

## Supplementary

### **Continuous methyl acrylate and acrylic acid making via co-activation reaction of aldehyde condensation and esterification catalyzed by siloxane-functionalized Vanadium Phosphorus Oxide-TiO<sub>2</sub> catalyst**

Jun Liu,<sup>ab</sup> Youjun Yan,<sup>a</sup> Meng Lian,<sup>a</sup> Yongqi Yang,<sup>a</sup> Hongchen Du,<sup>a</sup> Fangfang Liu,<sup>a</sup> Rongkai Pan,<sup>a</sup> Xinzhen Feng<sup>\*b</sup> and Weijie Ji<sup>b</sup>

a. Shandong Engineering Laboratory for Clean Utilization of Chemical Resources, Weifang University of Science and Technology, Weifang 262700, China.

b. Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, P. R. China.

### Catalyst preparation details

Benzyl alcohol was employed as the preparation media.  $V_2O_5$  was first refluxed in benzyl alcohol at 140 °C for 5 h, after that certain amount of PEG-6000 was introduced. One hour later, phosphoric acid (85%) was added drop wise to reach a P/V atomic ratio being 1.05/1.0. The suspension was refluxed for another 6 h, and then the solid was filtered out, and washed with acetone. It was further dried at 100 °C in air for 24 h to obtain catalyst precursor.

The precursor was activated at 400 °C for 15 h under a flowing  $O_2$  atmosphere (40 mL/min). The  $\delta$ -VOPO<sub>4</sub> phase were obtained.

The precursor was activated at 680 °C for 12 h under a flowing atmosphere (75%  $O_2/N_2$ , 60 mL/min). The  $\gamma$ -VOPO<sub>4</sub> phase were obtained.

Wet-solid mechanochemical method details. The wet-solid mechanochemical method was enforced by a mechanical ball-milling process. In the mechanical ball-milling process, stoichiometric  $\gamma$ -VOPO<sub>4</sub>,  $\delta$ -VOPO<sub>4</sub>, TiO<sub>2</sub>, and silane coupling agent (trimethoxy allyl silane or  $\gamma$ -glycidoxy propyl trimethoxy silane) were added into a 50 mL agate jar, then 50 little agate balls were added and 25 mL methyl alcohol was served as milling medium, finally the mixture was ball-milled for 12 h.

MCF-supported VPO samples were prepared via a simple impregnation approach which does not employ any organic solvent.  $NH_4VO_3$  of 2.34 g was dissolved in 90 mL deionized water, then certain amount of MCF was added at a V/Si atomic ratio of 1/2. Being stirred at 90 °C for 6 h, phosphoric acid (85%) with an atomic P/V ratio being 1 was added into the solution. 20 minutes later, the brown mixture was dried at 60 °C under vacuum, further calcined at 400 °C for 16 h in an air flow (60 mL/min).

### Characterization details

XPS. The binding energy (BE) was calibrated against the C1s signal (284.6 eV) of contaminant carbon. Elemental surface composition was estimated on the basis of peak areas normalized using Wagner factors. Relative surface concentration of V element with different oxidation state can be estimated through deconvolution analysis of the corresponding XPS peak. For the same batch of sample measured under identical

conditions as well as the same parameters adopted for deconvolution analysis, the  $V^{4+}/V^{5+}$  ratio of different samples is obtainable for comparison.

**NH<sub>3</sub>-TPD.** Catalyst of 50 mg was first heated in an Ar flow (40 mL/min) to 200 °C and kept at this temperature for 1 h. Then the sample was cooled to 100 °C in the Ar flow. After that, NH<sub>3</sub> adsorption was performed at 100 °C for 1 h. Finally, NH<sub>3</sub>-TPD was carried out in an Ar flow (40 mL/min) with the sample being heated to 500 °C at a rate of 10 °C/min. The amount of desorbed NH<sub>3</sub> (in μmol/g) was determined by a titration, in which a HCl solution (0.01 mol/L) was used to absorb the released NH<sub>3</sub>.

**<sup>31</sup>P-NMR.** The <sup>31</sup>P magic angle spinning solid state NMR spectra were recorded on a Bruker AVANCE AVIII WB 400 spectrometer at a resonance frequency of 162.31 MHz with a 4 mm MAS NMR rotor, a pulse width of 20 ms, and a delay time of 5 s between scans were applied.

#### Catalyst evaluation details

All the catalyst powders were pressed, crushed, and sieved to 20-40 mesh for activity evaluation. Two reactors were used for catalyst evaluation, one has an ID of 10 mm without a thermocouple jacket, and the other has an ID of 12 mm with a thermocouple jacket whose outside diameter is 3 mm. The reaction data derived from the two reactors were proved to be reproducible. Catalyst of 3 g was charged into the reactor, and the space above the catalyst bed was filled with quartz chips to preheat the in-coming liquid. Before feedstock introduction, the sample was heated up in a flow of N<sub>2</sub> (30 mL/min) to a desired temperature (360 °C) at a rate of 10 °C/min and kept at this temperature for 2.5 h. When a mixed HAc, HCHO, and CH<sub>3</sub>OH solution (2.5/1/1, n/n/n) was fed into the reactor with a LHSV of 1.33 mL·h<sup>-1</sup> (15.25 mmol·h<sup>-1</sup>, HAc-based), a mixture of N<sub>2</sub> and air (50 mL/min, 3 vol.% O<sub>2</sub> in N<sub>2</sub>) was served as carrier gas. The products were collected in a cold trap. After 2.5-h reaction, the collected liquid sample was analyzed using a gas chromatograph equipped with a flame ion detector (FID) and a HP-FFAP capillary column (0.32 mm × 25 m). Valeric acid and iso-butyl alcohol were used as internal standards for component quantification. All the catalysts were first evaluated by screening their performances in terms of the (MA + AA) Yield in the collected liquid sample based on HAc input. In these circumstances, the off-gas

was on-line analyzed by a GC equipped with TCD and TDX-01 packed column. It is worth noting that the formaldehyde component cannot be measured by GC analysis. In some cases, the unreacted HCHO content was analyzed by the iodometry method. Note that HAc is usually fed significantly excessive in amount over HCHO (in the current study the molar HAc/HCHO/CH<sub>3</sub>OH is 2.5:1:1) to obtain an overall better performance, the by-products such as acetone and CO<sub>x</sub> are mainly originated from HAc, thus the data associated with HAc conversion and particularly (AA + MA) selectivity based on the converted HAc is informative and meaningful to evaluate process economy. In addition, MAc was not regarded as a harmful by-product. In fact, it can continue to react with HCHO to produce AA/MA, thus there is no negative impact on a recycling manufacture process. For this reason, the molar quantity of generated MAc was treated as unreacted HAc when calculating the HAc conversion and (MA+AA) Selectivity (HAc-based).

Selectivity of AA ( $S_{AA}$ ) based on HAc is defined by equation S1:

$$S_{AA} = n_{(AA)equ} / (n_{(HAc)0} - n_{(HAc)measured} - n_{(MeOAc)measured}) \times 100\% \quad (S1)$$

Where  $n_{(AA)equ}$  is the molar quantity of HAc equivalent to AA,  $n_{(HAc)0}$  is the molar quantity of HAc fed into the reactor,  $n_{(HAc)measured}$  is the molar quantity of unreacted HAc, and  $n_{(MeOAc)measured}$  is the molar quantity of generated MeOAc.

Selectivity of MA ( $S_{MA}$ ) based on HAc is defined by equation S2:

$$S_{MA} = n_{(MA)equ} / (n_{(HAc)0} - n_{(HAc)measured} - n_{(MeOAc)measured}) \times 100\% \quad (S2)$$

Where  $n_{(MA)equ}$  is the molar quantity of HAc equivalent to MA,  $n_{(HAc)0}$  is the molar quantity of HAc fed into the reactor,  $n_{(HAc)measured}$  is the molar quantity of unreacted HAc, and  $n_{(MeOAc)measured}$  is the molar quantity of generated MAc.

Conversion of HAc ( $X_{HAc}$ ) is defined by equation S3:

$$X_{HAc} = (n_{(HAc)0} - n_{(HAc)measured} - n_{(MeOAc)measured}) / n_{(HAc)0} \times 100\% \quad (S3)$$

Where  $n_{(HAc)0}$  is the molar quantity of HAc fed into the reactor,  $n_{(HAc)measured}$  is the molar quantity of unreacted HAc, and  $n_{(MeOAc)measured}$  is the molar quantity of generated MeOAc.

Yield of AA and MA ( $Y_{MA+AA}$ ) is defined by equation S4:

$$Y_{MA+AA} = (n_{(MA)equ} + n_{(AA)equ}) / n_{(HAc)0} \times 100\% \quad (S4)$$

Where  $n_{(MA)_{\text{equ}}}$  is the molar quantity of HAc equivalent to MA,  $n_{(AA)_{\text{equ}}}$  is the molar quantity of HAc equivalent to AA,  $n_{(HAc)0}$  is the molar quantity of HAc fed into the reactor.

The carbon balance is calculated by equation S5:

$$\begin{aligned} \text{CB} = & (N_{\text{acetone}} \times n_{\text{acetone}} + N_{\text{methyl acetate}} \times n_{\text{methyl acetate}} + N_{\text{methanol}} \times n_{\text{methanol}} + N_{\text{methyl}} \\ & \text{acrylate} \times n_{\text{methyl acrylate}} + N_{\text{acetic acid}} \times n_{\text{acetic acid}} + N_{\text{acrylic acid}} \times n_{\text{acrylic acid}} + N_{\text{HCHO}} \times n_{\text{HCHO}} + \\ & N_{\text{CO}} \times n_{\text{CO}} + N_{\text{CO}_2} \times n_{\text{CO}_2})_{\text{measured}} / (N_{\text{acetic acid}} \times n_{(\text{acetic acid})0} + N_{\text{HCHO}} \times n_{(\text{HCHO})0} + \\ & N_{\text{methanol}} \times n_{(\text{methanol})0}) \times 100\% \quad (\text{S5}) \end{aligned}$$

Where N is the number of carbon in a specific molecule, n is the mole quantity of each component measured by GC and titration.

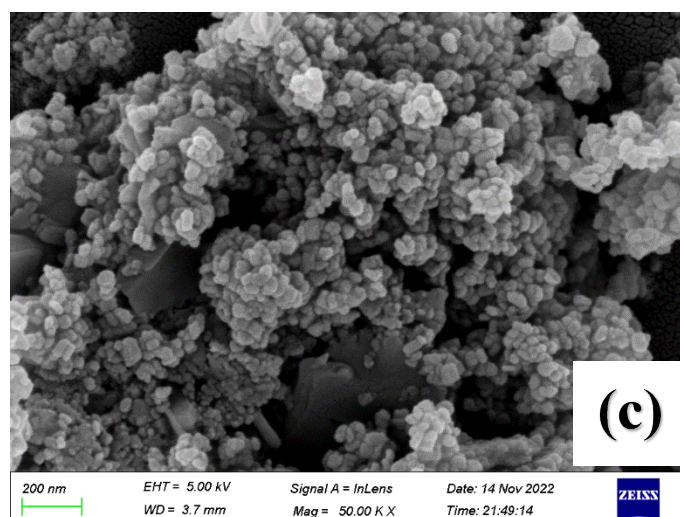
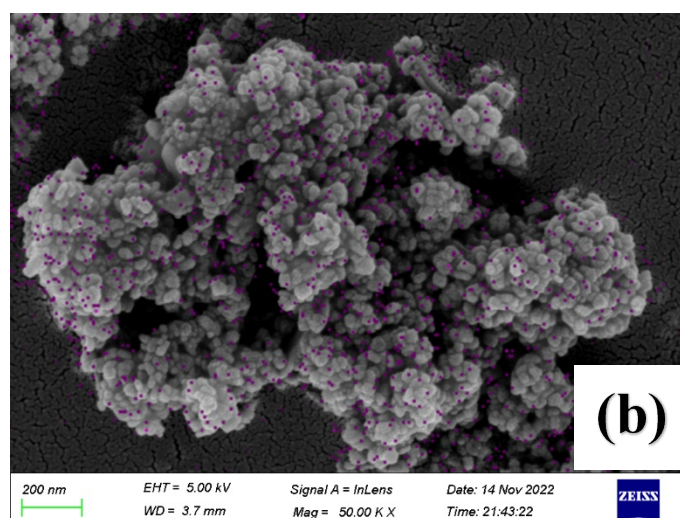
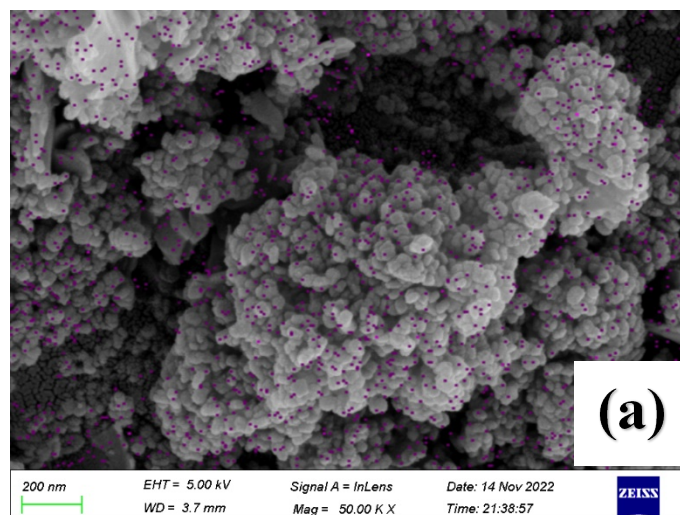


Fig. S1 SEM images of (a) Allyl-Si-V-Ti, (b) Glycidyl-Si-V-Ti, and (c) Unmodified V-Ti. The purple dots correspond to the distribution of Si element on the catalyst surface measured by EDX mapping.

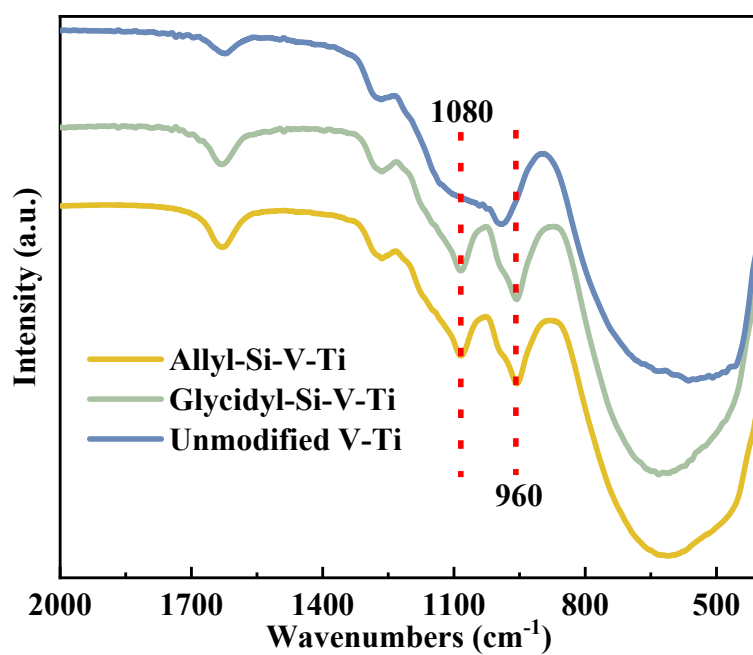


Fig. S2 FT-IR spectra of Allyl-Si-V-Ti, Glycidyl-Si-V-Ti, and Unmodified V-Ti.

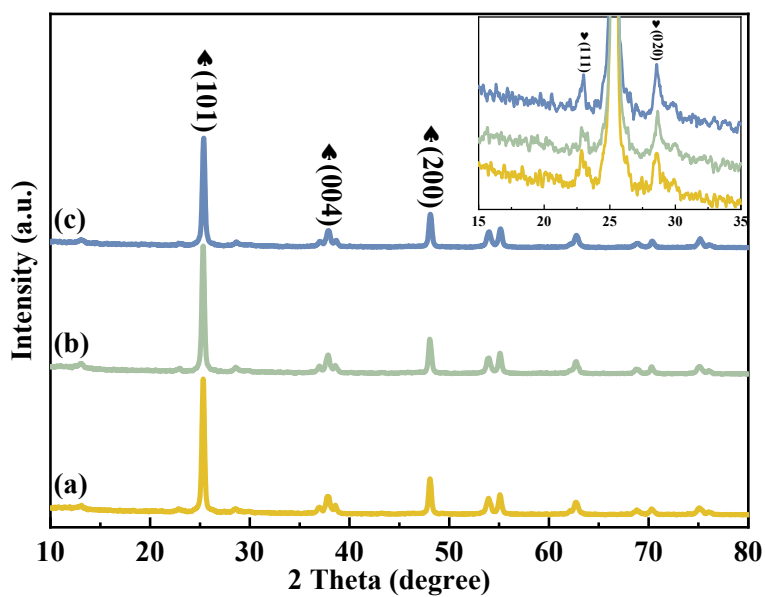


Fig. S3 XRD patterns of (a) Allyl-Si-V-Ti, (b) Glycidyl-Si-V-Ti, and (c) Unmodified V-Ti. ♠:  $\text{TiO}_2$ , ♥:  $\delta\text{-VOPO}_4$ .

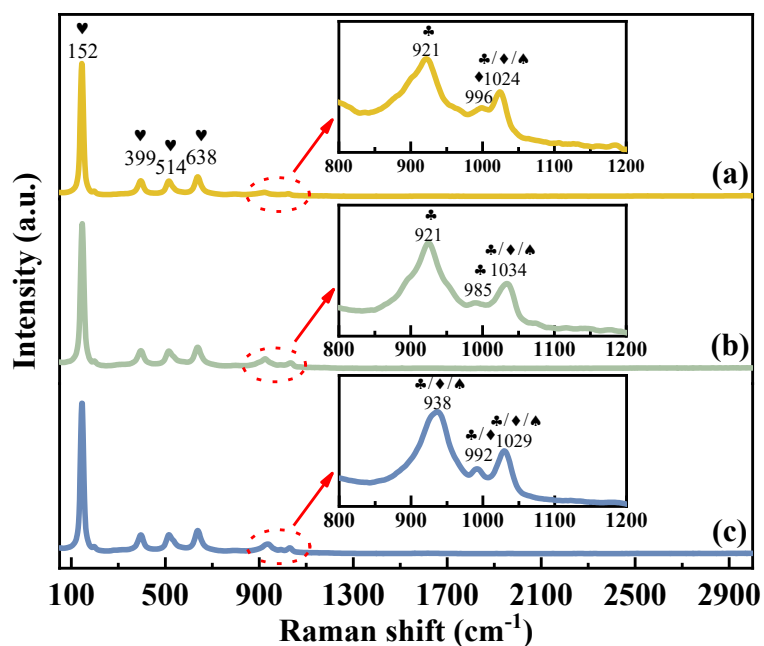


Fig. S4 Raman spectra of (a) Allyl-Si-V-Ti, (b) Glycidyl-Si-V-Ti, and (c) Unmodified V-Ti. ♥:  $\text{TiO}_2$ , ♣:  $(\text{VO})_2\text{P}_2\text{O}_7$ , ♦:  $\gamma\text{-VOPO}_4$ , ♠:  $\delta\text{-VOPO}_4$ .

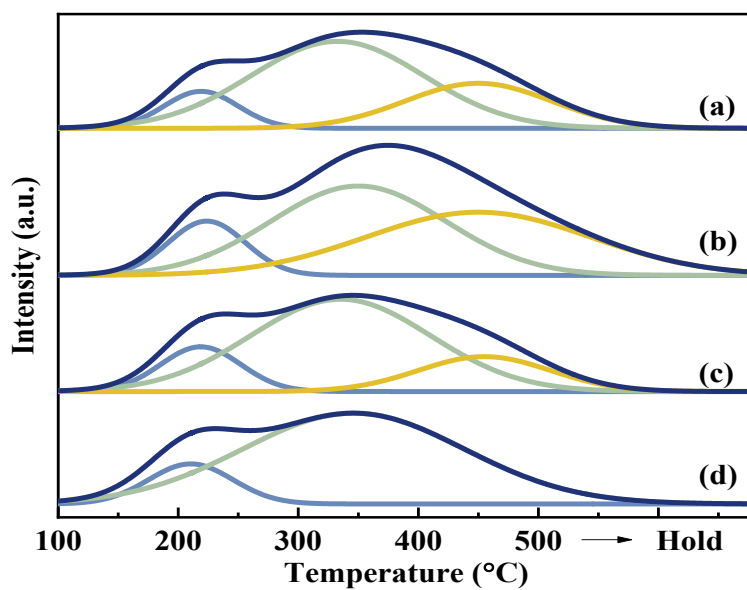


Fig. S5  $\text{NH}_3$ -TPD (Temperature Programmed Desorption) profiles of the catalysts, (a) Allyl-Si-V-Ti, (b) Glycidyl-Si-V-Ti, (c) Unmodified V-Ti, (d) VPO-MCF.



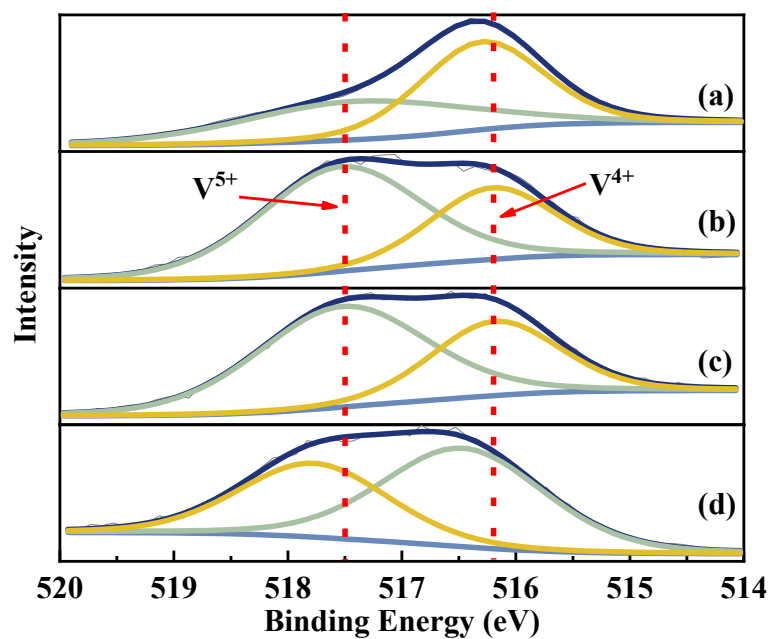


Fig. S6 V  $2p_{3/2}$  curve fitting analysis of the catalysts: (a) VPO-MCF, (b) Allyl-Si-V-Ti, (c) Unmodified V-Ti, and (d) Glycidyl-Si-V-Ti.

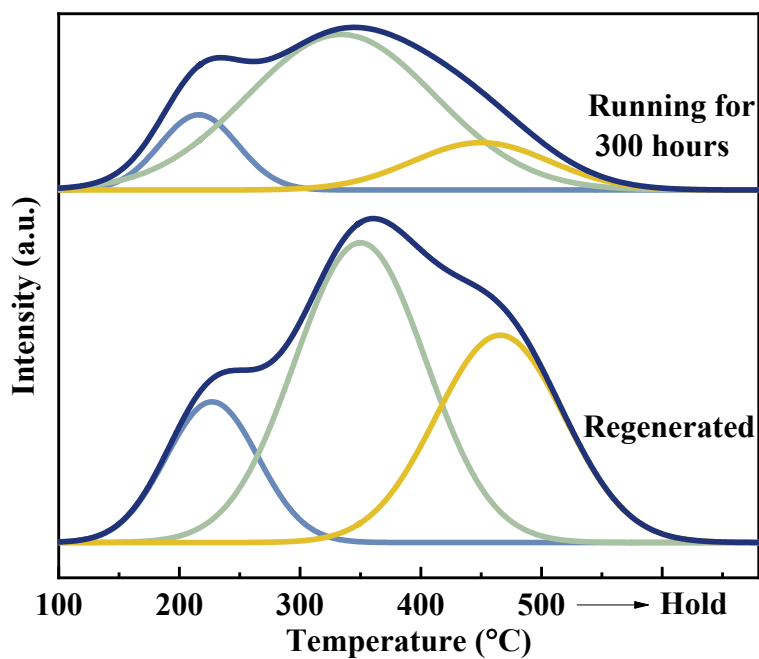


Fig. S7  $\text{NH}_3$ -TPD (Temperature Programmed Desorption) profiles of the used and regenerated catalysts.

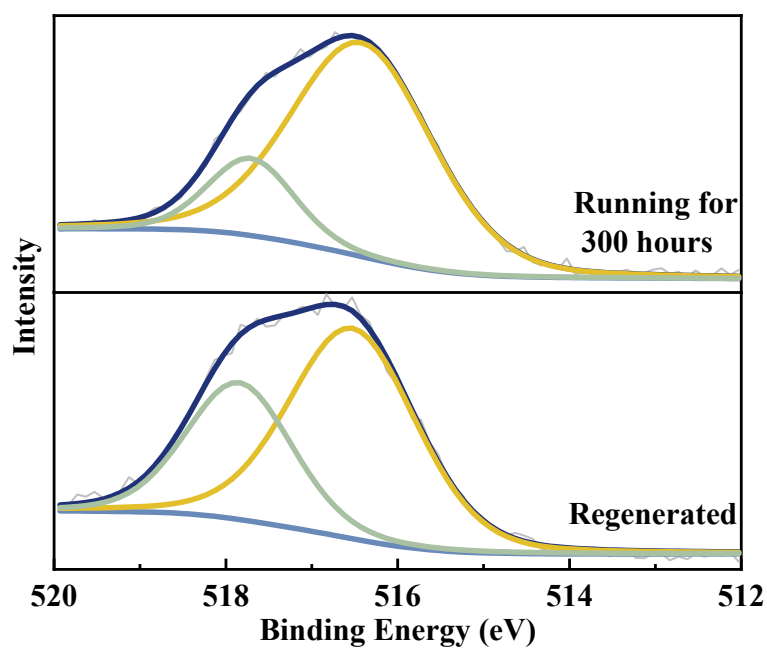


Fig. S8 V 2p<sub>3/2</sub> curve fitting analysis of the used and regenerated catalysts.

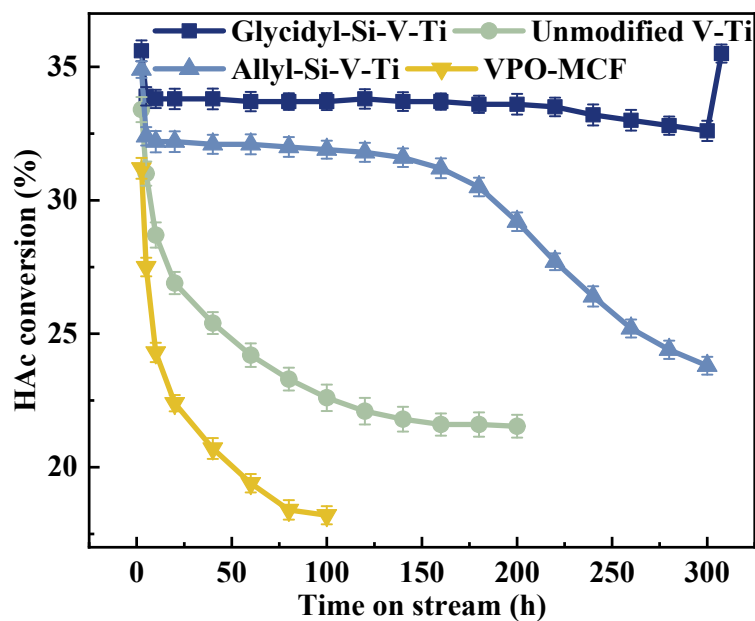


Fig. S9 Durability of HAC conversion versus time on steam. The reaction temperature and carrier flow rate was 360 °C and 50 mL·min<sup>-1</sup> (3.0 vol% O<sub>2</sub> in N<sub>2</sub>), respectively. The liquid feed was a HAC-HCHO-CH<sub>3</sub>OH mixture (2.5/1/1, n/n/n), with a LHSV of 1.33 mL·h<sup>-1</sup>.

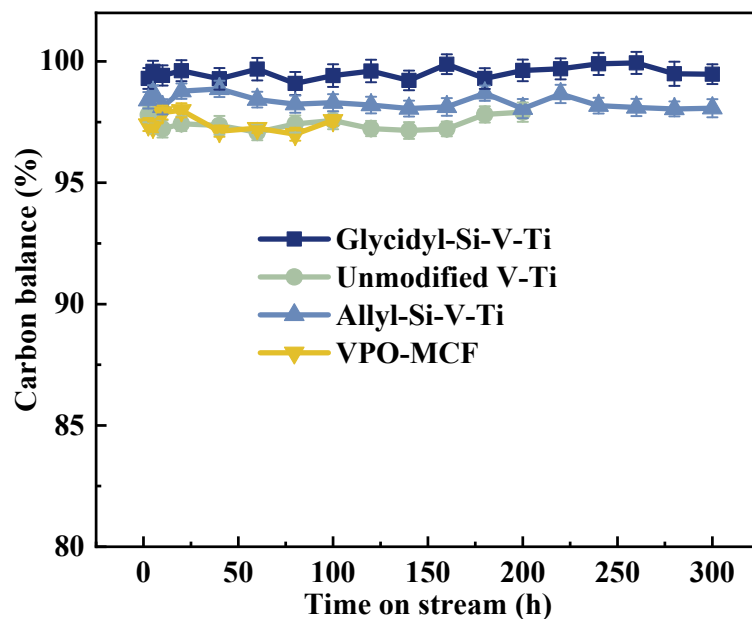


Fig. S10 Durability of carbon balance versus time on steam. The reaction temperature and carrier flow rate was 360 °C and 50 mL·min<sup>-1</sup> (3.0 vol% O<sub>2</sub> in N<sub>2</sub>), respectively. The liquid feed was a HAC-HCHO-CH<sub>3</sub>OH mixture (2.5/1/1, n/n/n), with a LHSV of 1.33 mL·h<sup>-1</sup>.

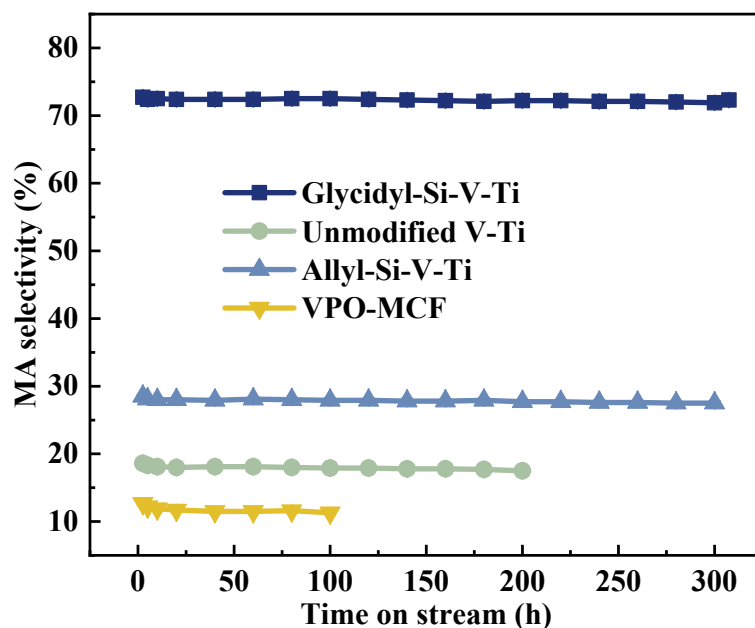


Fig. S11 Durability of MA selectivity versus time on steam. The reaction temperature and carrier flow rate was 360 °C and 50 mL·min<sup>-1</sup> (3.0 vol% O<sub>2</sub> in N<sub>2</sub>), respectively. The liquid feed was a HAC-HCHO-CH<sub>3</sub>OH mixture (2.5/1/1, n/n/n), with a LHSV of 1.33 mL·h<sup>-1</sup>.

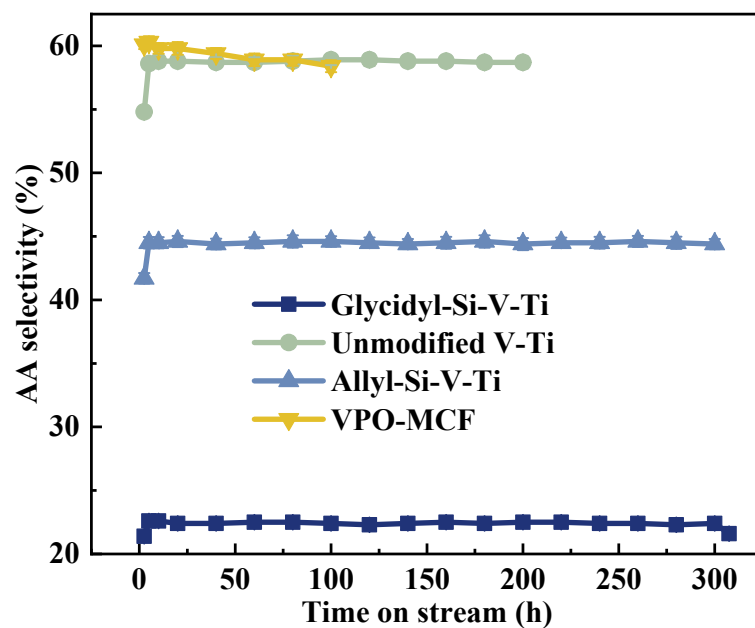


Fig. S12 Durability of AA selectivity versus time on steam. The reaction temperature and carrier flow rate was 360 °C and 50 mL·min<sup>-1</sup> (3.0 vol% O<sub>2</sub> in N<sub>2</sub>), respectively. The liquid feed was a HAC-HCHO-CH<sub>3</sub>OH mixture (2.5/1/1, n/n/n), with a LHSV of 1.33 mL·h<sup>-1</sup>.

**Table S1** The Crystallite size of the catalysts.

Catalysts	Crystallite size (nm)
Unmodified V-Ti	24.8
Glycidyl -Si-V-Ti	32.0
Allyl -Si-V-Ti	18.2

**Table S2** The catalytic performance of the reference catalysts.

Reference	Catalysts	(MA+AA) Yield (%)	(MA+AA) Selectivity (%)	Space-time-yield ( $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ )	Durability (h)
17	(NASICON)-type materials	/	71	37.2	6
18	B <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> nanocomposites	/	87	/	12
19	phase-modulated VPO	84.2 (HCHO-based)	74.4	4	110
20	Ba-La/Al <sub>2</sub> O <sub>3</sub>	/	93.9	/	300
Current work	Glycidyl-Si-V-Ti	33.5	94.1	/	300

**Table S3** XPS results derived of the catalysts.

Catalysts	Relative surface concentration (at %)						P/V	V <sup>4+</sup> /V <sup>5+</sup>
	C	V	P	O	Ti	Si	Ratio	Ratio
<b>Glycidyl -Si-V-Ti</b>	18.0	3.1	6.3	44.0	13.8	14.8	2.0	1.84
<b>Unmodified V-Ti</b>	16.9	2.8	6.2	61.4	12.7	/	2.2	1.88
<b>Allyl -Si-V-Ti</b>	16.7	3.0	6.8	46.1	13.5	13.9	2.3	1.79
<b>VPO -MCF</b>	17.1	2.8	6.5	25.8	12.6	35.2	2.3	0.80

**Table S4** The surface acidity of the catalysts.

Catalysts	Acid site distribution ( $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$ )			Total acidity
	Weak	Medium	Strong	( $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$ )
Running for 300 hours	17.2	85.9	19.2	189.4
Regenerated	38.2	115.6	78.5	196.4

**Table S5** XPS results derived of the catalysts.

<b>Catalysts</b>	<b>Relative surface concentration (at %)</b>						<b>P/V</b>	<b>V<sup>4+</sup>/V<sup>5+</sup></b>
	<b>C</b>	<b>V</b>	<b>P</b>	<b>O</b>	<b>Ti</b>	<b>Si</b>	<b>Ratio</b>	<b>Ratio</b>
Running for 300 hours	38.4	1.6	3.4	42.0	7.8	6.8	2.1	4.54
Regenerated	20.6	2.9	5.8	43.0	13.5	14.2	2.0	1.85