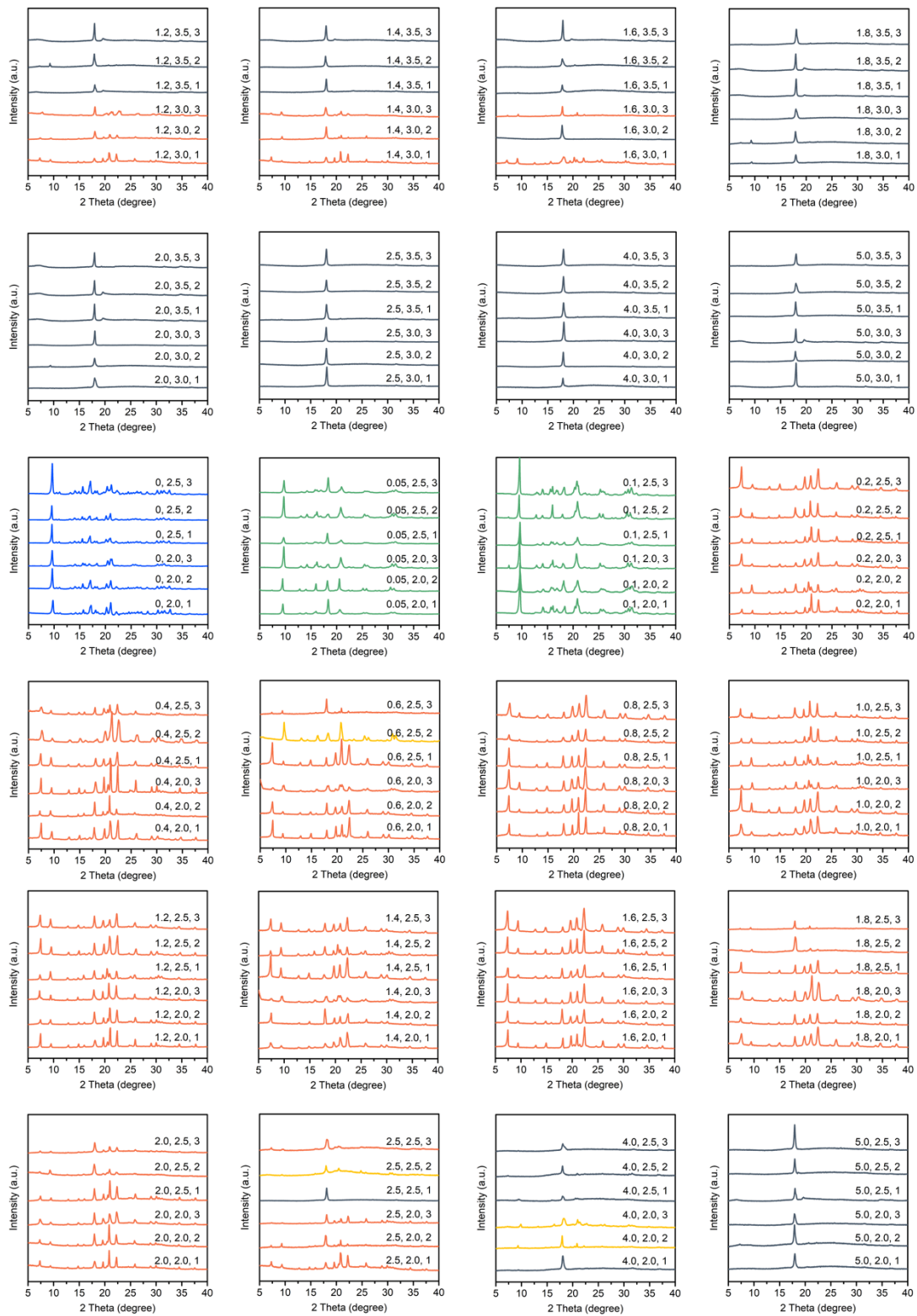


Fig. S8. XRD patterns for printed samples for every run (part 2).

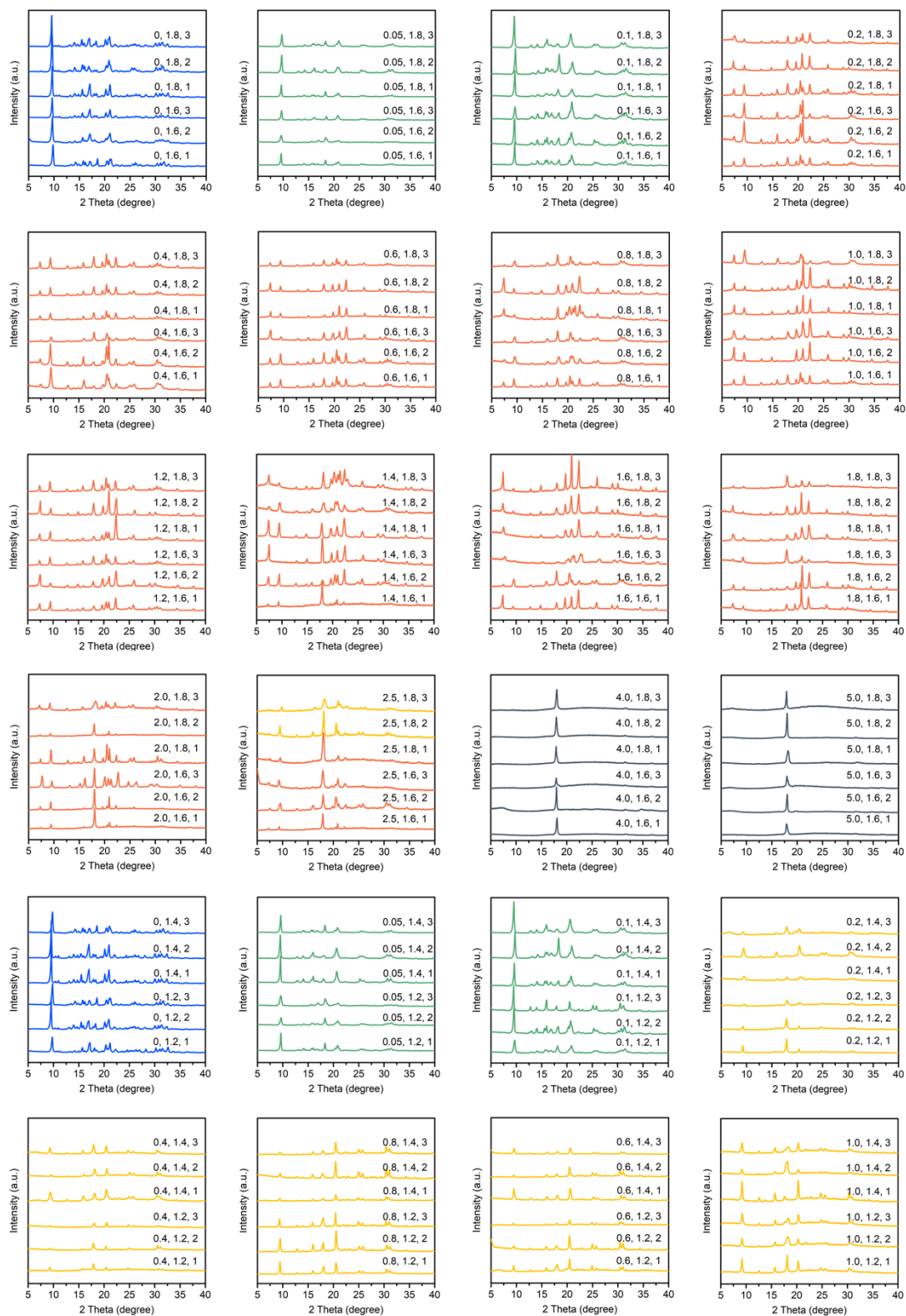


Fig. S9. XRD patterns for printed samples for every run (part 3).

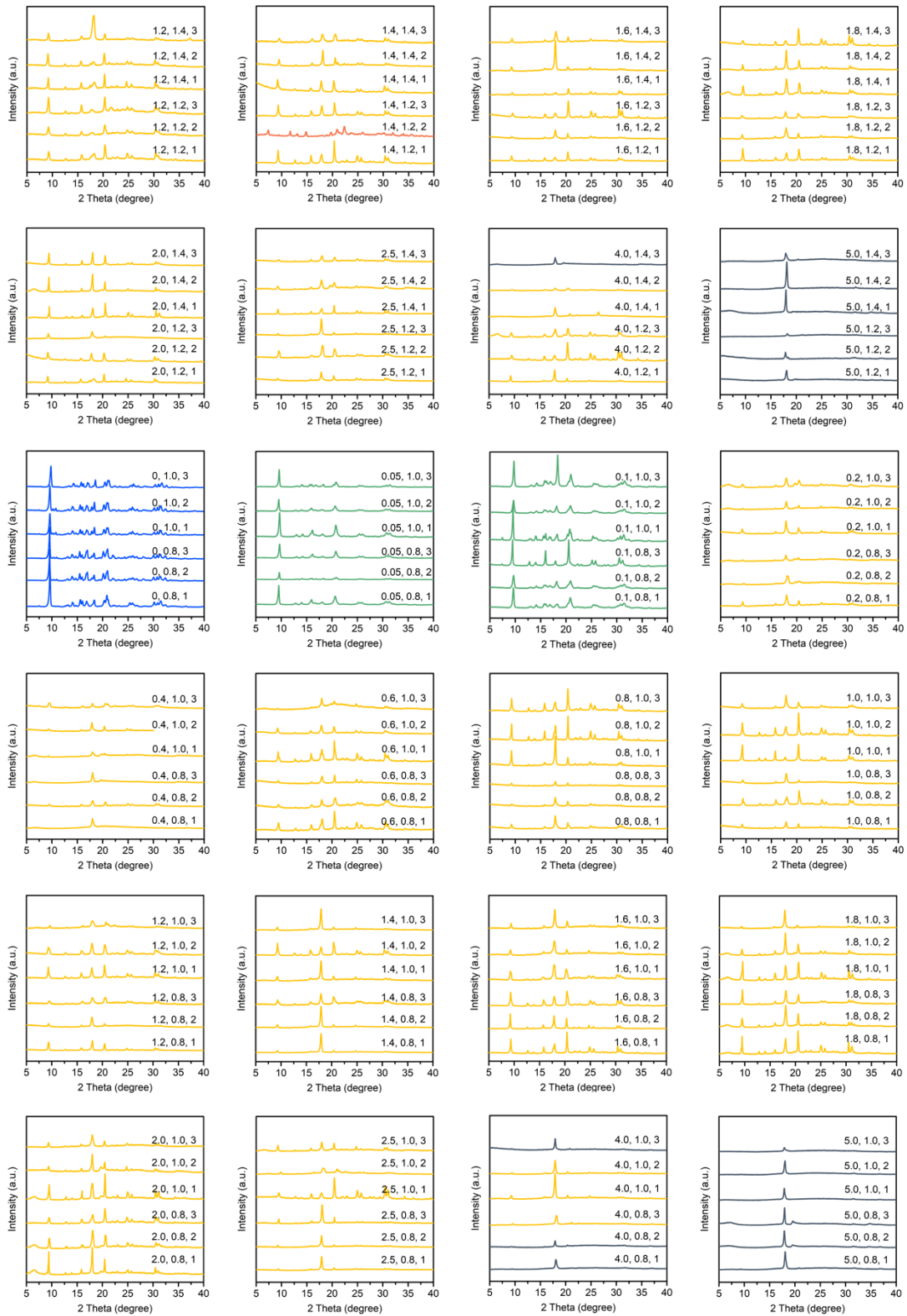


Fig. S10. XRD patterns for printed samples for every run (part 4).

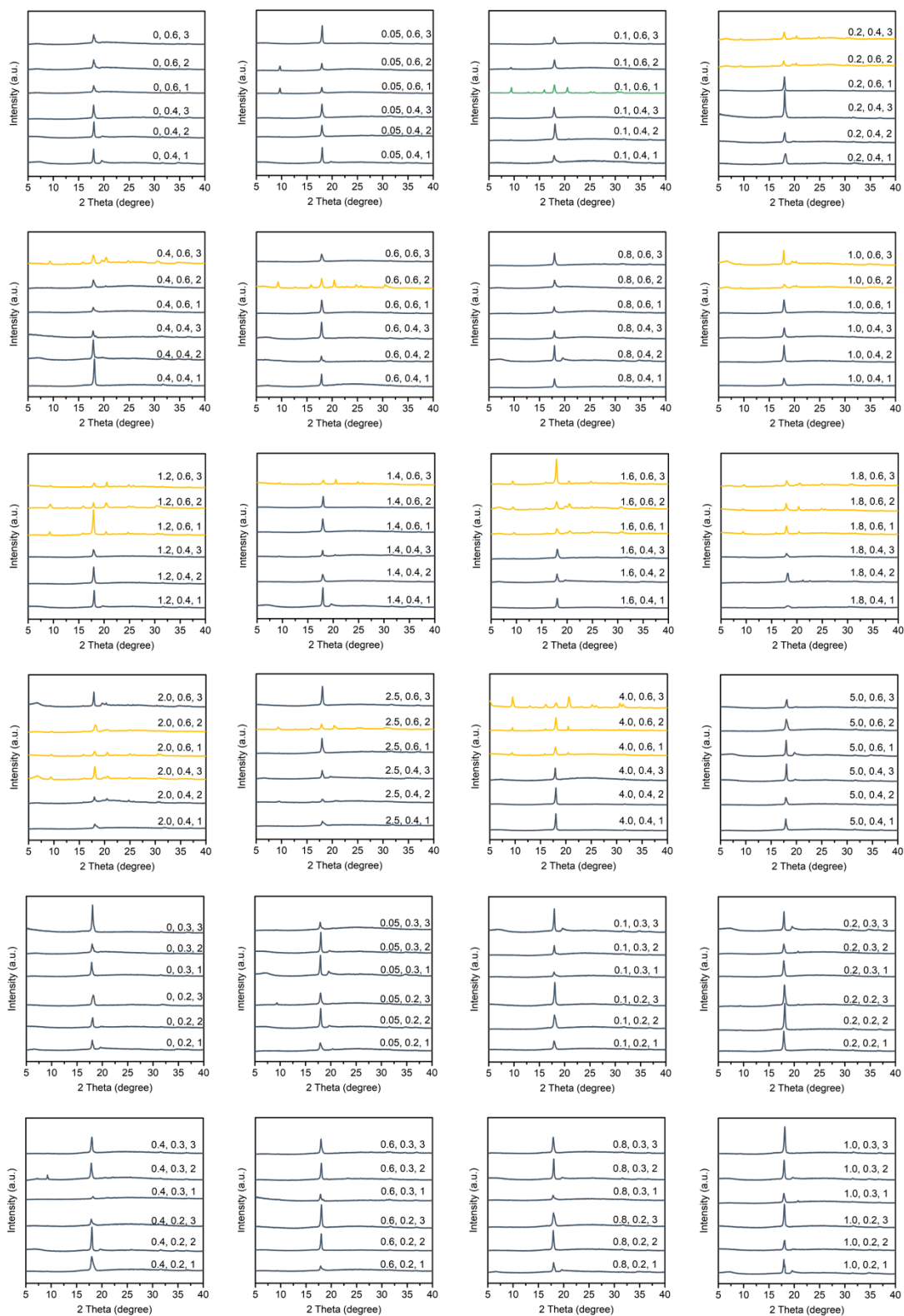


Fig. S11. XRD patterns for printed samples for every run (part 5).

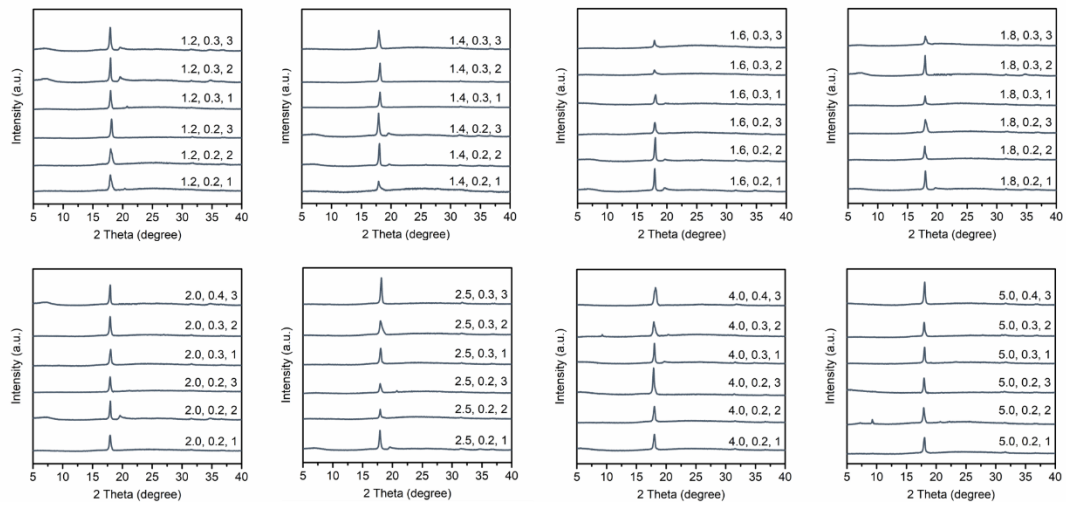


Fig. S12. XRD patterns for printed samples for every run (part 6).



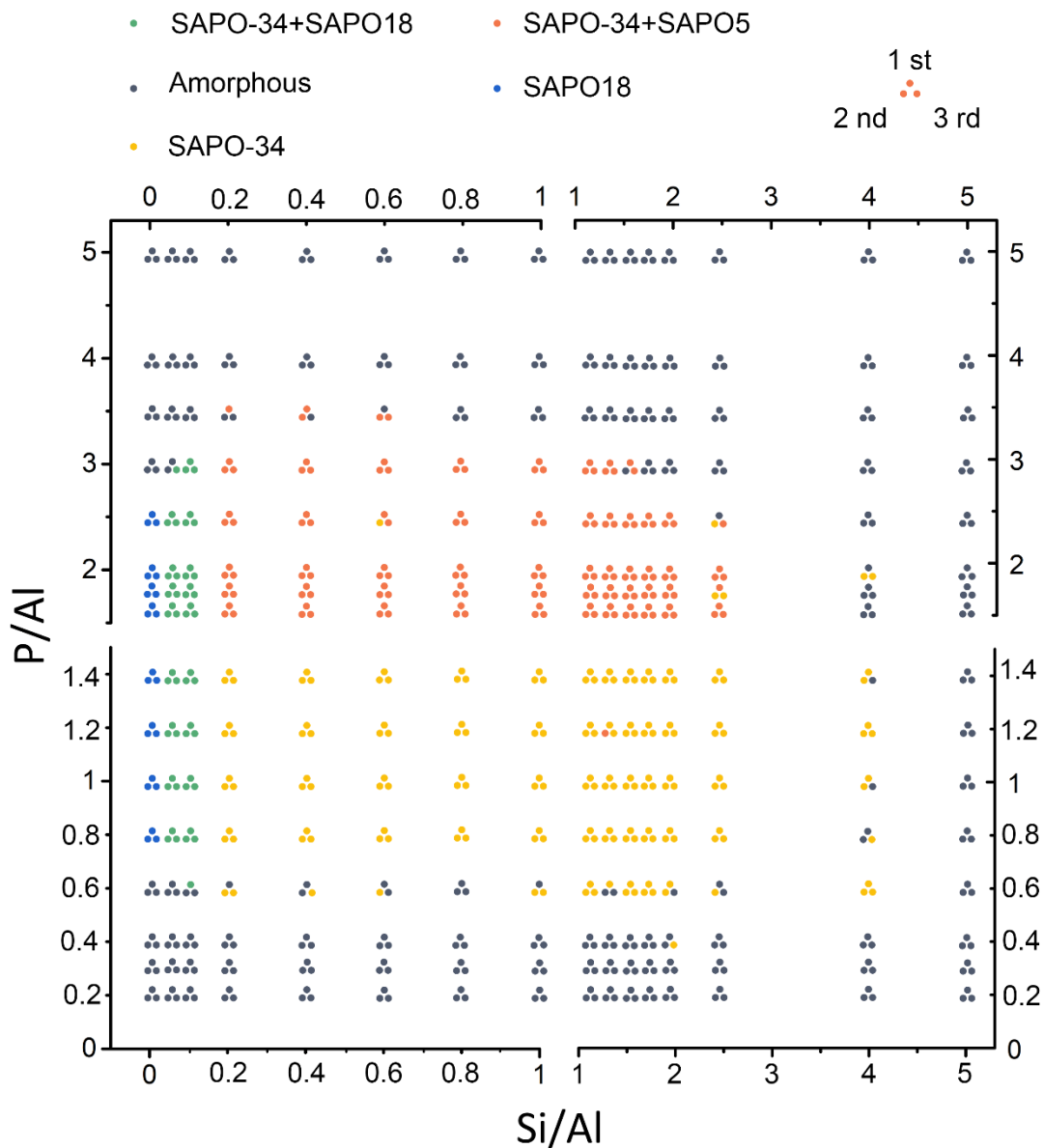


Fig. S13 A summary of XRD results for all the samples in three parallel tests. Most of the samples except a few located on the margin of two phases (e.g., Si/Al=0.2, P/Al=0.6) exhibit the same XRD patterns, suggesting that the printing technique is suitable and reproducible for SAPO systems with both low Si/Al ratios and high Si/Al ratios. The different XRD patterns for the samples on the margin of two phases are likely due to the randomness of nucleation process during the zeolite formation.

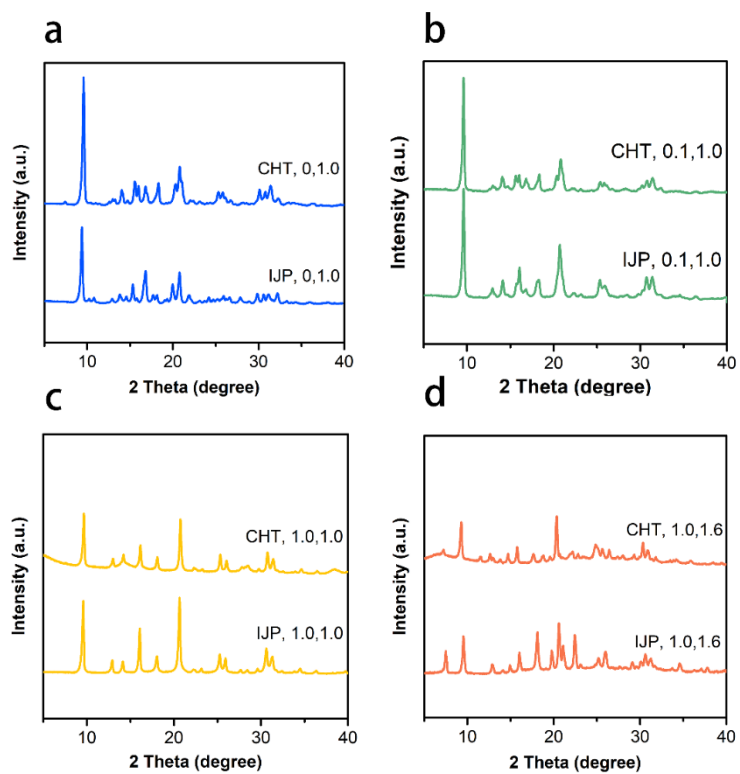


Fig. S14 XRD patterns of comparing experiments between CHT and IJP using the same formulations. a) Si/Al=0, P/Al=1. b) Si/Al=0.1, P/Al=1. a) Si/Al=1, P/Al=1. a) Si/Al=1, P/Al=1.6.

## References

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