

**Supplementary information**

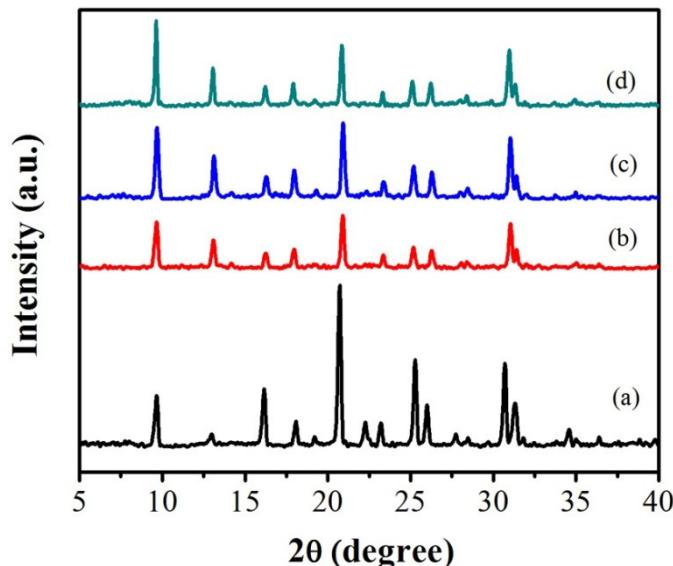
**Synthesis of sub-micrometric SAPO-34 by morpholine assisted two-step hydrothermal route and its excellent catalytic MTO performance**

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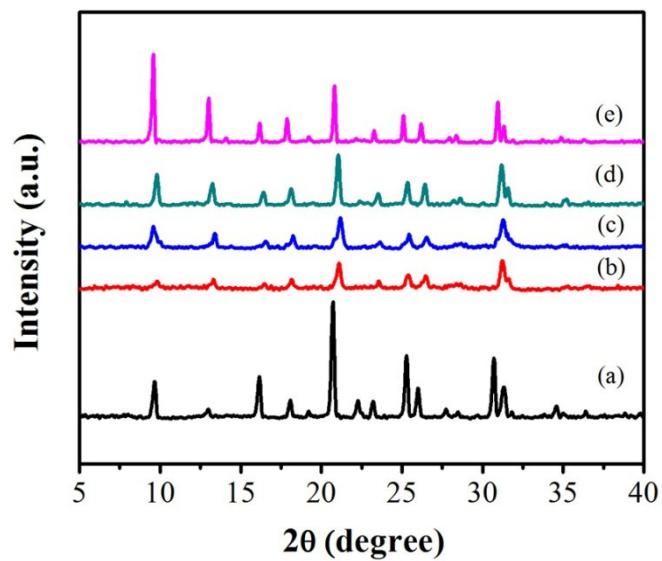
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**Fig.S1** XRD patterns of sample (a): SP-12 and samples synthesized by two-step crystallization without morpholine (b): SP-C2(4h), (c): SP-C2(8h) and (d): SP-C2(12h)



**Fig.S2** XRD patterns of sample (a): SP-12 and samples synthesized by two-step crystallization with morpholine (b): SP-MP(3h), (c): SP-MP(6h), (d): SP-MP(9h) and (e): SP-MP(12h)

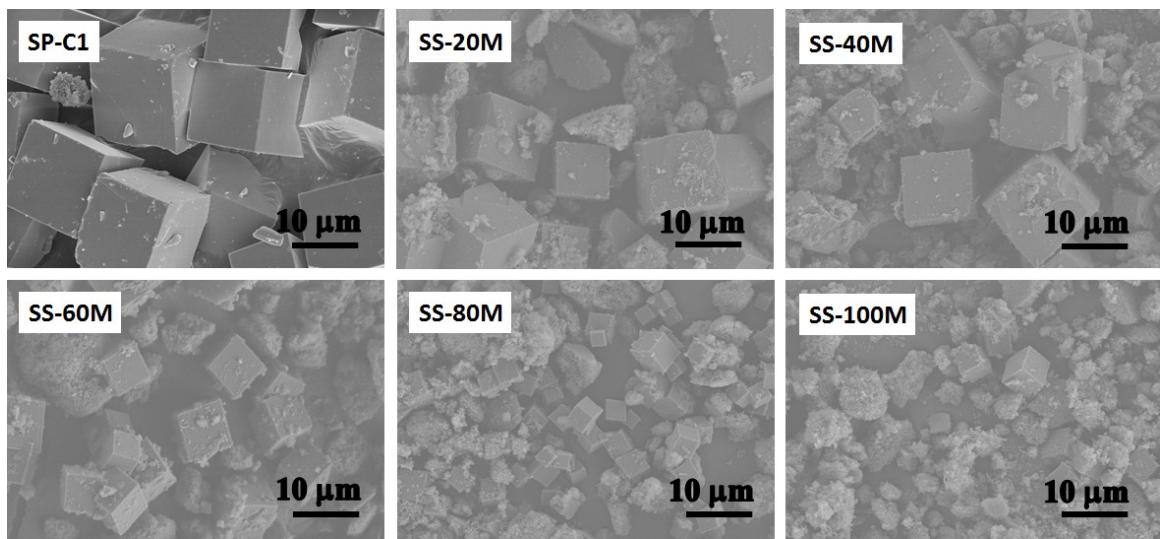


Fig. S3 SEM images of samples synthesized by single step crystallization having equi-amount of morpholine as with the two-step method.

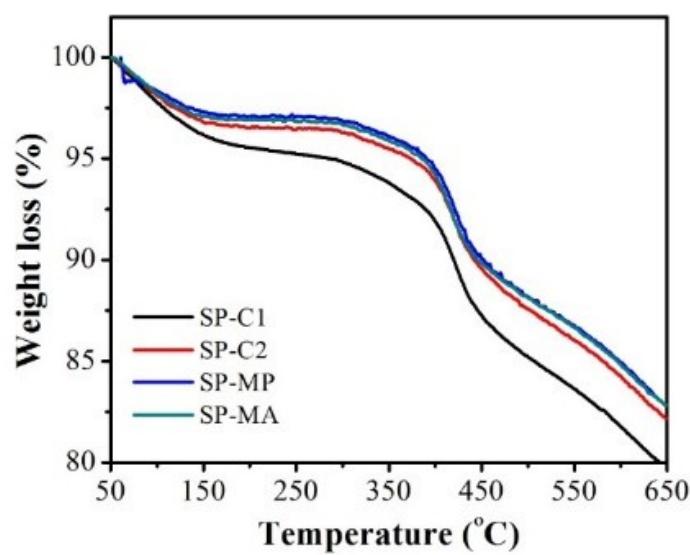


Fig S4. TG curves of the samples with different synthetic routes

**Table S1** Crystallite size of the samples calculated from XRD results

| Sample     | Crystallite size (nm) | Sample     | Crystallite size (nm) |
|------------|-----------------------|------------|-----------------------|
| SP-12h     | 54                    | SP-MP(3h)  | 29                    |
| SP-C2(4h)  | 52                    | SP-MP(6h)  | 39                    |
| SP-C2(8h)  | 57                    | SP-MP(9h)  | 48                    |
| SP-C2(12h) | 68                    | SP-MP(12h) | 50                    |

**Table S2** weight loss in TG curves over different samples

| Sample | < 200 °C / % | 200-440 °C / % | 440-650 °C / % | 200-650 °C / % | Total weight loss / % |
|--------|--------------|----------------|----------------|----------------|-----------------------|
| SP-C1  | 4.5          | 7.7            | 8.3            | 16.0           | 20.5                  |
| SP-C2  | 3.4          | 6.8            | 7.7            | 14.5           | 17.9                  |
| SP-MP  | 3.0          | 6.6            | 7.8            | 14.4           | 17.4                  |
| SP-MA  | 3.1          | 6.4            | 7.8            | 14.2           | 17.3                  |

**Table S3** Distribution of silicon species (%) by de-convolution of  $^{29}\text{Si}$  MAS NMR signals

| Sample    | ppm          | SP-C1 | SP-C2 | SP-MP | SP-MA |
|-----------|--------------|-------|-------|-------|-------|
| Defects   | -78 to -85   | 11.9  | 11.7  | 7.4   | 6.7   |
| Si4Al     | -91          | 28.6  | 24.7  | 59.8  | 48.1  |
| Si3AlSi   | -95          | 20.9  | 20.7  | 11.2  | 16.5  |
| Si2Al2Si  | -100         | 11.0  | 12.7  | 7.7   | 6.8   |
| Si1Al3Si  | -106         | 8.5   | 10.0  | 5.8   | 6.1   |
| Si4Si     | -110         | 13.9  | 15.3  | 10.2  | 11.2  |
| Si island | -100 to -110 | 33.5  | 38.0  | 23.8  | 24.0  |

**Table S4** Initial and final selectivity of olefin for conventional and medium replaced sample at 100% methanol conversion at WHSV = 2 h<sup>-1</sup> and 400 °C

| Sample | C <sub>2</sub> selectivity / % |       | C <sub>3</sub> selectivity / % |       | C <sub>4</sub> selectivity / % |       | Total/% |       |
|--------|--------------------------------|-------|--------------------------------|-------|--------------------------------|-------|---------|-------|
|        | Initial                        | Final | Initial                        | Final | Initial                        | Final | Initial | Final |
| SP-C1  | 25.1                           | 34.1  | 46.9                           | 44.9  | 18.5                           | 14.7  | 90.5    | 93.7  |
| SP-C2  | 25.4                           | 36.2  | 48.3                           | 45    | 18.2                           | 14.1  | 91.9    | 95.3  |
| SP-MP  | 26.9                           | 40.9  | 50.6                           | 43.7  | 16.6                           | 11.9  | 94.1    | 96.5  |
| SP-MA  | 28.1                           | 42.7  | 52.3                           | 43.5  | 16.1                           | 10.9  | 96.5    | 97.1  |