Supporting Information for

Vanadia Supported on Mesoporous Carbon Nitride as a Highly Efficient Catalyst for Hydroxylation of Benzene to Phenol

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Determination of the data of catalytic conversion and selectivity

All the reagents and products are analyzed by GC equipped by a FID detector coupled with a SE-54 capillary column. After a catalytic reaction, the resultant compounds revealed by the GC profile were only CH_3CN (solvent), benzene, phenol, and benzoquinone. No biphenyl, catechol, or hydroquinone was detected. Their quantitative calculation (i.e. conversion of benzene, and selectivity to phenol) was based on an area-normalization method.

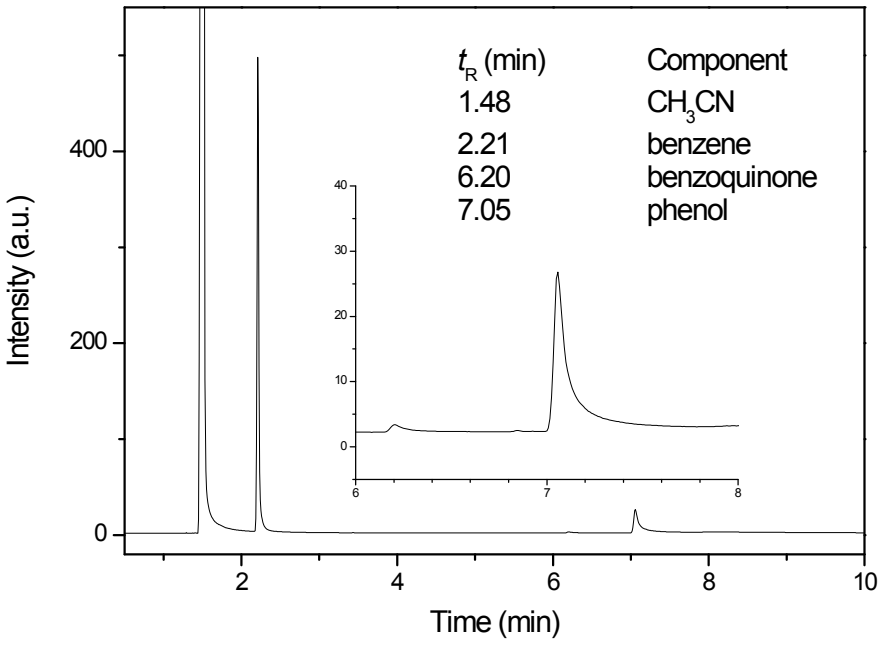


Fig. S1 A representative GC profile after the catalytic reaction.

A series of CH_3CN solutions containing benzene, phenol and benzoquinone with different concentrations were prepared. Wherein, the concentrations for the three solutes were close to ordinary values in a typical catalytic reaction of the present work. Next, the response factors (*f*) for phenol and benzoquinone on the basis of benzene were calculated as follows:

$$f_{\text{phenol}} = \frac{A_{\text{benzene}} / n_{\text{benzene}}}{A_{\text{phenol}} / n_{\text{phenol}}}, f_{\text{benzoquinone}} = \frac{A_{\text{benzene}} / n_{\text{benzene}}}{A_{\text{benzoquinone}} / n_{\text{benzoquinone}}}$$

where *A*, and *n* were the peak area of GC, and molar amount (or concentration, mol/L) of a compound, respectively.

The final conversion of benzene (*Conv.*) and selectivity to phenol (*Sel.*) were calculated as follows:

$$Conv. = \frac{A_{\text{phenol}} \times f_{\text{phenol}} + A_{\text{benzoquinone}} \times f_{\text{benzoquinone}}}{A_{\text{benzene}} + A_{\text{phenol}} \times f_{\text{phenol}} + A_{\text{benzoquinone}} \times f_{\text{benzoquinone}}}$$

$$Sel. = \frac{A_{\text{phenol}} \times f_{\text{phenol}}}{A_{\text{phenol}} \times f_{\text{phenol}} + A_{\text{benzoquinone}} \times f_{\text{benzoquinone}}}$$

The efficiency (E_{H2O2} or selective conversion) of H_2O_2 for the hydroxylation of benzene was calculated as follows:

$$E_{H_2O_2} = \frac{n_{\text{phenol}} + 2n_{\text{benzoquinone}}}{n_{H_2O_2,\text{feed}}} = \frac{n_{\text{benzene,feed}} \times Conv. \times Sel. + 2n_{\text{benzene,feed}} \times Conv. \times (1 - Sel.)}{n_{H_2O_2,\text{feed}}}$$

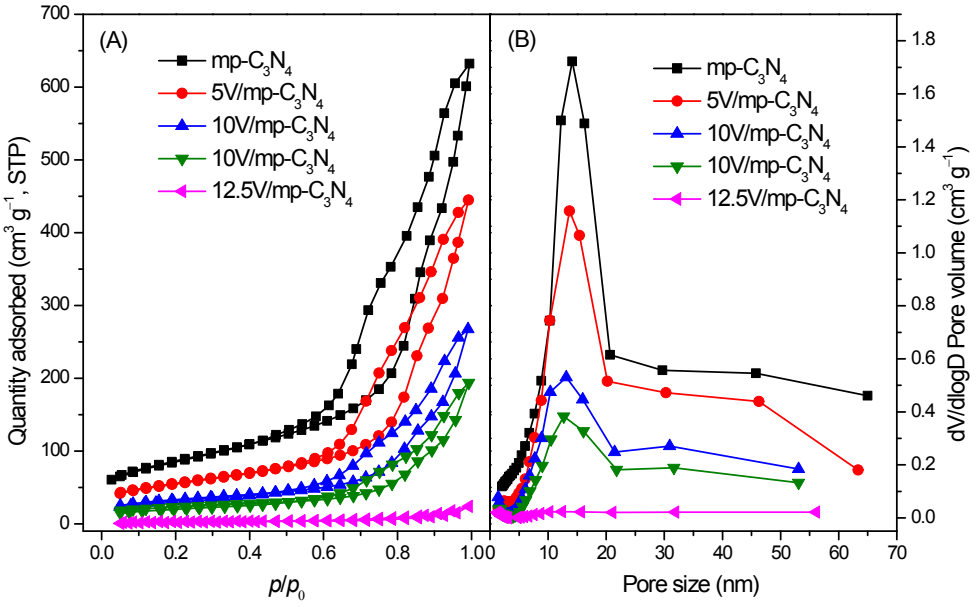


Fig. S2 N_2 adsorption–desorption isotherms (A) and pore size distributions (B) of V/mp-C_3N_4 samples.

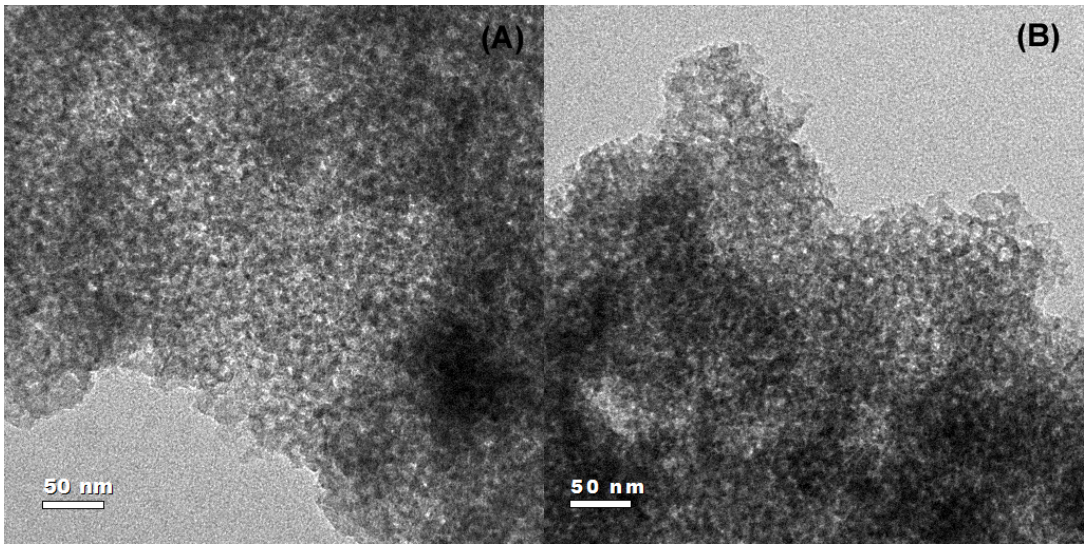


Fig. S3 TEM images of mp-C_3N_4 (A) and 10V/mp-C_3N_4 (B) materials.

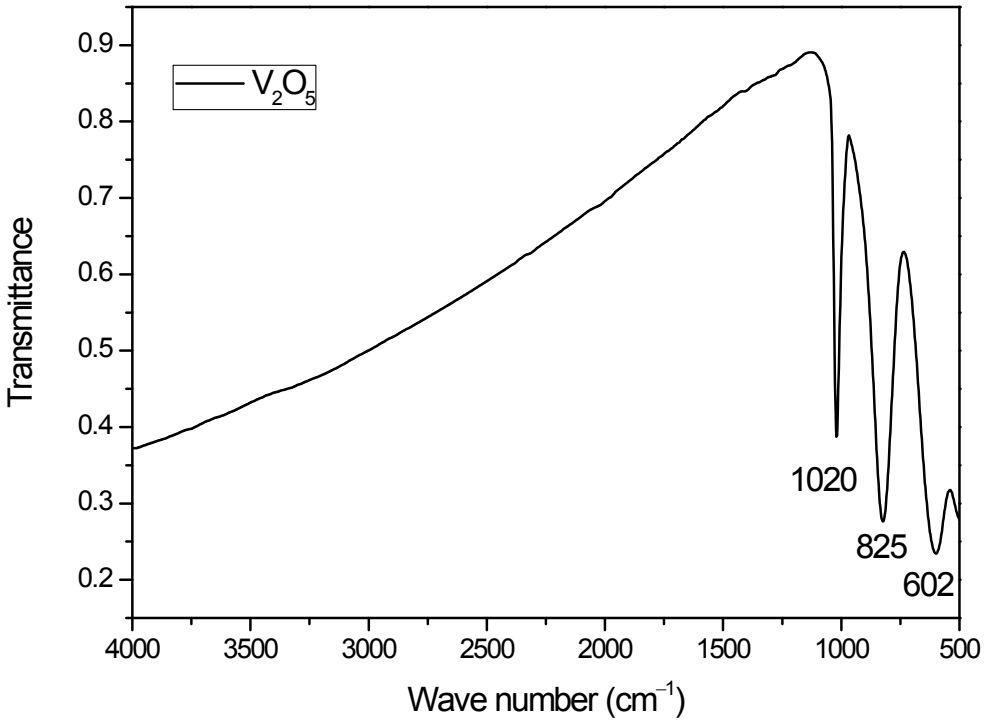


Fig. S4 FT-IR spectrum of V_2O_5.

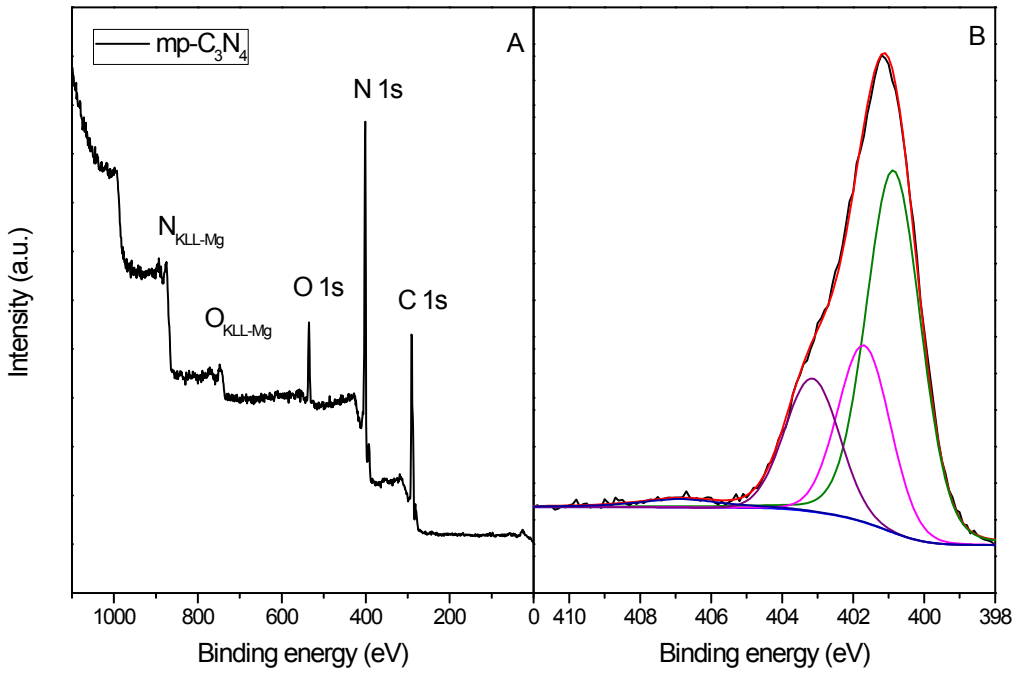
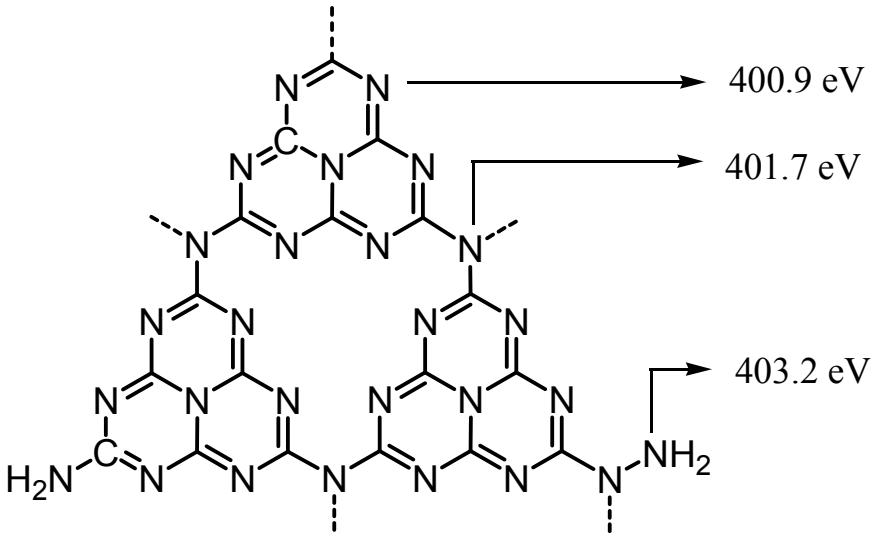


Fig. S5 XPS survey (A) and N 1s spectrum (B) of mp-C_3N_4.



Scheme S1 Various N species in mp-C_3N_4.

Table S1 Effects of the amounts of benzene and H_2O_2 catalyst on the catalytic performances on 10V/mp-C_3N_4[a].

Entry	$V_{benzene}$ (mL)	V_{H2O2} (mL)	$n_{H2O2}/n_{benzene}$	$W_{catal.}$ (mg)	Conv. (%)	Sel. (%)	Yield (%)	TOF (h^{-1})
1	1	3	2.6	60	21.3	92.4	19.7	1.16
2	1.5	3	1.8	60	18.7	95.9	18.0	1.59
3	2	3	1.3	60	10.2	97.1	9.9	1.17
4	1.5	1	0.6	60	2.8	97.1	2.7	0.24
5	1.5	2	1.2	60	10.8	96.7	10.4	0.92

[a] Reaction conditions: T = 60 °C, $V_{acetonitrile}$ = 6.0 mL, t = 3 h, and $W_{catal.}$ = 60 mg.