Supporting information

A neutralization-mediated extraction of amphiphilic organic molecules for obtaining high-quality mesoporous alumina

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Experimental Details

Materials

Aluminum *sec*-butoxide was purchased from Kanto Chemical Co. Ethanolic solution of gaseous hydrochloric acid (1 mol L^{-1} HCl in EtOH) was purchased from Yoneyama Yakuhin Kogyo Co. Ammonia (ca. 2.0 mol L^{-1} in ethanol), and triethanolamine (TEA) were obtained from Tokyo Chemical Industry (TCI) Co. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) was obtained from Sigma-Aldrich. Ethanol All other chemicals, such as triethylamine (Et_3N), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), pyridine (Py), concentrated hydrochloric acid (35-37 wt% aqueous solution), acetone, ethanol (99.5% EtOH), and tetrahydrofuran (THF), were obtained from FUJIFILM Wako Pure Chemical Co.

Characterization

Low- and wide-angle X-ray diffraction (XRD) patterns were recorded on Rigaku RINT 2100 diffractometers with monochromated Fe Kα and Cu Kα radiations. N_2 adsorption-desorption isotherms were measured at 77 K by using Anton Paar / Quantachrome Autosorb-iQ after the pretreatment at 110 °C for 6 h under vacuum. Pore size distribution curves were drawn with the Barrett-Joyner-Halenda (BJH) method using the desorption branch. Transmission electron spectroscopic (TEM) images were taken by using JEOL JEM-2010 operated at 200 kV. Field emission scanning electron microscopic (FE-SEM) images were taken by using HITACHI SU9000. Fourier transformed infrared (FT-IR) spectra were measured through common KBr pellet method with a resolution of 4 cm^{-1} using JASCO FT/IR-6100 or JASCO FT/IR-4X. Organic contents before and after extraction of amphophilic organic molecules were quantified by using CHN corder Thermo Finnigan FLASH EA1112. Size exclusion chromatograms (SEC) were recorded by using Waters Alliance HPLC System e2695 equipped with a refractive index (RI) detector model 2414. Ethanol (HPLC grade, FUJIFILM Wako Pure Chemical) was used as an eluent at a flow rate of 0.5 mL min^{-1}. Combustion ion chromatography was utilized for evaluating the amount of HCl in an as-synthesized nanocomposite by using Thermo Fisher Scientific Dionex Integrion HPIC System equipped with conductivity detector and suppressor ADRS-600 with aqueous solution of Potassium hydroxide (KOH) as an eluent. The mass loss during the heating up to 1100 °C with a heating rate of 10 ºC min^{-1} under a flow of air (100 mL min^{-1}) was checked by using a thermogravimeter with a differential thermal analyzer (TG-DTA, Rigaku Thermo plus EVO2 TG-DTA8122). Solid-state ^{13}C DD/MAS NMR spectra were recorded with a JEOL JNM-ECA600 spectrometer with a resonance frequency of 151 MHz when adamantane was used as an external standard (δ = 29.5 ppm).

Results and discussion

Supplementally Figures and Tables

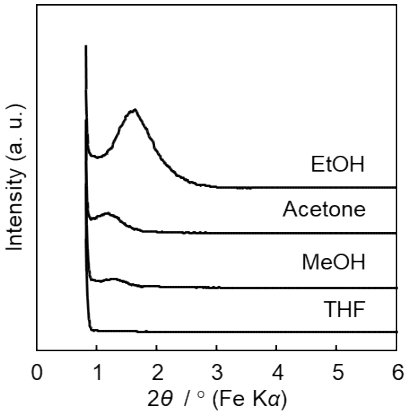

Fig. S1 Low-angle XRD patterns after the treatment of a mesostructured alumina, prepared using Pluronic P123 under the HCl mediated acidic conditions, with some solvents.

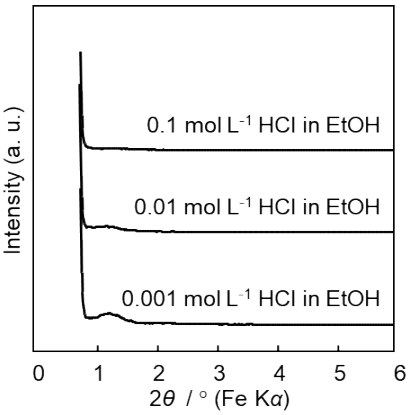

Fig. S2 Low-angle XRD patterns after the treatment of a mesostructured alumina, prepared using Pluronic P123 under the HCl mediated acidic conditions, with ethanolic solution of gaseous HCl.

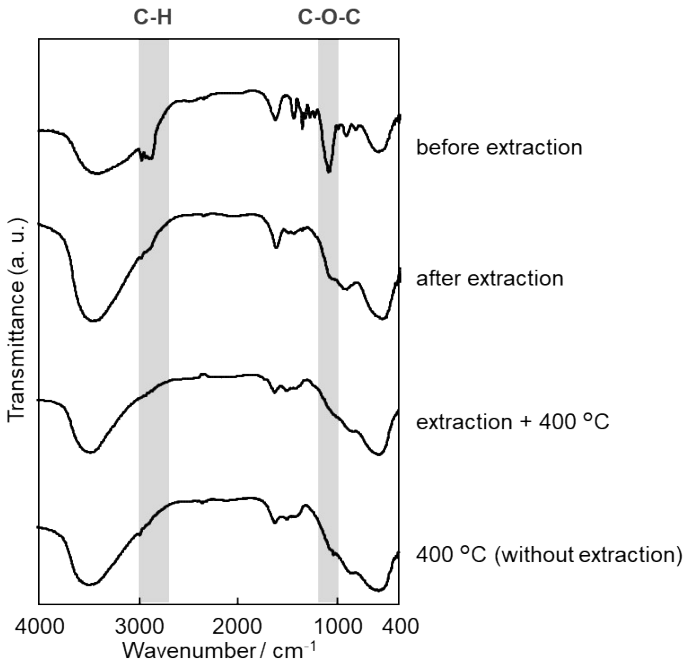

Fig. S3 FT-IR spectra of a mesostructured alumina, prepared using Pluronic P123 under the HCl mediated acidic conditions and those after the neutralization-mediated extraction by using EtOH with triethylamine (Et_3N), additional calcination at 400 °C and direct calcination at 400 °C without the extraction process.

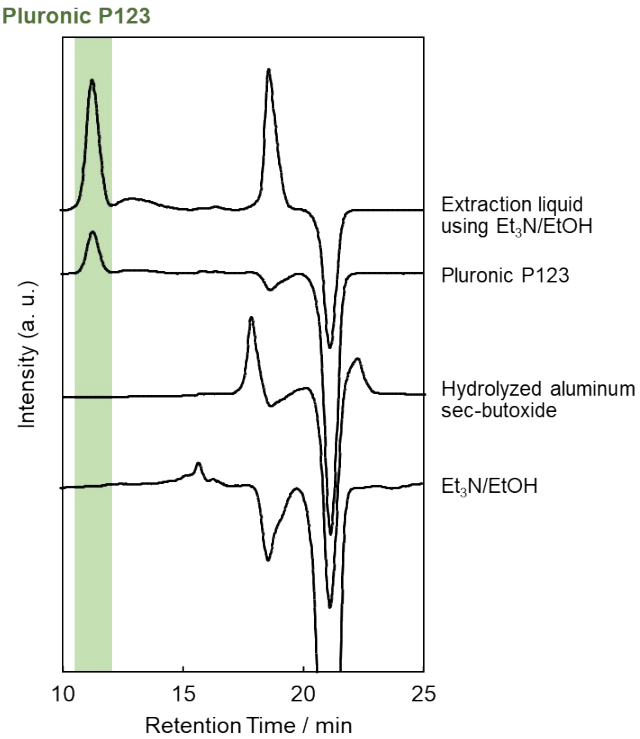

Fig. S4 Size-exclusion chromatography (SEC) traces of resultant solutions after the neutralization-mediated extraction by using Et_3N/EtOH.

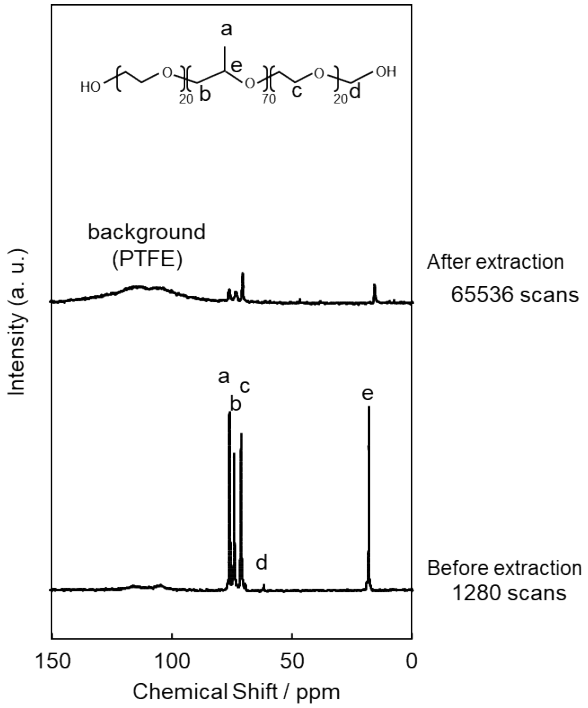

Fig. S5 Solid-state ^{13}C DD/MAS NMR spectra of successful mesoporous alumina before and after the neutralization-mediated extraction by using Et_3N/EtOH, with the assignment of signals to the molecular structure of Pluronic P123.

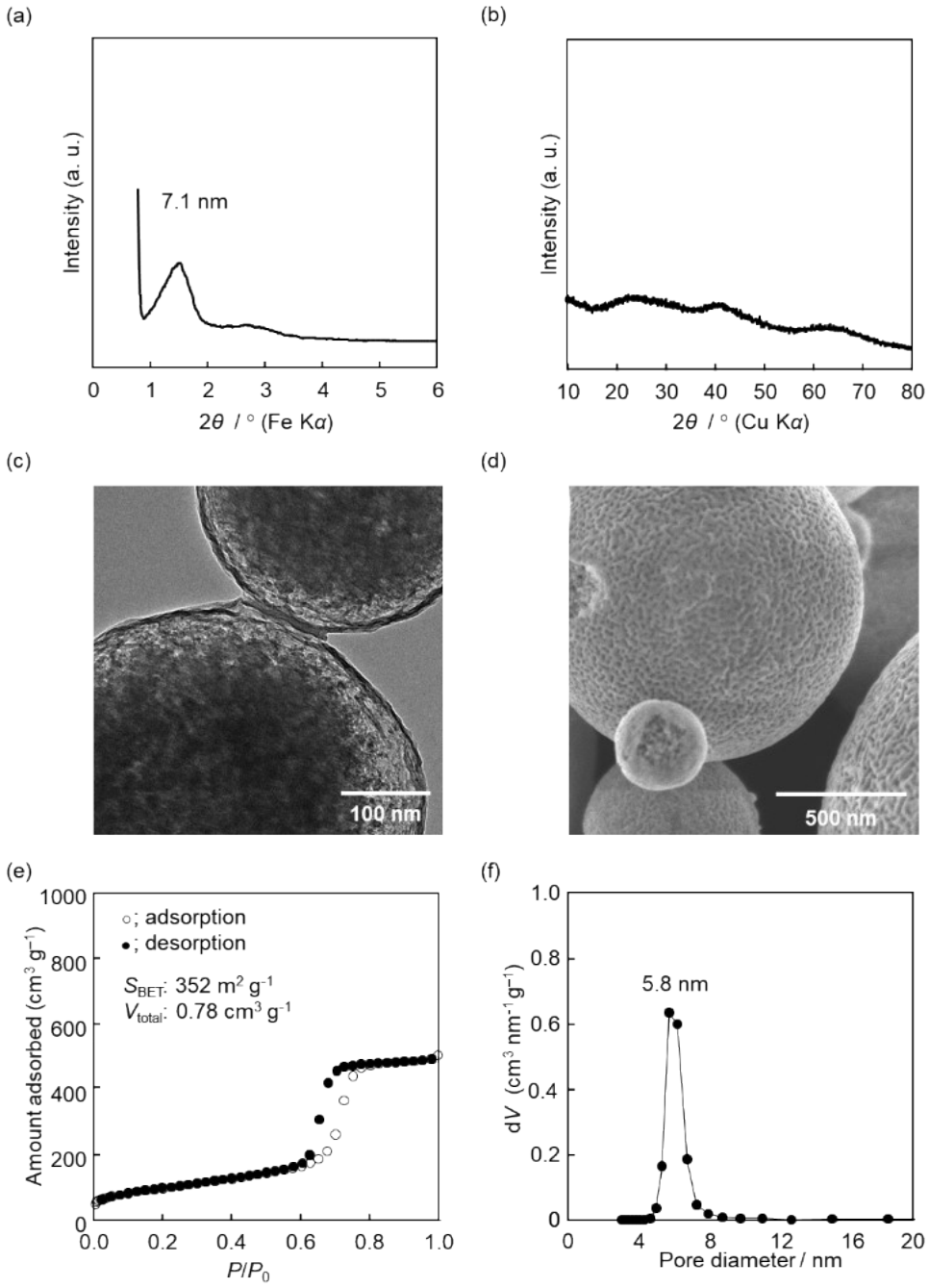

Fig. S6 (a) Low- and (b) wide-angle XRD patterns, (c) TEM and (d) SEM images, and (e) N_2 adsorption-desorption isotherm with (f) corresponding pore size distribution curve of successful mesoporous alumina after the extraction by using Et_3N/EtOH followed by calcination at 400 °C.

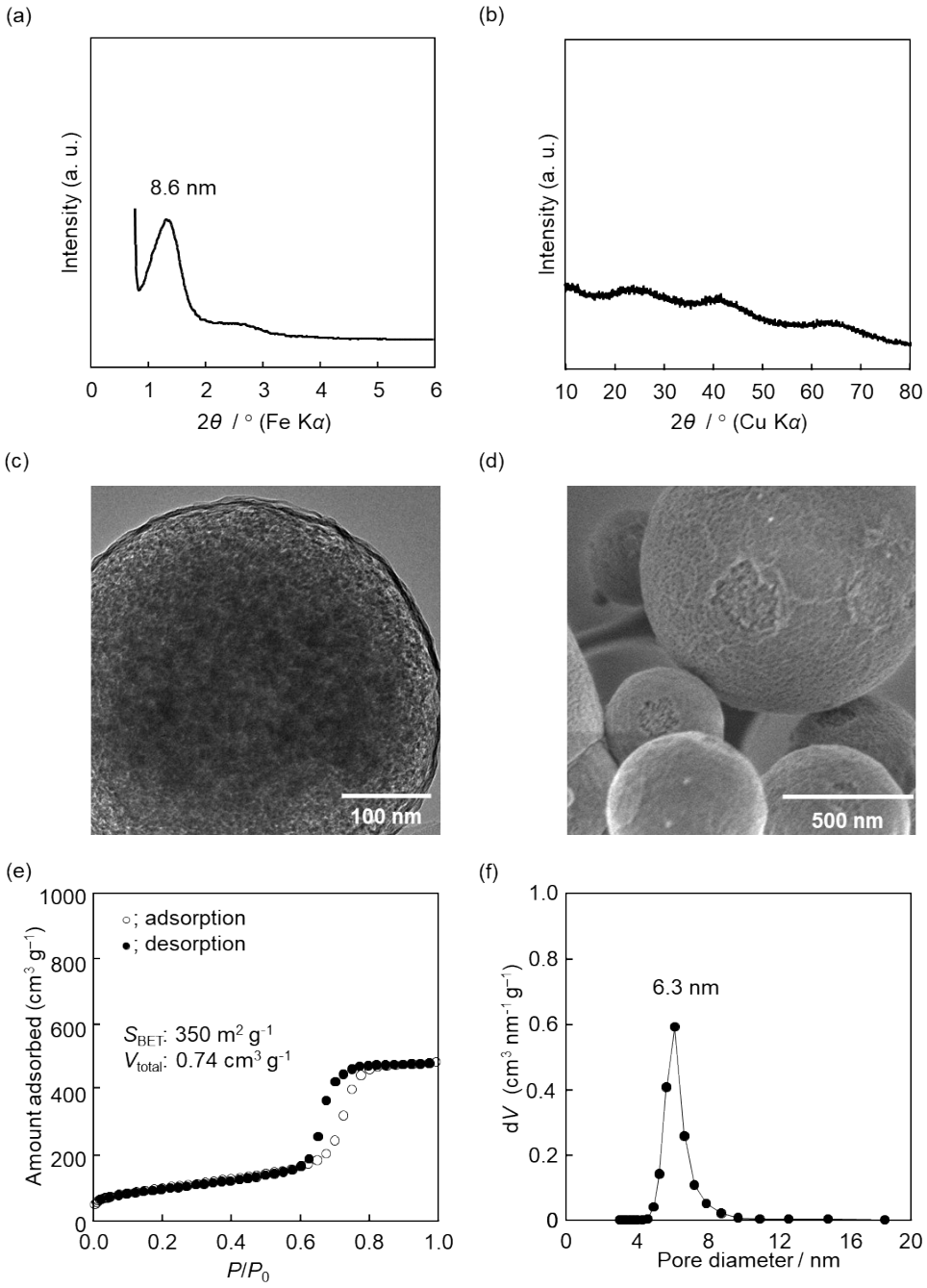

Fig. S7 (a) Low- and (b) wide-angle XRD patterns, (c) TEM and (d) SEM images, and (e) N_2 adsorption-desorption isotherm with (f) corresponding pore size distribution curve of mesoporous alumina after the common calcination at 400 °C without the extraction process.

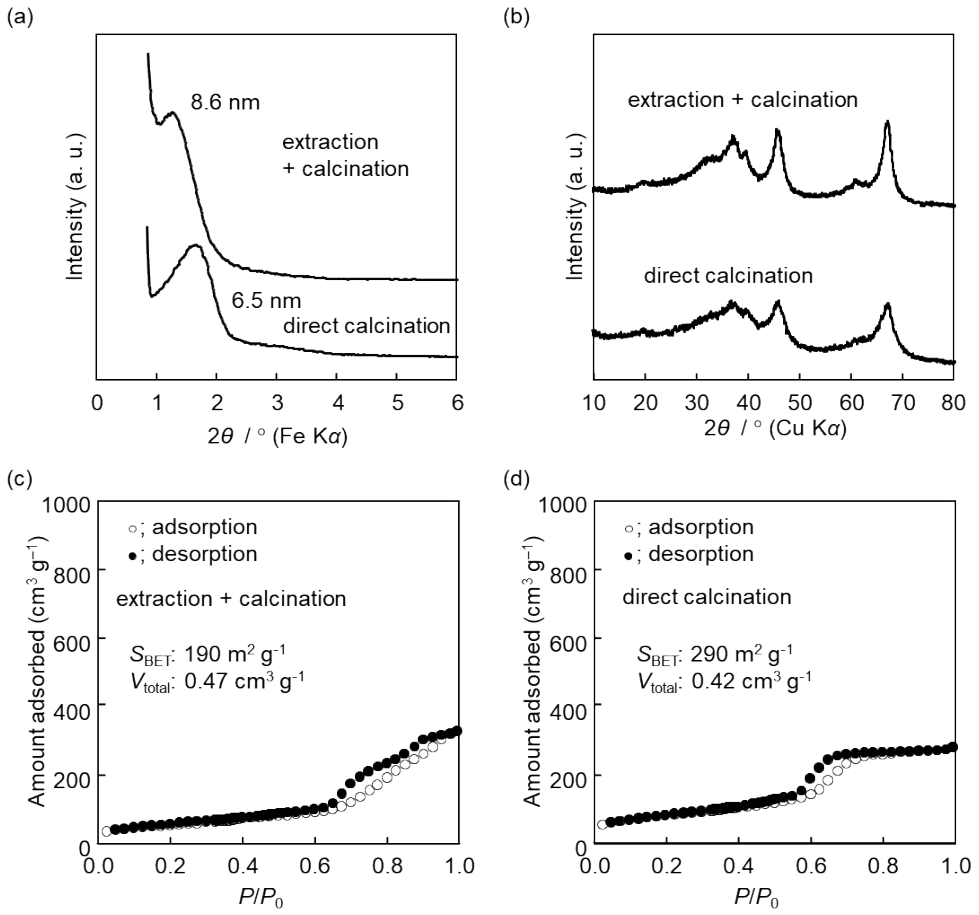

Fig. S8 (a) Low- and (b) wide-angle XRD patterns and (c, d) N_2 adsorption-desorption isotherm of mesoporous alumina calcined at 850 °C for crystallization to γ-Al_2O_3.

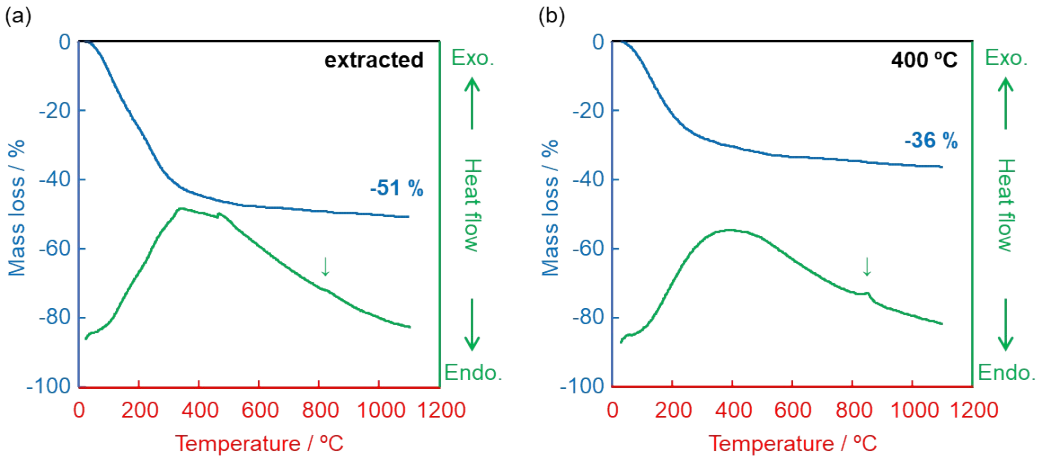

Fig. S9 TG-DTA curves of mesoporous alumina (a) extracted by using Et_3N/EtOH and (b) calcined at 400 ºC without the extraction process. The green arrows (↓) show the exothermic peak due to crystallization to γ-Al_2O_3.

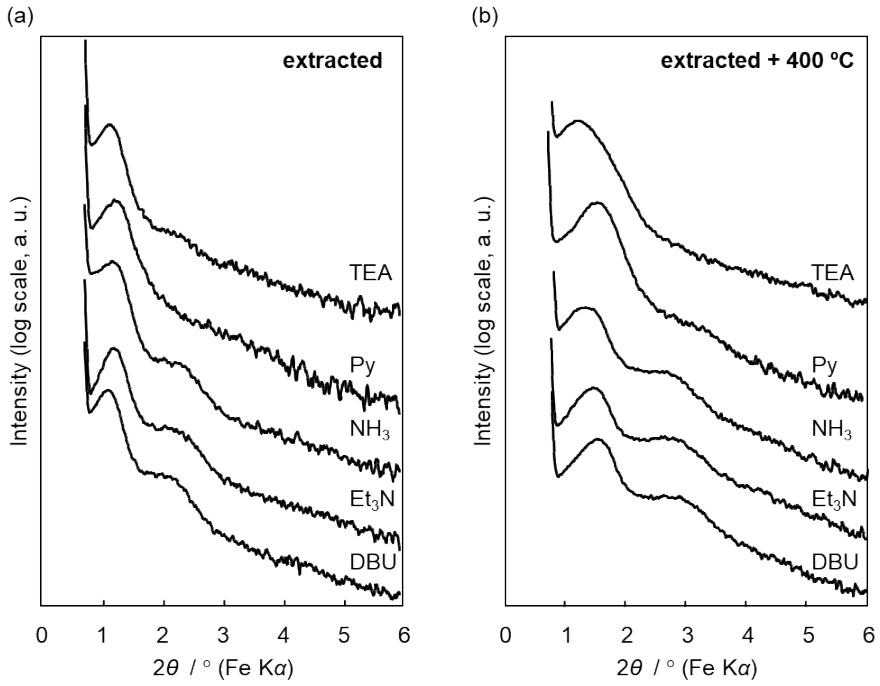

Fig. S10 Low-angle XRD patterns of mesostructured alumina, prepared using Pluronic P123 under the HCl mediated acidic conditions (a) after the treatment by using EtOH in the presence of various amines followed by (b) calcination at 400 °C.