

## Electronic Supplementary Information for *Chemical Communications*

### Dual functional catalysis of $[\text{Nb}_6\text{O}_{19}]^{8-}$ -modified Au/ $\text{Al}_2\text{O}_3$

Soichi Kikkawa,<sup>a,b</sup> Shoji Fukuda,<sup>a</sup> Jun Hirayama,<sup>a,b</sup> Naoki Shirai,<sup>a</sup> Ryo Takahata<sup>c</sup>,  
Kosuke Suzuki,<sup>d,e</sup> Kazuya Yamaguchi,<sup>d</sup> Toshiharu Teranishi<sup>c</sup> and Seiji Yamazoe<sup>\*a,b,e</sup>

- a. Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo, 192-0397, Japan
- b. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto, 615-8245, Japan
- c. Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.
- d. Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.
- e. Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Tokyo 102-0076, Japan.

\*Corresponding Author: Seiji YAMAZOE

E-mail: yamazoe@tmu.ac.jp

## Preparation of catalysts

Au/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the precipitation method using base according to the literature.<sup>1</sup> Au NPs were prepared by the addition of 1 M NaOH into an aqueous solution of HAuCl<sub>4</sub> (10 mM) with maintaining pH at ca. 9. The Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-7, <100 mesh powder, 1 g), which was supplied from Catalytic Society of Japan, was then dispersed into the solution. After stirring for 1h, the Al<sub>2</sub>O<sub>3</sub> powder was filtrated, washed, and dried at 333 K. The powder was reduced at 573 K for 2 h in the presence of 0.01 MPa of sufficient H<sub>2</sub> to obtain Au/Al<sub>2</sub>O<sub>3</sub>. The [Nb<sub>6</sub>O<sub>19</sub>]<sup>8-</sup>-modified Au/Al<sub>2</sub>O<sub>3</sub> was synthesized by the adsorption method. The Au/Al<sub>2</sub>O<sub>3</sub> was dispersed into the aqueous solution of K<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub>·14H<sub>2</sub>O (Mitsuwa Chemicals Co. Ltd., 0.8 mM) at a ratio of [Au atoms]:[Nb<sub>6</sub>O<sub>19</sub>] = 1:4, and this mixture was stirred for 10 min. After filtration, washing with pure water, and evacuation at 333 K, [Nb<sub>6</sub>O<sub>19</sub>]<sup>8-</sup>-modified Au/Al<sub>2</sub>O<sub>3</sub> (Nb6-Au/Al<sub>2</sub>O<sub>3</sub>) was obtained. [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup>-a and [SiW<sub>11</sub>O<sub>39</sub>]<sup>8-</sup>-modified Au/Al<sub>2</sub>O<sub>3</sub> (Ta6-Au/Al<sub>2</sub>O<sub>3</sub> and SiW11-Au/Al<sub>2</sub>O<sub>3</sub>, respectively) also prepared by using K<sub>8</sub>Ta<sub>6</sub>O<sub>19</sub>·16H<sub>2</sub>O (Mitsuwa Chemicals Co. Ltd) and K<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub> that was prepared according to the literature,<sup>2</sup> respectively. The [Nb<sub>6</sub>O<sub>19</sub>]<sup>8-</sup>-absorbed Al<sub>2</sub>O<sub>3</sub> (Nb6/Al<sub>2</sub>O<sub>3</sub>) was prepared by an absorption method. Al<sub>2</sub>O<sub>3</sub> was dispersed with K<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub> (0.04 mmol) and then dried up at 353 K.

## Characterizations

The loading amount of Au NPs, and [Nb<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> and [Ta<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> clusters were determined by ICP-AES spectrometer (ICPS-8100, Shimadzu). The structures of the prepared catalysts were characterized by PXRD (MiniFlex, Rigaku). The optical property was measured by UV-vis spectrometer (V-770, JASCO). The structure of the [Nb<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> precursor was confirmed by using a Fourier-transformed infrared spectrometer (FT/IR-4X, JASCO) equipped with an attenuated total reflection (ATR) unit. Nb K-edge XAS spectra were measured using BL01B1<sup>3</sup> beamline in SPring-8 (Japan Synchrotron Radiation Research Institute). The data reduction was carried out using xTunes software.<sup>4</sup> The particle size of the supported Au NPs was estimated by using HAADF-STEM equipped with EDX microanalyzer operating at 300 keV (JEM-3200FS, JEOL). The electronic states of Au NPs surface were evaluated by XP spectra (PHI5000 VersaProbe, ULVAC-PHI). The energy calibration was performed by using the C 1s signal at 284.6 eV.

## Catalytic reactions

The catalytic hydrogenation of *p*-nitrophenol, *p*-nitrobenzene, and *p*-nitrostyrene was performed using an autoclave reactor in methanol solution (catalyst: 5 mg, substrate: 62.1 μmol, methanol: 1 mL, H<sub>2</sub>: 1 MPa, reaction temperature: 353 K, reaction time: 2 h). Biphenyl was used as an internal standard. The products were analyzed by GC-FID. The conversion was calculated by the decreased amount of the substrate. The selectivity toward each product was calculated by the fraction of detected products. As a blank test, the reaction of over Au/Al<sub>2</sub>O<sub>3</sub> with the addition of K<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub> (1 mg) or K<sub>2</sub>CO<sub>3</sub> (1 mg) as a base was also carried out at the same reaction conditions. As for the reusability test, the samples were collected by centrifugation.

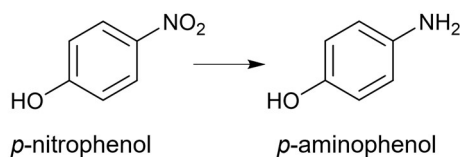
**Table S1** Contained amount of Au and Nb species measured by using ICP-AES<sup>a</sup>.

| Catalyst                              | Amount (mg) | Au <sup>b</sup> (μg) | Nb <sup>b</sup> (μg) | Ta <sup>b</sup> (μg) | Au (wt%) | Nb or Ta (wt%) | POM (wt%) | POM (μmol/g <sub>cat</sub> ) |
|---------------------------------------|-------------|----------------------|----------------------|----------------------|----------|----------------|-----------|------------------------------|
| Nb6-Au/Al <sub>2</sub> O <sub>3</sub> | 19.0        | 137                  | 84.5                 | n.d.                 | 0.72     | 0.44           | 0.69      | 8.0                          |
| Ta6-Au/Al <sub>2</sub> O <sub>3</sub> | 19.5        | 136                  | n.d.                 | 392                  | 0.70     | 2.0            | 2.6       | 18                           |
| Au/Al <sub>2</sub> O <sub>3</sub>     | 19.9        | 146                  | n.d.                 | n.d.                 | 0.73     | –              | –         | –                            |

<sup>a</sup>The sample for ICP-AES measurement was prepared as follows; ca. 20 mg of POM-Au/Al<sub>2</sub>O<sub>3</sub> was added into a mixture of HCl (Kanto Chemical Co., Inc., 35.0–37.0%, 1.2 mL), HNO<sub>3</sub> (Kanto Chemical Co., Inc., 60.0–61.0%, 0.4 mL), and HF (Kanto Chemical Co., Inc., >46.0%, 0.4 mL) and stirred at 423 K overnight. Then, the obtained clear solution without precipitates was diluted to the total volume of 20 mL.

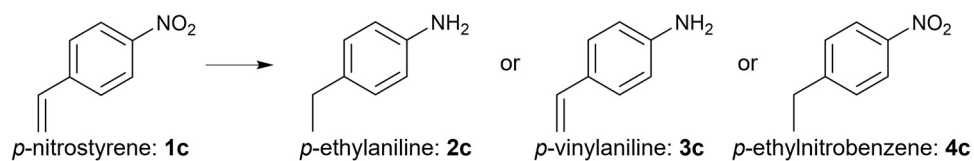
<sup>b</sup>The concentration of Au, Nb, and Ta were estimated by using the emission intensity at 242.8 nm, 316.3 nm, and 226.2 nm, respectively. The contained amount of those species were calculated as follows;

(Contained amount) (g) = (concentration of target element in measured solution) × (total volume of solution)

**Table S2** Reaction results for reduction of *p*-nitrophenol over Nb6-Au/Al<sub>2</sub>O<sub>3</sub><sup>a</sup>.

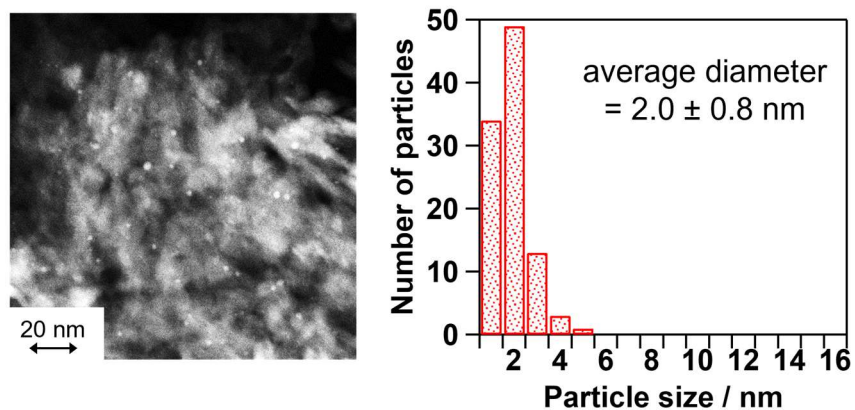
| Entry | Reaction time (h) | Conversion (%) |
|-------|-------------------|----------------|
| 1     | 2                 | 86             |
| 2     | 7                 | 95             |
| 3     | 18                | >99            |

<sup>a</sup> Catalyst, 5 mg; substrate, 62.1 μmol; methanol, 1 mL; H<sub>2</sub>, 1 MPa; reaction temperature, 353 K.

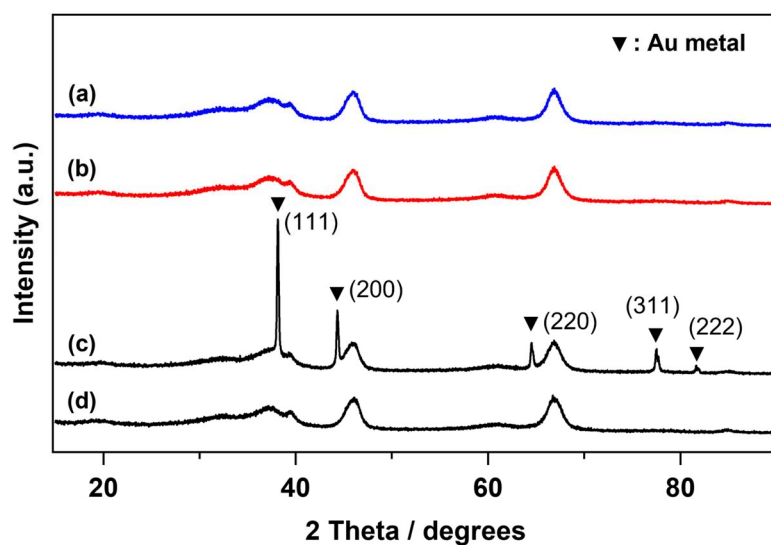
**Table S3** Reaction results for reduction of *p*-nitrostyrene (**1c**) over Nb6-Au/Al<sub>2</sub>O<sub>3</sub><sup>a</sup>.

| Entry | Catalyst                              | Time (h) | Conversion (%) | Selectivity (%) ( <b>2c:3c:4c</b> ) |
|-------|---------------------------------------|----------|----------------|-------------------------------------|
| 1     | Nb6-Au/Al <sub>2</sub> O <sub>3</sub> | 0.5      | 17             | 5:85:10                             |
| 2     | Nb6-Au/Al <sub>2</sub> O <sub>3</sub> | 1        | 85             | 33:56:11                            |
| 3     | Nb6-Au/Al <sub>2</sub> O <sub>3</sub> | 2        | 96             | 92:4:4                              |
| 4     | Au/Al <sub>2</sub> O <sub>3</sub>     | 2        | 21             | 3:97:<1                             |
| 5     | Au/Al <sub>2</sub> O <sub>3</sub>     | 4        | 47             | <1:99:<1                            |
| 6     | Au/Al <sub>2</sub> O <sub>3</sub>     | 6        | 98             | 21:73:6                             |

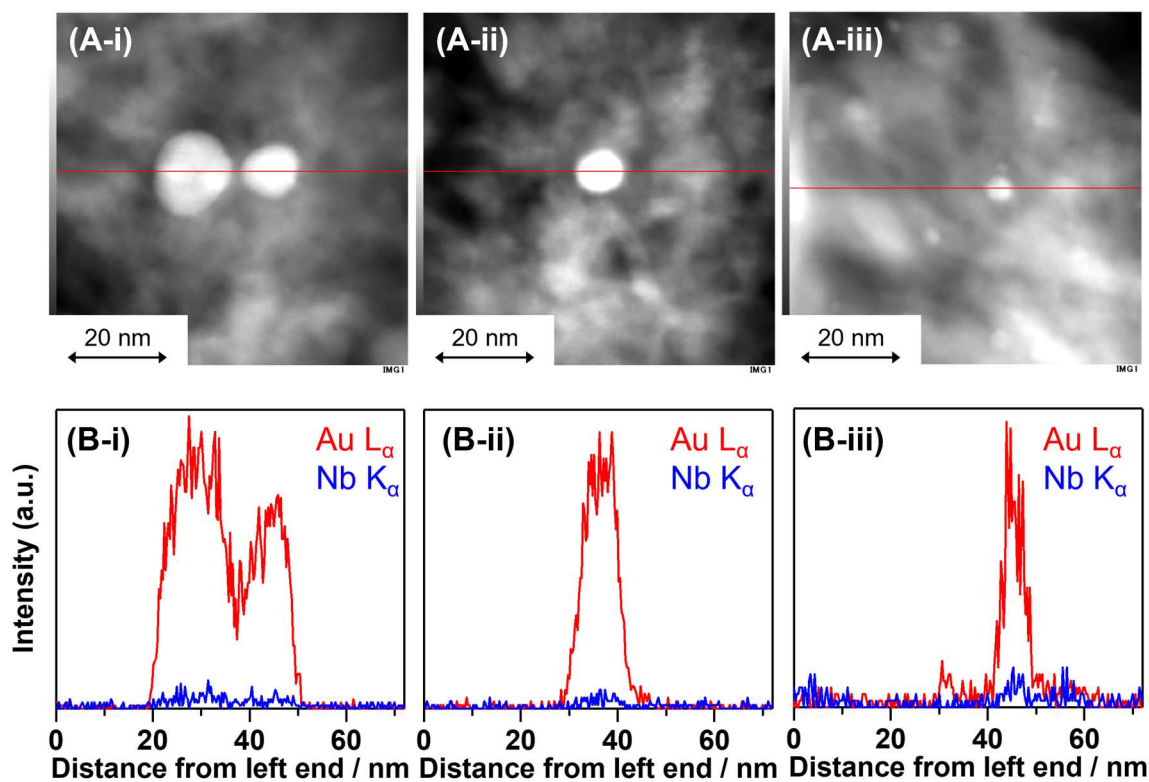
<sup>a</sup> Catalyst, 5 mg; substrate, 62.1 μmol; methanol, 1 mL; H<sub>2</sub>, 1 MPa; reaction temperature, 353 K.



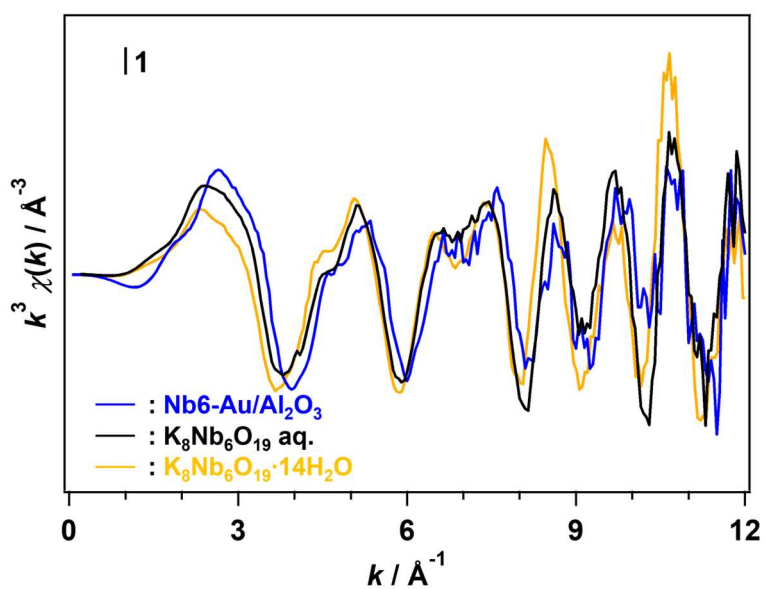
**Fig. S1** HAADF-STEM image and the size distribution of Au NPs of Au/Al<sub>2</sub>O<sub>3</sub>.



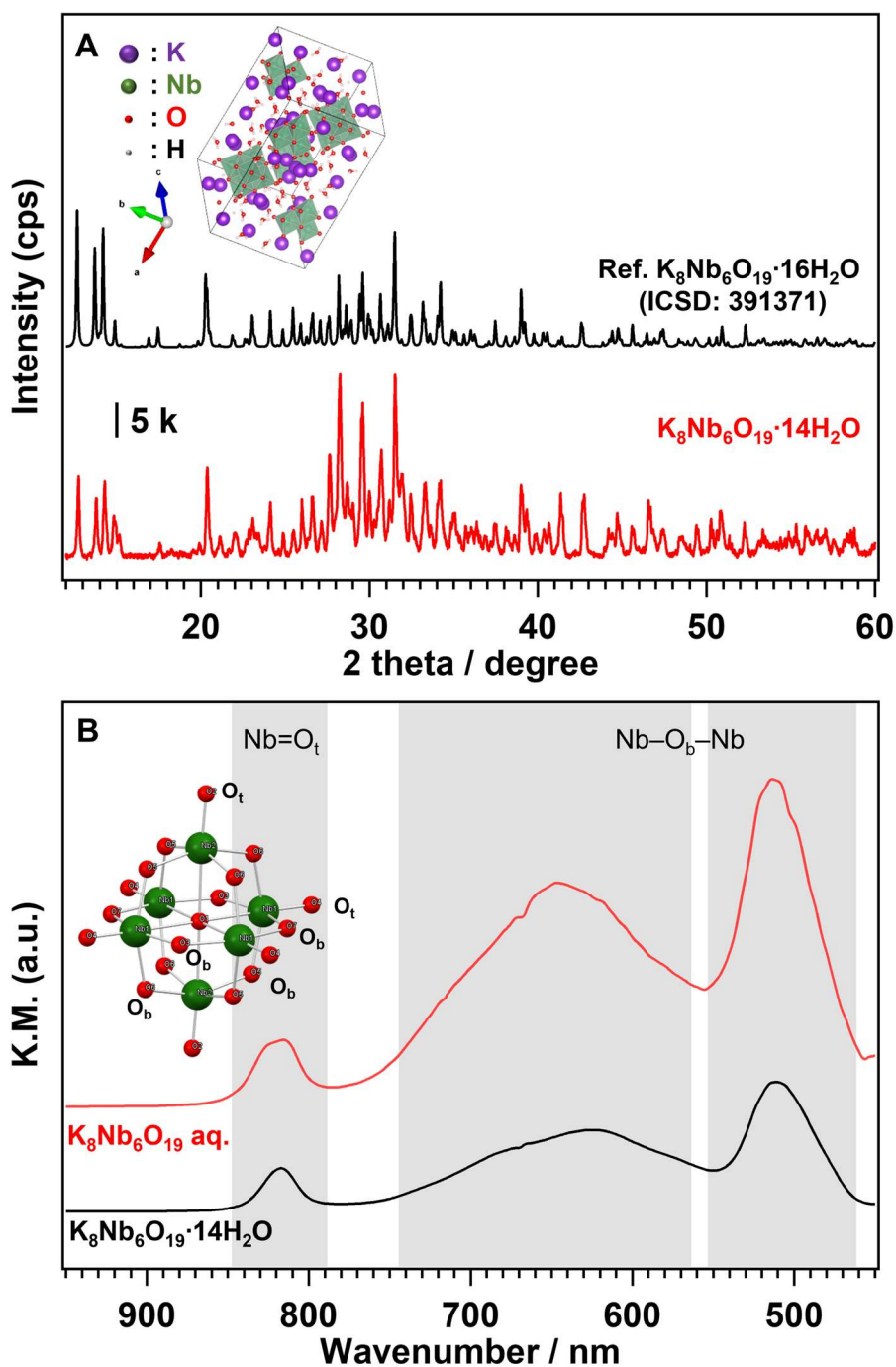
**Fig. S2** XRD patterns of (a) Nb<sub>6</sub>-Au/Al<sub>2</sub>O<sub>3</sub> and (b) Au/Al<sub>2</sub>O<sub>3</sub>. As references, (c) Au/Al<sub>2</sub>O<sub>3</sub> reduced at 773 K, and (d) Al<sub>2</sub>O<sub>3</sub> support.



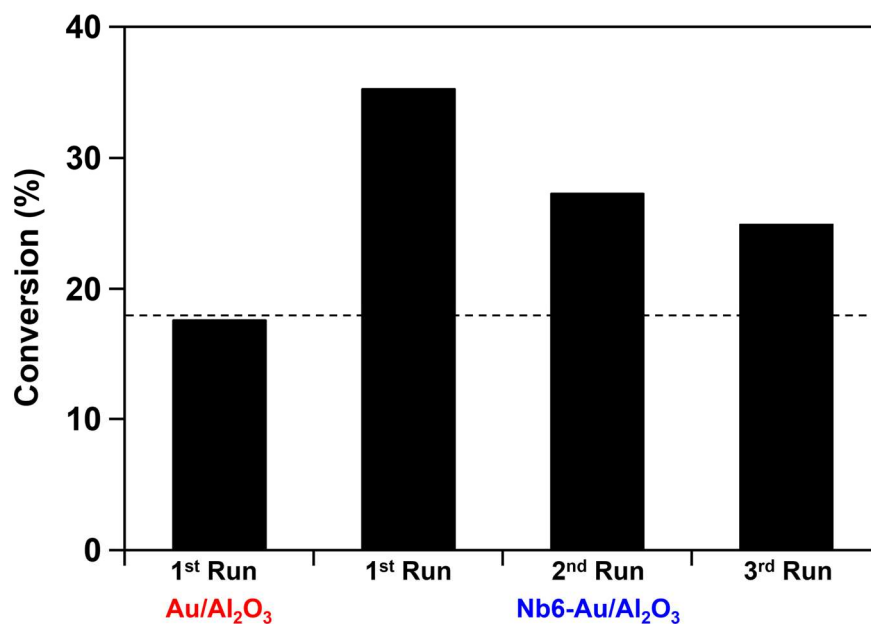
**Fig. S3(A)** STEM image of Au NPs and **(B)** the corresponding line analysis plots for the red line that were monitored at Au  $L_{\alpha}$ - and Nb  $K_{\alpha}$ -edges.



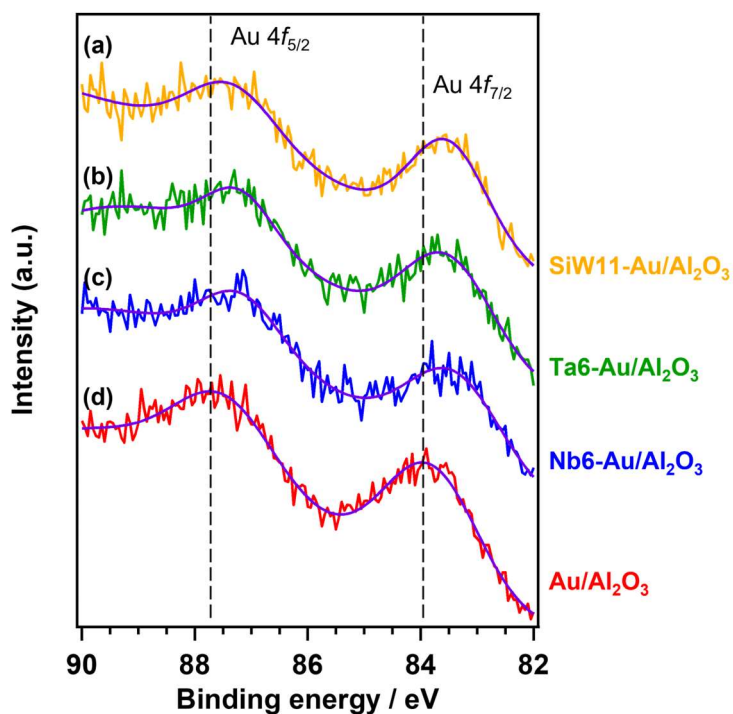
**Fig. S4** Nb K-edge EXAFS oscillations of Nb6-Au/ $Al_2O_3$  (blue), an aqueous solution of  $K_8Nb_6O_{19}$  (black), and  $K_8Nb_6O_{19} \cdot 14H_2O$  (yellow).



**Fig. S5(A)** XRD patterns of  $K_8Nb_6O_{19} \cdot 14H_2O$  and reference  $K_8Nb_6O_{19} \cdot 16H_2O$  (ICSD: 391371). **(B)** FT-IR spectra of  $K_8Nb_6O_{19} \cdot 14H_2O$  and the aqueous solution of  $K_8Nb_6O_{19}$ . The absorption bands assignable to the stretching vibration between Nb and terminal oxygen and that between Nb and bridged oxygen retained even in an aqueous solution.



**Fig. S6** Results for reusability test of Nb6-Au/Al<sub>2</sub>O<sub>3</sub>. Catalyst, 5 mg; substrate, 62.1  $\mu$ mol; methanol, 1 mL; H<sub>2</sub>, 1 MPa; reacton temperature, 353 K; reaction time, 1 h; The samples were collected by centrifugation for reuse.



**Fig. S7** XPS spectra of (a) SiW11-Au/Al<sub>2</sub>O<sub>3</sub>, (b) Ta6-Au/Al<sub>2</sub>O<sub>3</sub>, (c) Nb6-Au/Al<sub>2</sub>O<sub>3</sub>, and (d) Au/Al<sub>2</sub>O<sub>3</sub>.



## Reference

1. L. M. D. R. d. S. Martins, S. A. C. Carabineiro, J. Wang, B. G. M. Rocha, F. J. Maldonado Hódar and A. J. L. d. O. Pombeiro, *ChemCatChem*, 2017, **9**, 1211–1221.
2. A. Tézé and G. Hervé, *Inorg. Synth*, 1990, **27**, 88-98.
3. T. Uruga, H. Tanida, Y. Yoneda, K. Takeshita, S. Emura, M. Takahashi, M. Harada, Y. Nishihata, Y. Kubozono and T. Tanaka, *J. Synchrotron Radiat.*, 1999, **6**, 143–145.
4. H. Asakura, S. Yamazoe, T. Misumi, A. Fujita, T. Tsukuda and T. Tanaka, *Radiat. Phys. Chem.*, 2020, **175**, 108270–108273.