# How to achieve a highly selective yet simply available vanadium phosphorus oxide-based catalyst for sustainable acrylic acid production via acetic acid-formaldehyde condensation

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#### **Experimental details**

**Chemicals.** The following chemicals, ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%), Pluronic P123 triblock copolymer (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, averaged molecular weight = 5800, Alfa Aesar), 1,3,5-trimethylbezene (TMB), tetraethyl orthosilicate (TEOS), ammonium fluoride (NH<sub>4</sub>F), acetic acid ( $\geq$ 99.0%), were purchased in analytical grade. The porous silica spheres with an average pore diameter of 30 nm (Silica-30) and surface area of 100 m<sup>2</sup>/g was purchased from Alfa Aesar. The silica spheres with hierarchical pores (Silica-HP) was commercially obtained, the surface area was 166 m<sup>2</sup>/g and pore diameter 0.5~60 nm. The fumed silica with surface area of 400 m<sup>2</sup>/g was purchased from Aladdin. The commercial HCHO solution (37 wt.%) comprises a small fraction (ca. 8%) of methanol, to stabilize the HCHO component.

**Catalyst preparation.** Firstly, 0.02 mol  $NH_4VO_3$  was dissolved in 90 mL deionized water, then 0.02 mol  $H_3PO_4$  was added under stirring. After that, plenty of yellow precipitate was generated. The water was removed at 60 °C under vacuum and the VPO precursor was obtained.

The MCF and Silica-HP supported VPO samples were prepared via a simple deposition approach which does not employ any organic solvent. 0.02 mol NH<sub>4</sub>VO<sub>3</sub> was dissolved in 90 mL deionized water, then certain amount of MCF/ Silica-HP 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. The MCF support was prepared

according to the procedures described in literature.<sup>23</sup>

The catalyst  $\delta$ -VOPO<sub>4</sub>/ $\gamma$ -VOPO<sub>4</sub> (m/m = 3/1) was prepared according to the procedures described in literature.<sup>15</sup>

### Characterization

X-ray powder diffraction (XRD) and Raman measurements were conducted on the Philips X'Pert MPD Pro X-ray diffractometer and Renishanplc-Reflex Raman spectrometer, respectively.

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 (30 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 (30 mL/min) with the sample being heated to 450 °C at a rate of 10 °C/min. The amount of desorbed NH<sub>3</sub> (in  $\mu$ mol/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>. A NaOH solution (0.01 mol/L) was used as the titrant.

#### **Catalyst evaluation**

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 18 mm without a thermocouple jacket, and the other has an ID of 20 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 at a rate of 10 °C/min and kept at this temperature for 2.5 h. When a mixed solution of HAc and HCHO (molar ratio = 2.5) was fed, a mixture of N2 and air (40 mL/min, 3.9 vol.% O2 in N2) was served as carrier gas. The overall liquid feed rate was 4 mL/h (HCHO feed rate = 18.3 mmol/h). 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  $\times$  25 m). Valeric acid and iso-butyl alcohol were used as internal standards for component quantification. 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, therefore, the unreacted HCHO content was analyzed by the iodometry method.

Yield of AA+MA ( $Y_{AA+MA}$ ) based on HAc is defined by:

$$Y_{AA+MA} = n_{(AA+MA)equ}/n_0 \times 100\%$$

Where  $n_{(AA+MA)equ}$  is the molar quantity of HAc equivalent to (AA+MA),  $n_0$  is

the molar quantity of HAc fed into the reactor.

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

$$S_{AA+MA} = n_{(AA+MA)equ} / (n_{(HAc)0} - n_{(HAc)measured} - n_{(MAc)measured}) \times 100\%$$

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

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

## $X_{HAc} = (n_{(HAc)0} - n_{(HAc)measured} - n_{(MAc)measured})/n_{(HAc)0} \times 100\%$

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  $n_{(MAc)measured}$  is the molar quantity of generated MAc.

The carbon balance is calculated in terms of the following equation:

 $CB (0-2.5 h) = (N_{acetone} \times n_{acetone} + N_{methyl acetate} \times n_{methyl acetate} + N_{methanol} \times n_{methanol} + N_{methyl})$   $acrylate \times n_{methyl acrylate} + N_{acetic acid} \times n_{acetic acid} + N_{acrylic acid} \times n_{acrylic acid} + N_{formaldehyde} \times n_{formaldehyde}$   $+ N_{CO} \times n_{CO} + N_{CO2} \times n_{CO2})_{measured} / (N_{acetic acid} \times n_{0(acetic acid)} + N_{formaldehyde} \times n_{0(formaldehyde)} + N_{methanol} \times n_{0(methanol)}), where N is the number of carbon in a specific molecule, n is the mole quantity of each component measured by GC and titration.$ 



Fig. S1 XRD patterns of the VPO precursor.



Fig. S2 NH<sub>3</sub>-TPD profiles of (a)  $\delta$ -VOPO<sub>4</sub>/ $\gamma$ -VOPO<sub>4</sub> (m/m = 3/1), (b) unsupported VPO, (c) 33%-VPO/Silica-HP, (d) 33%-VPO/MCF.



Fig. S3 XRD patterns of the catalysts. Silica-HP: silica with hierarchical pores;  $\delta$ :  $\delta$ -VOPO<sub>4</sub>;  $\gamma$ :  $\gamma$ -VOPO<sub>4</sub>.



Fig. S4 HAc conversion, (MA+AA) selectivity, carbon balance, and (MA+AA) yield of the catalysts. Silica-30: silica with an average pore diameter of 30 nm.



Fig. S5 (MA+AA) selectivity, carbon balance, (MA+AA) yield and HAc conversion versus time on steam.



Fig. S6 Raman spectra of the catalysts.



Fig. S7 XRD patterns of the catalysts, Silica-30: silica with an average pore diameter of 30 nm.



Fig. S8 NH<sub>3</sub>-TPD profiles of 33%-VPO/Fumed SiO<sub>2</sub> and 33%-VPO/Silica-30.

Catalysts	Acid site distribution (µmol NH <sub>3</sub> /g <sub>cat</sub> )			Total acidity
	Weak	Medium	Strong	(µmol NH <sub>3</sub> /g <sub>cat</sub> )
Unsupported VPO	43.9	77.9	208.2	330.0
33%-VPO/MCF	57.8	108.3	/	166.1
33%-VPO/Silica-HP	48.8	124.7	/	173.5
$\delta$ -/ $\gamma$ -VOPO <sub>4</sub> (m/m=3/1)	61.5	149.7	238.9	450.1

Table S1 Surface acidity of the VPO catalysts determined by means of NH<sub>3</sub>-TPD.

Table S2 Surface acidity of the VPO catalysts determined by means of NH<sub>3</sub>-TPD.

Catalysts	Acid site distribution ( $\mu$ mol NH <sub>3</sub> /g <sub>cat</sub> )			Total acidity
	Weak	Medium	Strong	(µmol NH <sub>3</sub> /g <sub>cat</sub> )
33%-VPO/Fumed silica	20.2	72.6	16.9	109.7
33%-VPO/Silica-30	29.0	96.0	68.6	193.6