## **Supporting Information for**

## Niobium phytate prepared from phytic acid and NbCl<sub>5</sub>: Highly efficient and heterogeneous acid catalysts

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## **Catalyst characterization**

FT-IR spectra were recorded on Bruker Tensor 27 IR spectrometer and the sample was prepared by the KBr pellet method.

The BET surface area measurement and pore analysis were carried out by  $N_2$  adsorption at 77 K with Micromeritics ASAP 2020 V3.00 H (USA) surface area analyser.

X-ray diffraction (XRD) measurements were conducted on an X-ray diffractometer (D/MAX-RC, Japan) operated at 40 kV and 200 mA with Cu K $\alpha$  ( $\lambda$ =0.154 nm) radiation.

XPS measurements were carried out on an ESCAL Lab 220i-XL spectrometer at a pressure of  $\sim 3 \times 10^{-9}$  mbar (1 mbar=100 Pa) using Al K $\alpha$  as the excitation source (*hv*=1486.6 eV) and operated at 15 kV and 20 mA. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

TG analysis was performed on a thermogravimetric analysis system (Netzsch STA 409 PC/PG, Germany) in  $N_2$  atmosphere at a heating rate of 20 °C/min.

The scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 Scanning Electron Microscope operated at 15 kV. The samples were spray-coated with a thin layer of platinum before observation. The transmission electron microscopy (TEM) images were obtained using a TEM JeoL-1011 with an accelerating voltage of 120 kV. The sample was dispersed in ethanol with the aid of sonication and dropped on an amorphous carbon film, supported on a copper grid, for the TEM analysis.

Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was performed on Micromeritics' AutoChem 2950 HP Chemisorption Analyzer. The catalysts were charged into the quartz reactor, and the temperature was increased from room temperature to 150 °C at a rate of 10 °Cmin<sup>-1</sup> under a flow of He (50 cm<sup>3</sup>min<sup>-1</sup>), and then the catalyst was kept at 150 °C for 3 h. After that, the temperature was decreased to 30 °C. NH<sub>3</sub>/He (10/90, 50 cm<sup>3</sup>min<sup>-1</sup>) was pulsed into the reactor at 30 °C under a flow of He (10 cm<sup>3</sup>min<sup>-1</sup>) until the acid sites were saturated with NH<sub>3</sub>. The adsorbed NH<sub>3</sub> was removed by a flow of He (50 cm<sup>3</sup>min<sup>-1</sup>). When the baseline was stable, the temperature was increased from 30 °C to 300 °C for niobium phytate or to 500 °C for Nb<sub>2</sub>O<sub>5</sub> at a rate of 10 °C min<sup>-1</sup>.

The nature of the acid sites of the samples was determined by pyridine FT-IR on the Nicolet NEXUS 670 FT-IR spectrometer with a resolution of 2 cm<sup>-1</sup>. The samples were finely ground and pressed into a self-supporting wafer (diameter 15 mm, 42 mg). The wafers were evacuated in the IR cell at 250 °C for 1 h under a vacuum in order to remove physisorbed water. After the temperature decreased to room temperature, IR spectra were recorded in the range from 2500 to 1000 cm<sup>-1</sup>. Subsequently, the samples were followed by the adsorption of purified pyridine vapor at room temperature for 50 min. The Py-IR spectra were recorded after subsequent evacuation of the infrared cell at 200 °C. The spectra presented were obtained by subtracting the spectra recorded before and after pyridine adsorption. the quantity of Lewis acid sites was evaluated according to the equation in the literature (J. Catal., 1993, 141, 347-C(pyridine on Lewis sites)= $1.42IA(L)R^2/W$ . In the equation, 354): C=concentration (mmol/g catalyst); IA(L)=integrated absorbance of Lewis band (cm-1); R=radius of catalyst disk (cm); W=weight of disk (mg).

The contents of Nb and P in niobium phytate and the concentration of Nb in the reaction solution were determined by ICP-AES (VISTA-MPX). The content of C was obtained from elemental analysis by using the FLASH EA1112 analyzer.



Scheme S1. The chemical structure of phytic acid.



Fig. S1. UV-Vis spectra of niobium phytate and Nb<sub>2</sub>O<sub>5</sub>.



Fig. S2. The XPS spectra of Nb 3d in niobium phytate recovered after five times used.



**Fig. S3.** The XPS spectra of P 2p in niobium phytate recovered after five times used.



**Fig. S4**. Thermogram of niobium phytate. The weight loss (about 5%) up to 150 °C is attributable to the loss of intercalated and adsorbed water and ethanol molecules in the sample. The obvious weight loss (about 20%) occurred between 280 °C and 450 °C corresponds to the burning of organic fragments of the hybrid framework. The breaking of C-C, C-P and C-H bonds extended up to about 450 °C.



Fig. S5. NH<sub>3</sub>-TPD spectra of commercial Nb<sub>2</sub>O<sub>5</sub> and amorphous Nb<sub>2</sub>O<sub>5</sub>.

Element	Content of various elements on the surface (Atomic%) <sup>a</sup>		
	Fresh niobium phytate	Spent niobium phytate	
Nb	5.4	5.03	
Р	6.62	6.25	
С	46.52	47.76	
0	38.01	39.61	

**Table S1.** The contents of various elements on the surface of niobium phytatedetermined by XPS examination.

**Table S2.** Properties of niobium phytate and commercial  $Nb_2O_5$  determined by  $N_2$  adsorption-desorption method.

Entry	Sampla	BET surface area	Pore volume	Pore diameter
Entry	Sample	$(m^{2}/g)^{b}$	$(cm^3/g)^c$	(nm) <sup>d</sup>
1	Niobium phytate	30.9	0.11	12.4
2	Commercial Nb <sub>2</sub> O <sub>5</sub>	2.4	0.003	4.3
3	Amorphous Nb <sub>2</sub> O <sub>5</sub>	41.3	0.14	6.8

<sup>a</sup>The samples were degassed at 100 °C for 24 h. <sup>b</sup>Surface area based on multipoint BET method. <sup>c</sup>Pore volume based on BJH method. <sup>d</sup>Pore diameter based on BJH method.