

Supplementary Information

Novel hydrogen chemisorption properties of amorphous ceramic compounds consisting of *p*-block elements: exploring Lewis acid-base Al–N pair site formed *in-situ* within polymer-derived silicon-aluminum-nitrogen-based system

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In this study, aluminum (Al)-modified polysilazane, as a single-source precursor, was first synthesized by chemical modification of a commercially available Durazane[®] 1800, poly(vinylmethyl-co-methyl)silazane (PSZ, silicon nitride precursor) with alane *N,N*-dimethylethylamine (EtNMe₂·AlH₃—ADMEA). The reaction of PSZ and ADMEA relies on both dehydrocoupling and hydroalumination reactions (Fig. S1).

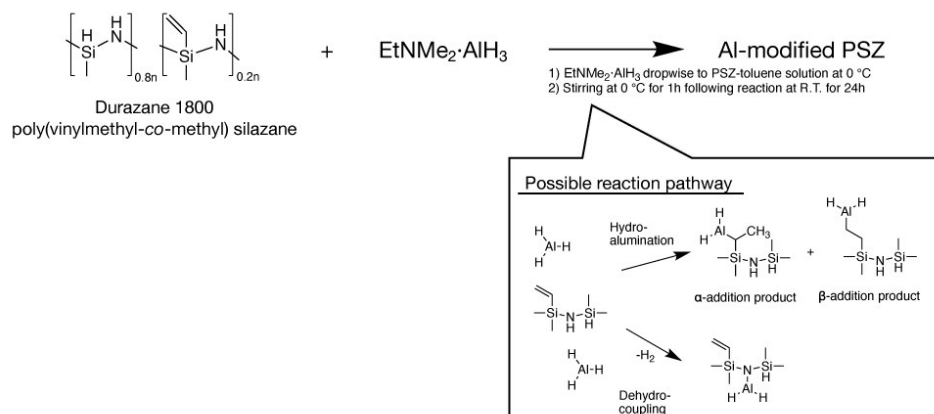


Fig. S1 Schematic representation of the synthesis of Al-modified PSZ through PDCs route.

The chemical modification performed in this study was monitored by attenuated total reflection fourier transform infra-red (ATR-FTIR) spectroscopy using FTIR spectrometer (FT/IR-4200IF, JASCO Corporation, Tokyo, Japan) with attachment of ATR equipment (ATR PRO 550S-S/570S-H, JASCO Corporation, Tokyo, Japan) at a resolution of 4 cm^{-1} . The typical ATR-FTIR spectra of Al-PSZ samples with different Al/Si atomic ratios shows in Fig. S2. The FT-IR spectra shows that the intensity of the bands corresponding to the C_{sp^2} -H band at 3048 and 1402 cm^{-1} slightly reduces. In parallel, the intensity of the bands assigned to N-H bands at 3381 and 1173 cm^{-1} reduces more significantly. These changes indicate both hydroalumination and dehydrocoupling reaction occur in parallel. FTIR (ATR/ cm^{-1}): ν (N-H) = 3350 (m); ν (C_{sp^2} -H) = 3048 (w); ν (C_{sp^3} -H) = 2950 (m), 2900 (vw); ν (Si-H) = 2130 (vs); ν (Al-H) = 1820 (m); ν (C=C) = 1596 (vw); δ (C-C, vinyl) = 1402 (w); δ (Si-CH₃) = 1250 (vs); δ (Si₂N-H) = 1175 (vs); δ (Si-N) = 840 – 1020 (vs); and δ (Si-C) = 700 – 850 (m).

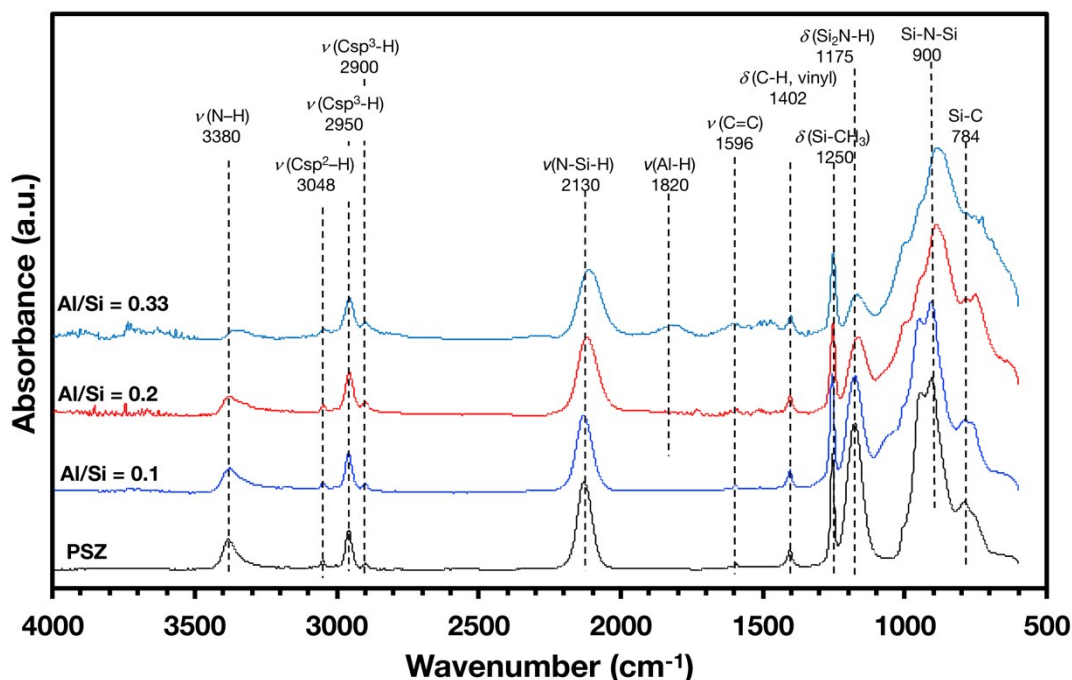


Fig. S2 ATR-FT-IR spectra for as-received PSZ and Al-modified PSZ.

In this study, Al-PSZ was pyrolyzed at 1000 °C under flowing ammonia (NH₃) to generate a silicon-aluminum-nitrogen-based ceramic. Powder X-ray diffraction (XRD) patterns of the pyrolyzed samples were measured on a flat sample stage, using Ni-filtered CuK α radiation (Model X'pert, Philips, Amsterdam, The Netherlands). The XRD patterns of as-pyrolyzed samples are shown in Fig. S3. The XRD pattern of as-pyrolyzed SiAlN (**SiAlN**) is X-ray amorphous and does not show any difference with the Al-free sample, *i.e.*, the as-pyrolyzed silicon nitride (**SiN**) sample, prepared through the same pyrolysis procedure.

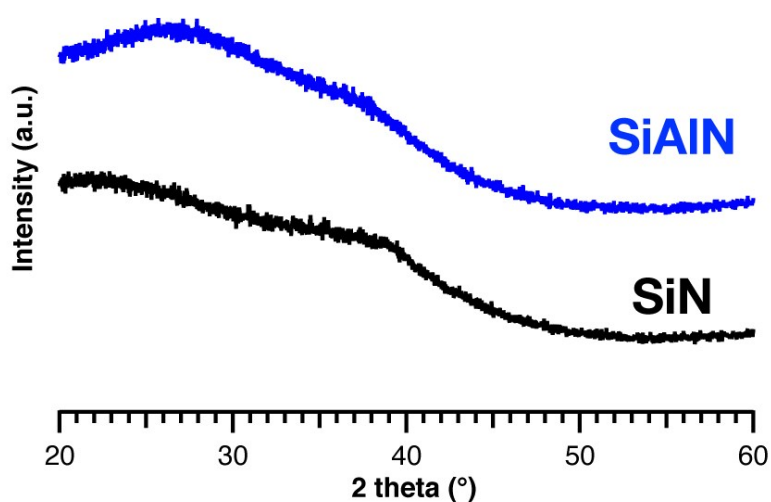


Fig. S3 Typical XRD patterns of samples after pyrolysis at 1000 °C under flowing NH₃.

Textural properties of pyrolyzed samples was evaluated by measuring N₂ adsorption and desorption isotherms at -196 °C under the relative pressures ranging from 0 to 0.99 (Model Belsorp Max, BEL Japan Inc., Osaka, Japan). The pore size distribution was analyzed by MP¹ and BJH² methods. The results are shown in Fig. S4. The **SiAlN** sample at -196 °C exhibited a type I+IV isotherms according to the IUPAC classifications^{3,4}, while the **SiN** sample showed no interaction with N₂ (Fig. S4a). The Brunauer-Emmett-Teller (BET) surface area ($S_{BET}^{N_2}$) of the **SiAlN** sample has been measured to be 165 m² g⁻¹. The pore size distribution curve (PSD) in the micropore range characterized by the MP meshod¹ exhibited a peak centered at 1.2 nm (Fig. S4b), whereas there was no distinct peak in the mesopore range by the BJH plot² although we can identify the existence of a certain porosity with a pore size range of approximately 2 to 4 nm (Fig. S4c). In addition, Fig. S5 shows a N₂ adsorption and desorption isotherm of the

SiAlN sample pyrolyzed at 700 °C which has low porosity due to the collapse and close of the pore.

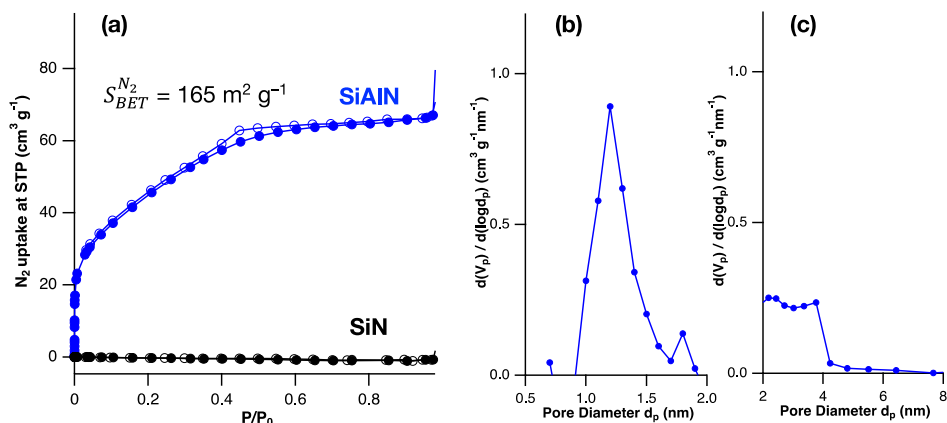


Fig. S4 (a) N₂ adsorption-desorption isotherms at –196 °C for the polymer-derived amorphous SiAlN and SiN samples, and pore size distribution curves of the SiAlN sample characterized by (b) MP plot and (c) BJH plot.

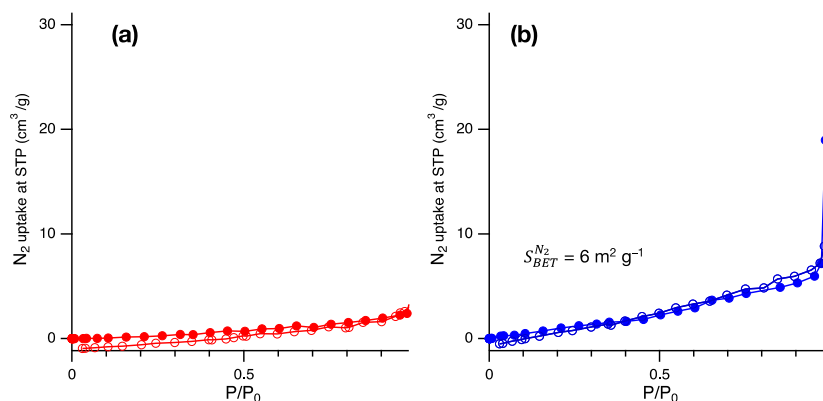


Fig. S5 Reference data of N₂ adsorption and desorption isotherms at –196 °C. Polymer-derived SiAlN pyrolyzed (a) at 1000 °C under N₂ and (b) at 700 °C under NH₃.

Thermalgravimetric (TG) analysis for the polymer-to-ceramic conversion was performed under flowing mixture of NH₃ and N₂ (60:40 in flow ratio) (Model TGA 92 16.18 Setaram, Inc., Newark, CA, USA) or He (Model JMS-Q1500GC, JEOL Ltd., Tokyo, Japan). The TG-curves under the mixed NH₃-N₂ gas flow were monitored up to 1000 °C with a heating rate of 5 °C min⁻¹ (Fig. S6), while those under He flow were monitored up to 1000 °C with a heating rate of 10 °C min⁻¹ (Fig. S7).

A contentious weight loss above 700 °C is identified during the conversion of the Al-modified PSZ leading to the SiAlN sample whereas no weight loss is identified above 800 °C during the conversion of PSZ into the SiN sample (Fig. S6), in contrast, such the difference

above 800 °C is not observed when the conversions of Al-modified PSZ and PSZ were monitored under He (Fig. S7).

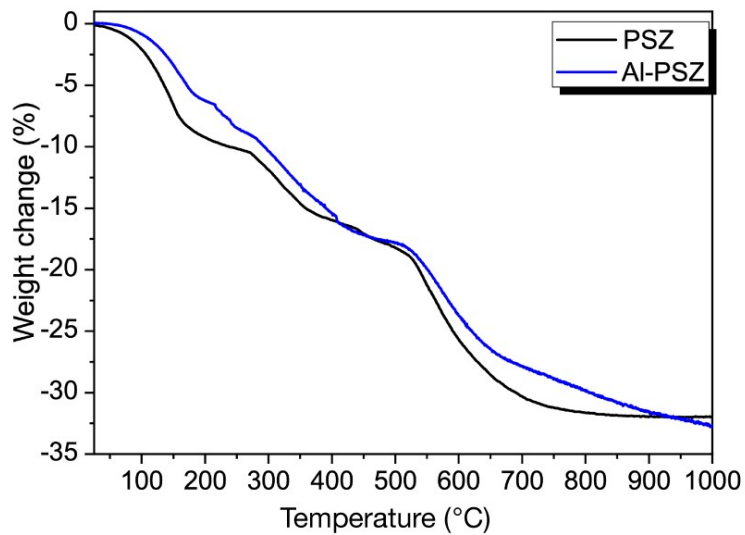


Fig. S6 TG-curves of PSZ and Al-PSZ under flowing $\text{NH}_3\text{-N}_2$ (60:40 in flow ratio) mixed gas.

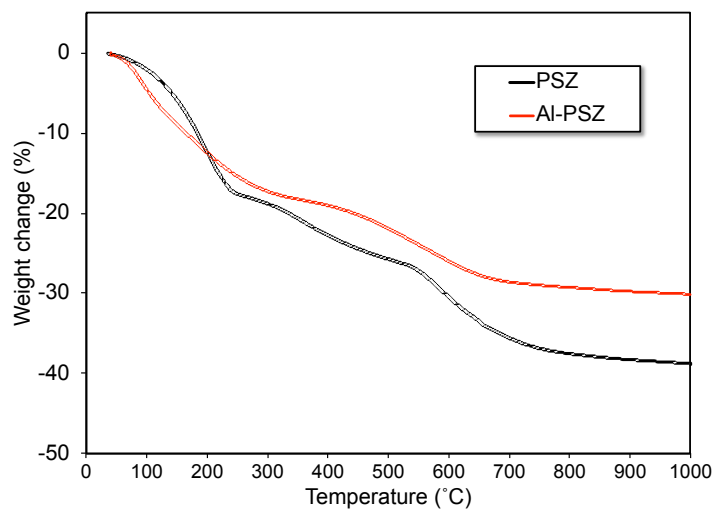


Fig. S7 TG-curves of PSZ and Al-PSZ under flowing He.

To investigate the chemical bonding-state of the **SiAlN** sample, X-ray photoelectron spectroscopic (XPS) measurements were performed using X-ray Photoelectron Spectrometer (PHI 5000, ULVAC-PHI, Inc., Japan) with an Al $K\alpha$ X-ray source operated at 14 kV and 14 mA. An alignment on the C 1s peak was performed before survey scans. The wide scan spectrum of **SiAlN** sample is shown in Fig. S8. Besides the intense lines of the constituent elements (N 1s, Si 2p and Al 2p) and unavoidable carbon contaminant, strong line of O 1s is observed. This indicates a certain amount of oxygen is present at the surface of the **SiAlN** sample. The summary of XPS characterization for amorphous SiAlN sample lists in Table S2.

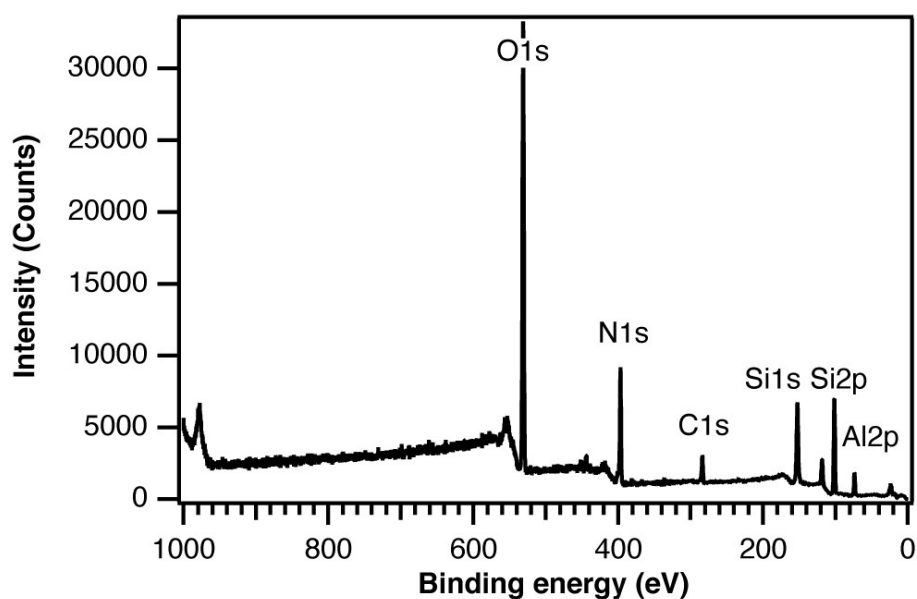


Fig. S8 Wide scan x-ray photoelectron spectrum of polymer-derived SiAlN.

Table S1 Summary of XPS characterization for amorphous SiAlN sample.
(a) Al 2p and (b) Si 2p.

| (a) | Band (Al 2p) | Binding energy (eV) | Area (%) |
|-----|--------------|---------------------|----------|
| | Al-N | 73.5 | 78.0 |
| | Al-O | 74.7 | 22.0 |
| (b) | Band (Si 2p) | Binding energy (eV) | Area (%) |
| | Si-N | 73.5 | 98.8 |
| | Si-O | 74.7 | 1.2 |

To study the H₂ adsorption and desorption properties, temperature-programmed-desorption of hydrogen (H₂-TPD) was performed using a catalyst analyzer (Model BELCAT-A, MicrotracBEL Corp., Osaka, Japan) fixed with a quadrupole mass spectrometer (Model BELMASS, MicrotracBEL Corp., Osaka, Japan). Prior to the measurement, the sample was maintained under Ar at 800 °C and subsequently exposed to H₂ at specific temperatures ($T_{H_2} = 100, 150$ °C) for 5 min. H₂-TPD profiles of the reference samples are shown in Fig. S9. The amorphous silicon nitride which is derived from the as-received PSZ, commercial crystalline AlN and HY zeolite samples show no desorption peak under the measurement condition ($T_{H_2} = 150$ °C), while the H₂-TPD profiles of the **H₂PTSiAlN** sample exhibits a single peak at approximately 100 to 350 °C under the same condition ($T_{H_2} = 150$ °C). As referential data, the volumetric amount of hydrogen desorption briefly estimated for the **H₂PTSiAlN** sample is approximately 1.1 mL g⁻¹ which was calculated based on the relative ratio of the peak area of H₂-TPD curve, $T_{H_2} = 150$ °C in Fig. S9, to that of well-known metal hydride, MgH₂ measured at our lab.

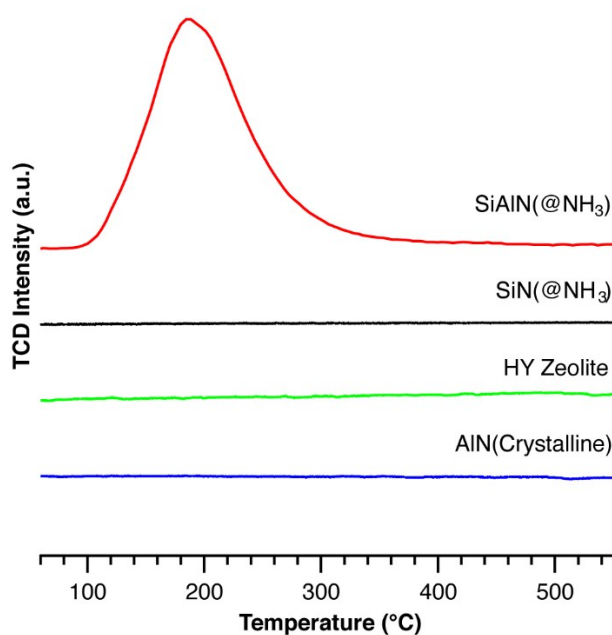


Fig. S9 Comparison of H₂-TPD profiles of **PTSiAlN** sample with those of reference samples of **SiN** sample, commercially available crystalline AlN and zeolite samples.

References

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