Electronic Supplementary Information (ESI†)

Selective catalytic oxidation of benzene to phenol by a vanadium oxide (V$_{nr}$) nanorod catalyst in CH$_3$CN using H$_2$O$_{2(aq)}$ and pyrazine-2-carboxylic acid (PCA)

Wondemagegn Hailemichael Wanna,[a,b] Damodar Janmanchi,[a] Natarajan Thiyagarajan,[a] Ravirala Ramu,[a,c] Yi-Fang Tsai,[a] Chih-Wen Pao,[d] and Steve S.-F. Yu[a,b,]*

From [a]Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan
[b]Sustainable Chemical Science and Technology, Taiwan International Graduate Program (TIGP), National Chiao-Tung University and Academia Sinica, Taiwan
[c]Sree Dattha Institute of Engineering & Science, Hyderabad, Telangana, India-501510
[d]National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan

*corresponding author:
 E-mail address: sfyu@gate.sinica.edu.tw

Table S1. Oxidation of benzene to *p*-benzoquinone (*p*-BQ) and phenol (PhOH) catalyzed by the various vanadium catalysts.[a]

Catalyst	TON[b]		Total TON[c]	Y_S [%][d]	Y_O [%][e]	OCE [%][f]	PhOH [%][g]	H_2O_2 (%) remained
	p-BQ	PhOH						
V_{nr}	1.75	11.74	13.49	4.21	7.03	12.10	87.03	25
V_{nr} (PCA)	1.30	25.54	26.83	8.37	13.99	63.93	95.17	77
V_2O_5	0.18	5.19	5.37	1.68	2.80	4.91	96.62	41
V_2O_5 (PCA)	0.55	9.58	10.13	3.16	5.28	8.97	94.59	38
$VOSO_4$	0.78	8.38	9.16	2.86	4.78	6.50	91.46	20
$VOSO_4$ (PCA)	0.58	9.11	9.70	3.03	5.06	7.56	94.00	29
VCl_3	0.68	6.12	6.80	2.12	3.55	13.13	89.98	70
VCl_3 (PCA)	0.48	6.93	7.41	2.31	3.86	12.14	93.50	66

[a]Conditions: Total volume of the reaction solution was 3 mL; Solvent: acetonitrile; Catalyst: V_{nr}/V_2O_5/$VOSO_4$/VCl_3 (0.014 mmol); Substrate: benzene (4.486 mmol); Oxidant: 35% H_2O_2(aq) (2.685 mmol); PCA (0.04 mmol); Temperature: 25 °C; Time: 5 h. Product quantification was conducted by GC analysis with nitrobenzene as the internal standard. [b]Turnover number (TON) for each of the oxygenated products, *p*-BQ and PhOH (mmol), respectively, was determined by calculating the number of millimoles of product per millimole of catalyst (based on V content). [c]The total TON of the products (*p*-BQ + PhOH). [d]Y_S [%]$_c$ = [substrate (mol)/H_2O_2 (mol)]×100. [e]Y_O [%]$_c$ = [products (mol)/H_2O_2 (mol)]×100. [f]Overall catalytic efficiency (OCE) = (2×*p*-BQ + PhOH)[TON]/[H_2O_2 consumed (equiv.)]. [g]Selectivity of PhOH = [(PhOH) (mol)/ [*p*-BQ + PhOH] (mol)]×100.

Table S2. Oxidation of benzene to *p*-benzoquinone (*p*-BQ) and phenol (PhOH) catalyzed by the vanadium oxide nanorod catalyst (**V$_{nr}$**) using various H$_2$O$_{2(aq)}$ concentrations.[a]

35%H$_2$O$_2$ (mmol)	TON[b] *p*-BQ	TON[b] PhOH	Total TON[c]	Y_S [%][d]	Y_O [%][e]	OCE [%][f]	PhOH [%][g]	H$_2$O$_2$ (%) remained
0.31	0.06	2.34	2.40	0.75	10.85	13.69	97.42	18
0.67	0.08	13.14	13.22	4.12	27.62	37.98	99.43	27
1.34	0.09	16.99	17.09	5.33	17.85	31.23	99.46	42
2.68	1.30	25.54	26.83	8.37	13.99	63.93	95.17	77
4.64	0.21	6.71	6.92	2.16	2.09	10.35	96.90	79
9.28	0.13	8.26	8.38	2.62	1.26	10.77	98.47	88

[a]Conditions: Total volume of the reaction solution was 3 mL, Solvent: acetonitrile; Catalyst: V$_{nr}$ (V content: 0.014 mmol), Substrate: benzene (4.486 mmol); PCA (0.04 mmol), Temperature: 25 °C; Time: 5 h. Product quantification was conducted by GC analysis with nitrobenzene as the internal standard; [b]Turnover number (TON) for each of the oxygenated products, *p*-BQ and PhOH (mmol), respectively, was determined by calculating the number of millimoles of product per millimole of catalyst (based on V content). [c]The total TON of the products (*p*-BQ + PhOH). [d]Ys [%]$_c$ = [substrate (mol)/H$_2$O$_2$ (mol)]×100. [e]Y$_O$ [%]$_c$ = [products (mol)/H$_2$O$_2$ (mol)]×100. [f]Overall catalytic efficiency (OCE) = (2×*p*-BQ + PhOH)[TON]/[H$_2$O$_2$ consumed. [g]Selectivity of PhOH = [(PhOH) (mol)/ [*p*-BQ + PhOH] (mol)]×100. (equiv.)]

Table S3. Oxidation of benzene to *p*-benzoquinone (*p*-BQ) and phenol (PhOH) catalyzed by the vanadium oxide nanorod catalyst (**V**$_{nr}$) using various $H_2O_{2(aq)}$ percentages.[a]

| % H$_2$O$_2$ | TON[b] | | Total TON[c] | Y_S [%][d] | Y_O [%][e] | OCE [%][f] | PhOH [%][g] | H$_2$O$_2$ (%) remained |
	p-BQ	PhOH						
5	0.09	3.32	3.42	1.07	12.45	25.07	97.26	49
10	0.16	7.03	7.19	2.24	13.13	28.29	97.73	52
20	0.23	10.81	11.04	3.45	10.08	28.92	97.88	64
35	1.30	25.54	26.83	8.37	13.99	63.93	95.17	77

[a]Conditions: Total volume of the reaction solution was 3 mL; Solvent: acetonitrile; Catalyst: V$_{nr}$ (V content: 0.014 mmol), Substrate: benzene (4.486 mmol); H$_2$O$_{2(aq)}$ (260 µL); PCA (0.04 mmol); Temperature: 25 °C; Time: 5 h. The products were determined using GC analysis with nitrobenzene as the internal standard. [b]Turnover number (TON) for each of the oxygenated products, *p*-BQ and PhOH (mmol), respectively, was determined by calculating the number of millimoles of product per millimole of catalyst (based on V content). [c]The total TON of the products (*p*-BQ + PhOH). [d]Y_S [%]$_c$ = [substrate (mol)/H$_2$O$_2$ (mol)]×100. [e]Y_O [%]$_c$ = [products (mol)/H$_2$O$_2$ (mol)]×100. [f]Overall catalytic efficiency (OCE) = (2×*p*-BQ + PhOH)[TON]/[H$_2$O$_2$ consumed (equiv.)]. [g]Selectivity of PhOH = [(PhOH) (mol)/ [*p*-BQ + PhOH] (mol)]×100.

Table S4. Oxidation of benzene to *p*-benzoquinone (*p*-BQ) and phenol (PhOH) catalyzed by the vanadium oxide nanorod catalyst (V_{nr}) in presence of PCA.[a]

Time (h)	TON[b] *p*-BQ	TON[b] PhOH	Total TON[c]	Y_S [%][d]	Y_O [%][e]	OCE [%][f]	PhOH [%][g]	H_2O_2 (%) remained
1 min	0.21	0.45	0.67	0.21	0.35	21.95	68.26	98
10 min	0.30	2.33	2.63	0.82	1.37	22.51	88.65	93
20 min	0.34	2.64	2.99	0.93	1.56	19.60	88.45	91
30 min	0.44	2.74	3.18	0.99	1.66	17.22	86.21	89
45 min	0.53	3.21	3.74	1.17	1.95	17.79	85.78	87
1	0.69	9.83	10.52	3.28	5.48	41.49	93.45	86
2	1.09	21.39	22.48	7.01	11.72	69.31	95.16	82
3	1.36	23.03	24.39	7.61	12.72	71.53	94.43	81
5	1.30	25.54	26.83	8.37	13.99	63.93	95.17	77
10	1.26	27.23	28.49	8.89	14.85	39.65	95.59	61
18	0.82	27.23	28.05	8.75	14.62	26.48	97.08	43
24	0.57	27.48	28.04	8.75	14.62	24.88	97.97	40
48	0.37	28.36	28.73	8.97	14.98	21.39	98.72	29

[a]Conditions: Total volume of the reaction solution was 3 mL; Solvent: acetonitrile; Catalyst: V_{nr} (V content: 0.014 mmol); Substrate: benzene (4.486 mmol); Oxidant: 35% $H_2O_{2(aq)}$ (2.685 mmol); PCA (0.04 mmol); Temperature: 25 °C. The products were determined using GC analysis with nitrobenzene as the internal standard. [b]Turnover number (TON) for each of the oxygenated products, *p*-BQ and PhOH (mmol), respectively, was determined by calculating the number of millimoles of product per millimole of catalyst (based on V content). [c]The total TON of the products (*p*-BQ + PhOH). [d]Y_s [%]$_c$ = [substrate (mol)/H_2O_2 (mol)]×100. [e]Y_O [%]$_c$ = [products (mol)/H_2O_2 (mol)]×100. [f]Overall catalytic efficiency (OCE) = (2×*p*-BQ + PhOH)[TON]/[H_2O_2 consumed (equiv.)]. [g]Selectivity of PhOH = [(PhOH) (mol)/ [*p*-BQ + PhOH] (mol)]×100.

Table S5. Oxidation of benzene to *p*-benzoquinone (*p*-BQ) and phenol (PhOH) catalyzed by the recycled vanadium oxide nanorod catalyst (**V_nr**).[a]

Catalyst	TON[b] *p*-BQ	TON[b] PhOH	Total TON[c]	Y_S [%][d]	Y_O [%][e]	OCE [%][f]	PhOH [%][g]	H_2O_2 (%) remained
V_nr(w/o PCA)	1.75	11.74	13.49	4.21	7.03	12.10	87.03	25
V_nr + (PCA)	1.30	25.54	26.83	8.37	13.99	63.93	95.17	77
1st recycled **V_nr** (w/o PCA)	1.65	15.73	17.38	5.42	9.06	12.49	90.50	32
1st recycled **V_nr** + (PCA)	2.04	20.34	22.38	6.99	11.67	31.15	90.88	65
2nd recycled **V_nr** (w/o PCA)	1.89	16.85	18.74	5.85	9.77	13.42	90.00	37
2nd recycled **V_nr** + (PCA)	2.14	20.75	22.90	7.15	11.94	22.30	92.72	54
V_nr leaching	-	1.75	1.75	0.03	0.05	2.32	100	57

[a]Conditions: Total volume of the reaction solution was 3 mL; Solvent: acetonitrile; **V_nr** (V content: 0.014 mmol), 1st recycled **V_nr** (V content: 0.012 mmol) ; 2nd recycled **V_nr** (V content: 0.011mmol), the leached **V_nr** (V content: 8.4×10^{-4} mmol), Substrate: benzene (4.486 mmol); Oxidant: 35% $H_2O_{2(aq)}$ (2.685 mmol); PCA (0.04 mmol); Temperature: 25 °C; Time: 5 h. The products were determined using GC analysis with nitrobenzene as the internal standard. [b]Turnover number (TON) for each of the oxygenated products, *p*-BQ and PhOH (mmol), respectively, was determined by calculating the number of millimoles of product per millimole of catalyst (based on V content). [c]The total TON of the products (*p*-BQ + PhOH). [d]Y_s [%]$_c$ = [substrate (mol)/H_2O_2 (mol)]×100. [e]Y_O [%]$_c$ = [products (mol)/H_2O_2 (mol)]×100. [f]Overall catalytic efficiency (OCE) = (2×*p*-BQ + PhOH)[TON]/[H_2O_2 consumed (equiv.)]. [g]Selectivity of PhOH = [(PhOH) (mol)/ [*p*-BQ + PhOH] (mol)]×100.

Table S6. Oxidation of toluene to benzaldehyde (**a**), methyl *p*-benzoquinone (**b**) benzyl alcohol (**c**), *o*-cresol (**d**), and *p*-cresol (**e**) catalyzed by the vanadium oxide nanorod catalyst (V_{nr}).[a]

Catalyst	TON[b]					Total TON[c]	Y_S [%][d]	Y_0 [%][e]	OCE [%][f]	sp^2/sp^3 [%][g]	H_2O_2 (%) remained
	a	**b**	**c**	**d**	**e**						
V_{nr}	3.33	0.74	0.36	1.01	1.13	6.57	2.06	3.43	8.06	44/56	33
V_{nr} (PCA)	6.9	4.6	1.64	4.02	3.41	20.57	6.44	10.73	25.05	58/42	31
V_{nr} (PCA,PPh₃)[h]	4.5	-	3.67	3.82	3.64	15.62	4.89	8.14	12.05	48/52	13

[a]Conditions: Total volume of the reaction solution was 3 mL; Solvent: acetonitrile; V_{nr} (V content: 0.014 mmol); Substrate: toluene (4.47 mmol); Oxidant: 35% $H_2O_{2(aq)}$ (2.685 mmol); PCA (0.04 mmol); Temperature: 25 °C; Time: 5 h. The products were determined using GC analysis with nitrobenzene as the internal standard. [b]Turnover number (TON) for each of the oxygenated products, **a–e** (mmol), respectively, was determined by calculating the number of millimoles of product per millimole of catalyst (based on V content). [c]The total TON of the products (**a+b+c+d+e**). [d]Y_s [%]$_c$ = [substrate (mol)/H_2O_2 (mol)]×100. [e]Y_O [%]$_c$ = [products (mol)/H_2O_2 (mol)]×100. [f]Overall catalytic efficiency (OCE) = (2×**a**+2×**b**+**c**+**d**+**e**)[TON]/ [H_2O_2 consumed (equiv.)]. [g]Selectivity for products, *o*-, *p*-cresols and methyl *p*-BQ = [(c+d+e)(mol)/all oxidation products (mol)]×100. [h]PPh₃ was added after 5 h of reaction time and continued stirring for additional 30 min.

Table S7. The XPS characterization of vanadium oxide catalysts.

Samples	XPS	
	V/O	V^{4+}/V^{5+}
V_{nr}	0.037	0.301
$V_{nr(cal)}$	0.274	0.218
1st recycled **V_{nr}** + (PCA)	0.222	0.639
V_2O_5 commercial	0.364	0.118

2. Figures
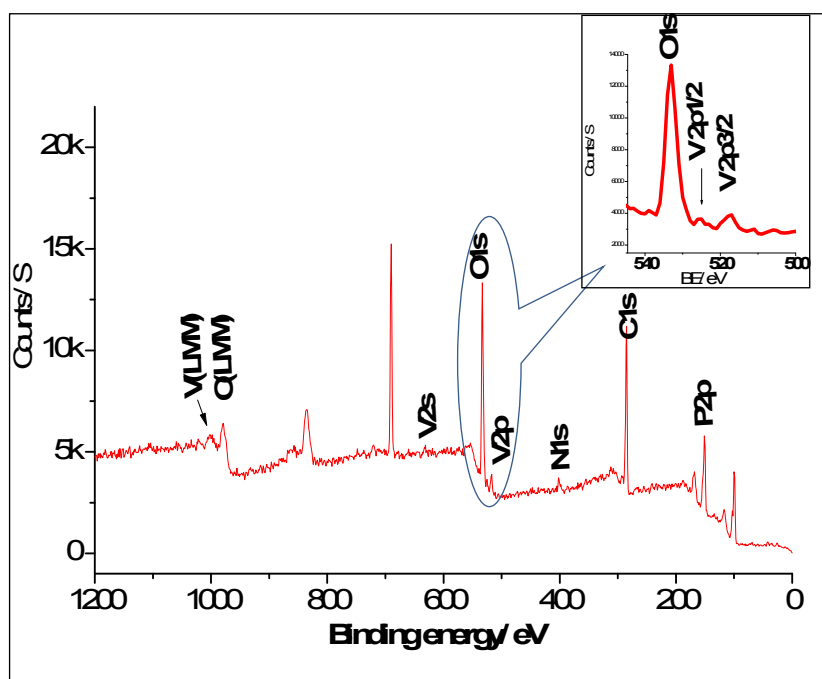
Fig. S1. The XPS survey spectrum of vanadium oxide nanorod (V_{nr}) catalyst.
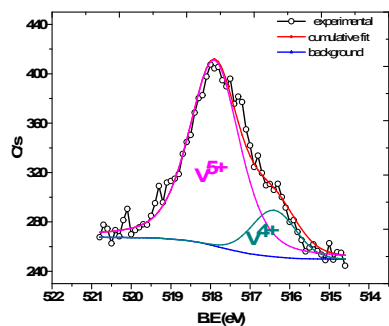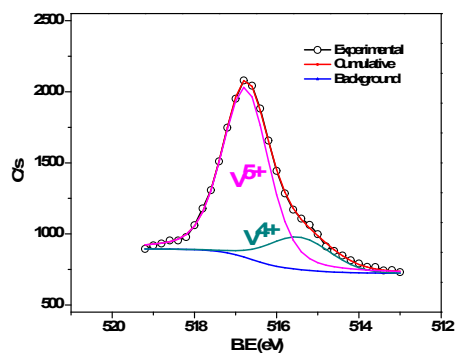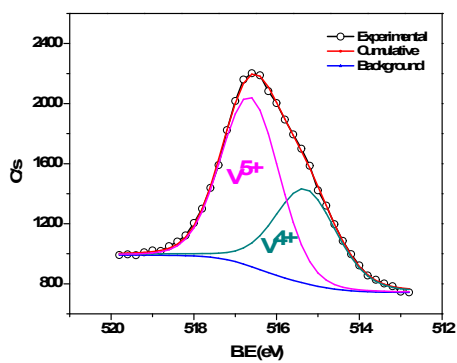

(a)

(b)
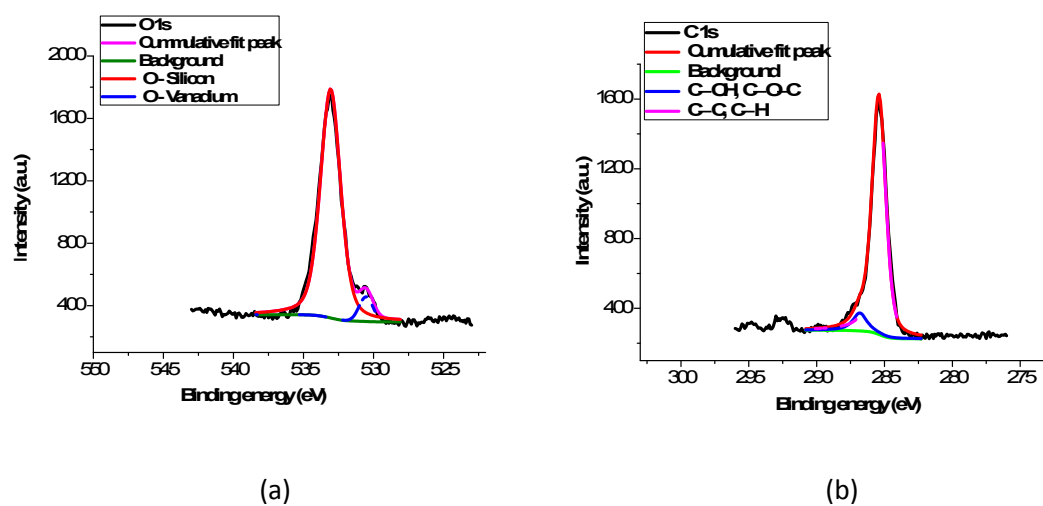
Fig. S2. The high-resolution XPS spectra of vanadium oxide nanorod (V_{nr}) catalyst de-convoluted presented for: (a) O 1s and (b) C 1s. (Si-O signal contribution is from the Si sample holder)
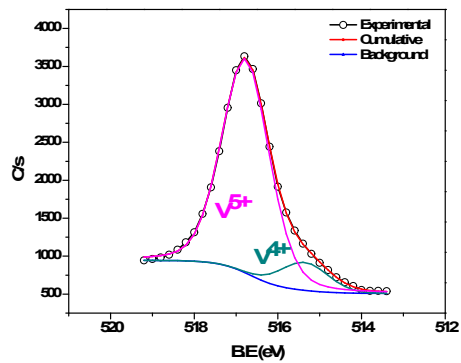
Fig. S3. The high-resolution XPS spectra of vanadium oxide catalysts were deconvoluted presented for V 2p3/2. (a) V_{nr}; (b) calcined V_{nr}; (c) 1st recycled V_{nr} and (d) V_2O_5 commercial catalyst.
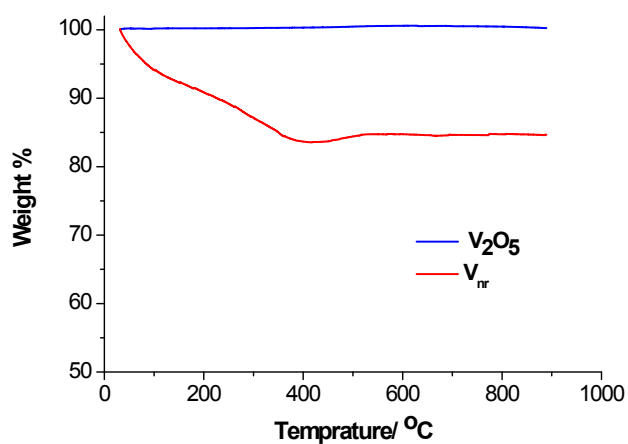
Fig. S4. Thermogravimetric analysis (TGA) diagram of vanadium oxide nanorod (V_{nr}) catalyst and commercialized bulk V_2O_5 powder.
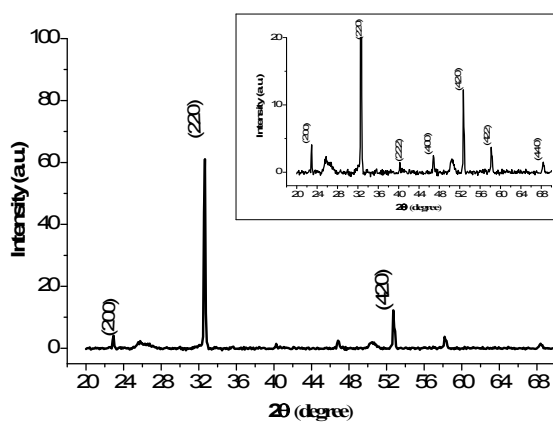
Fig. S5. X-ray diffraction (XRD) spectra of vanadium oxide nanorods (V_{nr}) catalyst.
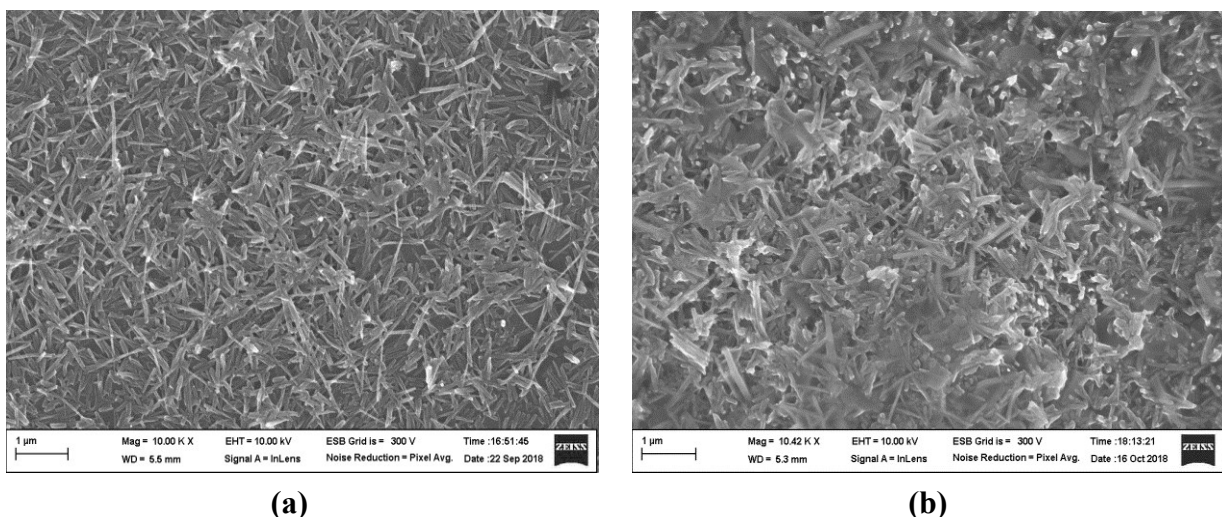
Fig. S6. Scanning Electron Microscopy (SEM) image of the vanadium oxide catalyst: (a) the **V_{nr}** catalyst; (b) the 1st recycled **V_{nr}** from **V_{nr}** catalyzed reaction mixtures in normal reaction condition with the addition of PCA.
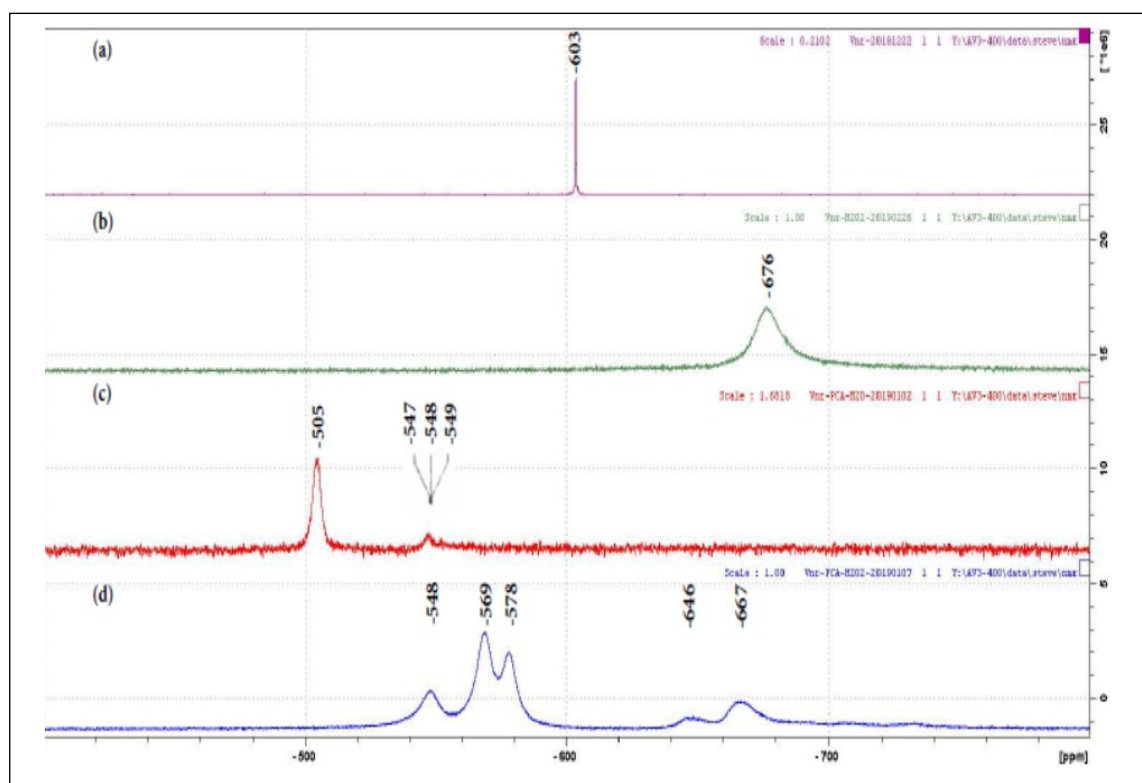
Fig. S7. ^{51}V NMR spectra of solutions of vanadium oxide nanorod in ethanol-*d*1. (a) **V_{nr}** (V content: 0.014 mmol) (b) **V_{nr}** (V content: 0.014 mmol) + 35% H_2O_2 (2.685 mmol); (c) **V_{nr}** (V content: 0.014 mmol) + PCA (0.04 mmol); (d) **V_{nr}** (V content:0.014 mmol) + PCA (0.04 mmol) + 35% H_2O_2 (2.685 mmol).
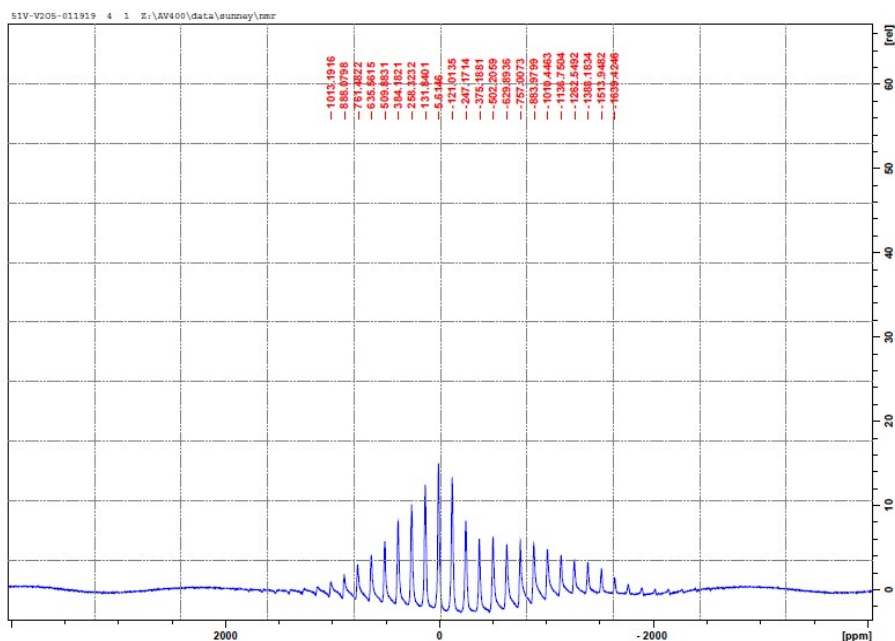
Fig. S8. [51]V-MAS–NMR experimental spectra of vanadium oxide nanorod (V_{nr}) catalyst.

3. Mechanistic study of catalytic oxidation of benzene to phenol using $^{18}O_2$ or $H_2^{18}O_2$.


(a)   (b)   (c)
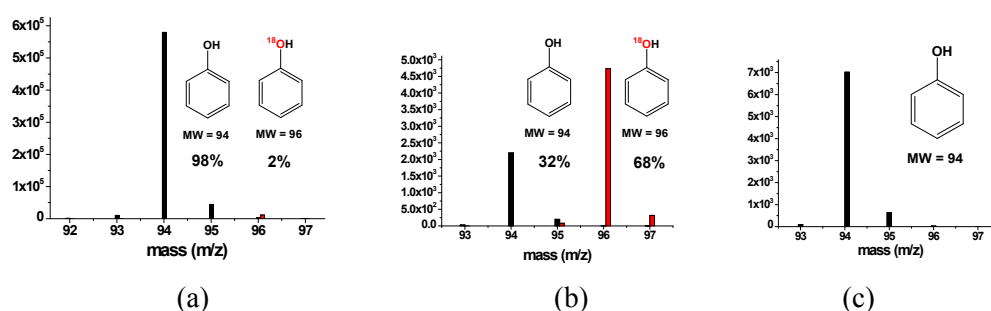
Fig. S9. The oxygen-isotopic distribution of PhOH under the reaction mixtures of vanadium catalyst, V_{nr} containing (a) 35% $H_2^{16}O_{2(aq)}$ enriched at 1 atm of $^{18}O_2$ and (b) 35% $H_2^{18}O_2$ in H_2O at 1 atm N_2 in CH_3CN. The reactions were proceeded for 3 h. The ratios of PhOH:^{18}O-PhOH derived from the deconvolution of the mass spec of ^{16}O enriched PhOH were 98:2 and 32:68, respectively; the mass spec of the parent ^{16}O-enriched PhOH is represented in (c).

4. Determination of NIH-shift ratios of 4-[^{2}H$_{0,1}$]toluene catalyzed by vanadium oxide catalyst in CH$_3$CN by the addition of H$_2$O$_{2(aq)}$ using GC-MS

Synthesis of 4-[^{2}H$_{0,1}$]toluenes:

4-[^{2}H$_{0,1}$]toluenes were synthesized by carrying out a hydrolysis of (4-methylphenyl)magnesium bromide, which was prepared by the reaction of 4-bromotoluene with magnesium in anhydrous tetrahydrofuran and with D$_2$O according to the reported procedure.[1]
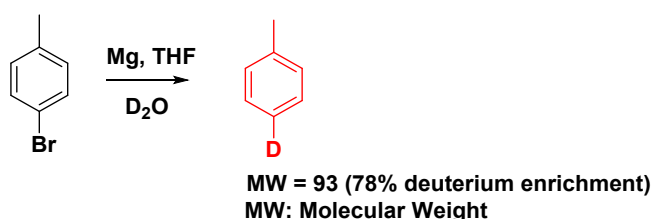
Scheme S1. Preparation of 4-[^{2}H$_{0,1}$]toluenes.
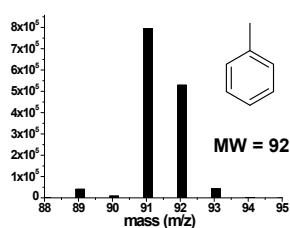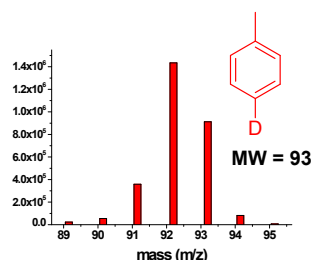
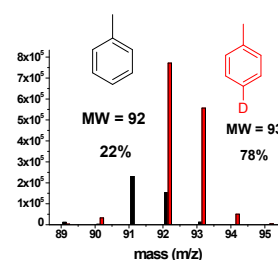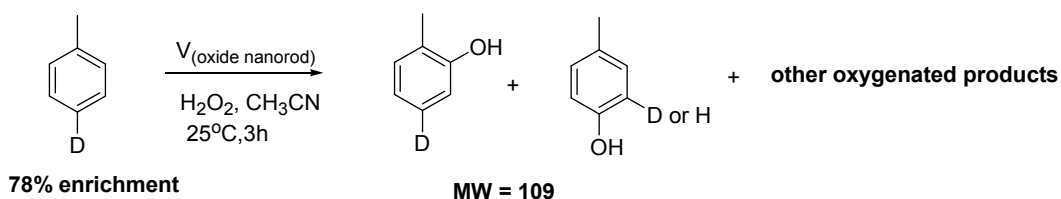**Fig. S10 (a)** toluene   **Fig. S10 (b)** 4-[^{2}H$_{0,1}$]toluene   **Fig. S10 (c)** toluene:4-[^{2}H$_1$]toluene = 22%:78%

Scheme S2. Total volume of the reaction solution was 3 mL; Solvent: acetonitrile; Catalyst: Vanadium oxide nanorod (V content: 0.014 mmol); Substrate: 4-[^{2}H$_{0,1}$]toluenes (with a deuterium enrichment of 78%) (4.47 mmol); Oxidant: 35% H$_2$O$_{2(aq)}$ (2.685 mmol); Reaction time: 3 h; Temperature: 25°C.
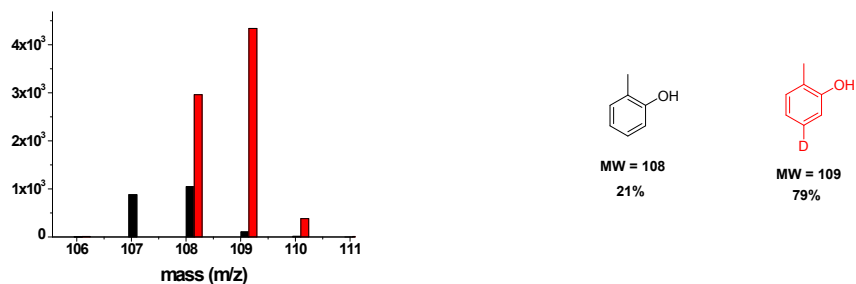
Fig. S11. The mass spectra of the oxygenated product, 4-[^{2}H$_{0,1}$]-o-cresols.
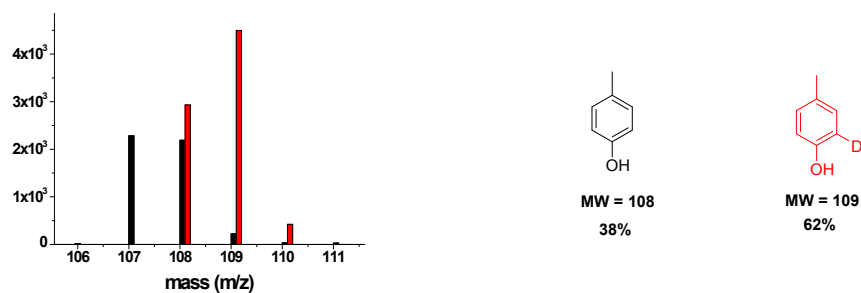

Fig. S12. The mass spectra of the oxygenated product, 3-[^{2}H$_{0,1}$]-p-cresol. (Deuterium enrichment (78%) for the reactant, 4-[^{2}H$_{0,1}$]toluenes).

NIH-shift ratio of the deuterium (62%) remaining in the oxidation product 3-[^{2}H$_{0,1}$]-p-cresols of 4-[^{2}H$_{0,1}$]toluenes (78% deuterium enrichment) = 62%/78% = 80%

Reference

1 Y. Morimoto, S. Bunno, N. Fujieda, H. Sugimoto and S. Itoh, *J. Am. Chem. Soc.,* 2015, **137**, 5867-5870.