## **Supporting Information for**

# A Schiff-base Type Vanadyl Complex Grafted on Mesoporous

Carbon Nitride: A New Efficient Catalyst for Hydroxylation of

### **Benzene to Phenol**

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#### **Preparation of SBA-15**

The SBA-15 material was prepared using Pluronic P123 triblock copolymer  $(EO_{20}PO_{70}EO_{20}, Sigma-Aldrich)$  as a template. Briefly, 4.0 g Pluronic P123 was dissolved in 150 mL of 1.6 mol L<sup>-1</sup> HCl solution, followed by elevation of the reaction temperature to 30 °C. After that, 8.8 g TEOS was added, and the solution was further stirred at 40 °C for 24 h. The milky solution was transferred into an autoclave and aged at 130 °C for 24 h. Afterwards, the white precipitate was filtered off and dried overnight at 60 °C. The resultant solid was calcined at 550 °C for 5 h to remove the surfactant. Finally, SBA-15 was obtained with a mass of *ca*. 2.4 g.

#### Preparation of VOac-SBA15-NH<sub>2</sub> and VOac-CNTs-NH<sub>2</sub>

The preparation of vanadyl complexes immobilized on SBA-15 and CNTs materials were based on previously reported approaches <sup>1, 2</sup>.

#### (a) VOac-SBA15-NH<sub>2</sub>

SBA-15 powder was first dried at 120 °C for 2 h. Next, 2.0 g of dried SBA-15 and 1.18 mL of 3-aminopropyltriethoxysilane (APTES) were added into 100 mL of toluene and the mixture was refluxed at 100 °C for 2 h under an argon atmosphere. The resultant material was filtrated and washed by 40 mL of toluene, followed by a second refluxing with 80 mL of toluene. After that, the precipitation was dried at 60 °C for 2 h under vacuum, and the final white solid was labeled as SBA15-NH<sub>3</sub>. The preparation of VOac-SBA15-NH<sub>3</sub> was prepared in the same way like VOac-CND.

(b) VOac-CNTs-NH<sub>2</sub>

0.7 g of previously dried CNTs and 0.4 mL of APTES were added into 50 mL of toluene and the mixture was refluxed at 100 °C for 2 h under an argon atmosphere. The resultant material was filtrated and washed by 40 mL of toluene, followed by a second refluxing with 80 mL of toluene. After that, the precipitation was dried at 60 °C for 2 h under vacuum, and the final black solid was labeled as CNTs-NH<sub>3</sub>. The preparation of VOac-CNTs-NH<sub>3</sub> was prepared in the same way like VOac-CND.

References:

1 C. Pereira, J. F. Silva, A. M. Pereira, J. P. Araújo, G. Blanco, J. M. Pintado and C. Freire, *Catal. Sci. Technol.*, 2011, 1, 784-793.

2 B. Jarrais, A. R. Silva and C. Freire, Eur. J. Inorg. Chem., 2005, 4582-4589.



Fig. S1 XRD pattern of VO(acac)<sub>2</sub>.



Fig. S2 Raman spectra of CND and VOac-CND materials.



Fig. S3 SAXS pattern of SBA-15.



**Fig. S4** TEM images of CND material. A and B were recorded along with the [110] and [100] directions, respectively.



Fig. S5 FT-IR spectra of VOac-CND materials grafted with 50, 100, 175 mg of VO(acac)<sub>2</sub>.



**Fig. S6** N<sub>2</sub> adsorption–desorption isotherms (A) and the corresponding pore size distributions (B) of the fresh and used VOac-CND catalysts after four catalytic runs, as well as Cuac-CND.

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Sample	$S_{\rm BET} ({ m m}^2~{ m g}^{-1})$	Pore size (nm) <sup><i>a</i></sup>	Pore volume (cm <sup><math>3</math></sup> g <sup><math>-1</math></sup> )
SBA-15	564	9.7	1.12
CND	488	5.4	0.57
VOac-CND <sup>b</sup>	<mark>368</mark>	<mark>5.3</mark>	0.48
VOac-CND <sup>c</sup>	<mark>365</mark>	<mark>5.0</mark>	0.45
VOac-CND <sup>d</sup>	328	4.6	0.38
VOac-CND <sup>e</sup>	312	4.6	0.38
CuOac-CND	424	4.9	0.50

 Table S1 Textural parameters of CND and the grafted acetylacetonate-containing

complexes.

<sup>*a*</sup> Determined by the adsorption branches. <sup>*b*</sup> Grafted with 50 mg of VO(acac)<sub>2</sub>. <sup>*c*</sup> Grafted with 100 mg of VO(acac)<sub>2</sub>. <sup>*d*</sup> Grafted with 175 mg of VO(acac)<sub>2</sub>. <sup>*e*</sup> After four catalytic runs for VOac-CND grafted with 175 mg of VO(acac)<sub>2</sub>.



Fig. S7 FT-IR spectra of the fresh and used VOac-CND catalysts subjected to four catalytic runs.



Fig. S8 FT-IR spectrum of Cuac-CND-120.



**Fig. S9** FT-IR spectra of SBA-15, SBA-15-NH<sub>2</sub>, and VOac-SBA-15-NH<sub>2</sub> materials. The v,  $\delta$ , and  $\gamma$  indicate the vibrations of stretching, bending, and rocking, respectively. It should be noted that the band of v(Si–OH) overlaps with that of v(V=O) at *ca*. 970 cm<sup>-1</sup>. However, upon grafting with APTES, the original signal associated with v(Si–OH) disappeared, suggesting that the Si–OH groups of SBA-15 have reacted with

amino groups of APTES. While, after the following immobilization of VO(acac)<sub>2</sub>, a new band located at *ca*. 960<sup>-1</sup> cm<sup>-1</sup> reappeared. Obviously, the new band was not indexed as v(Si-OH) but v(V=O) signals, confirming the presence of vanadyl species on SBA-15-NH<sub>2</sub>.