Supplementary Information (SI) for Catalysis Science & Technology.

Electronic Supplementary information

Lewis acid catalysis of phosphorous-modified $CaNb_2O_6$ for xylose dehydration to furfural

Zijian Wang,‡[a,b] Ryota Osuga,‡[a] Koichiro Endo,[a] Daniele Padovan,[a] Satoshi Suganuma,[a] Atsushi Fukuoka,[a] Hideki Kato,[c] and Kiyotaka Nakajima*[a]

[a] *Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan*

[b] *Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan.*

[c] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

Author information

Corresponding Author

*E-mail; nakajima@cat.hokudai.ac.jp

Tel: +81 (0)11 706 9132

‡ These authors contributed equally.

Notes

The authors declare no competing financial interest.

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Experimental.

Chemicals.

$NbCl_5$ was purchased from HIGH PURITY CHEMICALS. Hydrogen peroxide (30–35 wt%), phosphoric acid (>85 wt%), toluene, and chloroform were supplied by KANTO CHEMICAL CO., INC. Ammonia aqueous solution (28 wt%), L-lactic acid, calcium nitrate tetrahydrate, sulfuric acid (>95 wt%), D(+)-xylose, and pyridine (dehydrated) were obtained from FUJIFILM Wako Pure Chemical Corporation. Scandium trifluoromethanesulfonate, furfural, and chlorobenzene were received from Tokyo Chemical Industry (TCI). Amberlyst-15 was supplied by Sigma-Aldrich. H-Beta was provided by the Catalysis Society of Japan (JRC-Z-HB150).

Catalysts preparation.

$CaNb_2O_6$ was synthesized by the amorphous metal complex (AMC) method using water-soluble niobium lactate ($Nb(CH_3CH(OH)COO)(CH_3CH(O)COO)_2$ denoted as Nb-LA).[S1, S2] $NbCl_5$ (25 g) was slowly added to 300 mL of distilled water, after which the pH was adjusted to 7.0 using ammonia aqueous solution. The mixture was then stirred at 600 rpm for 3 h. After adjusting the pH of the solution to 7.0, the precipitate was recovered by filtration and washed with distilled water to remove Cl^- ions, obtaining wet paste of amorphous Nb_2O_5. The amorphous Nb_2O_5 (10 mmol) was added to a mixture of lactic acid (80 mmol) and hydrogen peroxide (200 mmol). After adjustment of the pH to 4.5 with ammonia aqueous solution, the mixture was stirred at 60 °C for 1 h and at 90 °C overnight to obtain Nb-LA. The mixture of calcium nitrate tetrahydrate (10 mmol) and lactic acid (30 mmol) and 5 mL of distill water was sonicated until the solid was completely dissolved. After the addition of an aqueous Nb-LA solution (20 mmol), the solution was gelled at 110 °C for 1 h and heated stepwise (250 °C for 1 h, 450 °C for 3 h) with a slow ramping rate to form a black powder. Carbonaceous species derived from lactic acid were then removed by high-temperature calcination in a muffle oven at 700 °C for 5 h to obtain $CaNb_2O_6$. The same preparation processes were applied to T-phase Nb_2O_5 simply using 10 mmol of Nb precursor without calcium nitrate tetrahydrate. $CaNb_2O_6$ and Nb_2O_5 were treated with phosphoric acid to immobilize phosphate moiety on their surfaces. Typically, the sample (1 g) was added to an aqueous phosphoric acid solution (1M, 200 mL) and stirred at room temperature for two days. The solid was recovered by filtration and washed with water until the pH of the filtrate became neutral and then dried overnight in an oven to obtain a phosphate-immobilized sample (P-$CaNb_2O_6$ and P-Nb_2O_5).

Characterization.

X-ray diffraction (XRD) measurement was performed on an Ultima IV Rigaku diffractometer set at 40 kV and 40 mA using Cu Kα radiation ($\lambda = 1.5418$ Å). Nitrogen adsorption experiment was conducted at 77 K using a Micromeritics 3-Flex instrument after the sample was degassed at 150°C for 1 h. Brunauer-Emmett-Teller (BET) surface area was calculated over a relative pressure (P/P_0) range from 0.05 to 0.30. X-ray photoelectron spectroscopy (XPS) was performed using a JEOL JPS-9010MC. Data analysis was carried out using CasaXPS software. Fourier transform (FT) infrared (IR) spectra were obtained using a JASCO FT/IT-4100 with a mercury cadmium telluride (MCT) detector. The self-supported disk (20 mm, 40–90 mg) was placed in an IR cell connected to a closed gas-circulation system and pretreated at 300 °C for 1 h under vacuum to remove physisorbed water. Pyridine or chloroform was used as a probe molecule for characterizing acidity and basicity, respectively. The spectra were recorded with 4 cm^{-1} resolution and 64 scans. Thermogravimetric analysis (TGA) was performed on a Rigaku Thermo plus Evo2 instrument. Samples (10 mg) were heated from 30 to 800 °C with the ramping rate of 10 °C min^{-1} at a constant airflow of 50 mL min^{-1}.

Xylose dehydration to frufural.

The catalytic reaction was typically conducted in a pressure-resistant spherical glass reactor using 75 mg of xylose in 2 mL of water and 8 mL of toluene with 300 mg of catalyst. In this system, toluene functions as an extraction solvent for furfural, and contributes to improving the selectivity of furfural.[S3] The reaction mixture was heated in an oil bath. After the reaction, the reactor was completely cooled in the ice bath, and the reaction mixture was separated by centrifugation. The aqueous phase was analyzed using a Shimadzu LC-2030C Plus high-performance liquid chromatograph. The mobile phase consisted of a 5 mmol L^{-1} sulfuric acid solution. The reactants were separated using a BIO-RAD Aminex HPX-87H column and detected by a refractive index detector (RID-20A) and an ultraviolet detector (245 nm). The organic phase was quantified using chlorobenzene as an internal standard and analyzed by a gas chromatograph (GC, Shimadzu, GC-2025AF) equipped with a flame ionization detector (FID). Conversion, yields and selectivity were calculated based on the following equations. In this study, the detectable product is limited only to furfural, meaning that by-products are defined as “humin-type undetectable species”.

$$Conversion = 100\% * \frac{Moles\ of\ xylose_{initial} - Moles\ of\ sylose_{final}}{Moles\ of\ xylose_{initial}} \quad \textbf{(1)}$$

$$Yield_{fufural} = 100\% * \frac{Moles\ of\ furfural_{final}}{Moles\ of\ xylose_{initial}} \quad \textbf{(2)}$$

$$Yield_{by-products} = Moles\ of\ xylose_{initial} - Yield_{fufural} \quad \textbf{(3)}$$

$$Selectivity_{furfural} = 100\% * \frac{Yield_{fufural}}{Conversion} \quad \textbf{(4)}$$

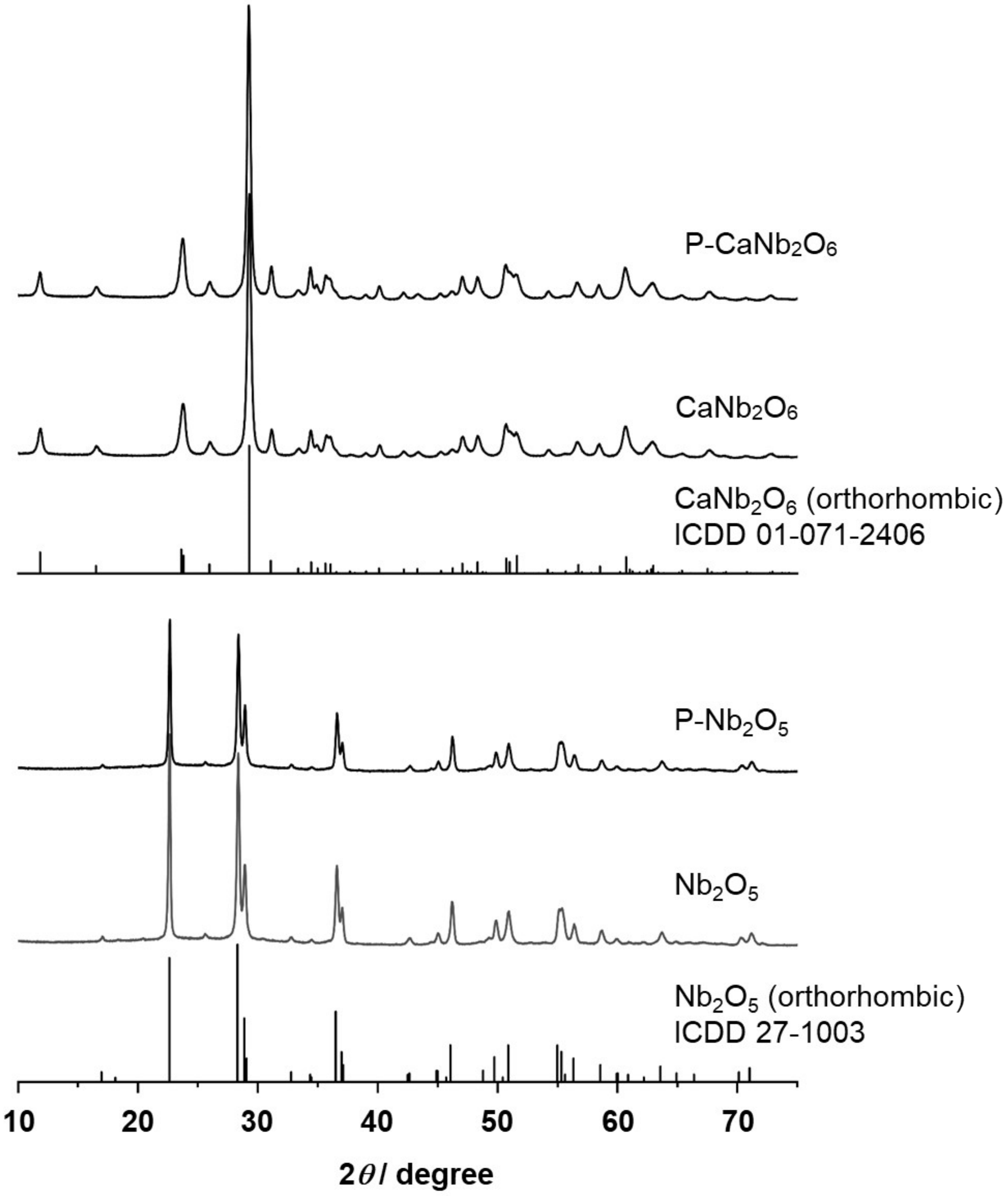

Fig. S1. XRD patterns for prepared samples.

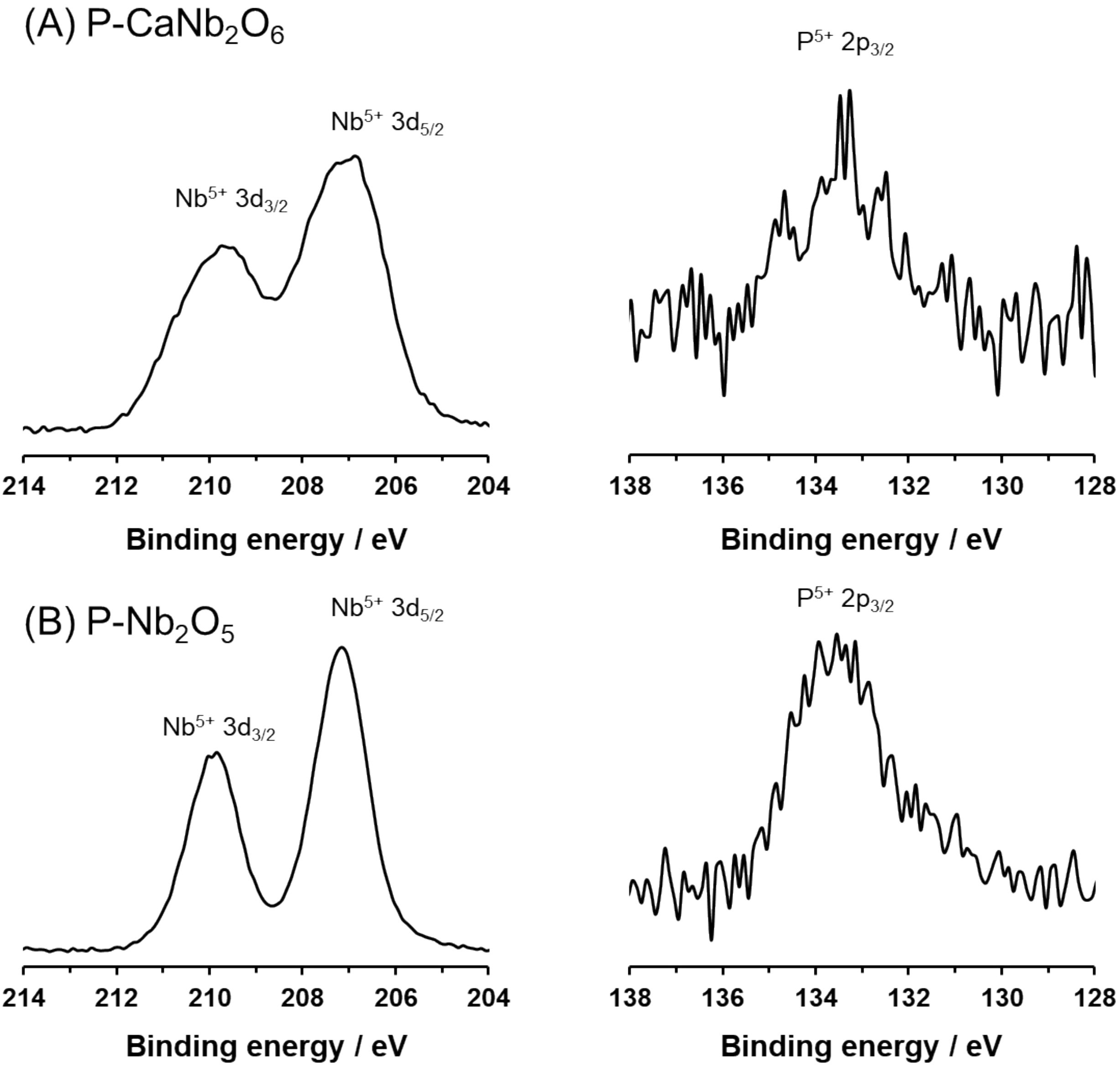

Fig. S2. XPS data of (A) P-CaNb$_2$O$_6$ and (B) P-Nb$_2$O$_5$.

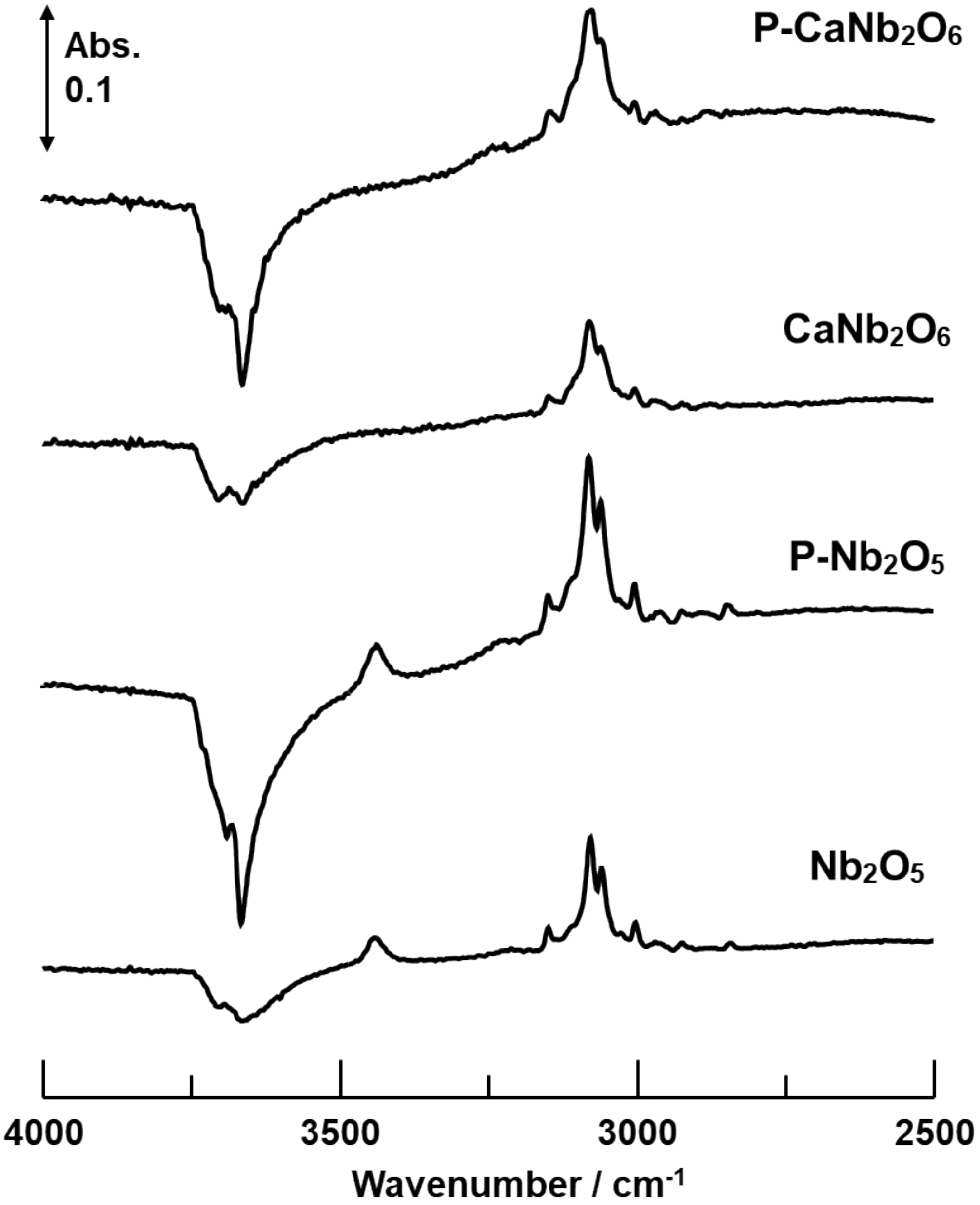

Fig. S3. Difference IR spectra in O-H and C-H stretching vibrations of adsorbed pyridine species on each catalyst at 30 °C.

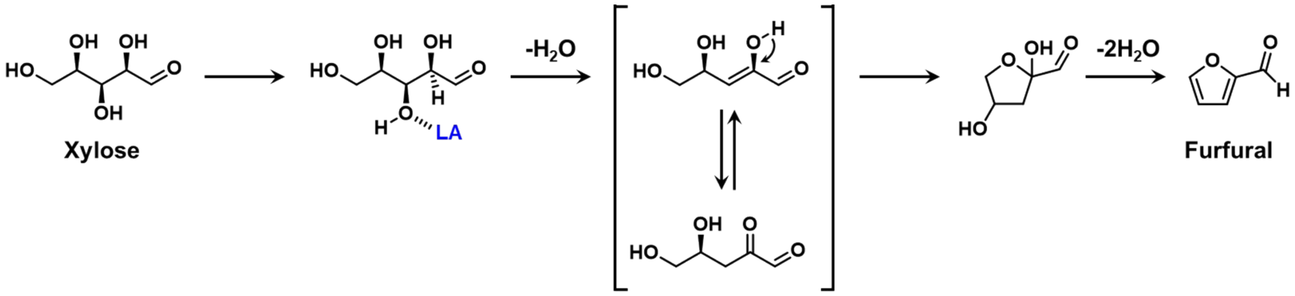

Fig. S4. Proposed reaction mechanism for xylose dehydration over Lewis acidic metal oxides via stepwise dehydration.[S3].

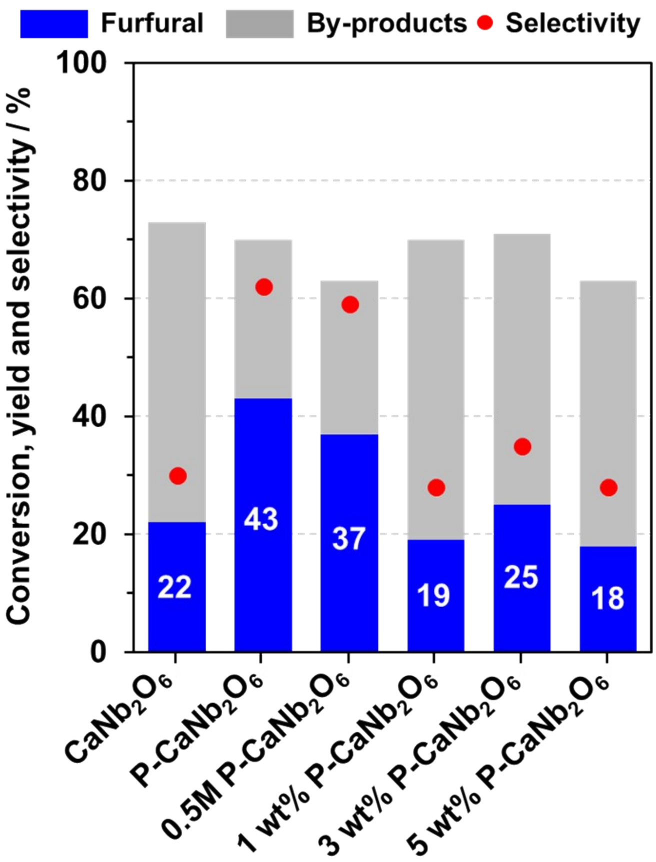

Fig. S5. Effect of phosphate loading (wet-impregnation vs equilibrium adsorption) on the catalytic activity of the resulting $CaNb_2O_6$. Reaction conditions: xylose, 75 mg; catalyst, 300 mg; toluene, 8 mL; water, 2 mL, temperature, 120 °C, time, 5 h. By-products indicate undetectable products, calculated by subtracting the total yield of detectable products (only furfural in this study) from the xylose conversion. The sum of the blue and gray bars means the xylose conversion.

To investigate the effect of phosphate loading on the activity of the resulting P-$CaNb_2O_6$, we synthesized several P-$CaNb_2O_6$ samples by both a conventional wet-impregnation method and an equilibrium adsorption method. In the wet-impregnation method, the samples were denoted as X % P-$CaNb_2O_6$ where X represents the weight percentage of phosphate species impregnated onto $CaNb_2O_6$. In the equilibrium adsorption method, phosphoric acid solutions with two different concentrations (0.5 M and 1.0 M) were employed to prepare P-$CaNb_2O_6$. The samples prepared with 0.5 M and 1 M solutions were denoted as P-$CaNb_2O_6$ and 0.5M P-$CaNb_2O_6$, respectively. No significant difference in the activity between P-Nb_2O_6 and 0.5M P-$CaNb_2O_6$ suggests that the $CaNb_2O_6$ surface is saturated to a similar extent with phosphate groups in both treatments, affording comparable sample. In contrast, the impregnated catalysts exhibited similar activity to bare $CaNb_2O_6$, meaning that phosphate species immobilized via the equilibrium adsorption method are essential for enhancing the acid properties and, consequently, improving the catalytic activity.

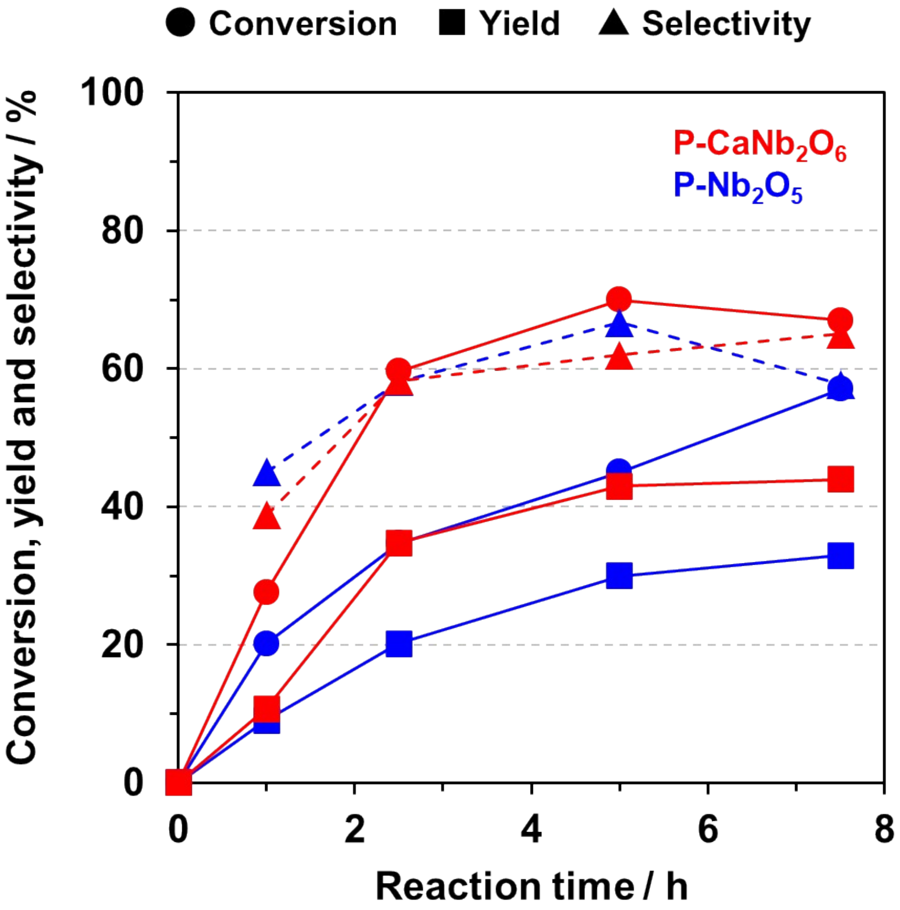

Fig. S6. Time course for xylose dehydration with P-$CaNb_2O_6$ and P-Nb_2O_5. Reaction conditions: Xylose, 75 mg; catalyst, 300 mg; toluene, 8 mL; water, 2 mL, temperature, 120 °C.

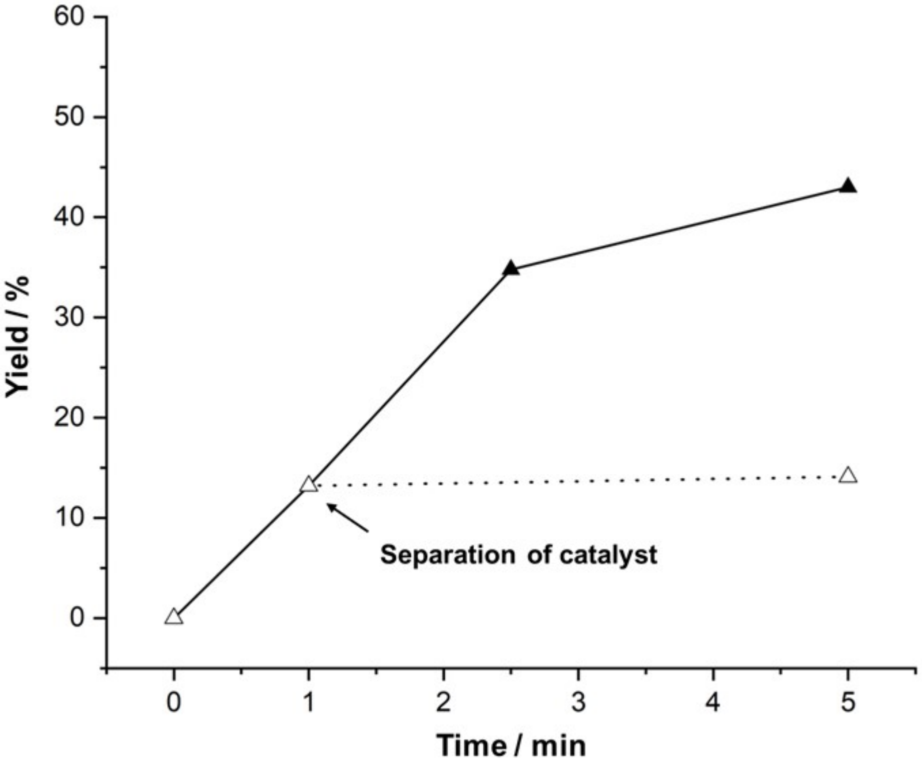

Fig. S7. Leaching test for P-$CaNb_2O_6$. Reaction conditions: Xylose, 75 mg; catalyst, 300 mg; toluene, 8 mL; water, 2 mL, temperature, 120 °C.

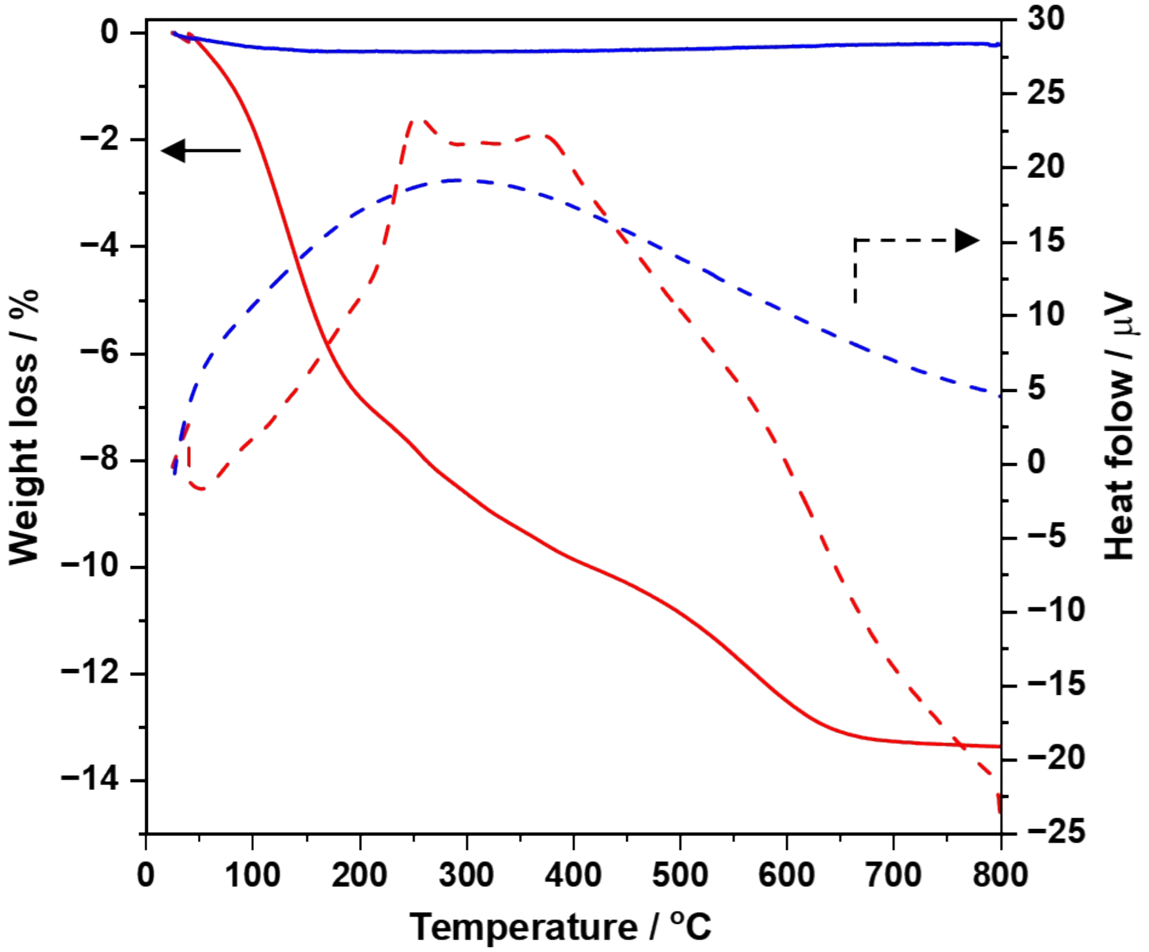

Fig. S8. TG-DTA profiles for P-$CaNb_2O_6$ before (blue) and after (red) the reaction.

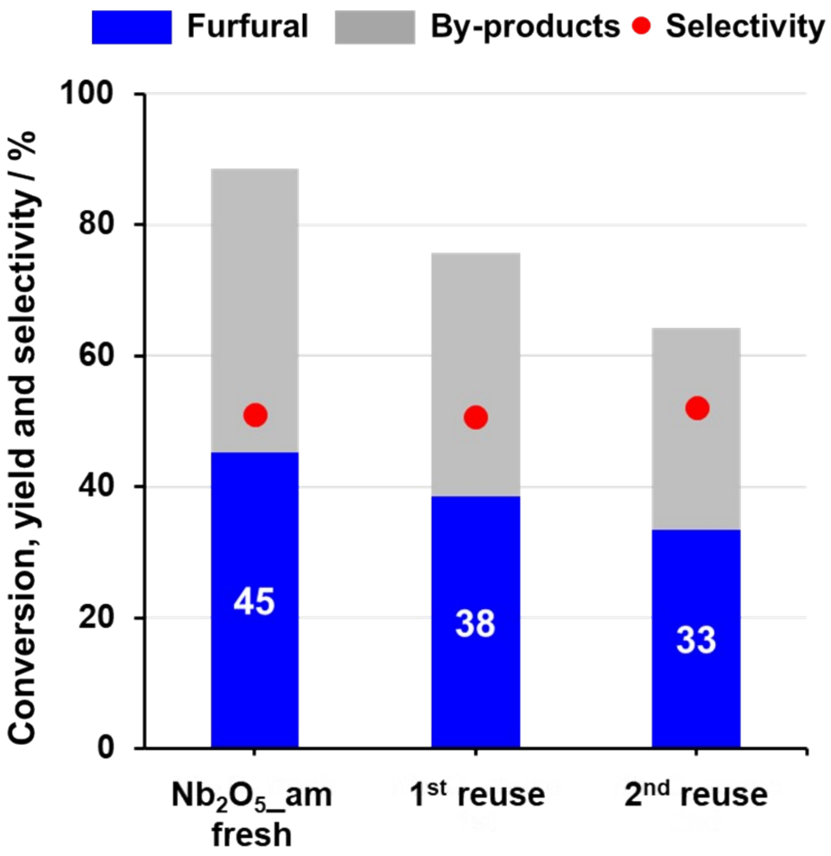

Fig. S9. The reusability test of Nb$_2$O$_5$-am for xylose dehydration. Reaction conditions: Xylose, 75 mg; catalyst, 300 mg; toluene, 8 mL; water, 2 mL, temperature, 120 °C; time, 5 h. By-products indicate undetectable products, calculated by subtracting the total yield of detectable products (only furfural in this study) from the xylose conversion. The sum of the blue and gray bars means the xylose conversion.

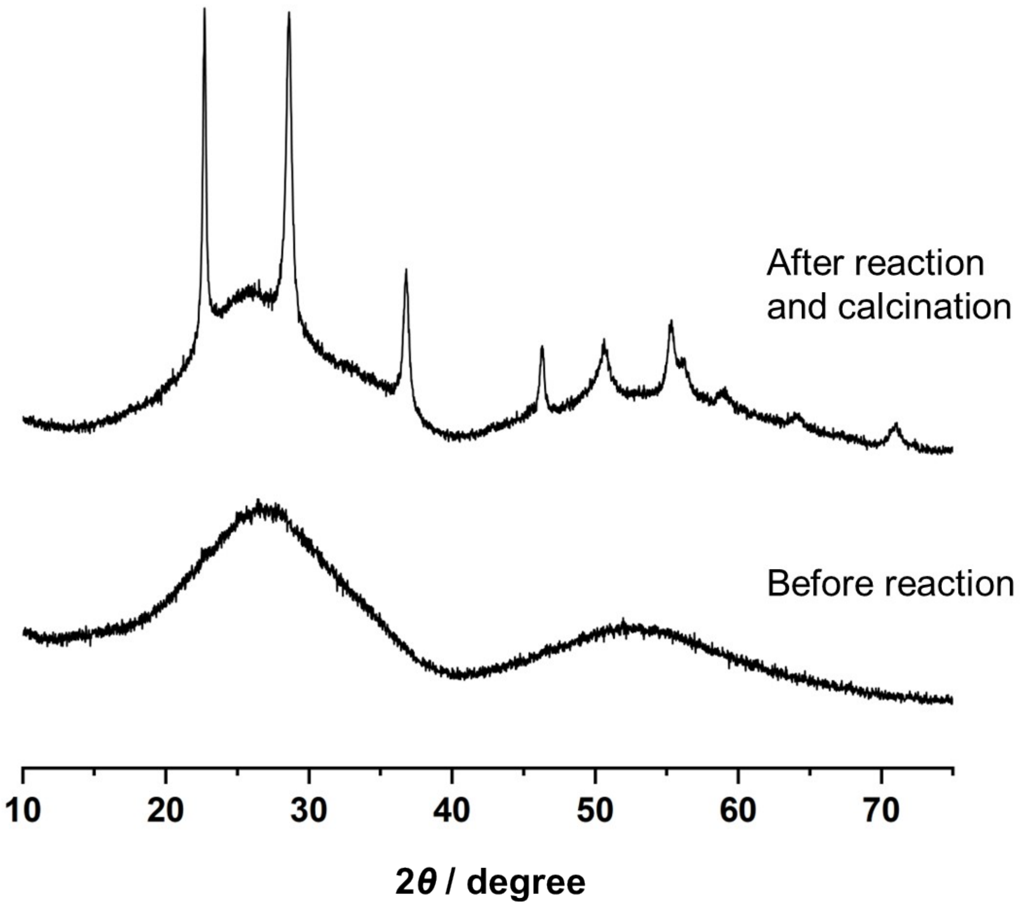

Fig. S10. XRD patterns of Nb_2O_5-am before and after reaction.

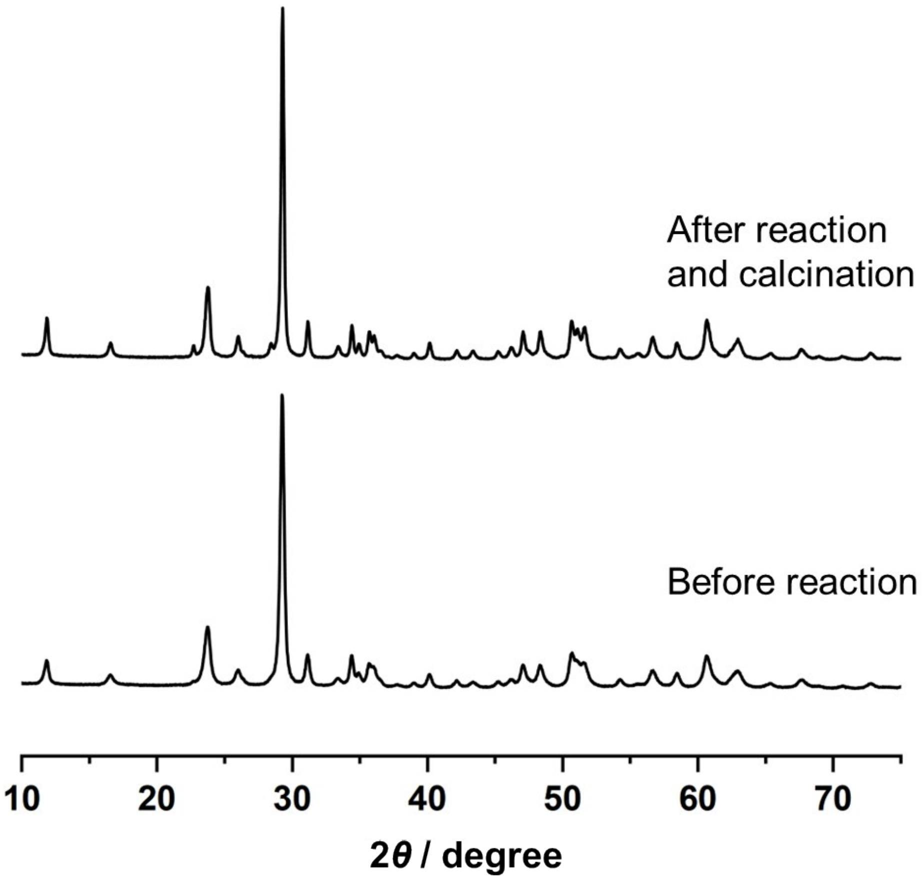

Fig. S11. XRD patterns of $CaNb_2O_6$ before and after reaction.

Supplementary references

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