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Melting-assisted solvent-free synthesis of hierarchical SAPO-34 with enhanced methanol to olefins (MTO) performance

Ziyu Liu[a], Shu Ren[a], Xing Yu[a,c], Xinqing Chen[a,*], Gang Wang[a], Xian Wu[a,c], Gan Yu [a,b], Minghuang Qiu[a], Chengguang Yang[a], and Yuhan Sun[a,b,*]

[a] *CAS Key Laboratory of Low-carbon Conversion Science and Engineering, Shanghai Advanced Reasearch Institute, Chinese Academy of Science, Shanghai, 201202, China.* [b]*ShanghaiTech University, Shanghai, 201210,China.* [c]*Shanghai University, Shanghai 200444, China.* [c]*Shanghai University, Shanghai 200444, China*

**Corresponding authors: chenxq@sari.ac.cn; sunyh@sari.ac.cn; Fax: +86 21 20350958; Tel: +86 21 20350958*

Supporting information:

Materials:

SAPO-34 was hydrothermally synthesized from the gel with a composition of $1Al_2O3:0.44SiO_2:1.1P_2O_5:2.25TEA:35H_2O$. Pseudoboehmite, phosphoric acid (85 wt%) and silica sol (40 wt%) were used as the sources of aluminum, phosphorus and silicon, respectively. Phosphoric acid was added to the pseudoboehmite and silica sol solution, which was then stirred for 1 h until a uniform gel was obtained. To the resultant, triethylamine (TEA) and SAPO-34 crystal seeds were successively added, and the stirring was maintained for 1h to form a uniform reaction mixture, which was then sealed in a 120 ml autoclave and heated from room temperature to 165℃within 420min, then kept for 33 h . Finally, the crystal was calcined in 600℃ for 5 h in order to remove the template agents named as SP34. Post-synthesis treatment of as-synthesized SAPO-34 was carried out at 100℃ for 6 h with solid-state oxalic acid and designated as SP34-x(x is the percentage of oxalic acid, 2%, 3%, 5%, 10%). In addition, the SP34-5% was treated at different temperature (80℃-140℃), and these samples were noted as SP34-80, SP34-100, SP34-120, SP34-140 respectively.

Characterizations

The crystallinity and phase purity of the samples were characterized by powder X-ray diffraction on a Bruker AXS D8 diffractometer using Cu Kα radiation (λ=1.5418 Å). The crystal size and morphology was observed with a high resolution scanning electron microscopy (SEM) on a JSM-6700Felectron microscope (JEOL, Japan). Low-temperature nitrogen adsorption isotherms were carried out on a Micromeritics 2020 analyzer at -196℃ after activation in vacuum at 300℃ for 6 h. Surface Area (S_{BET}) and micropore volume (Vmicro) were determined by applying the BET and t-plot methods, respectively. Pore size distribution and volume of mesopores (Vmeso) were obtained by applying the BJH model to the adsorption branch of the isotherm. Mercury penetration measurements were conducted on a Micromeritics AutoPore IV 9500. The solid-state MAS NMR experiments were performed on a Bruker AVANCE III 400 WB spectrometer. Chemical compositions were determined with X-ray fluorescence (XRF) analysis carried out on an AXIOS with Rh radiation.

Thermogravimetric (TG) analysis was performed on NETZSCH STA 449 F3 instrument in air at a heating rate of 10°C/min from room temperature to 1000°C. NH_3-TPD analysis was carried out on an automated chemisorption analyzer (TP-5080) from 100 to 600°C with a temperature increase of 10℃/min.

Catalytic Test: Methanol to Olefin Reaction (MTO)

The catalytic tests of MTO reactions were performed in a quartz tubular fixed-bed steel reactor with a length of 50 cm and an inner diameter of 10 mm under atmospheric pressure. A 3.0 g (20–40 mesh) of prepared catalyst was loaded in the center of quartz reactor. The samples were pretreated under an air flow of 10 mL/min for 1 h after the temperature of reactor reached 400^0C in order to activate the catalyst, and then methanol was pumped in the reactor with a WHSV of 1 h^{-1}. The analysis of the reaction products was performed by using an off-line gas chromatograph (GC-2014C) equipped with a frame ionization detector (FID) and a thermal conductivity detector (TCD). The conversion and selectivity were calculated on CH_2 basis and dimethyl ether (DME) was considered as the reactant in the calculation.

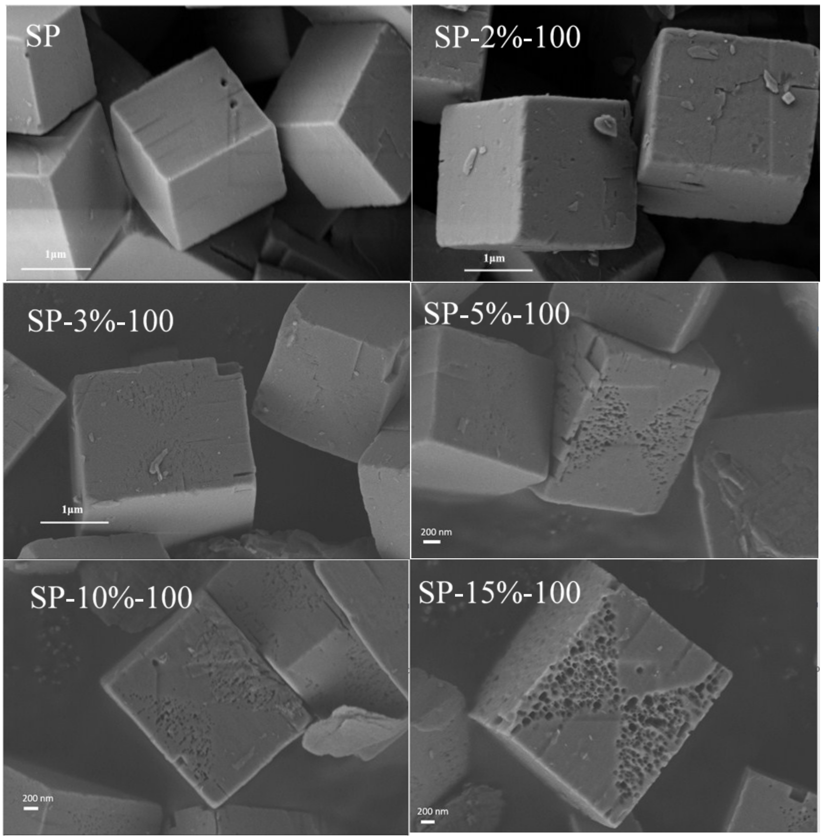

Figure S1. SEM images of SP34 and SP34-x samples.

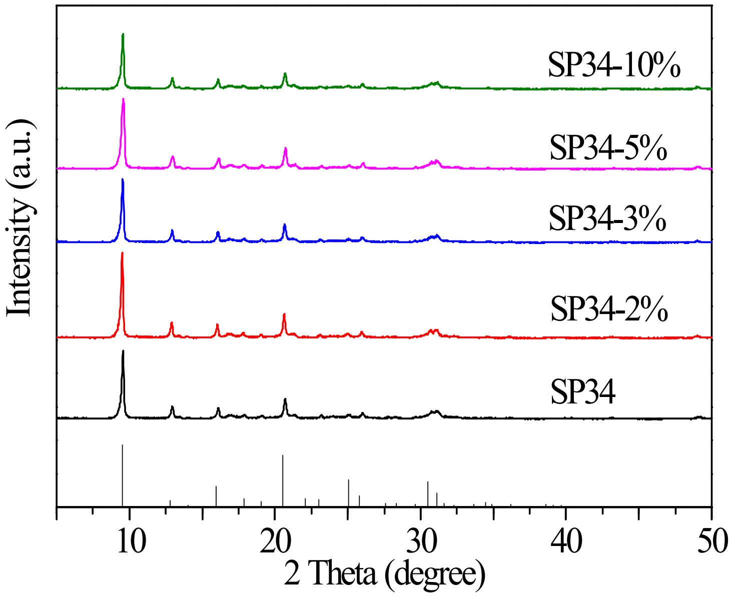

Figure S2. XRD patterns of SP34 and SP34-x samples

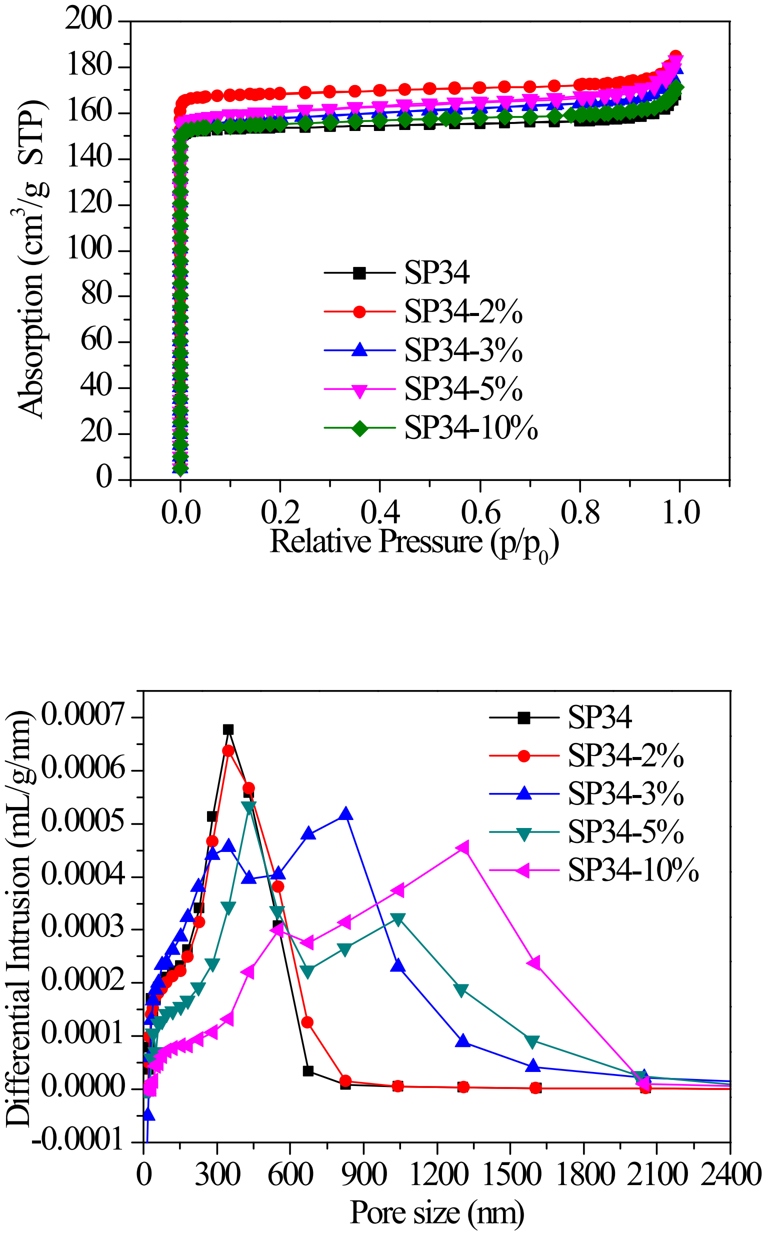

Figure S3. N_2 adsorption-desorption isotherms and pore size distribution (PSD) of SP34 and SP34-x samples

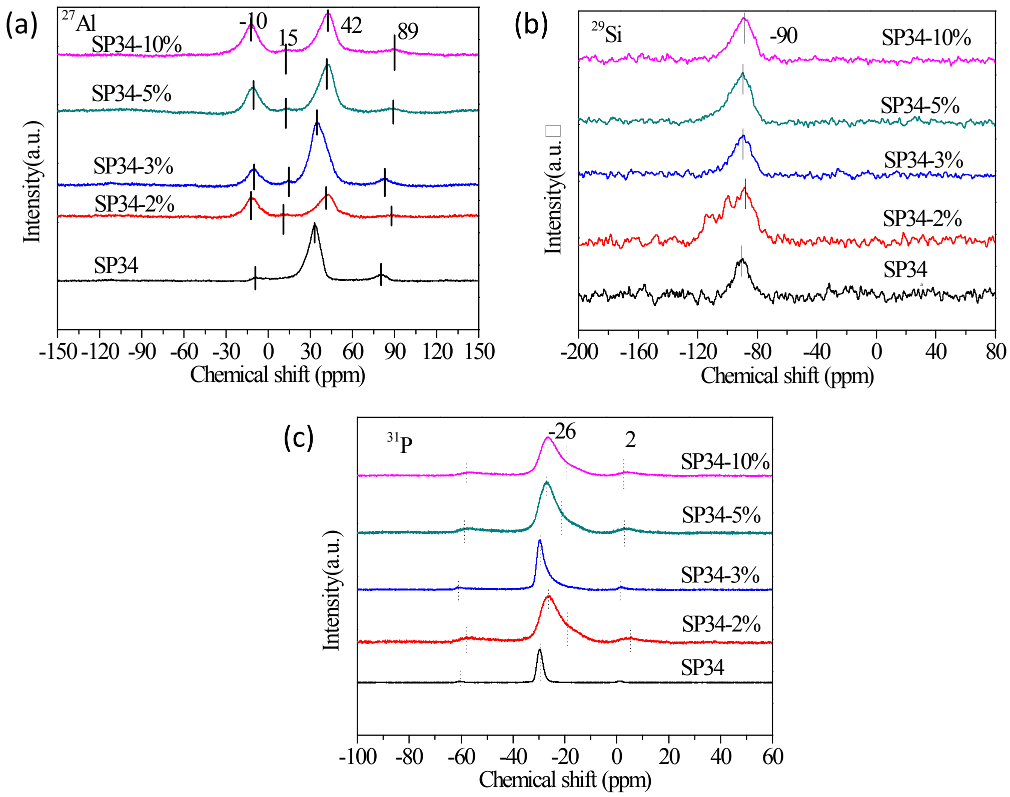

Figure S4. (a) ^{27}Al , (b) ^{29}Si, (c) ^{31}P MAS NMR spectra of SP34 and SP34-x samples.

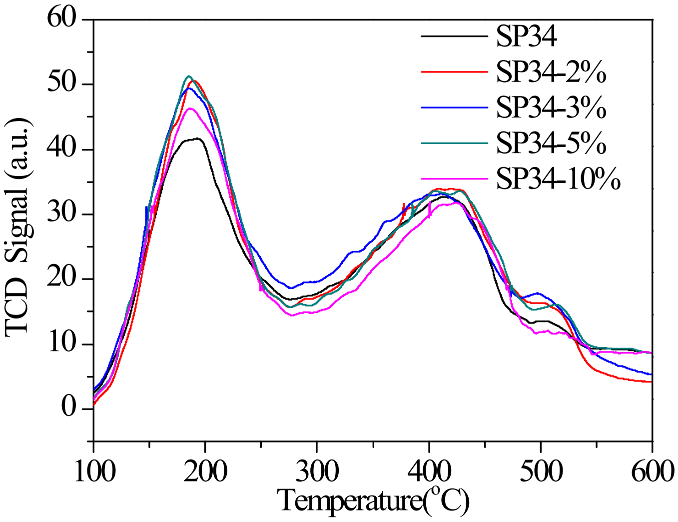

Figure S5. NH_3-TPD of SP34 and SP34-x samples.

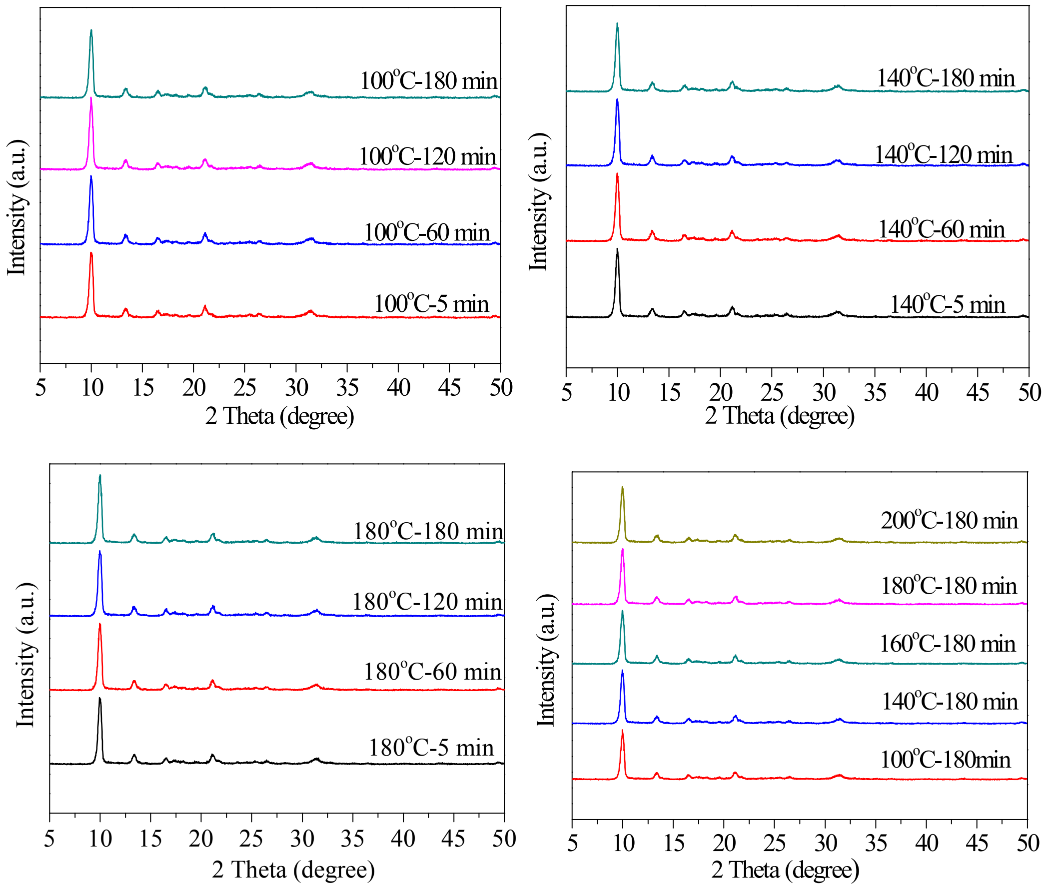

Figure S6. In-situ XRD patterns of SP34-5% sample at different treating temperatures.

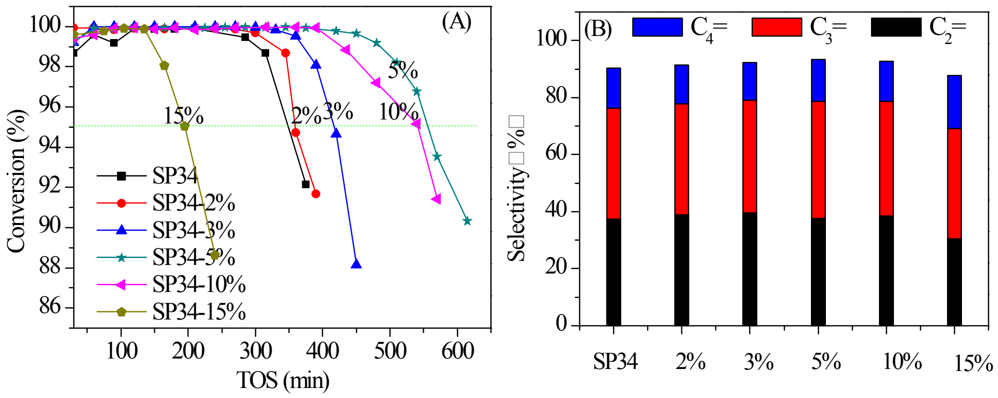

Figure S7. (A) Catalytic conversion of methanol and (B) light olefins selectivity of SP34 and SP34-x samples for MTO reaction at 400^{o}C with WHSV of 1 h^{-1} at atmospheric pressure.

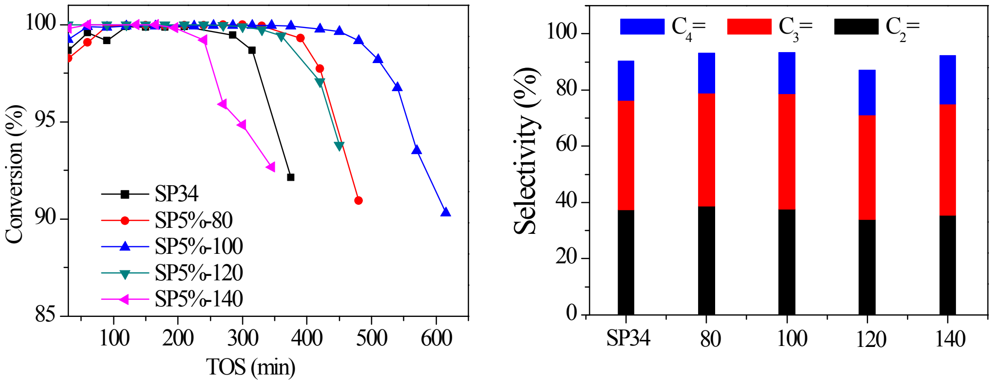

Figure S8 (A) Catalytic conversion of methanol and (B) light olefins selectivity of SP34 and SP34-5% samples after treating at different temperatures, for MTO reaction at 400°C with WHSV of 1 h^{-1} at atmospheric pressure.

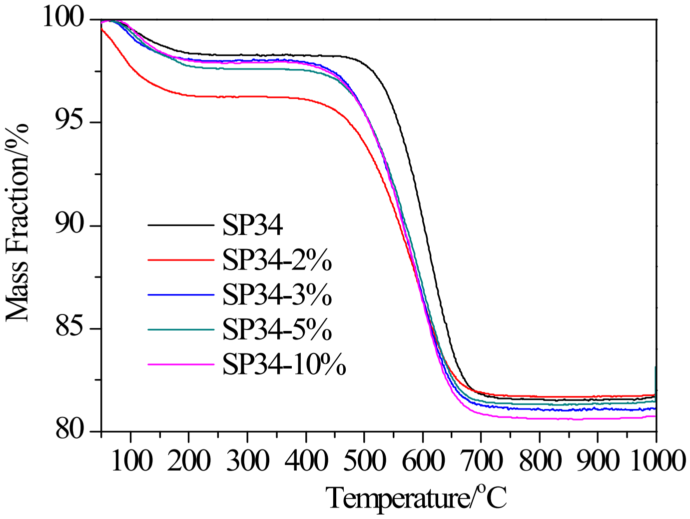

Figure S9. TG analysis of SP34 and SP34-x samples

Table S1. Textural properties of the prepared SP34 and SP34-x samples.

Samples	S_{BET} ($m^2 g^{-1}$)	S_{micro} ($m^2 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_{meso} ($cm^3 g^{-1}$)
SP34	625	610	0.23	0.01
SP34-2%	712	704	0.26	0.02
SP34-3%	667	657	0.24	0.02
SP34-5%	673	658	0.24	0.03
SP34-10%	656	647	0.24	0.02

Table S2. The life time and coking formation rate of SP34 and SP34-x samples

Samples	SP34	SP-2%	SP-3%	SP-5%	SP-10%
TOS (min)	340	360	430	580	540
Coke (%, g/g_{cat})	16.58	14.50	16.63	16.50	16.00
R_{coke} (mg/(min·g_{cat}))	0.49	0.40	0.39	0.28	0.30
P_{coke} (g/g_{MeOH})	0.029	0.024	0.023	0.017	0.018

R_{coke} (g/(min.g_{cat}))=Coke amount (g)/reaction time (min). P_{coke} (g/g_{cat})=Coke amount (g)/methanol feedstock (g)

Table S3. The distributions of coking species on spent catalysts analyzed by GC-MS.

The main coke species	Retention time (min)	SP34	SP34-2%	SP34-3%	SP34-5%	SP34-10%
Benzene homologues	4.0-13.9	4.1%	5.2%	9.51%	9.8%	12.1%
Naphthalene and indene derivatives	14.0-20.7	13.7%	21.0%	26.94%	28.3%	29.9%
Phenanthrene and anthracene derivatives	20.8-24.2	33.2%	40.2%	39.5%	35.7%	38.5%
Pyrene and Benzanthracene ect.	>24.2	49.0%	33.7%	24.0%	26.3%	19.4%