Supplementary Information

Highly Efficient Honeycomb Hypocrystalline V-P-C Catalysts for Sustainable Production of Acrylic Acid via Glycerol Dehydration-Oxidation

Xiaobing Zhao,[a] Weichen Wang,[a] Jun Liu, *,[a] Meng Lian,[a] Youjun Yan, [a] Guofu Huang,[a] Yongwei Li[a] and Xinzhen Feng [b]

[a]Peninsula Engineering Research Center of Comprehensive Brine Utilization, 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, China

*e-mail: liujun@wfust.edu.cn

Table S1. H_2-TPR profiles of the catalysts

Catalyst	V^{5+}		V^{4+}		V^{4+}/V^{5+} ratio
	Temp. / ℃	H_2 consumption / (mmol/mol V)	Temp. / ℃	H_2 consumption / (mmol/mol V)	
VPO-PPOA	527	5.28	811	1.53	0.29
VPO-HPAA	538	5.17	821	1.60	0.31
VPO-EDTPMA	499	2.42	822	5.23	2.16

PPOA: phenylphosphonic acid; HPAA: *n*-hexylphosphonic acid; EDTPMA: ethylenediamine tetramethylphosphonic acid.

Table S2. Elemental composition of the catalysts

Catalyst	C / %	N / %	O / %	P / %	V / %
VPO-PPOA	48.33	0	42.61	5.77	3.29
VPO-HPAA	52.93	0	35.85	7.06	4.17
VPO-EDTPMA	48.52	0	40.29	6.18	5.02

PPOA: phenylphosphonic acid; HPAA: *n*-hexylphosphonic acid; EDTPMA: ethylenediamine tetramethylphosphonic acid.

Table S3. XPS results of V 2p for the catalysts

Catalyst	V^{5+} / %	V^{4+} / %
VPO-PPOA	68.7	31.3
VPO-HPAA	69.8	30.2
VPO-EDTPMA	40.5	59.5

PPOA: phenylphosphonic acid; HPAA: *n*-hexylphosphonic acid; EDTPMA: ethylenediamine tetramethylphosphonic acid.

Table S4. XPS results of O 1s for the catalysts

Catalyst	O_L / %	O_V / %
VPO-PPOA	70.9	29.1
VPO-HPAA	70.8	29.2
VPO-EDTPMA	56.8	43.2

PPOA: phenylphosphonic acid; HPAA: *n*-hexylphosphonic acid; EDTPMA: ethylenediamine tetramethylphosphonic acid.

Table S5. The surface acidity of the catalysts

Catalyst	Acid site distribution / (μmol NH_3 g_{cat}^{-1})			Total acidity / (μmol NH_3 g_{cat}^{-1})
	Weak	Medium	Strong	
VPO-PPOA	10.64	42.26	50.90	0.29
VPO-HPAA	7.86	36.67	40.86	0.31
VPO-EDTPMA	18.32	59.74	–	2.16

PPOA: phenylphosphonic acid; HPAA: *n*-hexylphosphonic acid; EDTPMA: ethylenediamine tetramethylphosphonic acid.

Table S6. Catalytic activity of the catalysts

Catalyst		Conversion / %	Selectivity / %	Carbon balance / %
Catalyst precursor	VPO-PPOAA	6.80 ± 0.52	5.38 ± 0.08	95.35 ± 0.54
	VPO-HPAAA	10.45 ± 0.48	8.74 ± 0.06	93.04 ± 0.21
	VPO-EDTPMA	4.97 ± 0.55	7.35 ± 0.08	96.83 ± 0.38
Activated catalyst	VPO-PPOAA	96.34 ± 0.87	41.73 ± 0.38	87.23 ± 0.36
	VPO-HPAAA	90.86 ± 0.69	44.25 ± 0.42	88.21 ± 0.42
	VPO-EDTPMA	89.04 ± 0.71	53.37 ± 0.44	93.32 ± 0.39

PPOA: phenylphosphonic acid; HPAA: *n*-hexylphosphonic acid; EDTPMA: ethylenediamine tetramethylphosphonic acid.

Table S7. Literature data for the gas-phase conversion of glycerol over the acid catalysts

Reference	Catalyst	Conversion / %	Selectivity / %	Formation rate / ($mmol^{-1}$ g^{-1} h^{-1})
1	Mo-V	100	57	9.28
2	V/H-b	87.6	46.3	–
3	Mo-V	100	33.5	5.50
4	$Mo_xV_yO_z$	97	32	5.05
Current	VPO-EDTPMA	90	53.4	26.0

EDTPMA: ethylenediamine tetramethylphosphonic acid.

References

1. Rasteiro, L. F.; Vieira, L. H.; Santilli, C. V.; Martins, L.; *RSC Adv.* **2018**, *8*, 11975. [Crossref]
2. Silva, T. Q.; dos Santos, M. B.; Santiago, A. A. C.; Santana, D. O.; Cruz, F. T.; Andrade, H. C. S.; Mascarenhas, A. J. S.; *Catal. Today* **2017**, *289*, 38. [Crossref]
3. Rasteiro, L. F.; Vieira, L. H.; Possato, L. G.; Pulcinelli, S. H.; Santilli, C. V.; Martins, L.; *Catal. Today* **2017**, *296*, 10. [Crossref]
4. Possato, L. G.; Cassinelli, W. H.; Meyer, C. I.; Garetto, T.; Pulcinelli, S. H.; Santilli, C. V.; Martins, L.; *Appl. Catal., A* **2017**, *532*, 1. [Crossref]