Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2014

Supporting Information for Hydrothermal synthesis of octahedra-based layered niobium oxide and its catalytic activity as a solid acid Toru Murayama, Junli Chen, Jun Hirata, Keeko Matsumoto and Wataru Ueda *Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan*

Entry	7 Sample	Cal. Temp. /°C	Crystallinity	d(001)	Morphology (particle size /nm)	BET surface) area / m ² g ⁻¹	t-plot / m² g-1	Mesopore volume ^a / cm ³ g ⁻¹	Acid amounts ^t / mmol g ⁻¹	Conversion of benzyl alcohol/ % (yield of benzyl anisole/ %)
1	Ammonium niobium oxalate (CBMM)	400	Deformed orthorombic	3.922	2 Rod(10×50~100)	193	202	0.563	0.152	100° (93.9)°, 51.7 ^d (36.4) ^d
2	Ammonium niobium oxalate (Aldrich)	400	Deformed orthorombic	3.917	7 Rod(10×50~100)	188	195	0.466	0.161	100° (94.6)°, 48.8 ^d (35.8) ^d

Table S1 Results of the characterization of niobium oxides obtained by using ammonium niobium oxide.

^a Calculated by the BJH method, ^b Acid amounts were calculated by NH₃-TPD, ^c reaction conditions: benzyl alcohol (1.0 mmol), anisole (50 mmol), catalyst (0.1 g), 100 °C, 30 min, ^d reaction conditions: benzyl alcohol (10 mmol), anisole (100 mmol), catalyst (0.1 g), 100 °C, 120 min.



Fig. S1 XRD pattern (left) and structure model (right) of a morphous Mo_3VO_x .



Fig. S2 Effects of the amount of niobic acid precursor on the XRD pattern of as-synthesized niobium oxide. ((a) 4 mmol, (b) 3 mmol, (c) 2 mmol, (d) 0.5 mmol and (e) 0.25 mmol (based on Nb) in 40 mL deionized water.) Niobium oxide synthesized from 4 mmol niobic acid is denoted as NbO-NA(c) and that synthesized from 0.25 mmol is denoted as NbO-NA(d) in the text.



Fig. S3 Effects of the concentration of ammonium niobium oxalate on XRD patterns for as-synthesized niobium oxides (a) and calcined samples (b).(The samples were calcined at 400 $^{\circ}$ C for 4 hours under air.) Niobium oxide synthesized from 0.15 mol L⁻¹ ammonium niobium oxalate is denoted as NbO-ANO in the text.



Fig. S4 Effects of the concentration of oxalic acid in precursor solution on the XRD pattern of niobium oxide. (As-synthesized sample (a), after calcination at 400 °C (b), small angle of calcined sample (c), amount of niobic acid was 2 mol (based on Nb) in 40 mL deionized water.) Niobiumoxide synthesized from niobic acid and 0.25 mol L^{-1} oxalic acid is denoted as NbO-NA(o) in the text.



Fig. S5 STEM images of niobium oxides (a, a': NbO-ANO, b: NbO-NA(d), c: NbO-NA(c), d: NbO-NA(o), e:NbO-cal).



Fig. S6 N₂ adsorption isotherms of NbO-ANO, NbO-NA(d), NbO-NA(c), NbO-NA(o), NbO-cal and orthorhombic Mo_3VO_x as a reference. (Samples were calcined at 400 °C for 4 hours under air beforehand, except for NbO-pyro (300 °C for 4 hours).)



Fig. S7 TG and TPD profiles of as-synthesized NbO-ANO. (Weight loss was 6.7% calculated from TG, corresponding to 3.51 mmol/g as Nb₂O₅. 0.714 mmol/g of NH₃ and 0.11 mmol/g of CO₂ were desorbed from TPD, respectively.)



Fig. S8 XPS spectra of NbO-ANO and NbO-cal. (Samples were calcined at 400 °C for 4 hours under air.) The charge of niobium was 5+ for the NbO-ANO sample.



Fig. S9 Time course of alkylation reaction for conditon II in Table 2. (●: conversion of benzyl alcohol, ■: yield of benzyl anisole)



Fig. S10 NH_3 -TPD spectra of various niobium oxides.



Fig. S11 Catalytic activity of reused NbO-ANO for the alkylation reaction. (Reaction condition is the same as the condition II in Table 2)



Fig. S12 TPD spectra of various niobium oxides for m/z=16. (The desorption amount of NH_3 was calculated from these profiles (NbO-ANO: 0.645 mmol g⁻¹, NbO-ANO(K⁺): 0.096 mmol g⁻¹, NbO-ANO(NH₄⁺): 0.523 mmol g⁻¹).