Electronic Supplementary Information (ESI)

Title: Preparation, characterization and catalytic performance of Mo–V–O oxide layers linked by alkylamines

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All chemicals were purchased from Wako Pure Chemical Industries, Ltd. These chemicals were used as purchase without further purification. Distilled water was prepared by using Yamato Autostill WG25 (Tokyo, Japan).

Material synthesis. In a 100–mL beaker, 25 mL $VOSO_4 \cdot nH_2O$ solution ($M_V = 0.10$ mol L^{-1},) was added into 25 mL $(NH_4)_6Mo_7O_{24}.4H_2O$ ammonium heptamolybdate tetrahydrate (AHM) solution ($M_{Mo} = 0.42$ mol L^{-1}). The above mixture was stirred for 10 min at rt. with N_2 bubbling (30 mL min^{-1}), and then the desired amount of alkylamine was added. The mixture was adjusted with NaOH to pH = 3.20, stirred for 1 h at r.t, and then transferred into a 60–mL Teflon–lined autoclave. The autoclave was placed at 175 ^oC for 48 h. The resulting precipitate was then filtered out, washed with chloroform (50 mL × 3), ethanol (50 mL × 3) and acetone (30 mL × 3), and then dried under ambient condition. The sample was degassed from rt. to 300 ^oC at the ramping rate of 10 ^oC min^{-1} in a 50 mL min^{-1} N_2 flow, and kept at 300 ^oC for 30 min.

General characterization. Powder X–ray diffraction (**XRD**) measurements were performed with a Rigaku, RINT Ultima+ diffractometer with Cu K_α radiation (K_α 1.54056 Å) and X–ray power of 40 kV/20mA. Shirley background correction procedures and least-squares fittings methods were adopted for data processing. Field emission scanning electron microscopy (**FE–SEM**) was performed on a JSM–7400F (JEOL). Samples for SEM were dusted on an adhesive conductive carbon paper attached on a brass mount. Specific surface areas were measured by N_2 adsorption at 77 K using Brunauer–Emmett–Teller method (**BET**) over Autosorb 6AG (Quantachrome Instruments). Infrared spectra (**FT–IR**) were recorded on a PERKIN ELMER FTIR spectrometer. The sample pellet of 1.5 mm in diameter was prepared by pressing a mixture of sample and KBr. The IR spectra were recorded by accumulating 32 scans at a spectra resolution of 2 cm^{-1}. UV-Vis spectra were measured with V-570 apparatus (JASCO). The measurements of thermogravimetric analysis (**TGA**) were performed in a TG–8120 (Rigaku) thermogravimetric analyzer. The dry air provided by a pressured tank with the flow rate of 30 mL min^{-1} was used as carrier. The catalyst sample and standard one were loaded into alumina two pans and heated at 10 ^{o}C min^{-1}. The baseline was subtracted from a blank run without loading sample. The measurements of temperature programmed oxidation-mass spectrometer (**TPO–MS)** were conducted on Anelva Quadrupole Mass Specrometer (M–100QA) with 20% O_2/Helium (30 mL min^{-1}) as carrier. Sorption uptake measurments were obtained by means of batch experiments.[1]

Catalysis. We used stirred batch reactor for catalytic tests. The volume of the reactor was ca. 15 mL. In a typical reaction, the catalyst (0.02 g) and magnetic stir bar were initially loaded into the reactor. The oxygen/air provided by gas tank was inflated into the reactor at room temperature through a needle connected with a side-mouth sealed with Teflon septum, through which a mixture of alcohol (0.25 mmol), toluene, and internal standard (p-xylene, 0.04 mL) was injected by a syringe. The total reaction volume was 1.75 mL adjusted by toluene. The reactor was placed into an oil bath which was thermally stabilized at 80 ^{o}C. Aliquots were collected at intervals to monitor the conversion and selectivity. Reactant and product concentrations were measured by gas chromatography using flame ionization detector (Shimazu Classic–5000, 60 m TC WAX column), operated with a heating program: 100 ^{o}C for 10 min, ramp 10 ^{o}C min^{-1} to 230 ^{o}C, and 230 ^{o}C for 25 min.

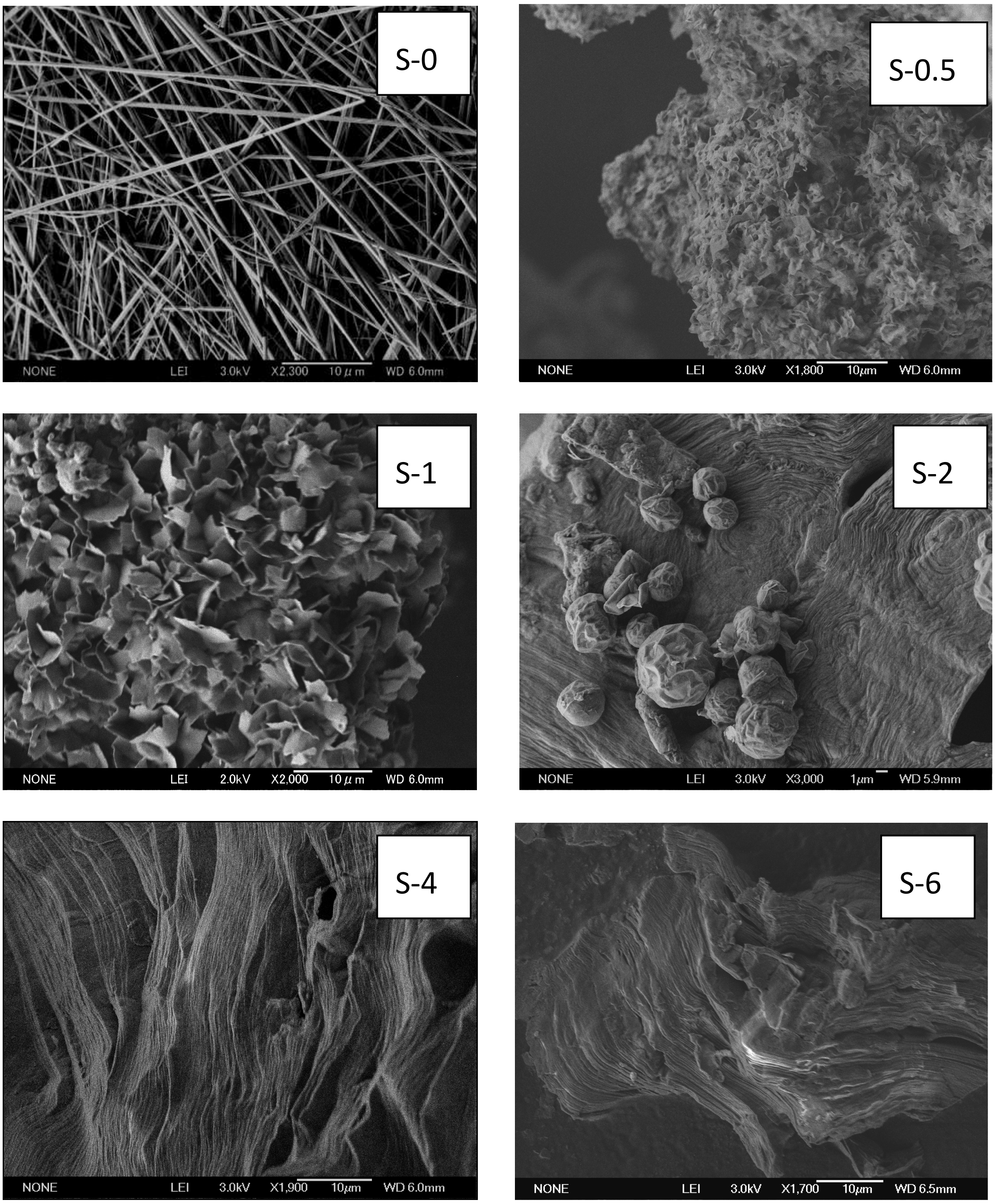

Fig. S1 Representative SEM images of the as-prepared materials

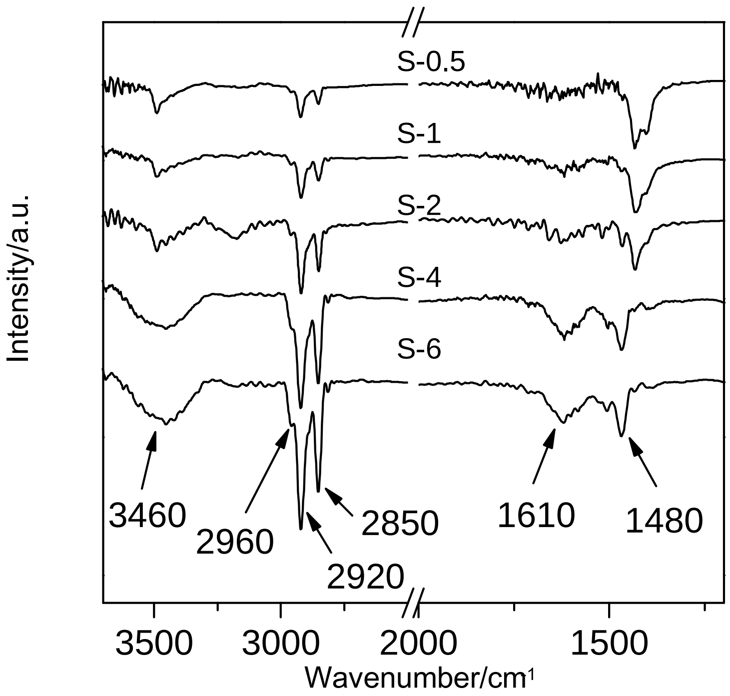

Fig. S2. FT–IR spectra of S–n hybrid materials. In IR spectra the peaks at 2960, 2920 cm^{-1} and 1480 cm^{-1} are due to the ν_{as}(C–H), ν_s(C–H) and $\delta(CH_2)$ vibration modes of $CH_3(CH_2)_{15}NH_2$.

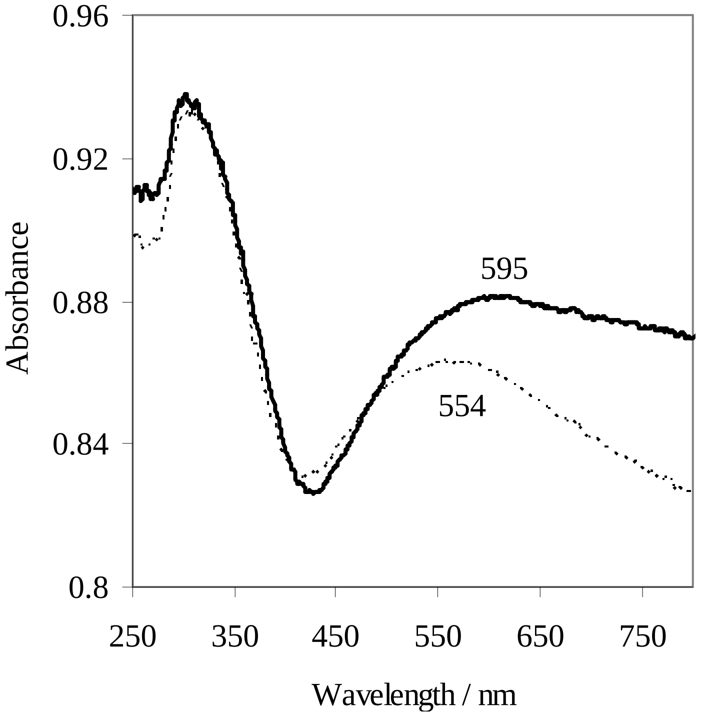

Fig. S3 UV–Vis spectra of the hybrid material (dark line, S-4) and the Mo–V–O crystalline oxide calcined in N_2 (dash line).

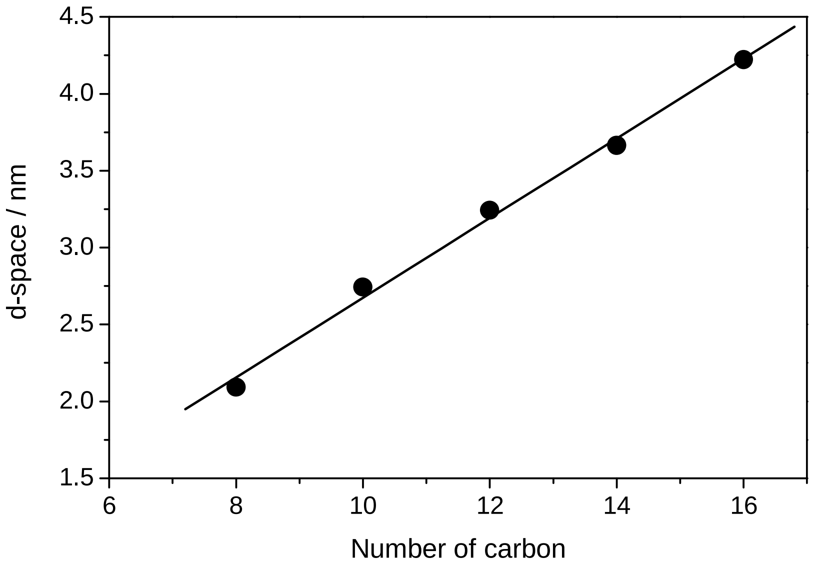

Fig. S4 A plot of d-space value versus the number of carbon atoms in alkylamines.

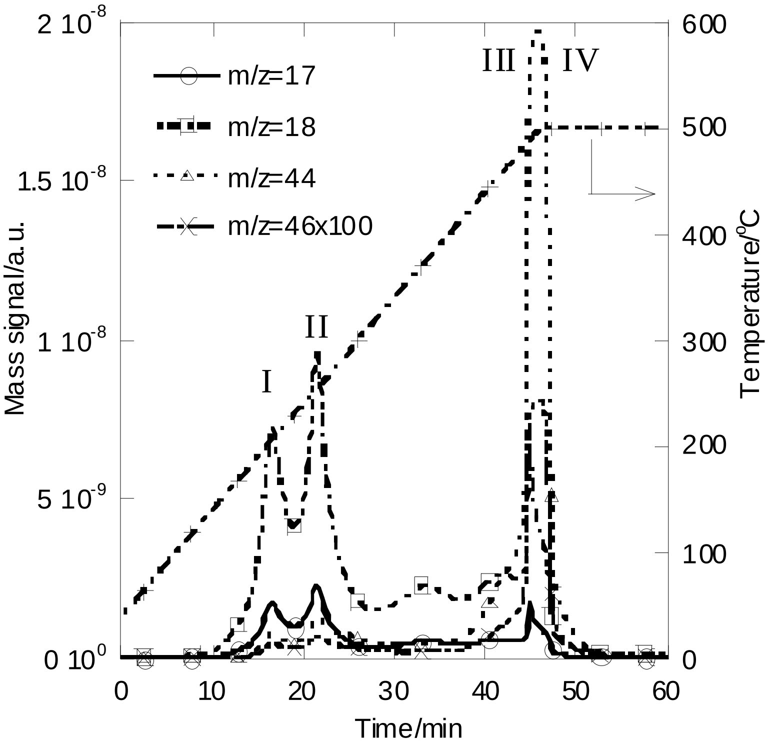

Fig. S5 Temperature programmed oxidation--mass spectrometry profile of S–4.

Reference

1 K. M. A. De Meyer, S. Chempath, J. F. M. Denayer, J. A. Martens, R. Q. Snurr and G. V. Baron, *J. Phys. Chem. B*, 2003, **107**, 10760-10766.