

# Supporting Information – Structural Studies of Bulk to Nano-size Niobium Oxides with Correlation to Their Acidity

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## S1. Niobium oxide synthesis

### S1.1 Materials

All chemicals were in analytical grade of over 99% purity from Wako Pure Chemical Industries unless otherwise stated. Nb<sub>2</sub>O<sub>5</sub> (≥99.9%) was purchased from Alfa Aesar (Johnson Matthey) for use as a precursor in order to compare its properties and performance to the niobium oxides.

### S1.2 Preparation of mesoporous Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O

Mesoporous Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O was synthesized using a mixture of niobium(V) ethoxide (Nb(OEt)<sub>5</sub>, Kojundo Chemical Laboratory, (5.0 g) and distilled water (200mL) stirred at room temperature for 24 h. The resulting precipitate was filtered, washed with distilled water and soaked in 0.1 M HCl solution overnight (~12 h). The resulting white precipitate was repeatedly washed with distilled water until the filtrate became neutral and was then dried at 200 °C for 5h [1].

### S1.3 Preparations of H<sub>3</sub>ONb<sub>3</sub>O<sub>8</sub> and HNb<sub>3</sub>O<sub>8</sub>

Layered niobate was prepared by conventional solid-state reactions in an alumina crucible [2,3]. K<sub>2</sub>CO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> were mixed in molar ratios of 1.1:3 and calcined at 600 °C for 2 h and 900 °C for 3 h for the synthesis of KNb<sub>3</sub>O<sub>8</sub>. The obtained KNb<sub>3</sub>O<sub>8</sub> was converted to H<sub>3</sub>ONb<sub>3</sub>O<sub>8</sub> by immersion in 6.0 M HCl at 60 °C for 1 week whilst replacing the acid solution with fresh solutions each day. The resulting precipitate was filtered, washed with distilled water repeatedly until the filtrate became neutral and was then dried at 60 °C overnight (~12 h). The obtained H<sub>3</sub>ONb<sub>3</sub>O<sub>8</sub> was converted to HNb<sub>3</sub>O<sub>8</sub> by calcination at 150 °C for 3 h.

### S1.4 Preparations of single molecular layer niobate (hy-Nb-TEOA) and reduced layer niobate nanosheets (hy-Nb) by hydrothermal method

The niobate molecular sheets were synthesized by hydrothermal method using amine surfactants in ammonia solution. In a typical experiment, 1.989 g of Nb(OEt)<sub>5</sub> (0.00625 mol) was mixed with 3.735 g of triethanolamine (TEOA) (0.025 mol), which is stable against hydrolysis at room temperature. The mixed solution was added to 25 mL of aqueous NH<sub>3</sub> and the final pH of the mixture was kept at 12.8. The mixture was then transferred to a 45 mL of Teflon autoclave, which was aged at 160 °C for 24 h. The resulting product was centrifuged at 6000 rpm and a colloidal suspension with small amount of white precipitate was obtained. After the removal of the precipitate fraction, the yellowish supernatant colloid was collected, filtered and washed with distilled water. The product was dried at 60 °C overnight (~12 h) and was christened as hy-Nb-TEOA precursor.

Acid treatment of hy-Nb-TEOA was performed using HNO<sub>3</sub> aqueous solution. A 6.0 M HNO<sub>3</sub> aqueous solution was added to the colloidal suspension until pH became around 2.0, resulting in aggregation as a precipitate. The aggregated sample was filtered, washed with distilled water

repeatedly until the filtrate became neutral. The product was dried at 60 °C overnight (~12 h) and was christened as hy-Nb-TEOA.

A hydrothermal synthesis of Nb(OEt)<sub>5</sub> without TEOA in aqueous NH<sub>3</sub> were performed in a similar way to examine the role of TEOA. After centrifugation at 3500 rpm for 10 min, a white precipitate with a clear supernatant was collected. The precipitate was then washed with ethanol and dried at 60 °C overnight (~12 h). The obtained sample was christened as hy-Nb precursor.

Acid treatment of hy-Nb was performed using HNO<sub>3</sub> aqueous solution. The sample of hy-Nb was stirred in 1.0 M HNO<sub>3</sub> aqueous solution. After several hours, the collected sample was washed with distilled water repeatedly until the filtrate became neutral. The product was dried at 60 °C overnight (~12 h) and was christened as hy-Nb.

Note: The same synthetic procedures and TMP <sup>31</sup>P NMR analysis procedures have been used in our previous work on niobium oxides.[4]

## S2. Surface area measurements

Specific surface areas were derived from the corresponding adsorption isotherms with a conventional BET nitrogen adsorption apparatus (BELSORP18SP, Bell Japan Inc.).

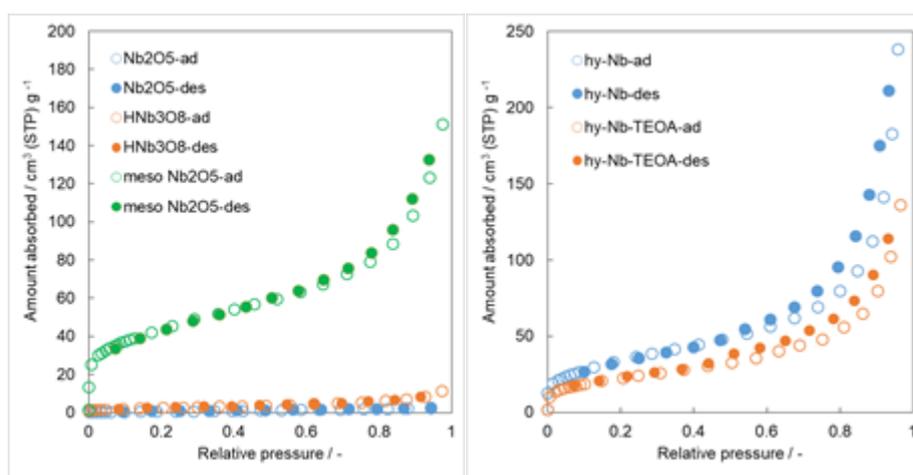


Figure S1. (a,b) N<sub>2</sub> adsorption–desorption isotherms of various niobium oxides. Open and closed circles express adsorption and desorption branches, respectively. The pore size analysis for mesoporous niobium oxide should be referred to a review paper in this area [1].

## S3. TMP <sup>31</sup>P MAS NMR analysis

### S3.1 Background

Pioneered by Lunsford and co-workers, TMP was first adopted as a probe molecule to characterize the acidity of zeolite based on the observed <sup>31</sup>P chemical shift ( $\delta^{31}\text{P}$ ). [5] Thereafter, the technique has been widely utilized for acidity characterization of various solid acid catalysts. [6] Figure S2 shows three scenarios of interaction between TMP and substrate: (a) chemisorbed on Lewis acid centers, (b) physisorbed on hydroxyls (hydrogen bonding interactions), and (c) chemisorbed on Brønsted acid sites (i.e., formation of TMPH<sup>+</sup> Ionic complexes).

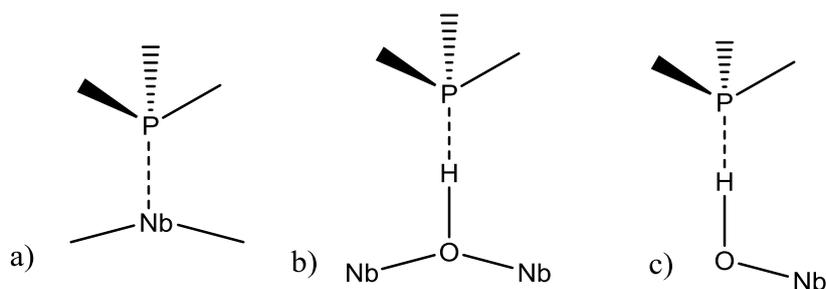


Figure S2. The structures of adsorbed trimethylphosphine a) Lewis chemisorbed form, b) physisorbed form and c) Brønsted chemisorbed form.

The  $\delta^{31}\text{P}$  of adsorbed TMP spans over a wide range (-20~-58 ppm) when interacting with various LA centers on different solid acids, whereas a  $\text{TMPH}^+$  ionic complex formed when a TMP molecule adsorbs onto a BA proton tends to give rise to a  $^{31}\text{P}$  resonance in a much narrower range of -2 to -6 ppm. Therefore, Brønsted (proton donor) and Lewis acid (electron acceptor) sites present in a solid acid catalyst can be readily distinguished using  $^{31}\text{P}$  ssNMR of adsorbed TMP.

### S3.2 The system setup and preparation of TMP-adsorbed samples.

About 150 mg of sample were loaded to a glass tube and pre-treated at 423 K for 2 h under vacuum ( $10^{-1}$  Pa). After reaching room temperature, the sample was loaded with 1 mmol TMP per g catalyst and TMP is vaporized under the low pressure conditions (system set-up, see [7]). To promote TMP adsorption, the sample tube was then immersed in liquid nitrogen. After about 10 min the pressure of the isolated system reaches a plateau, meaning the equilibrium state between gaseous and adsorbed TMP has been obtained. Excess TMP was then removed carefully via a short vacuum treatment. The above steps were repeated three times for sample equilibration and a more accurate final TMP adsorption on the sample surface. The glass tube was finally flame sealed for storage and transferred to a Bruker 4 mm  $\text{ZrO}_2$  rotor with a Kel-F endcap under nitrogen atmosphere, as a preparation for the NMR measurement.

### S3.3 $^{31}\text{P}$ MAS NMR experiments

Solid state magic angle spinning (MAS) NMR experiments were carried out at room temperature using a Bruker Avance III 400WB spectrometer. High power decoupling (HPDEC) was used for quantitative  $^{31}\text{P}$  analysis in order to remove additional peak broadening due to proton spin effects.[7] Considering the long relaxation times of  $^{31}\text{P}$  nuclei, a  $30^\circ$  pulse with a width of  $1.20\ \mu\text{s}$  and 15 s delay time was used. The radiofrequency for decoupling was 59 kHz and the spectra were collected between 200 and -200 ppm, with a scanning number of 800. The  $^{31}\text{P}$  chemical shifts were reported relative to 85 % aqueous solution of  $\text{H}_3\text{PO}_4$  using  $\text{NH}_4\text{H}_2\text{PO}_4$  as a secondary standard (0.81 ppm). The quantity of adsorbed TMP molecules was calculated according to the calibration line (Figure S3) established by running standard samples with various adsorbed TMP concentrations.

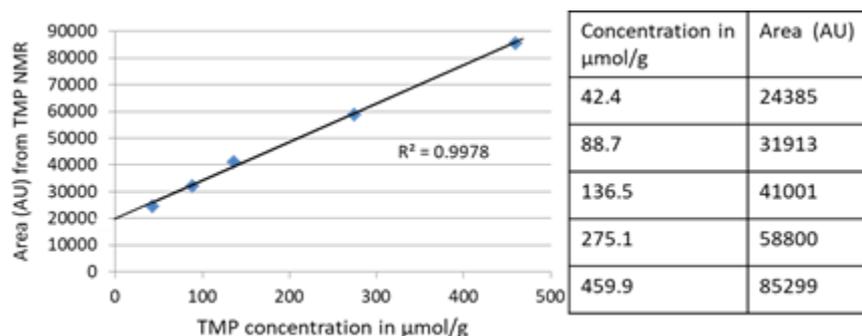
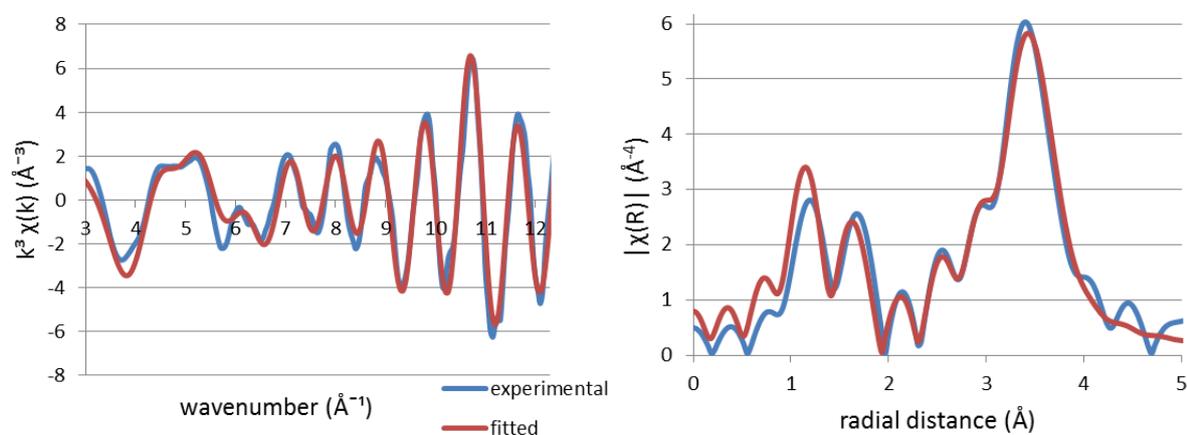


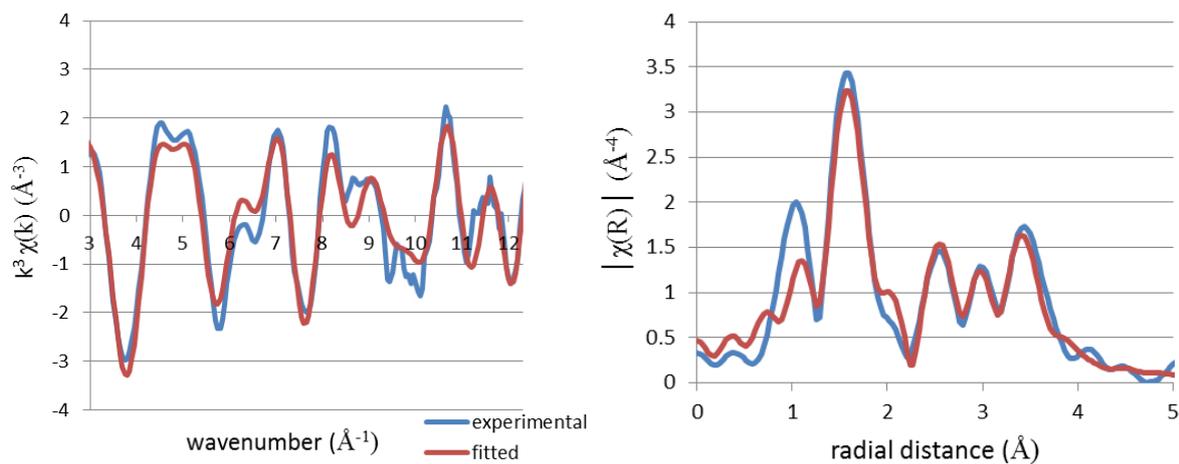
Figure S3. Calibration line established by various standard samples with known adsorbed TMP concentration.

#### S4. Nb K-edge X-ray absorption fine structure (XAFS) analysis

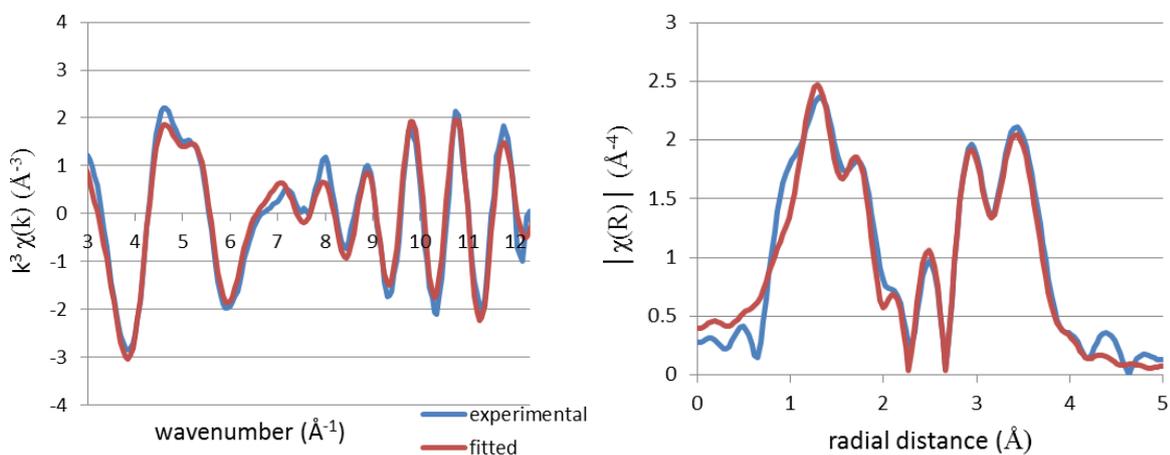
XAFS (extended x-ray absorption fine structure) gives insights into oxidation state and atomic neighbourhood, especially with regard to bond distances and to some extent also coordination numbers. XAFS spectra depict the absorption coefficient of a sample with respect to energy, which is commonly divided into X-ray absorption near edge structure (XANES) and the Extended X-Ray Absorption Fine Structure (EXAFS). Structural parameters (radial distance, bond distance information to neighbouring atoms) can be obtained by fitting of the model function to the measured EXAFS spectra through transforming the normalised oscillatory part of the absorption coefficient to  $k$  space and further to Fourier Transform ( $R$ ) space. [8-10] Here, Nb K-edge absorption analysis has been done for the different niobium oxides. In Figure S4, the fitted  $k$  and  $R$  ranges are displayed for each sample with only the first shell neighbours ( $1^{\text{st}}$  O-shell) of Nb taken into consideration. It is to note that for valid results the correlation factor  $R$  between experimental result and fitting should always be within 2% and enot, the difference in absorption energy between experimental and calculated result, should always be within  $\pm 8$ . The coordination numbers of Nb can further be derived from here, however only within 20% error and given as average numbers over the whole crystal structure, meaning that decimals are common.



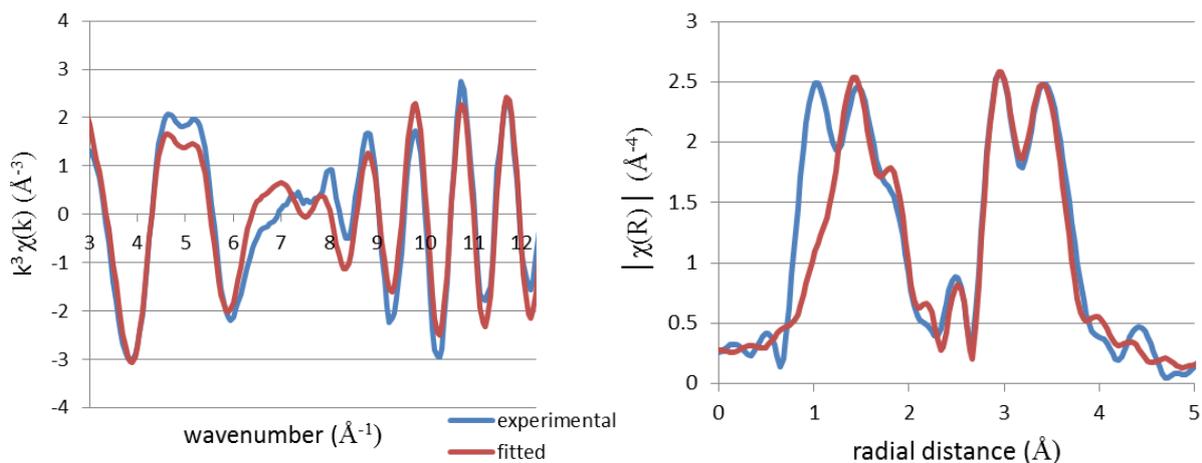
a)  $\text{Nb}_2\text{O}_5$ :  $R = 2.0\%$ ,  $k$  range 3-12.3,  $R$  range 1.2-4, enot = -7.6



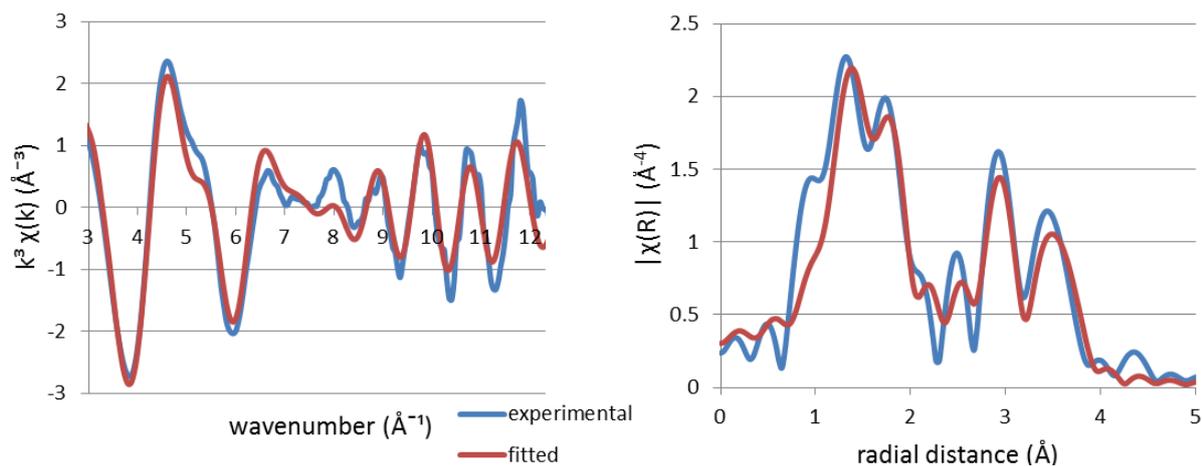
b) HNb<sub>3</sub>O<sub>8</sub>: R = 1.0%, k range 3-12.3, R range 1.2-2.8, enot = 2.1



c) hy-Nb: R = 0.5%, k range 3-12.3, R range 1.2-2.65, enot = 6.3



d) hy-Nb-TEOA: R = 1.1%, k range 3-12.3, R range 1.2-2.65, enot = 7.6



e) mesoporous Nb<sub>2</sub>O<sub>5</sub>\*nH<sub>2</sub>O: R = 2.0%, k range 3-12.3, R range 1.2-4, enot = 6.2

Figure S4. (a-e) k and R space transformations of Nb K-edge EXAFS spectra for the different niobium oxides

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