Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Selective Oxidation of Methacrolein to Methacrylic Acid over $H_4PMo_{11}VO_{40}/C_3N_4$-SBA-15

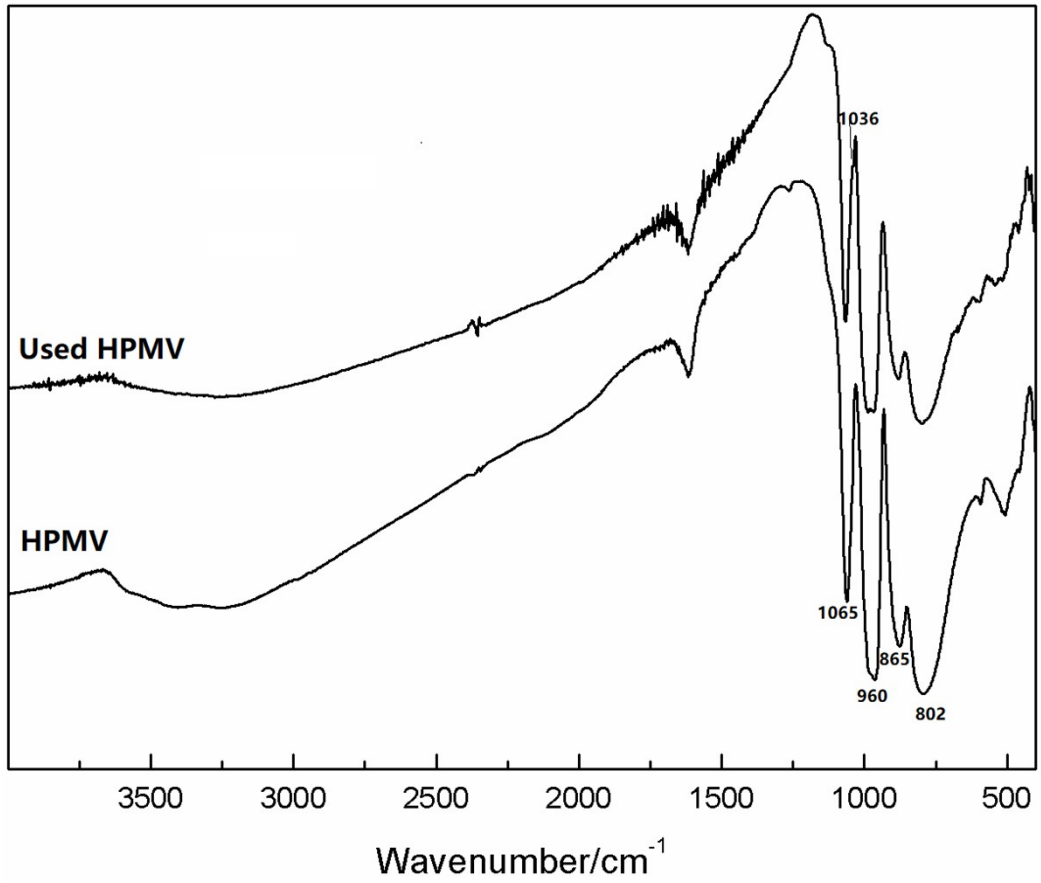


Figure S1. FT-IR spectra of HPMV before calcination (HPMV) and after reaction (Used HPMV)

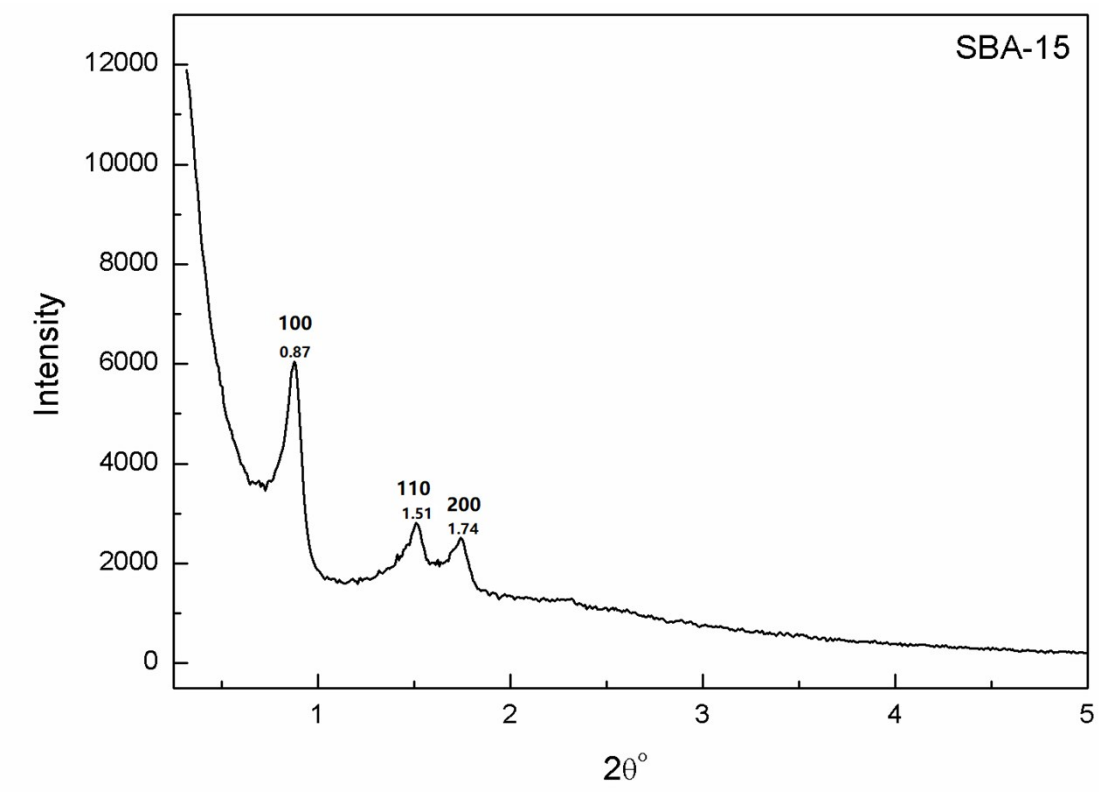


Figure S2. Small angle XRD patterns of SBA-15

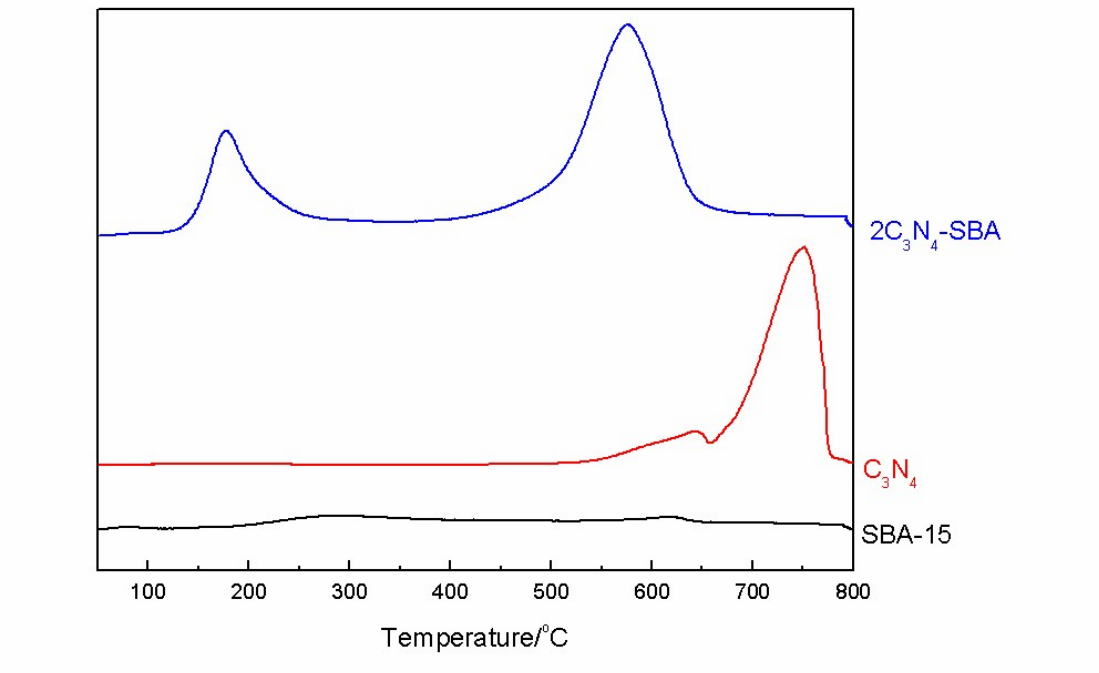


Figure S3. CO_2-TPD curves of SBA-15, C_3N_4 and C_3N_4-SBA

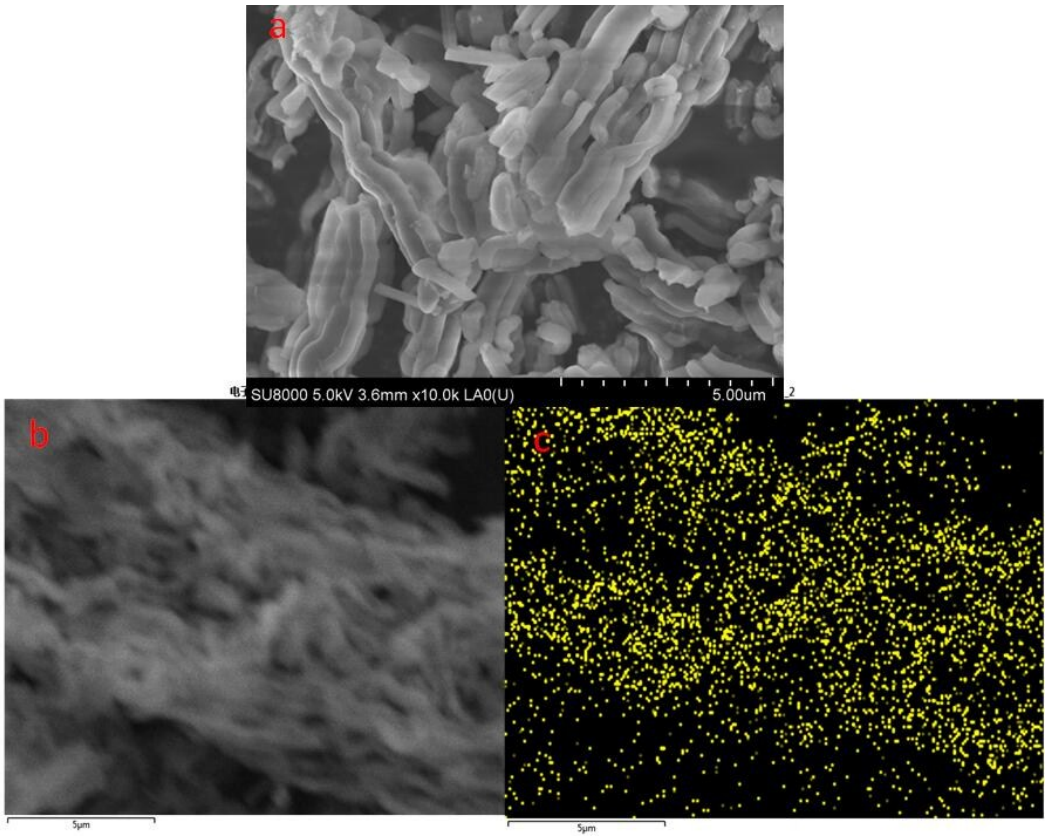


Figure S4. The SEM image of SBA-15 (a) and CN-SBA (b) and N dispersion of CN-SBA (c)

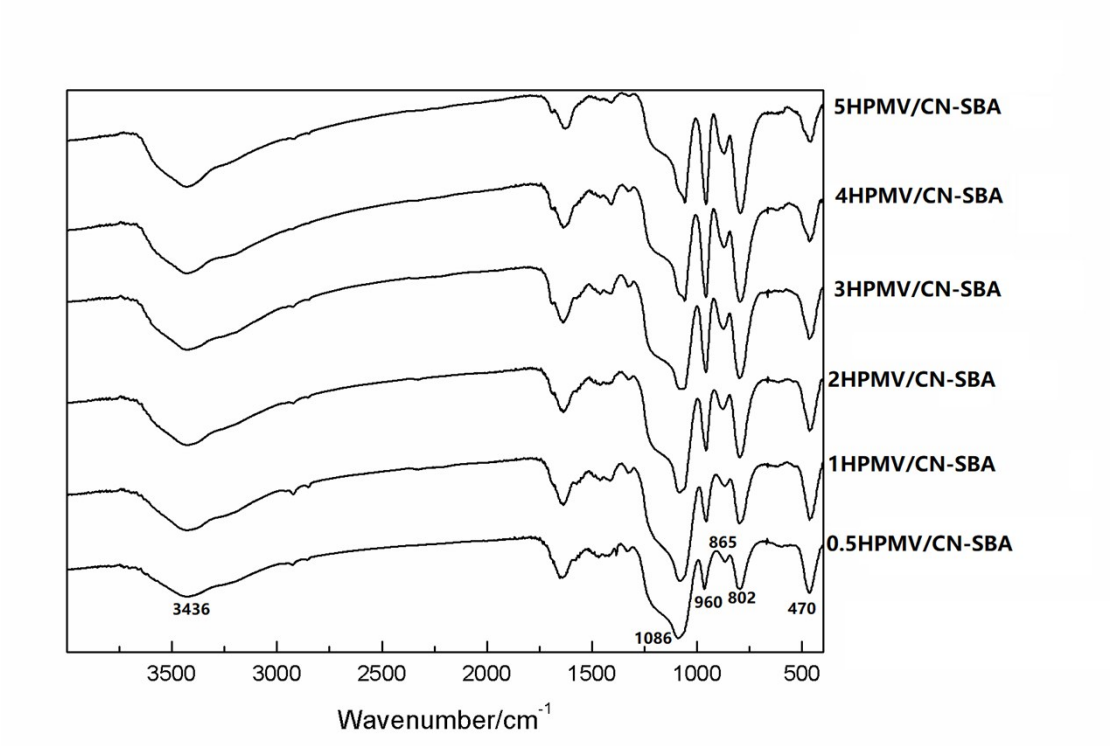


Figure S5. FT-IR spectra of HPMV/CN-SBA catalysts before calcination with different HPMV loading amount. Catalysts were prepared at 80 ^{o}C with 2 h mixing

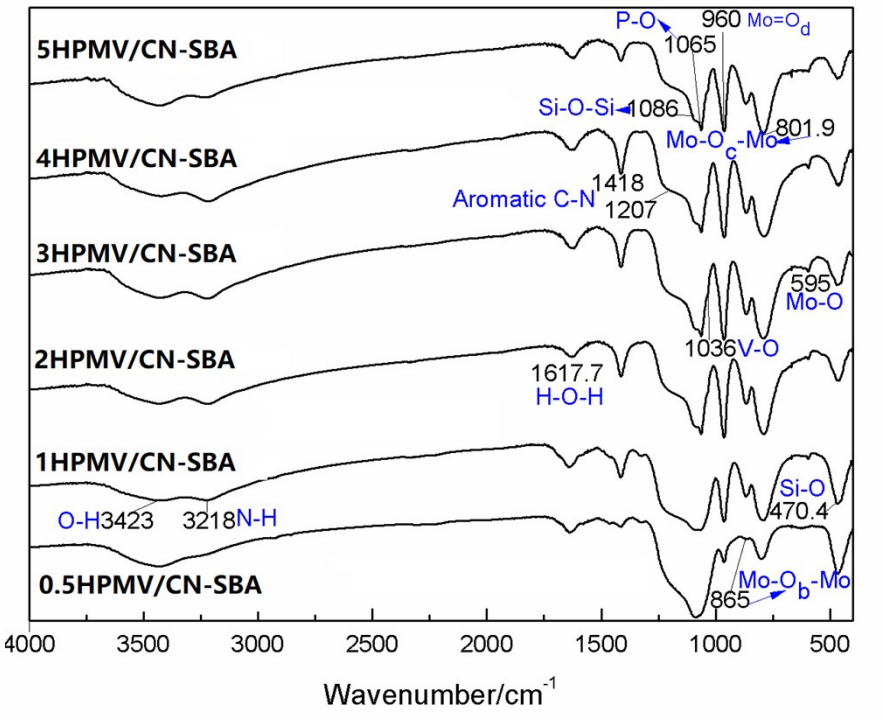


Figure S6. FT-IR spectra of HPMV/CN-SBA catalysts following calcinations with different HPMV loading. Catalysts were prepared at 80 °C with 2 hours mixing and calcined at 360 °C for 12 h)

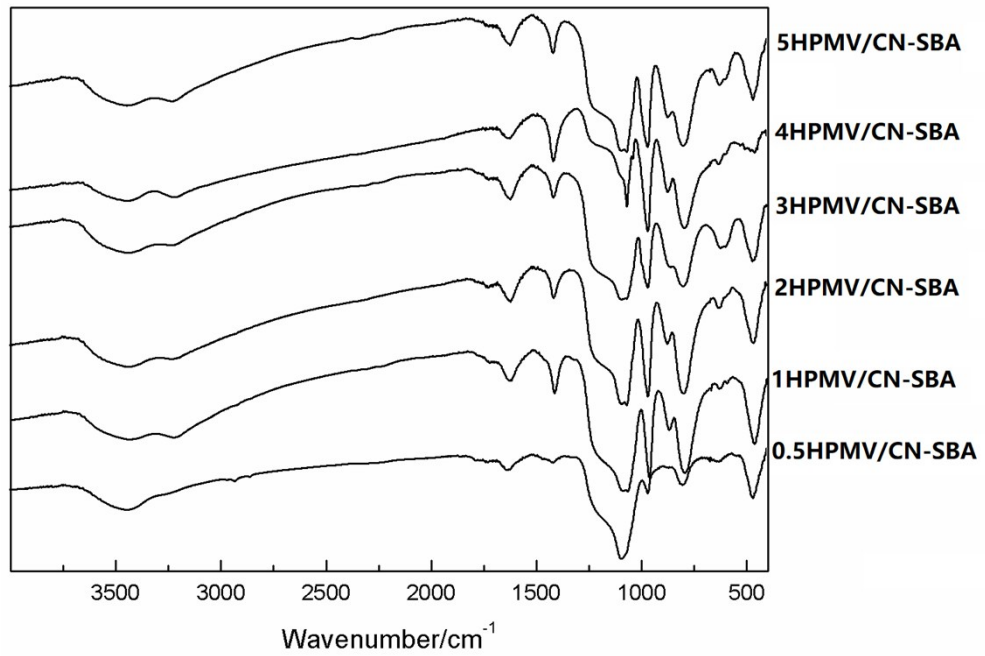


Figure S7. FT-IR spectra of HPMV-CN-SBA catalysts post reaction with different HPMV loading. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h. MAL reaction conditions were: the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1, and 17.8, with the

balance N_2 at 310 ^oC with 16 h.

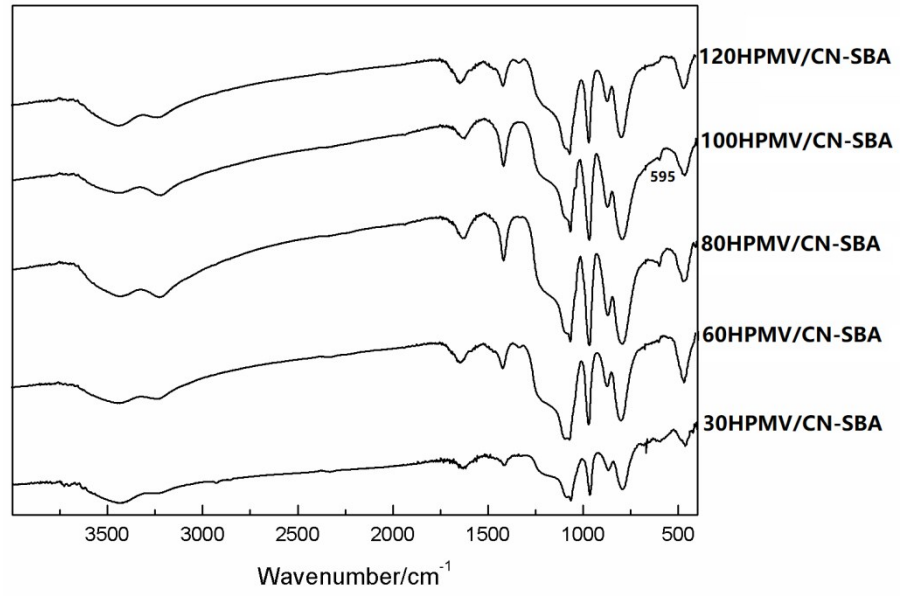


Figure S8. FT-IR spectra of calcined 2HPMV/CN-SBA synthesized at different temperature. Catalysts were prepared at temperature ranging from 30-120 oC with 2 h mixing and calcined at 360 ^oC for 12 h. Catalysts synthesis temperature indicated by prefix to HPMV/CN-SBA

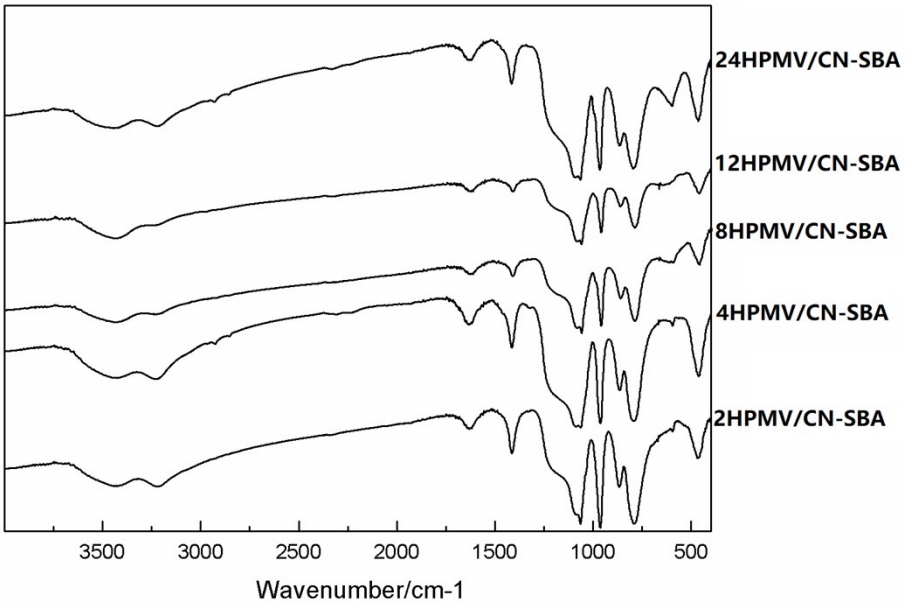


Figure S9. FT-IR spectra of calcined 2HPMV/CN-SBA synthesized with different mixing times. Catalysts were prepared at mixing times ranging from 2-24 h at a temperature of 80 ^oC and calcined at 360 ^oC for 12 h. Catalysts mixing time during synthesis indicated by prefix to HPMV/CN-SBA

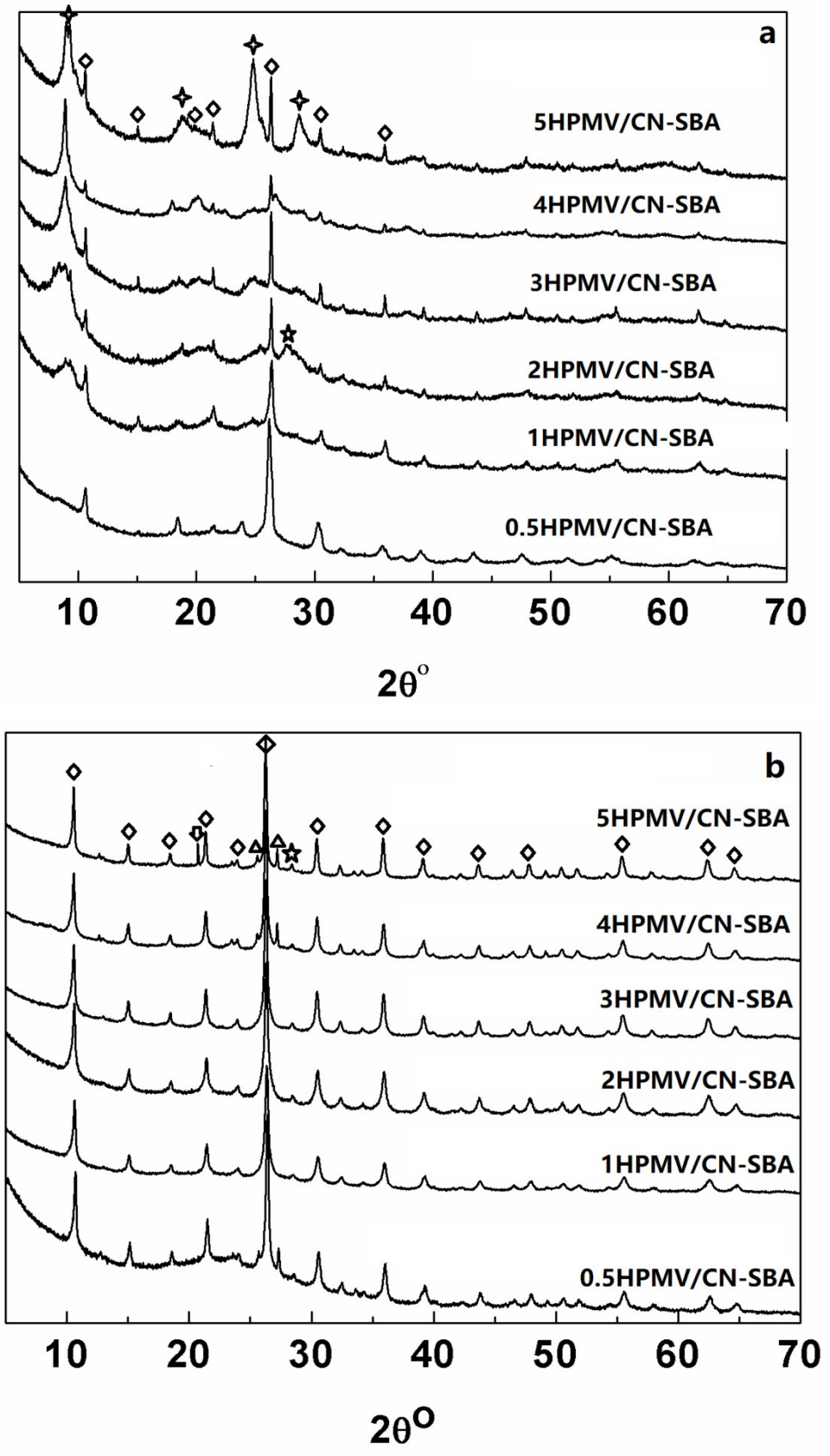


Figure S10. XRD patterns of supported catalysts with different supporting amount before (a) and after calcination (b) (quadrangular star, HPMV; arrow, V_2O_5;

△, MoO_3; ◇, $(NH_4)xH_{4-x}PMo_{11}VO_{40}$; ☆, C_3N_4)

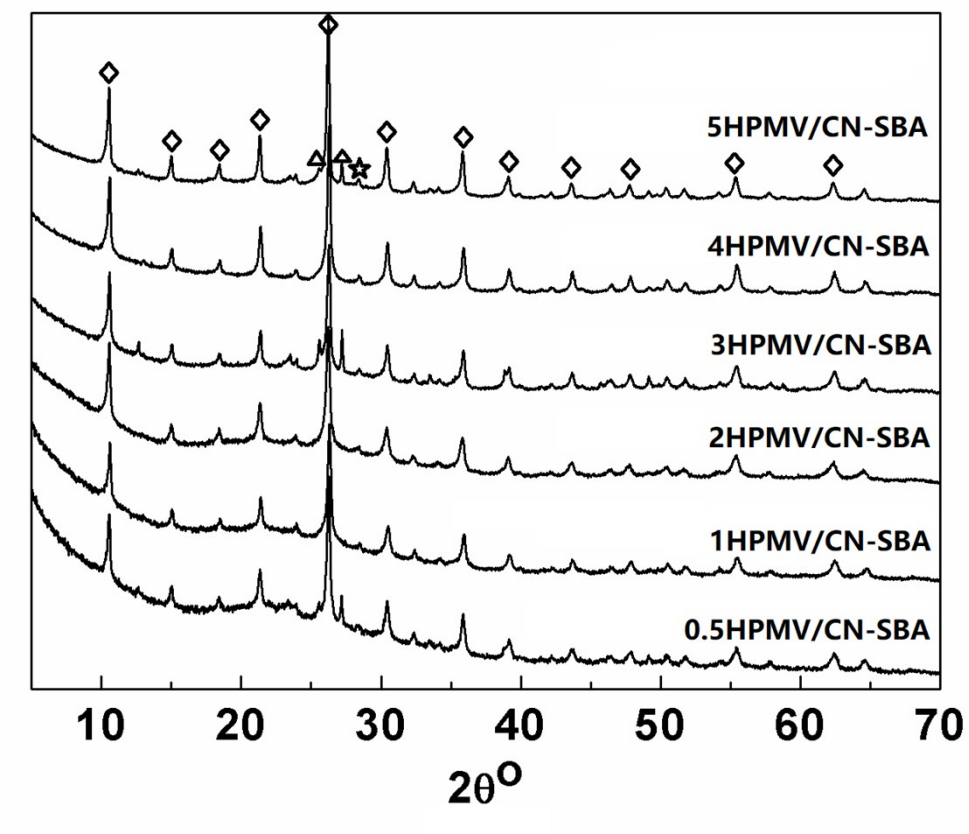


Figure S11. XRD patterns of HPMV/CN-SBA catalysts post-reaction with different HPMV loadings. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h. Reaction conditions were the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1, and 17.8, with the balance N_2 at 310 °C with 16 h. Peak identification: quadrangular star = HPAV; arrow = V_2O_5; △ = MoO_3; ◇ = $(NH_4)xH_{4-x}PMo_{11}VO_{40}$; ☆ = C_3N_4)

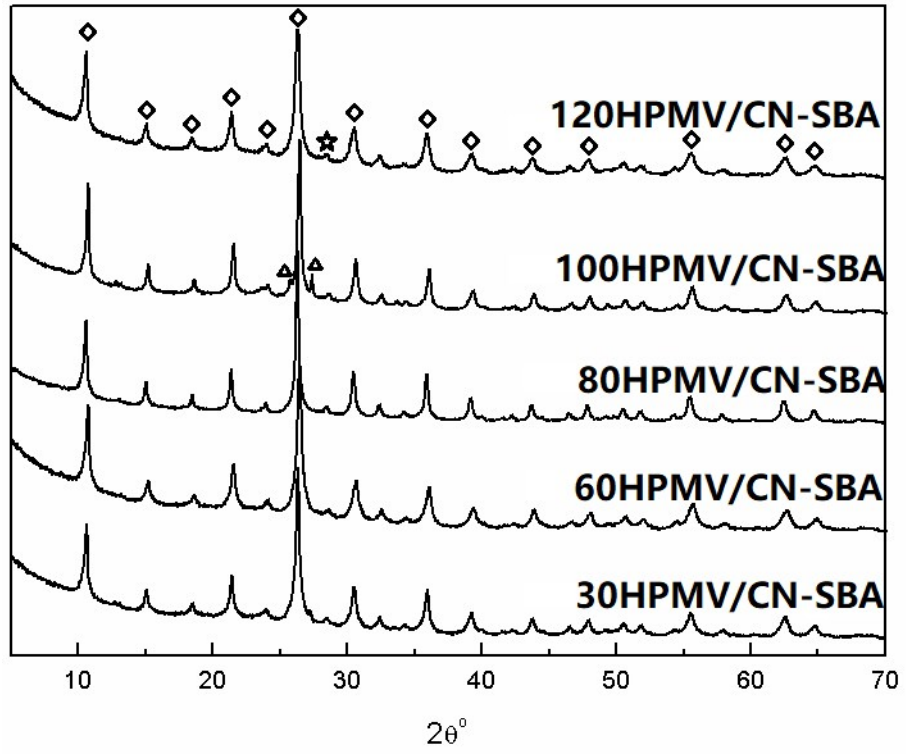


Figure S12. XRD patterns of calcined 2HPMV/CN-SBA synthesized at different temperatures. Catalysts were prepared at temperatures ranging from 30-120 °C with 2 h mixing and calcined at 360 °C for 12 h. Catalyst synthesis temperature indicated by prefix to HPMV/CN-SBA. Peak identification: △ = MoO_3; ◇ = $(NH_4)xH_{4-x}PMo_{11}VO_{40}$; ☆ = C_3N_4

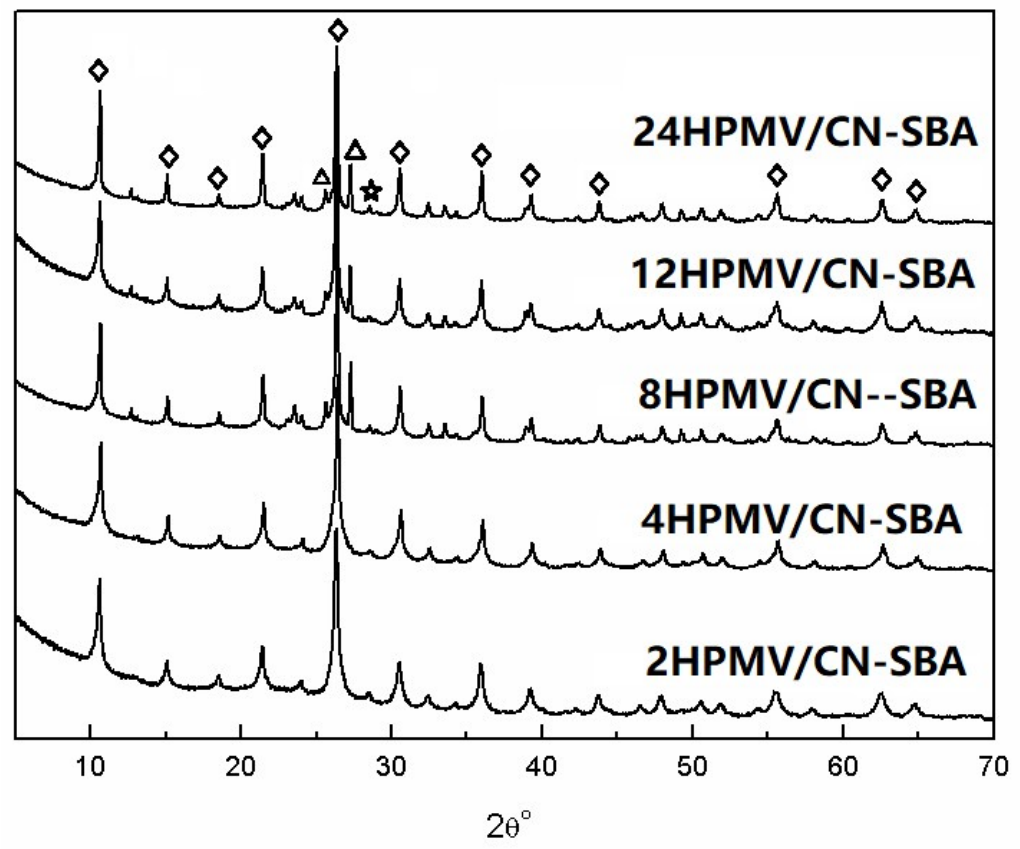


Figure S13. XRD patterns of calcined 2HPMV/CN-SBA synthesized with different mixing times. Catalysts were prepared at mixing times ranging from 2-24 h at a temperature of 80 °C and calcined at 360 °C for 12 h. Catalyst mixing time during synthesis indicated by prefix to HPMV/CN-SBA. Peak identification: △ = MoO_3; ◇ = $(NH_4)xH_{4-x}PMo_{11}VO_{40}$; ☆ = C_3N_4

Table S1. Crystalline diameter of supported catalysts

Catalysts	Crystalline diameter/nm
0.5HPAV/C_3N_4-SBA	24.4
1HPAV/C_3N_4-SBA	28.3
2HPAV/C_3N_4-SBA	59.8
3HPAV/C_3N_4-SBA	64.1
4HPAV/C_3N_4-SBA	28.4
5HPAV/C_3N_4-SBA	72.1
Calcined 0.5HPAV/C_3N_4-SBA	29.3
Calcined 1HPAV/C_3N_4-SBA	27.5
Calcined 2HPAV/C_3N_4-SBA	26.5
Calcined 3HPAV/C_3N_4-SBA	31.2
Calcined 4HPAV/C_3N_4-SBA	35.4
Calcined 5HPAV/C_3N_4-SBA	44.1

Used 0.5HPAV/C_3N_4-SBA	33.5
Used 1HPAV/C_3N_4-SBA	30.3
Used 2HPAV/C_3N_4-SBA	29.2
Used 3HPAV/C_3N_4-SBA	33.7
Used 4HPAV/C_3N_4-SBA	33.5
Used 5HPAV/C_3N_4-SBA	38.8
Calcined 4^tHPAV/C_3N_4-SBA	26.3
Calcined 8^tHPAV/C_3N_4-SBA	23.4
Calcined 12^tHPAV/C_3N_4-SBA	31.4
Calcined 24^tHPAV/C_3N_4-SBA	26.7
Calcined 30^cHPAV/C_3N_4-SBA	29.4
Calcined 60^cHPAV/C_3N_4-SBA	44.7
Calcined 100^cHPAV/C_3N_4-SBA	46.2
Calcined 120^cHPAV/C_3N_4-SBA	49.0

The crystalline diameters of supported catalysts was calculated by Scherrer formula, $D_{hkl}=k\lambda/\beta cos\theta_{hkl}$ (Where k is shape factor, cubic is 0.9; λ is the wavelength of X-ray (1.075 nm); β is FWHM (radian); θ_{hkl} is diffraction angle which is around 13^o (radian).).

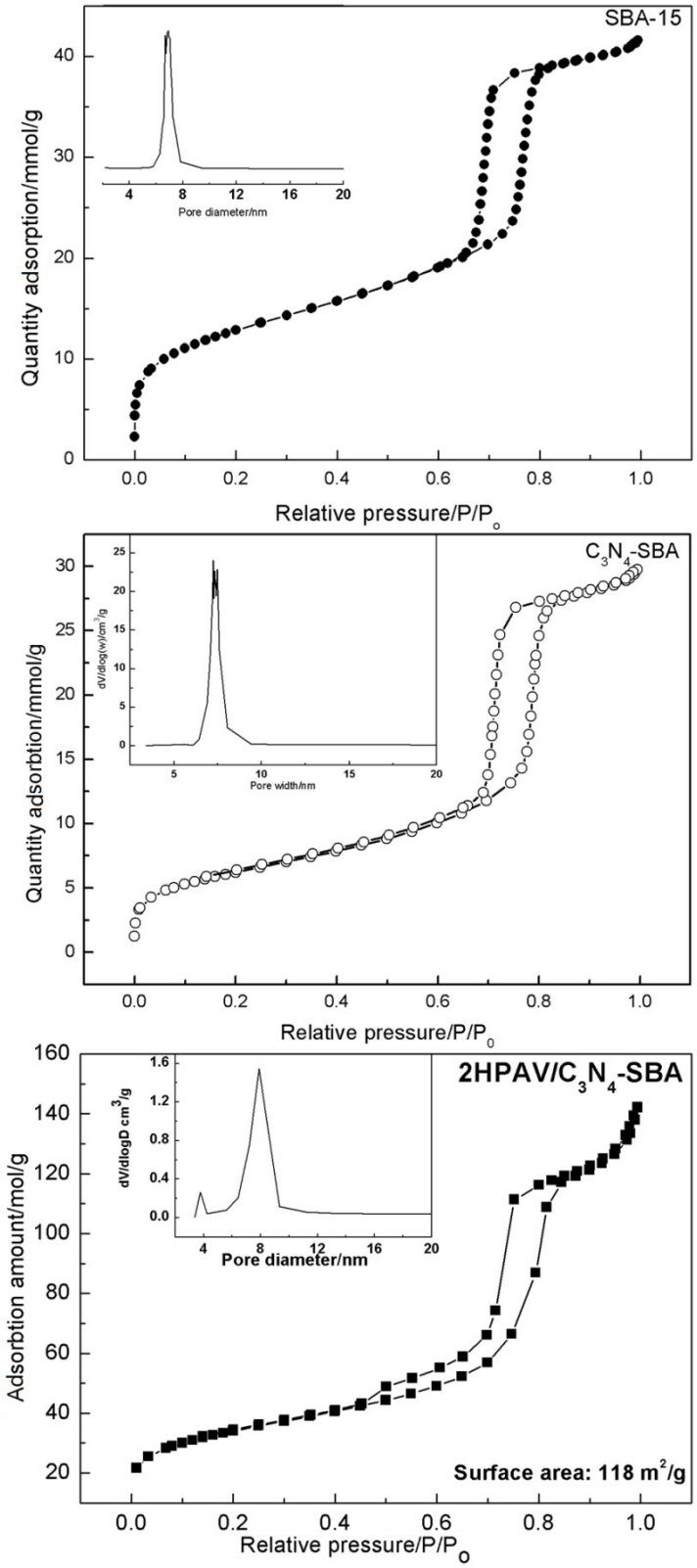


Figure S14. Nitrogen adsorption/desorption isotherms and (inset) pore size distribution of SBA-15, CN-SBA and 2HPMV/CN-SBA

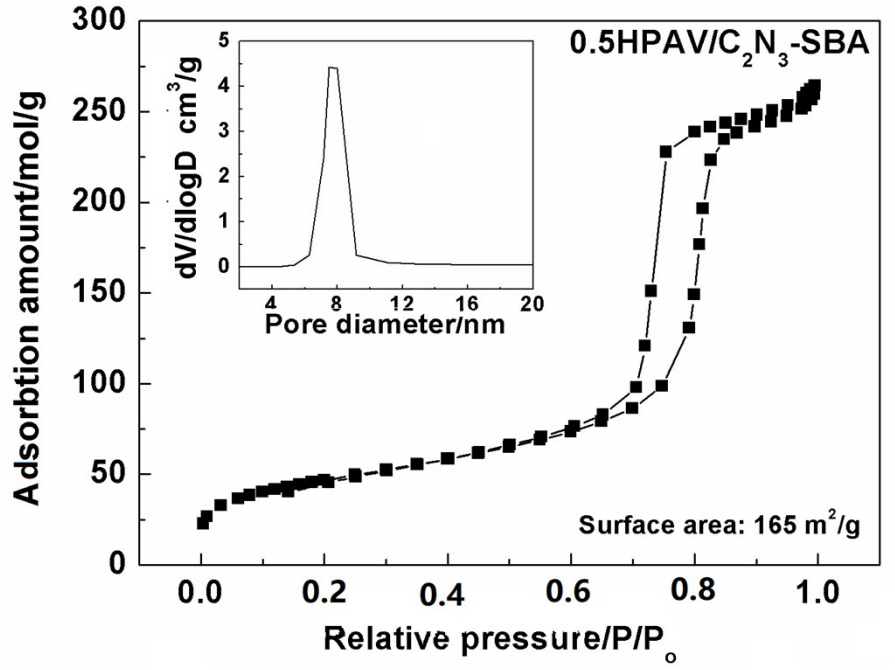


Figure S15. Nitrogen adsorption/desorption isotherms and (inset) pore size distribution of calcined 0.5HPMV/CN-SBA

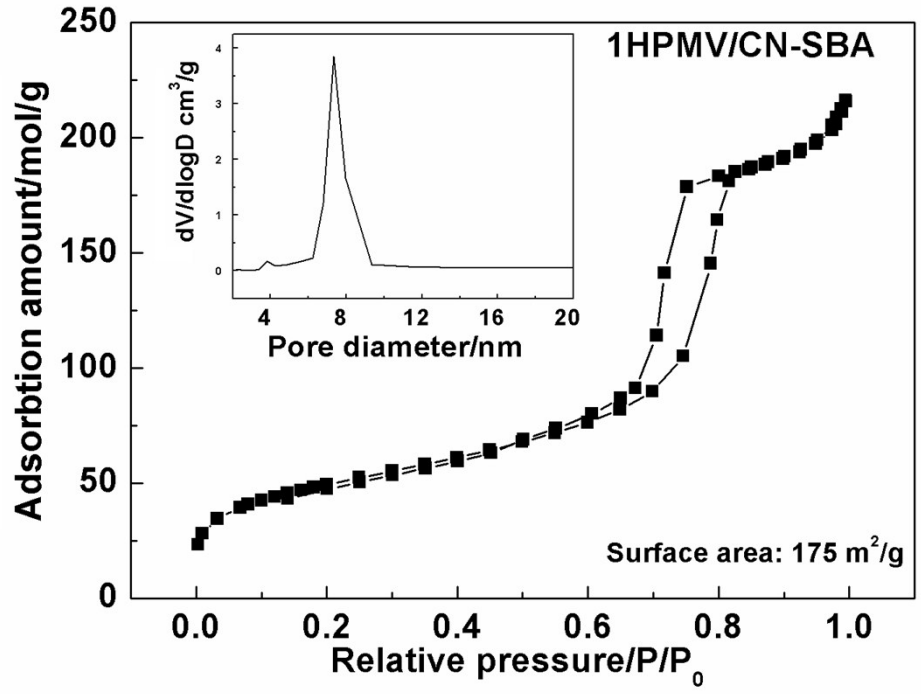


Figure S16. Nitrogen adsorption/desorption isotherms and (inset) pore size distribution of calcined 1HPMV/CN-SBA

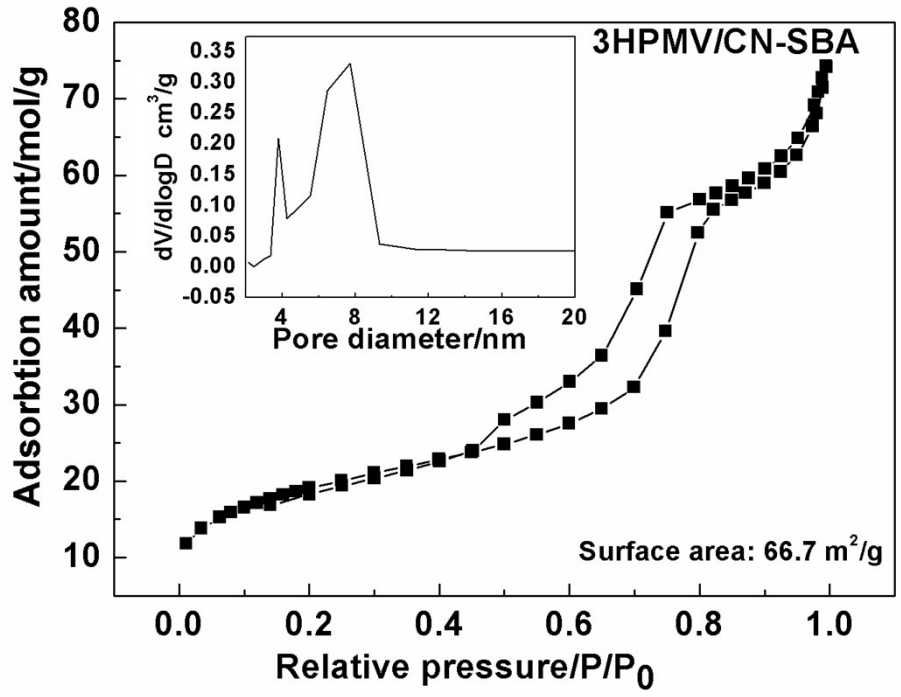


Figure S17. Nitrogen adsorption/desorption isotherms and (inset) pore size distribution of calcined 3HPMV/CN-SBA

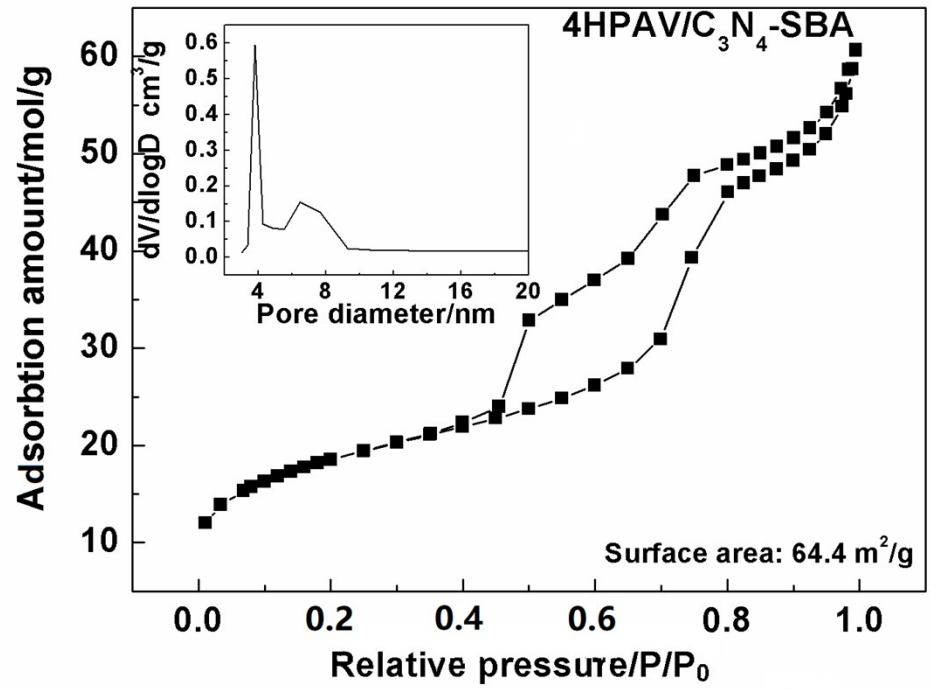


Figure S18. Nitrogen adsorption/desorption isotherms and (inset) pore size distribution of calcined 4HPMV/CN-SBA

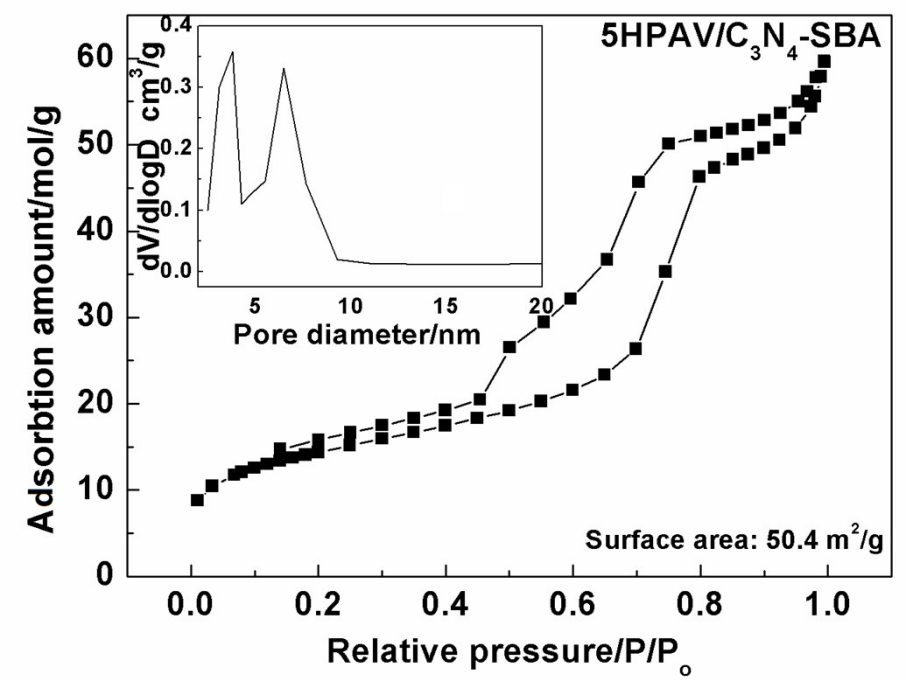


Figure S19. Nitrogen adsorption/desorption isotherms and (inset) pore size distribution of calcined 5HPMV/CN-SBA

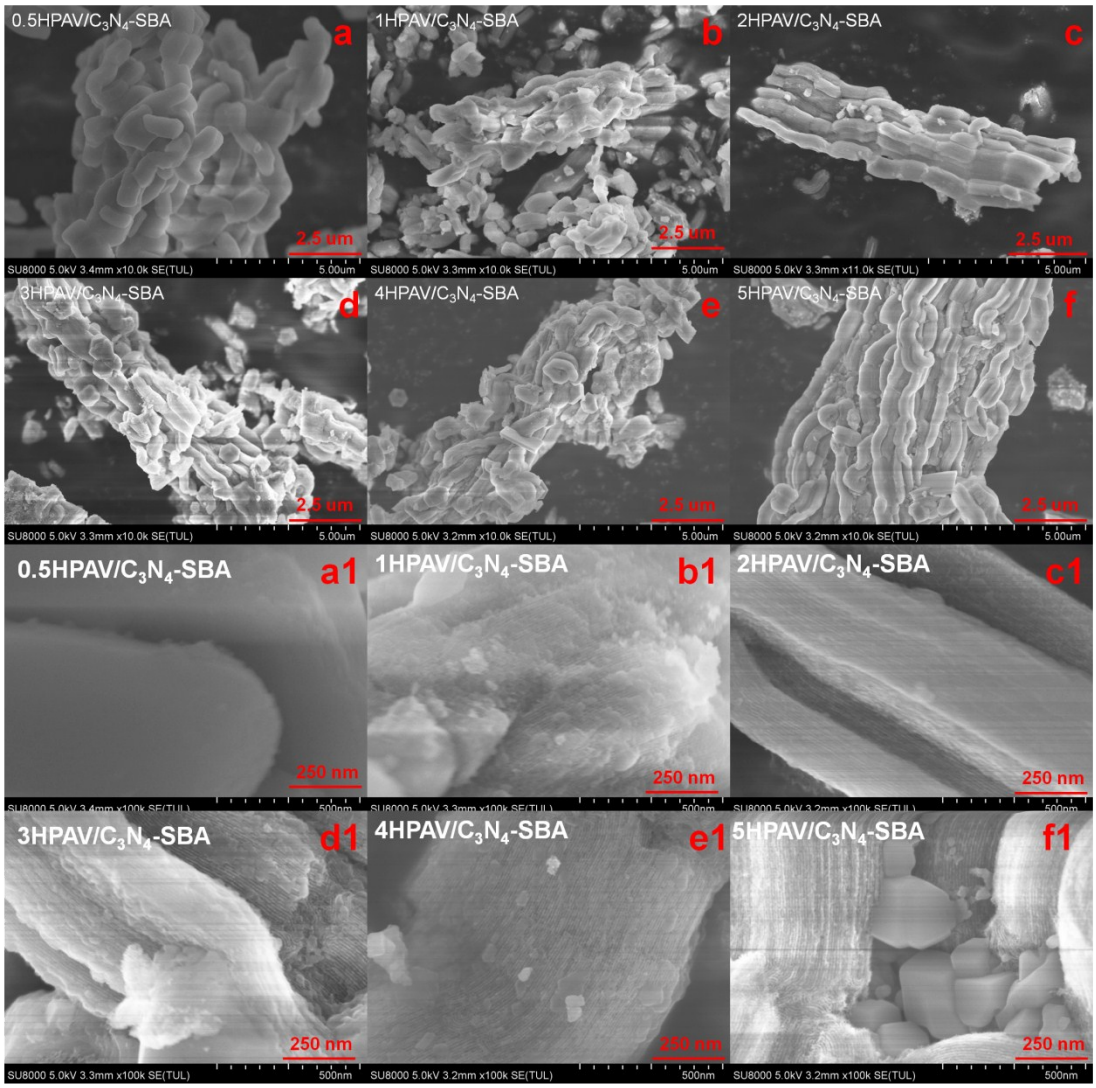


Figure S20. SEM images of HPMV/CN-SBA catalysts with different HPMV loadings (a, a1) 0.5HPMV/CN-SBA, (b, b1) 1HPMV/CN-SBA, (c, c1) 2HPMV/CN-SBA (d, d1) 3HPMV/CN-SBA, (e, e1) 4HPMV/CN-SBA, (f, f1) 5HPMV/CN-SBA

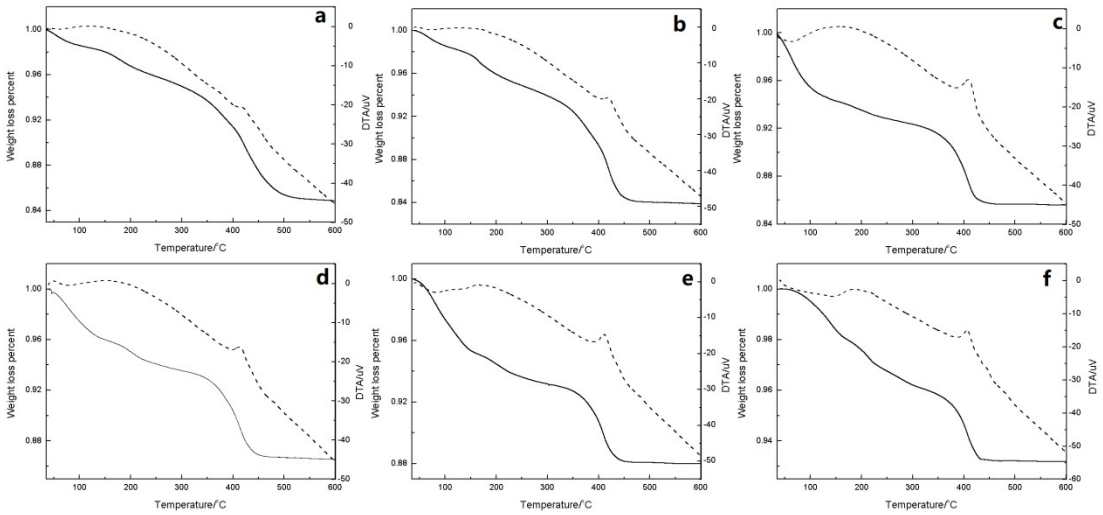


Figure S21. TG-DTA curves of HPMV/CN-SBA catalysts with different HPMV loadings (a) 0.5HPMV/CN-SBA, (b) 1HPMV/CN-SBA, (c) 2HPMV/CN-SBA (d) 3HPMV/CN-SBA, (e) 4HPMV/CN-SBA, (f) 5HPMV/CN-SBA

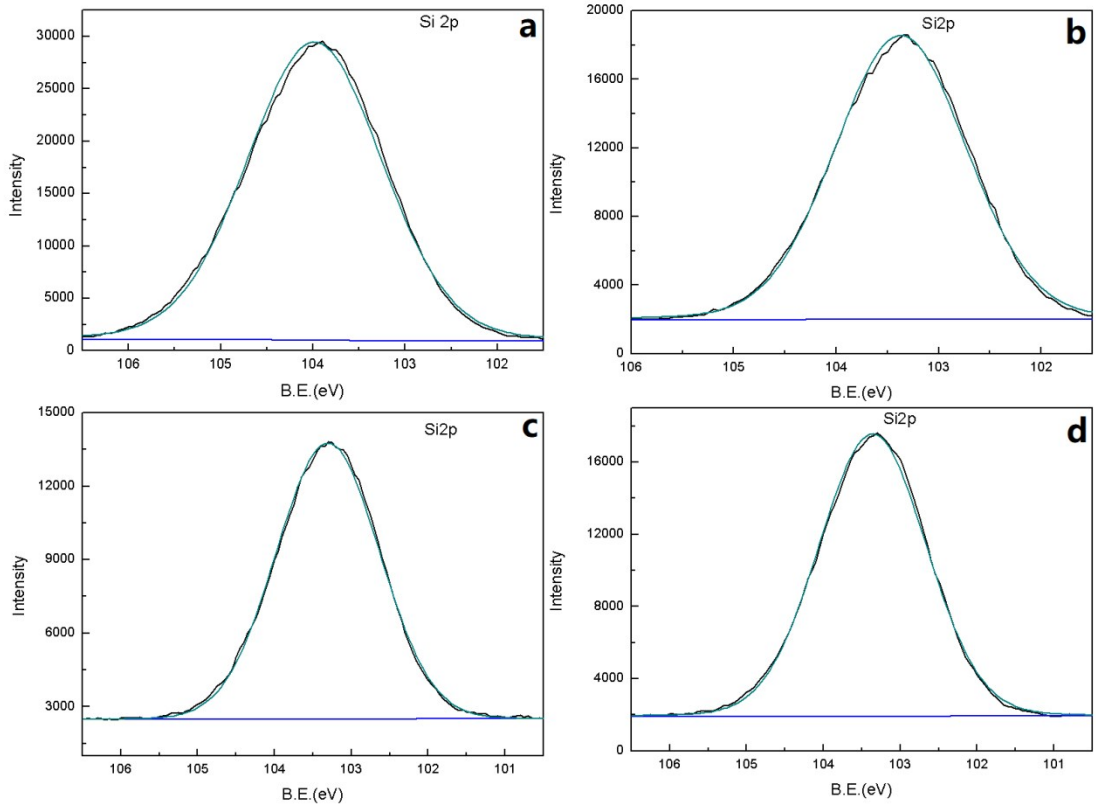


Figure S22. XPS spectra of Si 2p for (a) CN-SBA, and 3HPMV/CN-SBA (b) before calcination, (c) after calcination and (d) post-reaction. Catalysts were prepared at 80 ^{o}C with 2 h mixing and calcined at 360 ^{o}C for 12 h. Reaction conditions were: the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1,

and 17.8, with the balance N_2 at 310 °C with 16 h.

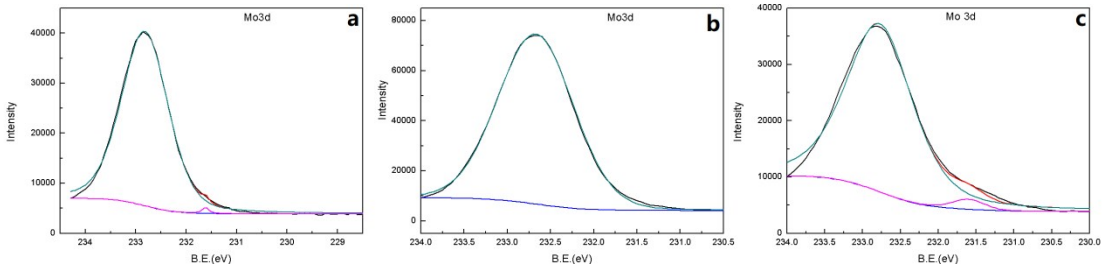


Figure S23. XPS spectra of Mo 3d for 3HPAV/CN-SBA (a) before calcination, (b) after calcination and (c) post-reaction. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h. Reaction conditions were: the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1, and 17.8, with the balance N_2 at 310 °C with 16 h.

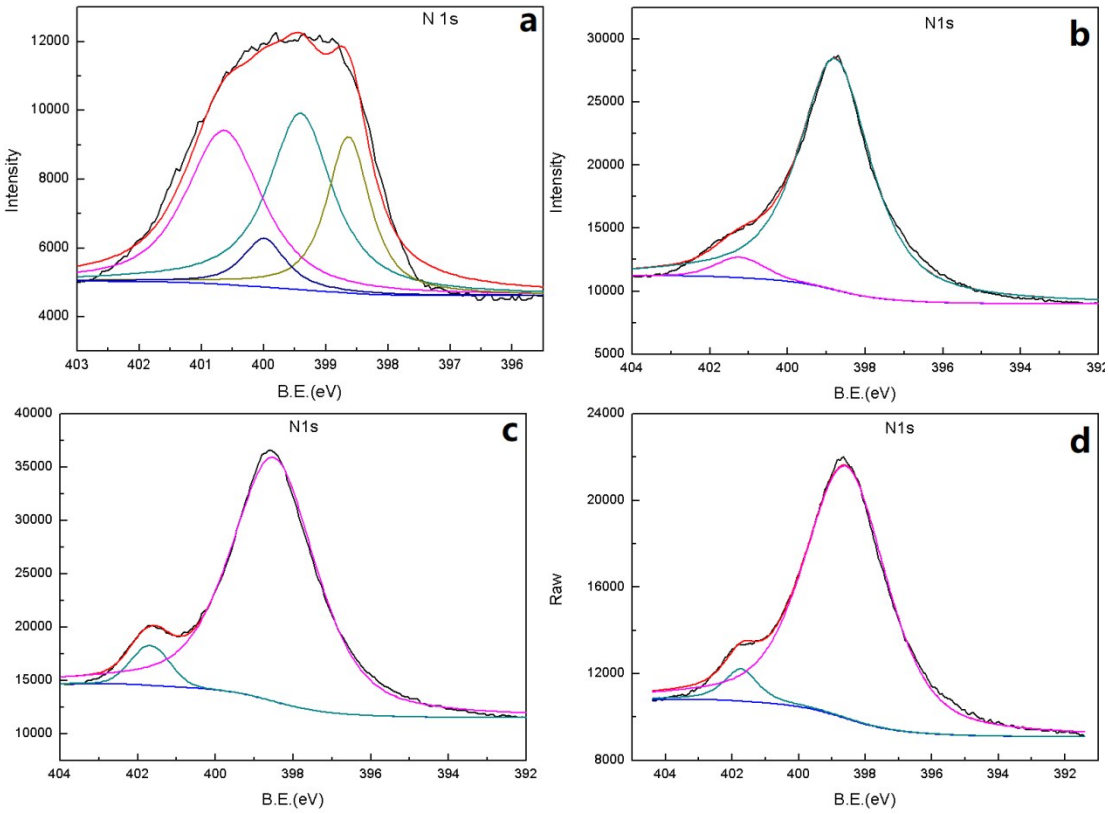


Figure S24. XPS spectra of XPS spectra of N 1s for (a) CN-SBA and 3HPMV/CN-SBA (b) before calcination, (c) after calcination and (d) post-reaction. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h. Reaction conditions were: the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1, and 17.8, with the balance N_2 at 310 °C with 16 h.

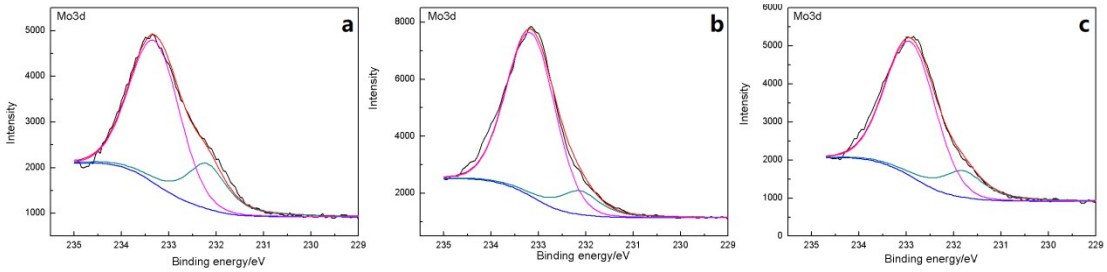


Figure S25. XPS spectra of Mo 3d for 3HPMV/SBA (a) before calcination, (b) after calcination and (c) post-reaction. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h. Reaction conditions were: the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1, and 17.8, with the balance N_2 at 310 °C with 16 h.

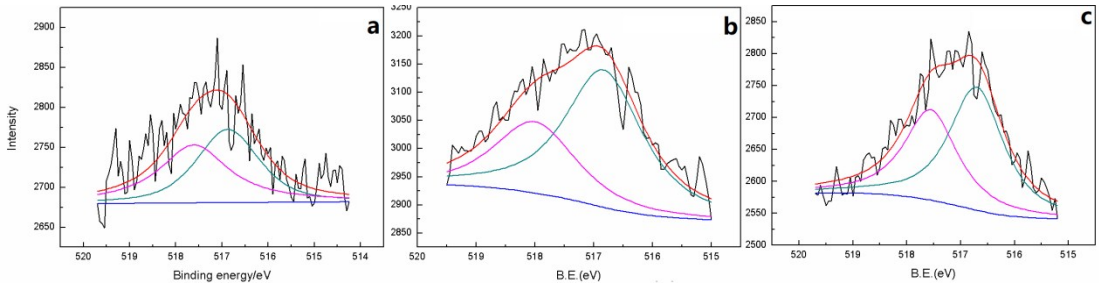


Figure S26. XPS spectra of V 2p for HPMV/SBA (a) before calcination, (b) after calcination and (c) post-reaction. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h. Reaction conditions were: the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1, and 17.8, with the balance N_2 at 310 °C with 16 h.

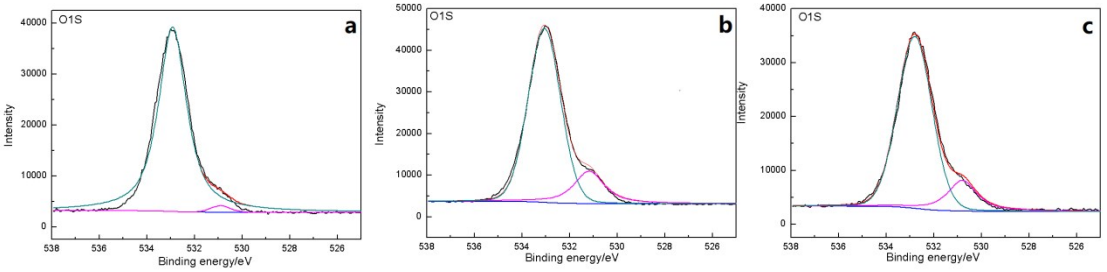


Figure S27. XPS spectra of O 1s for HPAV/SBA (a) before calcination, (b) after calcination and (c) post-reaction.

Table S2. Binding energies of N 1s, O1s, Mo 3d, V 2p and Si 2p for CN-SBA, 3HPMV/CN-SBA catalyst before calcinations, after calcinations or post-reaction

N 1s

Catalysts	*Peak1/ eV*	*Pea k2/eV*	*Pea k3/eV*	*Pea k4/eV*	*Area ratio of different peaks*

CN-SBA	400.6	400.0	399.4	398.6	5.3:1:5.6:3.2
3HPMV/CN-SBA	401.2			398.8	1:20.2
Calcined 3HPMV/CN-SBA	401.7			398.5	1:16.3
Post-reaction 3HPMV/CN-SBA	401.7			398.6	1:17.5

V 2p

Catalysts	*Peak 1/eV*	*Peak 2/eV*	*Area ratio of Peak 1 and Peak 2*
3HPMV/CN-SBA	517.1	516.1	1.2:1
Calcined 3HPMV/CN-SBA	517.2	516.1	1.8:1
Used 3HPMV/CN-SBA	517.4	516.5	1:1.3
HPMV/SBA	517.60	516.70	2.0:1
Calcined HPMV/SBA	517.56	516.81	1:1
Post-reaction HPMV/SBA	517.51	516.65	1.1:1

Mo 3d

Catalysts	*Peak 1/eV*	*Peak 2/eV*	*Area ratio of Peak 1 and Peak 2*
3HPMV/CN-SBA	232.8	231.6	144.3:1
Calcined 3HPMV/CN-SBA	232.7	--	--
Used 3HPMV/CN-SBA	232.8	231.6	40.3:1
4HPMV/SBA	233.30	232.20	3:1
Calcined 4HPMV/SBA	233.20	232.13	5.8:1
Post-reaction 4HPMV/SBA	232.91	231.80	4.5:1

Si 2p

Catalysts	*Peak 1/eV*
CN-SBA	103.4
3HPMV/CN-SBA	103.4
Calcined 3HPMV/CN-SBA	103.3
Post-reaction 3HPMV/CN-SBA	103.4

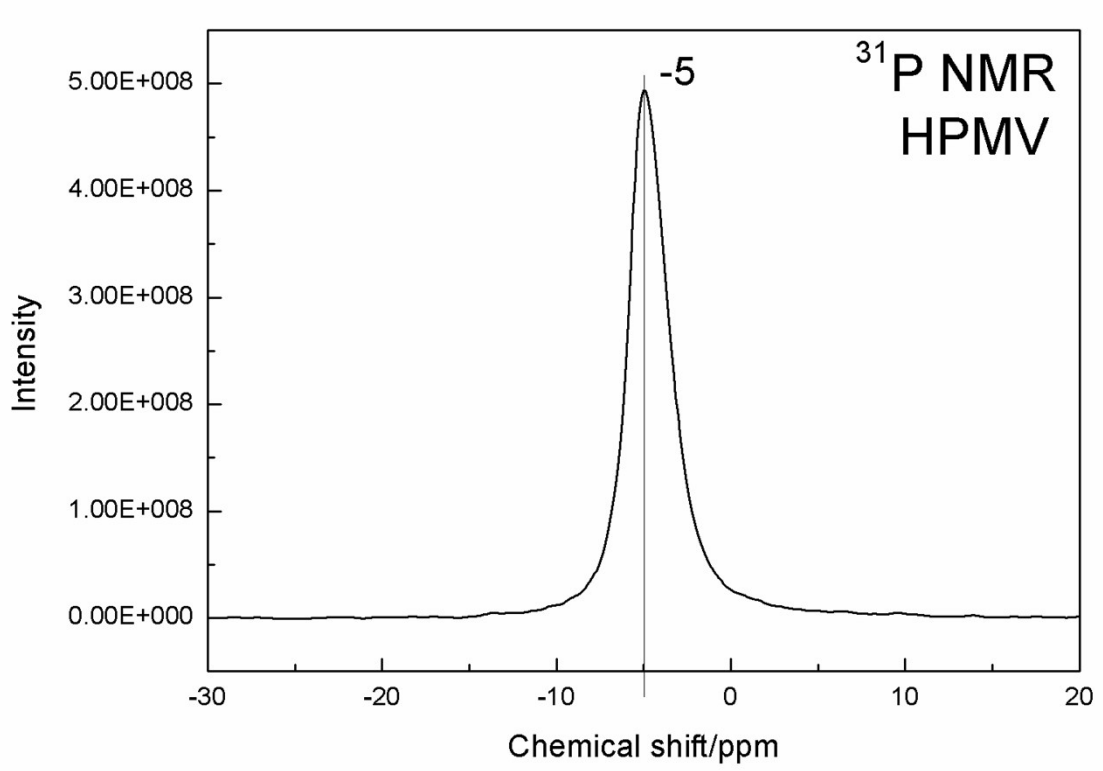
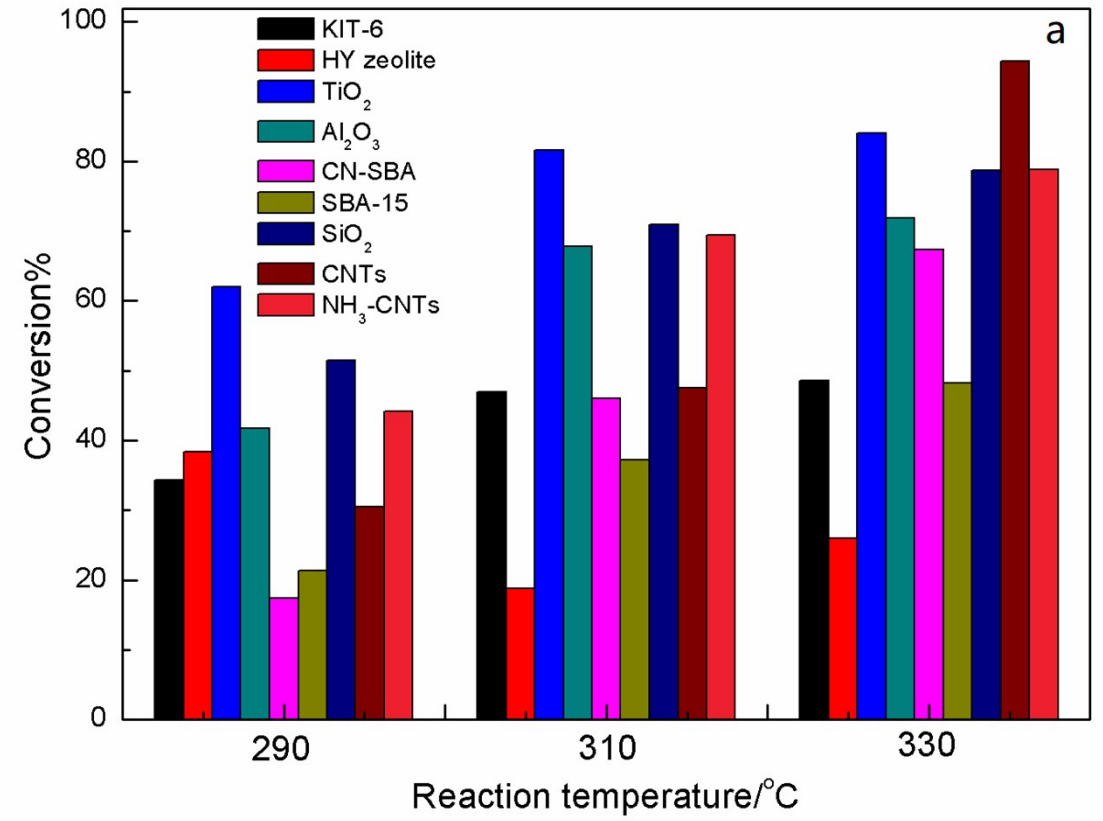


Figure S28. ^{31}P NMR spectrum of HPMV



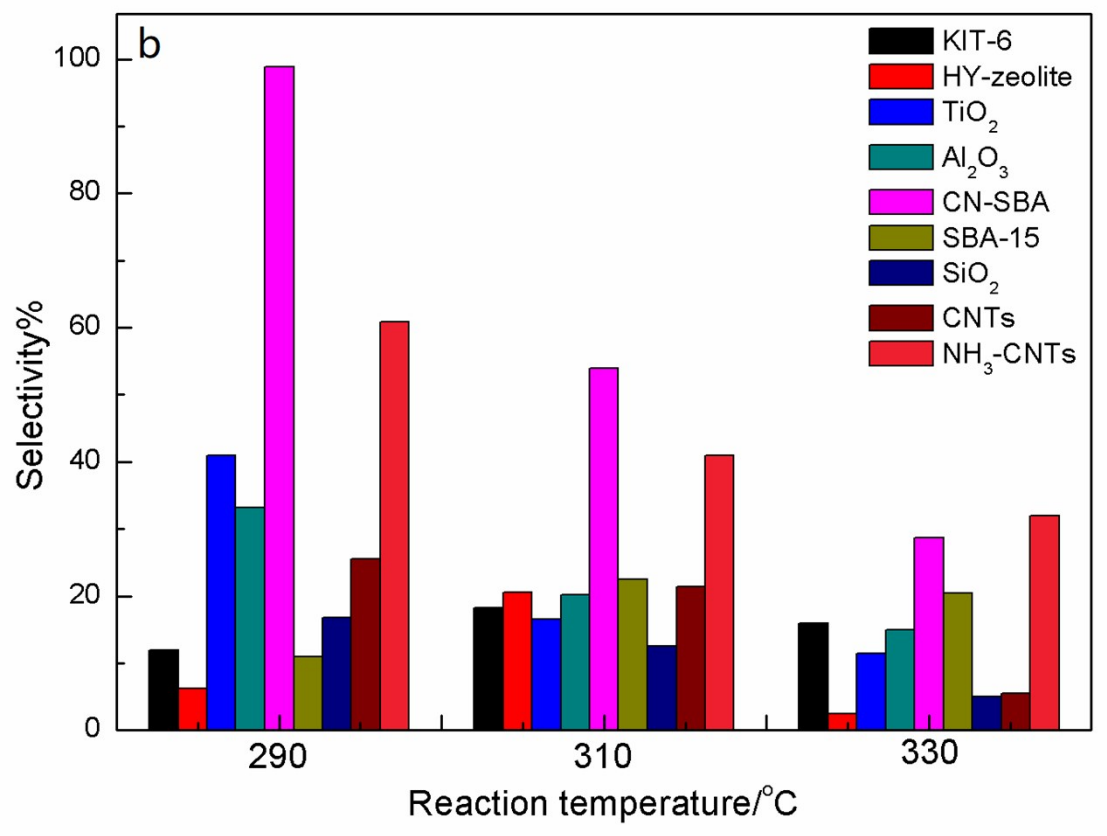


Figure S29. MAL conversion and MAA selectivity over HPMV supported on KIT-6, HY zeolite, TiO_2, Al_2O_3, CN-SBA, SBA-15, SiO_2, CNTs, NH3-CNTs at 290, 310 and 330 °C, respectively. The volume ratio of MAL, O_2 and H_2O in the reactant stream were 4.4 vol.%, 11.1 vol.%, 17.8 vol.%, respectively, N_2 balance.

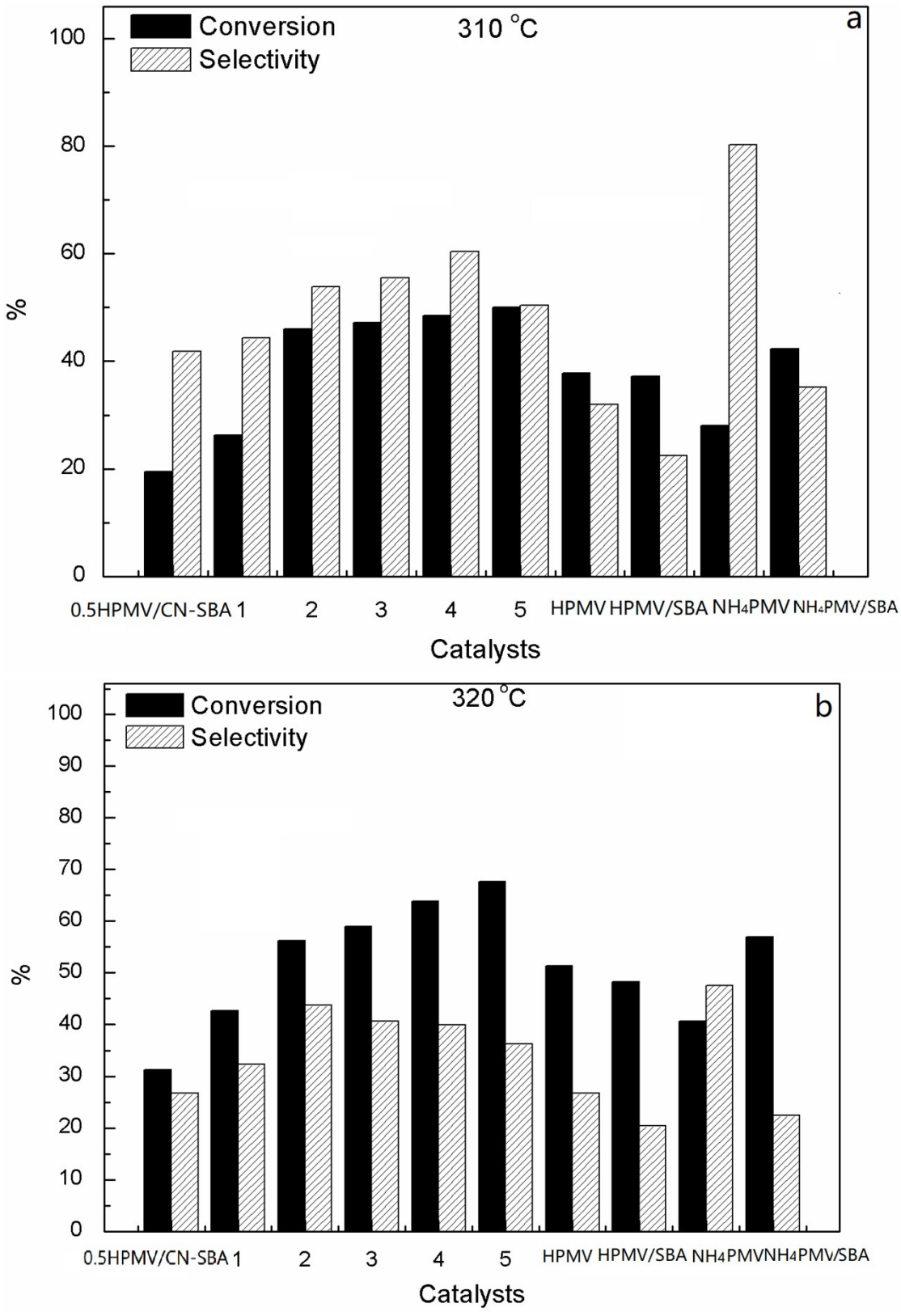


Figure S30. MAL conversion and MAA selectivity over 0.5HPMV/CN-SBA, 1HPM/CN-SBA (1), 2HPMV/CN-SBA (2), 3HPMV/CN-SBA (3), 4HPMV/CN-SBA (4), 5HPMV/CN-SBA (5), HPMV, HPMV/SBA-15, NHPMV and NHPMV/SBA at (a) 310 °C and (b) 320 °C. The volume ratio of MAL, O_2 and H_2O in the reactant

stream were 4.4 vol.%, 11.1 vol.%, 17.8 vol.%, respectively, N_2 balance.

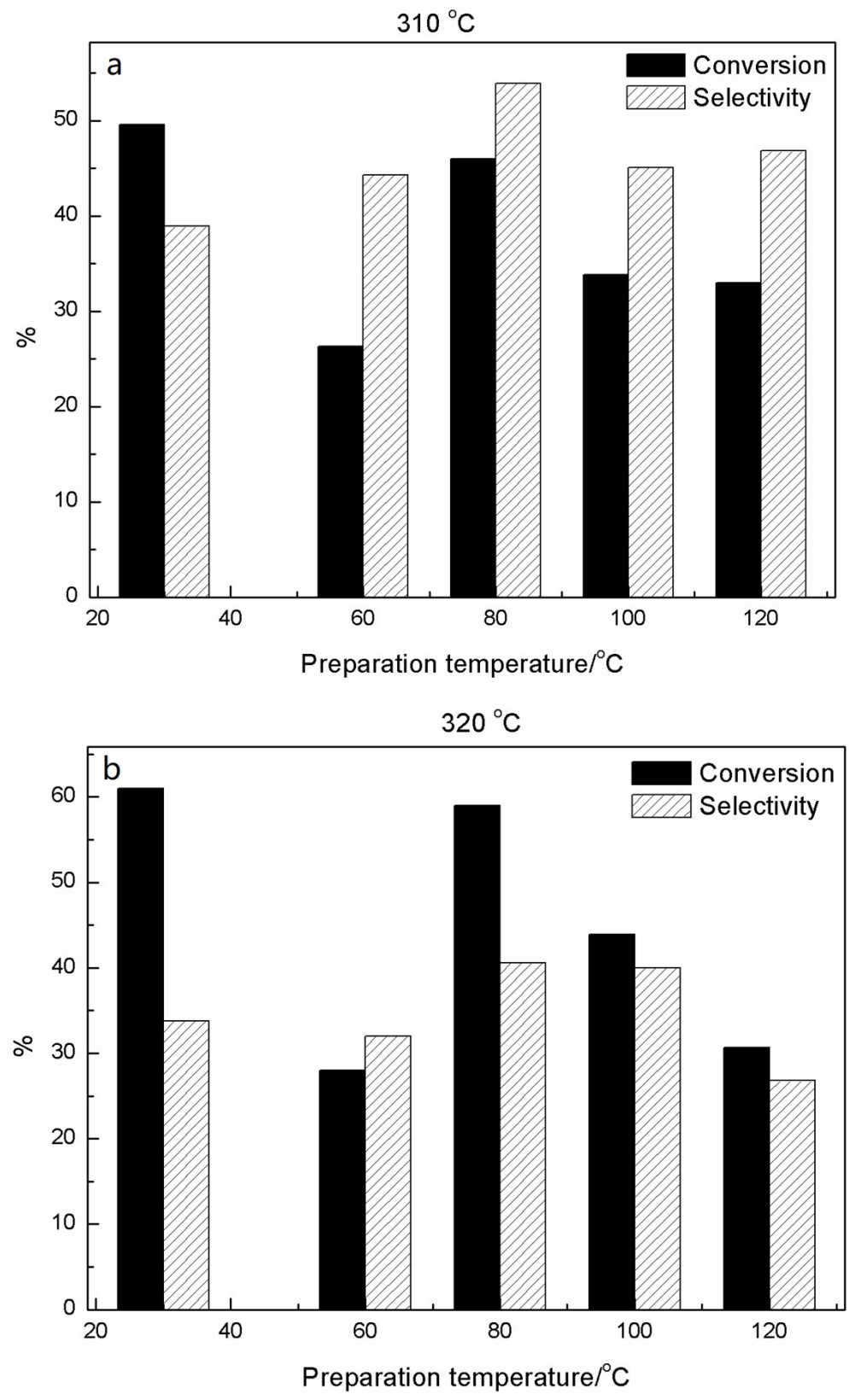


Figure S31. Effect of synthesis temperature on MAL conversion and MAA selectivity over 2HPMV/CN-SBA at reaction temperatures of (a) 310 °C and (b) 320

°C. The volume ratio of MAL, O_2 and H_2O in the reactant stream were 4.4 vol.%, 11.1 vol.%, 17.8 vol.%, respectively, N_2 balance.

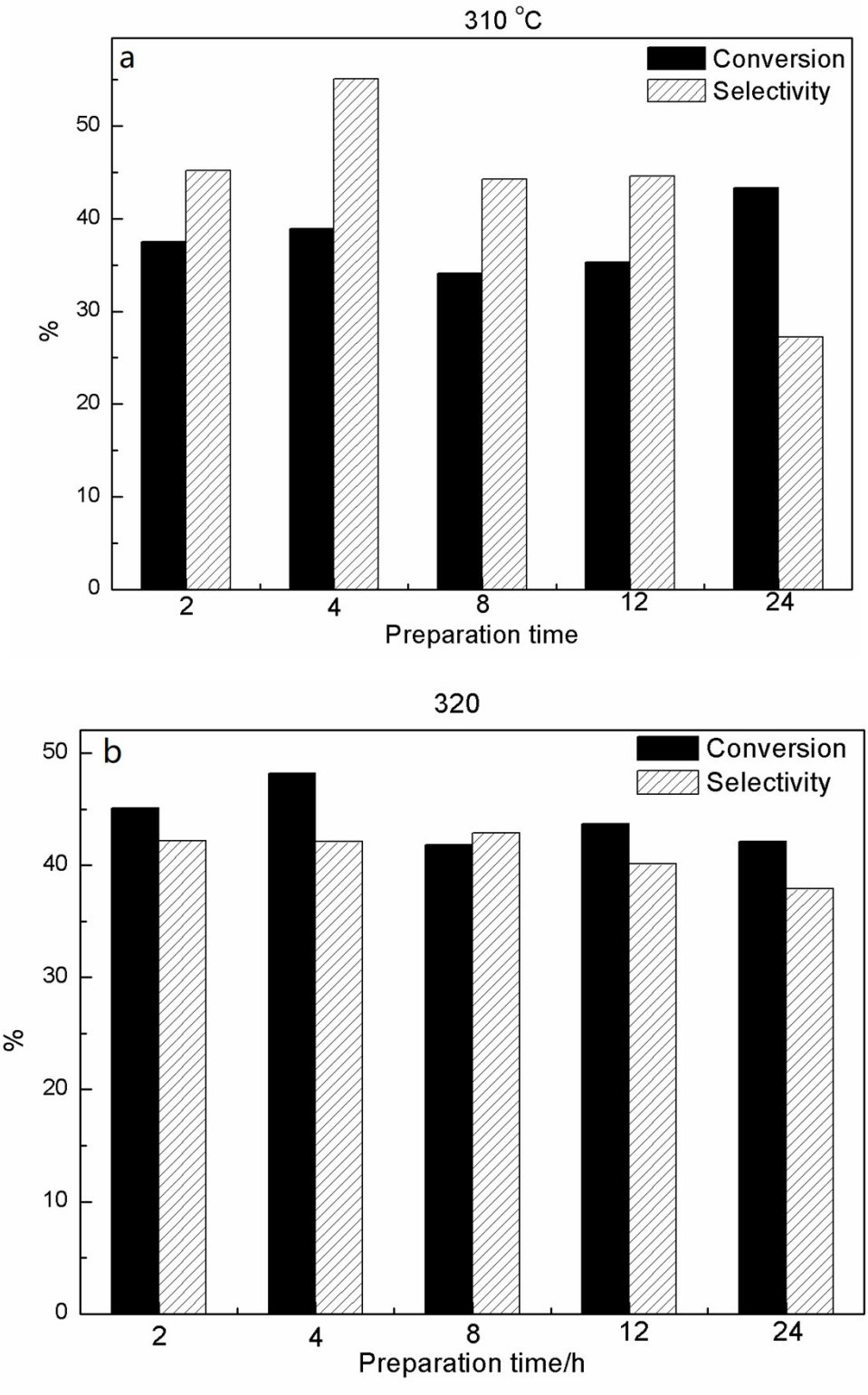


Figure S32. Effect of mixing time during synthesis on MAL conversion and MAA selectivity over 2HPMV/CN-SBA at reaction temperatures of (a) 310 °C and (b)

320 °C. The volume ratio of MAL, O_2 and H_2O in the reactant stream were 4.4 vol.%, 11.1 vol.%, 17.8 vol.%, respectively, N_2 balance.

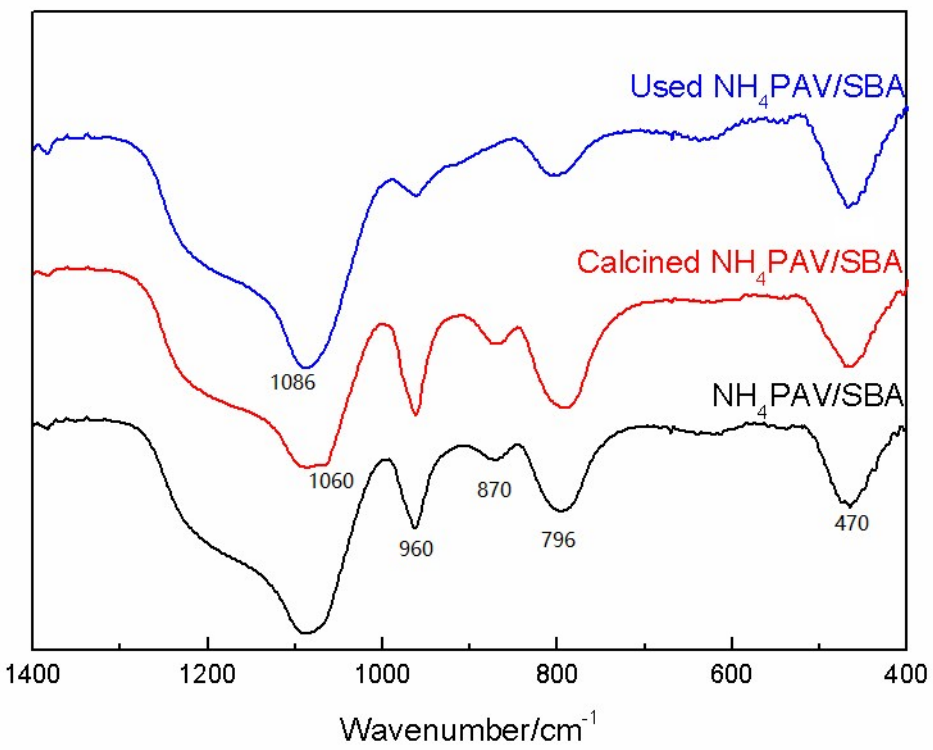


Figure S33. FT-IR spectra of NHPMV/SBA before calcination, after calcination and post-reaction. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h. Reaction conditions were: the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1, and 17.8, with the balance N_2 at 310 °C with 16 h.

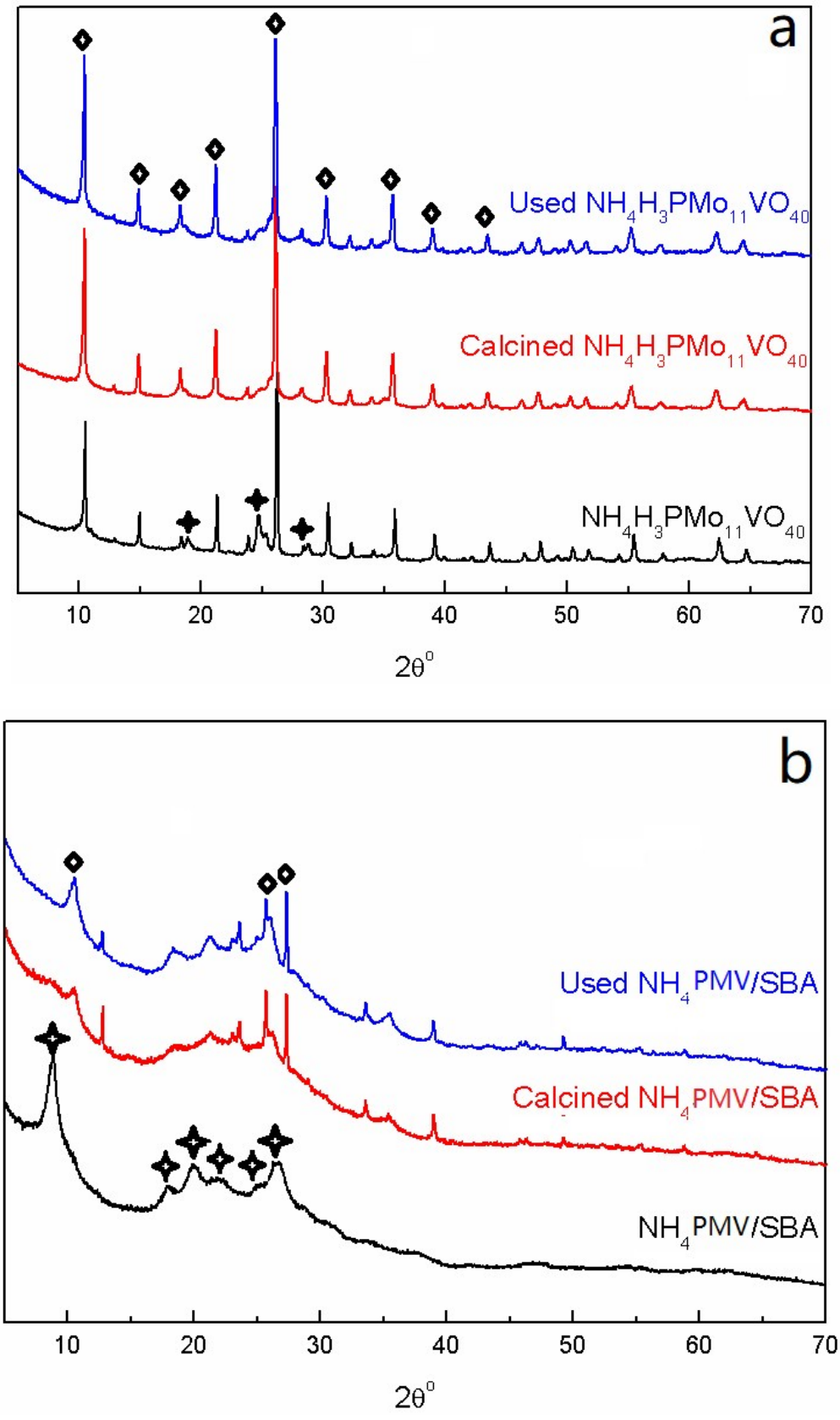


Figure S34. XRD patterns of NH_4PMV, NH_4PMV/SBA before calcination, after calcination and post-reaction. Catalysts were prepared at 80 °C with 2 h mixing and

calcined at 360 °C for 12 h. Reaction conditions were the volume percent (vol.%) of MAL, O_2 and H_2O in the reactant stream was 4.4, 11.1, and 17.8, with the balance N_2 at 310 °C with 16 h.. Peak identification: quadrangular star = HPAV ◇ = $(NH_4)xH_{4-x}PMo_{11}VO_{40}$.

Table S3. Weak and strong acid sites and amount of each for calcined neat HPMV, neat NH_4PMV and HPMV/CN-SBA catalysts with different HPMV loadings. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h.

Catalysts	*Weak acid sites (°C)*	*Acid amount 1 (mmol/g)*	*Strong acid sites (°C)*	*Acid amount 2 (mmol/g)*
0.5HPMV/CN-SBA	115	0.176	448	0.156
1HPMV/CN-SBA	116	0.151	445	0.287
2HPMV/CN-SBA	127	0.081	453	0.376
3HPMV/CN-SBA	113	0.127	456	0.373
4HPMV/CN-SBA	213	0.123	459	0.390
5HPMV /CN-SBA	110	0.167	459	0.410
HPMV	114	0.396	467	0.298
NH_4PMV	113	0.148	471	0.340

Table S4. $(NH_4)_xH_{4-x}$PMV crystal diameter for calcined HPMV/CN-SBA catalysts with different HPMV loadings. Catalysts were prepared at 80 °C with 2 h mixing and calcined at 360 °C for 12 h. Values determined from XRD profiles using Scherrer equation.

Catalysts	*Crystalline diameter/nm*
0.5HPAV/C_3N_4-SBA	24.4
1HPAV/C_3N_4-SBA	28.3
2HPAV/C_3N_4-SBA	59.8
3HPAV/C_3N_4-SBA	64.1
4HPAV/C_3N_4-SBA	68.4
5HPAV/C_3N_4-SBA	72.1