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SUPPORTING INFORMATION

for

Conversion of methane to acetonitrile over GaN catalysts derived from gallium nitrate hydrate co-pyrolyzing with melamine, melem, or g-C_3N_4: the influence of nitrogen precursors

Korawich Trangwachirachai,[a] Chin-Han Chen,[a] Ai-Lin Huang,[a] Jyh-Fu Lee,[b]

Chi-Liang Chen,[b] and Yu-Chuan Lin[a,*]

[a]Department of Chemical Engineering, National Cheng Kung University

No. 1 University Rd., Tainan 70101, Taiwan

[b]National Synchrotron Radiation Research Center

101 Hsin-Ann Rd., Hsinchu 30076, Taiwan

[*] Corresponding author's Tel.: (886) 6 275 7575 ext. 62668; Fax: (886) 6 234 4496; E-mail: yclin768@mail.ncku.edu.tw

Table S1. The concentrations of Ga and N of used samples

Catalyst	Ga (wt%)[a]	N (wt%)[b]	N/Ga molar ratio
c-GaN	80.3	8.6	0.53
GaN-(melamine)-(1)	75.6	15.5	1.02
GaN-(melem)-(1)	72.5	15.4	1.06
GaN-(C_3N_4)-(0.5)	73.9	15.1	1.02
GaN-(C_3N_4)-(1)	73.7	15.4	1.04
GaN-(C_3N_4)-(2)	75.9	15.2	1.00

[a]Estimated by ICP-MS；[b]Estimated by EA

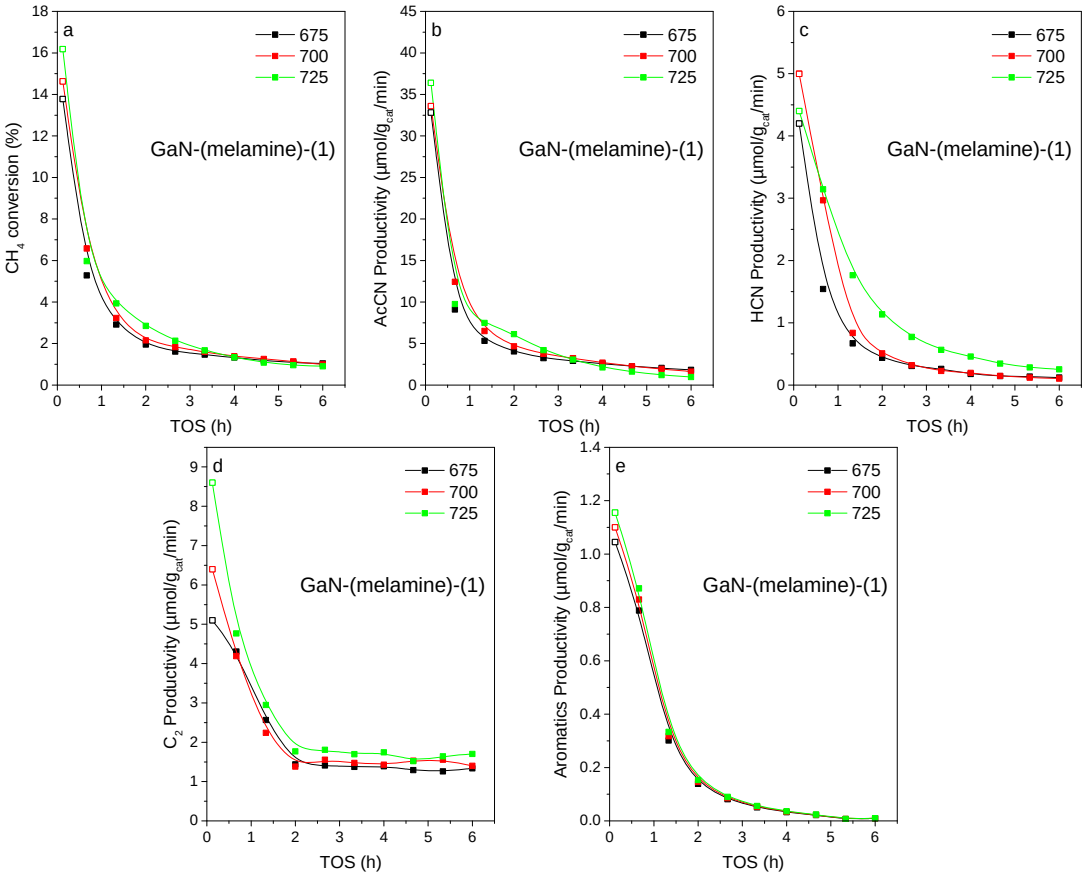

Figure S1. The TOS profiles of (a) CH_4 conversion and productivities of (b) AcCN, (c) HCN, (d) C_2, and (e) aromatics at 675, 700, and 725 °C with GHSV = 3000 $mL_{CH_4}/g/h$ by testing GaN-(melamine)-(1). The open symbol means the initial activity calculated by using the MS signals; the closed symbol, calculated by the GC responses.

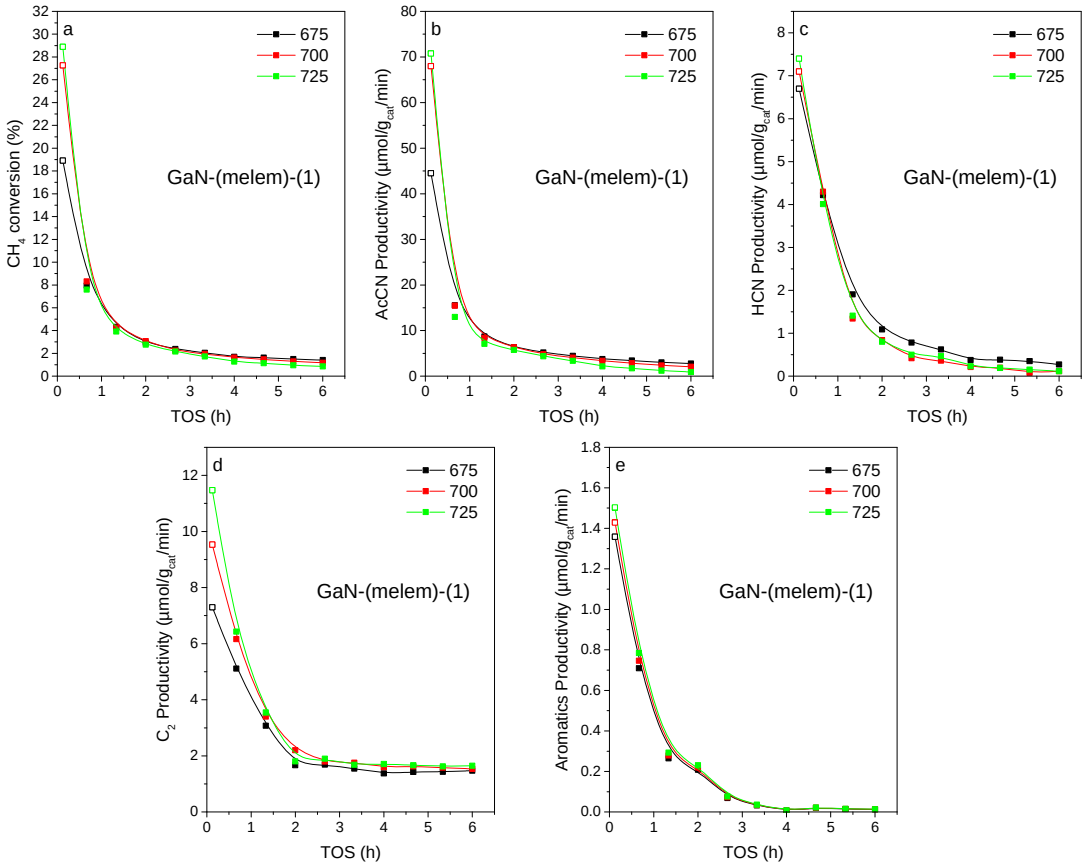

Figure S2. The TOS profiles of (a) CH_4 conversion and productivities of (b) AcCN, (c) HCN, (d) C_2, and (e) aromatics at 675, 700, and 725 °C with GHSV = 3000 $mL_{CH_4}/g/h$ by testing GaN-(melem)-(1). The open symbol means the initial activity calculated by using the MS signals; the closed symbol, calculated by the GC responses.

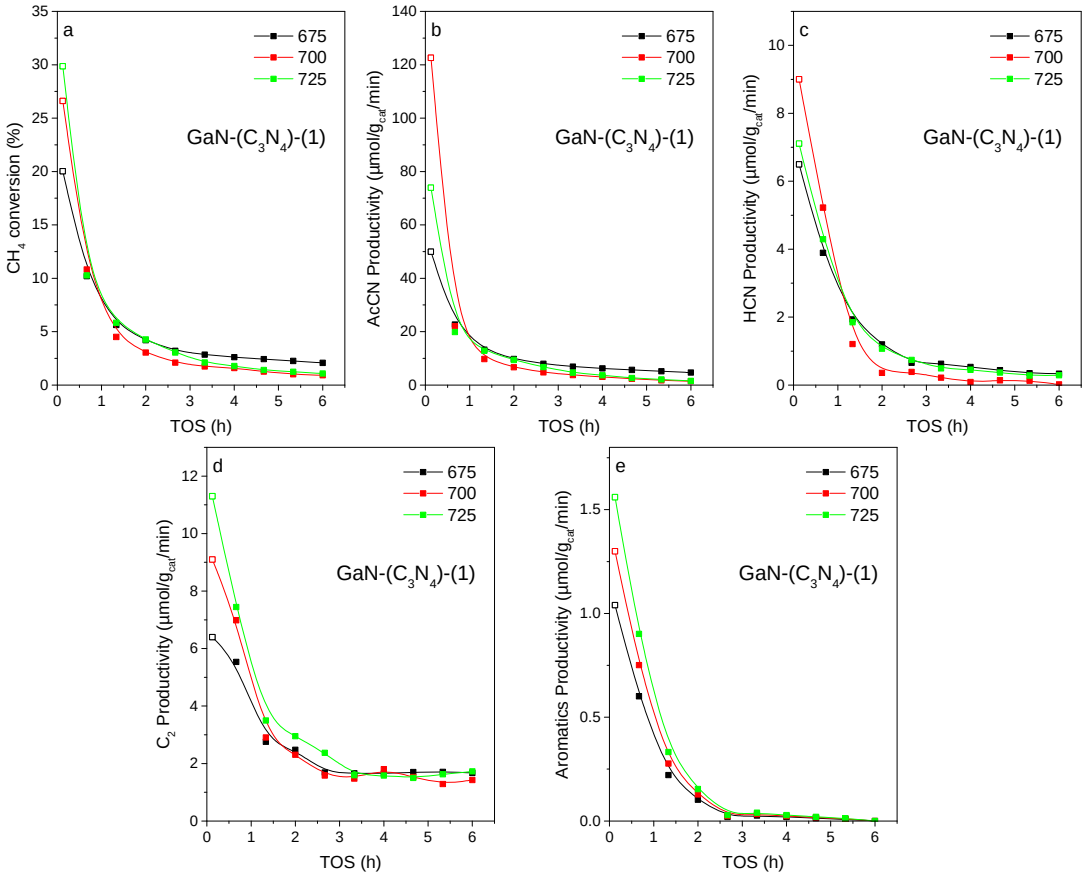

Figure S3. The TOS profiles of (a) CH_4 conversion and productivities of (b) AcCN, (c) HCN, (d) C_2, and (e) aromatics at 675, 700, and 725 °C with GHSV = 3000 $mL_{CH_4}/g/h$ by testing GaN-(C_3N_4)-(1). The open symbol means the initial activity calculated by using the MS signals; the closed symbol, calculated by the GC responses.

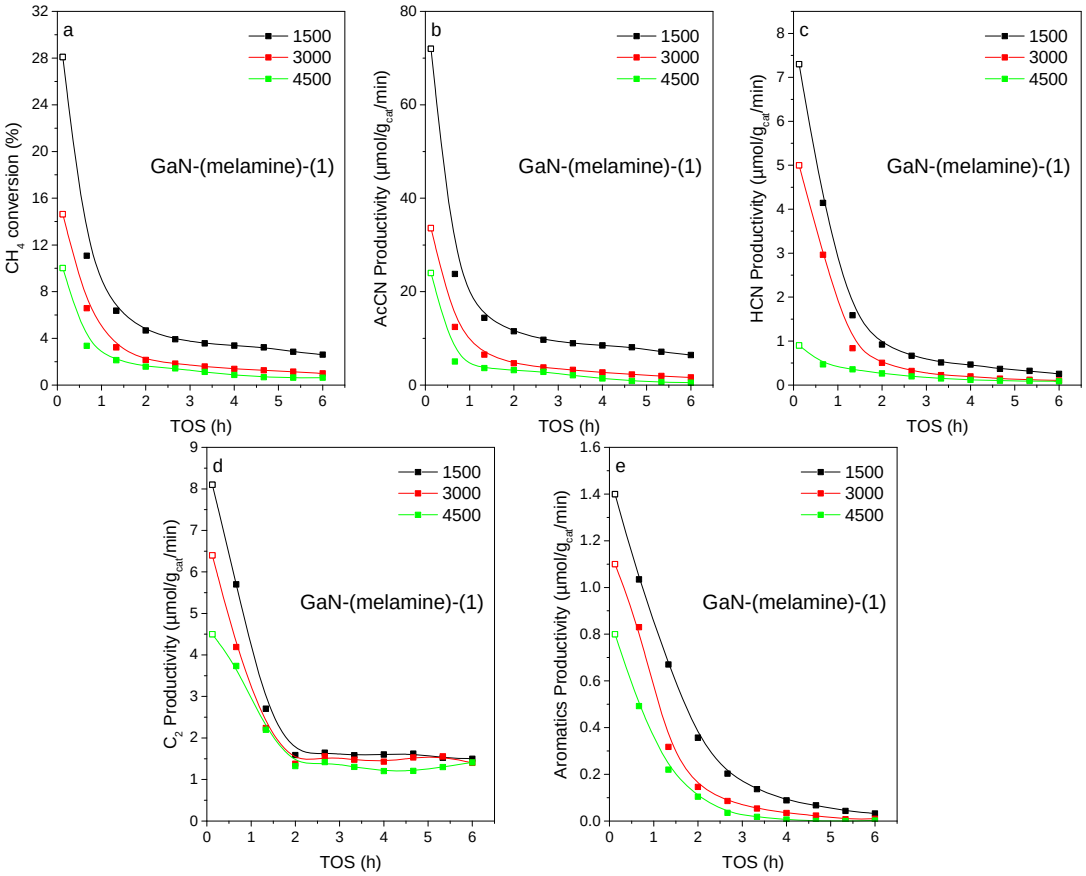

Figure S4. The TOS profiles of (a) CH_4 conversion and productivities of (b) AcCN, (c) HCN, (d) C_2, and (e) aromatics at 700 °C with GHSVs = 1500, 3000, and 4500 $mL_{CH_4}/g/h$ by testing GaN-(melamine)-(1). The open symbol means the initial activity calculated by using the MS signals; the closed symbol, calculated by the GC responses.

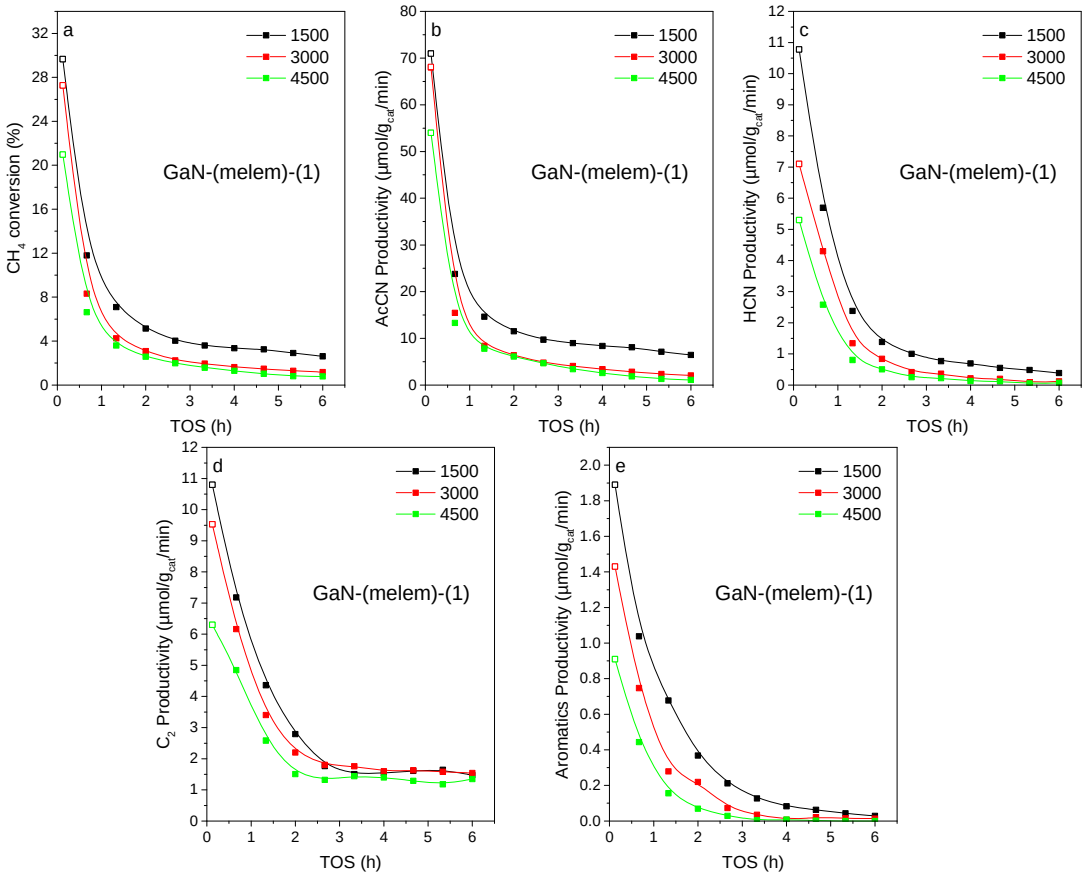

Figure S5. The TOS profiles of (a) CH_4 conversion and productivities of (b) AcCN, (c) HCN, (d) C_2, and (e) aromatics at 700 °C with GHSVs = 1500, 3000, and 4500 $mL_{CH_4}/g/h$ by testing GaN-(melem)-(1). The open symbol means the initial activity calculated by using the MS signals; the closed symbol, calculated by the GC responses.

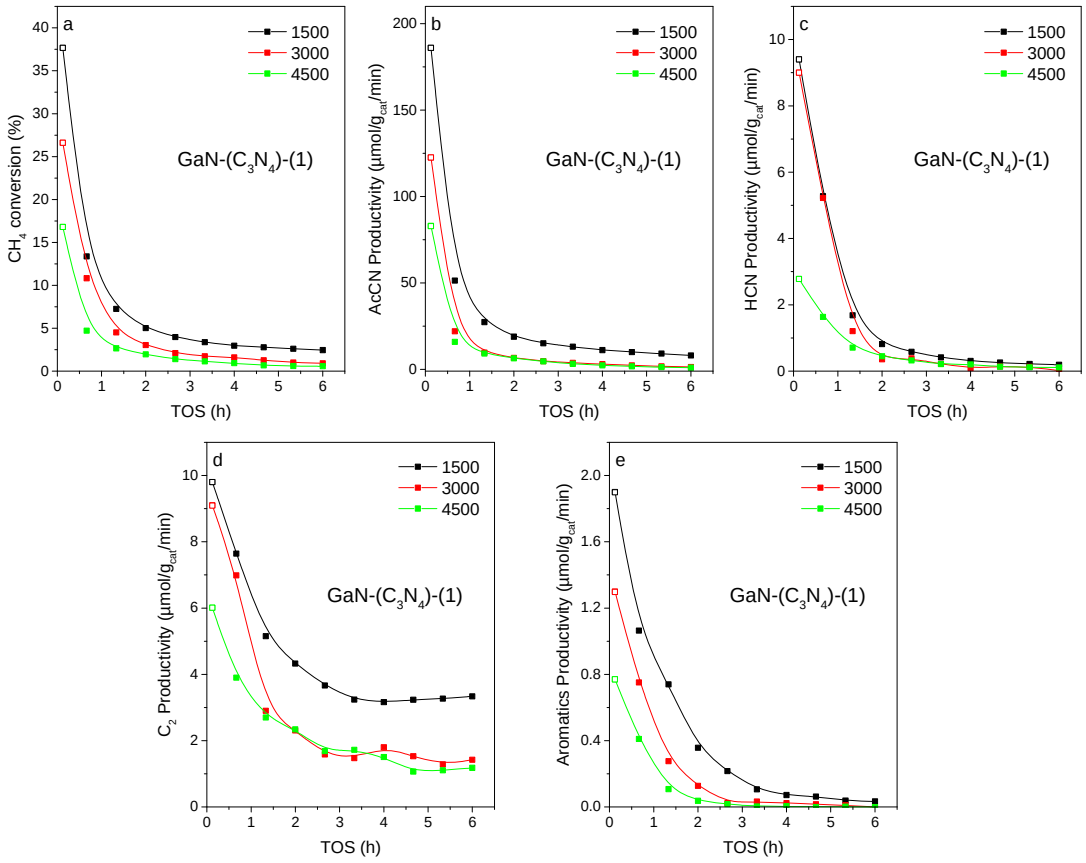

Figure S6. The TOS profiles of (a) CH_4 conversion and productivities of (b) AcCN, (c) HCN, (d) C_2, and (e) aromatics at 700 °C with GHSVs = 1500, 3000, and 4500 $mL_{CH_4}/g/h$ by testing GaN-(C_3N_4)-(1). The open symbol means the initial activity calculated by using the MS signals; the closed symbol, calculated by the GC responses.

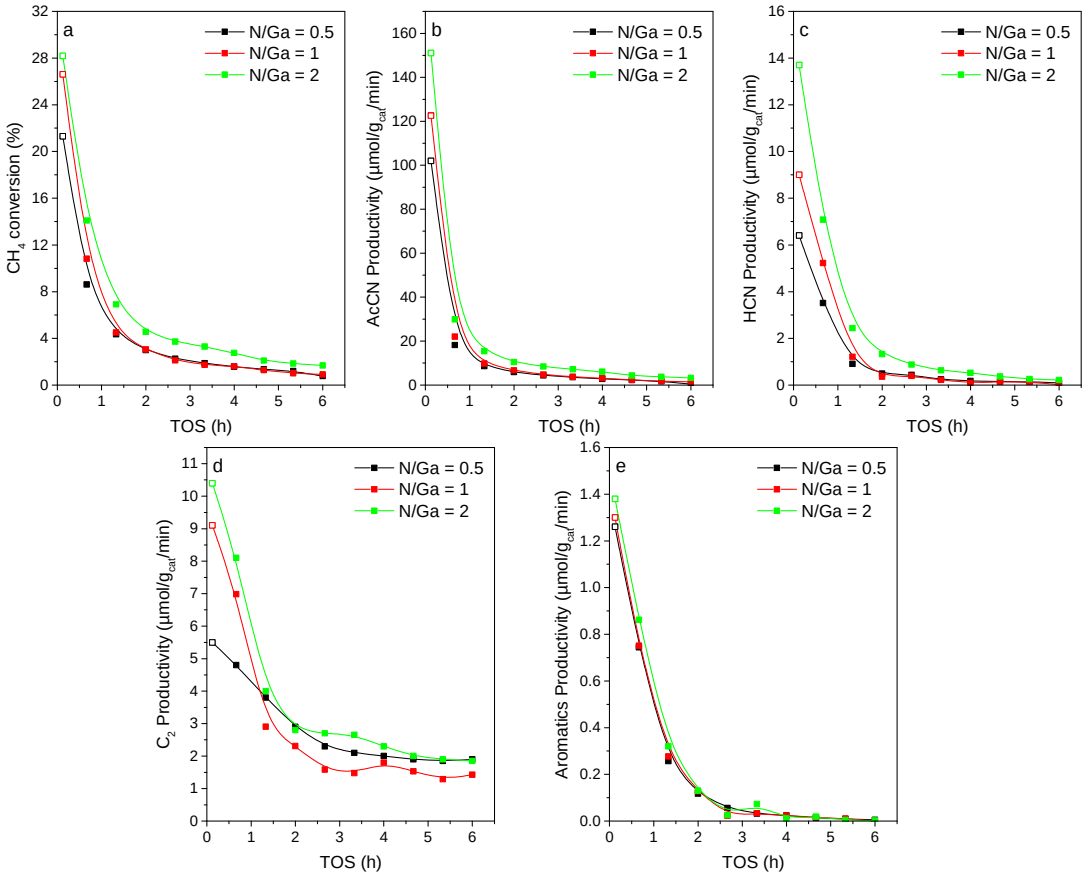

Figure S7. The TOS profiles of (a) CH_4 conversion and productivities of (b) AcCN, (c) HCN, (d) C_2, and (e) aromatics at 700 °C with GHSV = 3000 $mL_{CH_4}/g/h$ by testing GaN-(C_3N_4)-(0.5, 1, and 2) catalysts. The open symbol means the initial activity calculated by using the MS signals; the closed symbol, calculated by the GC responses.

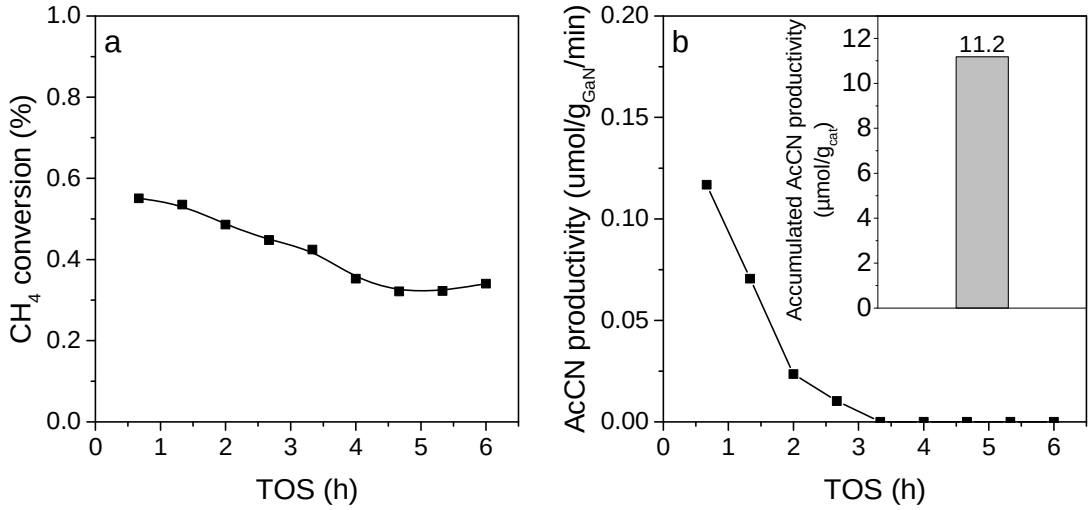

Figure S8. (a) The methane conversion and (b) AcCN productivity of c-GaN at 700 °C with GHSV = 3000 $mL_{CH_4}/g/h$.

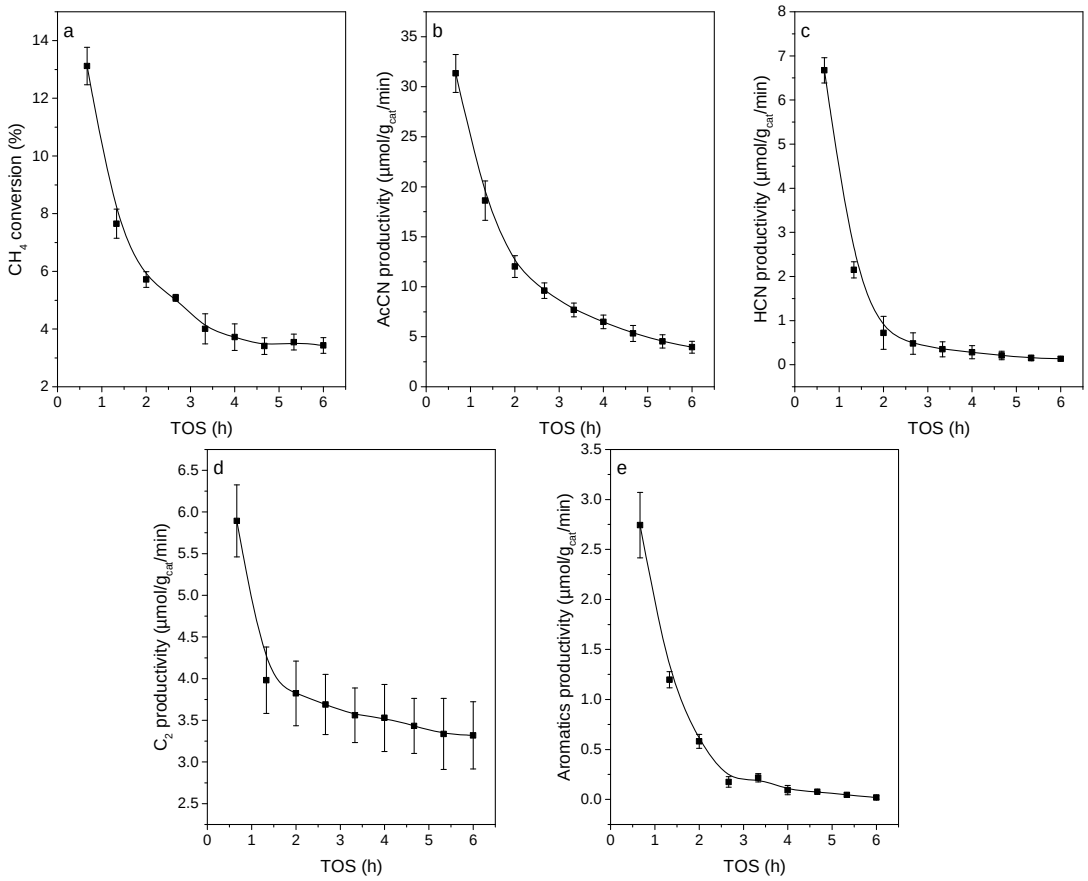

Figure S9. The TOS profiles of a reproducibility testing of (a) CH_4 conversion and productivities of (b) AcCN, (c) HCN, (d) C_2, and (e) aromatics at 700 °C with GHSV = 3000 $mL_{CH_4}/g/h$ by testing GaN-(C_3N_4)-(2).

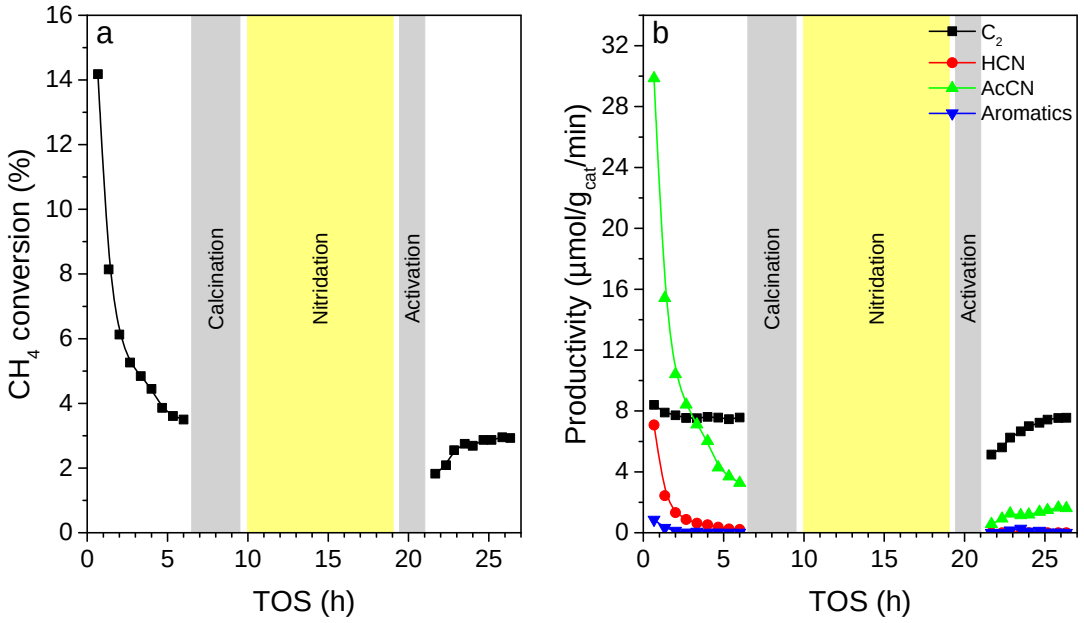

Figure S10. (a) Methane conversion and (b) productivities of AcCN, C_2, HCN, and aromatics of the regeneration test of GaN-(C_3N_4)-(2) using the calcination-nitridation method.

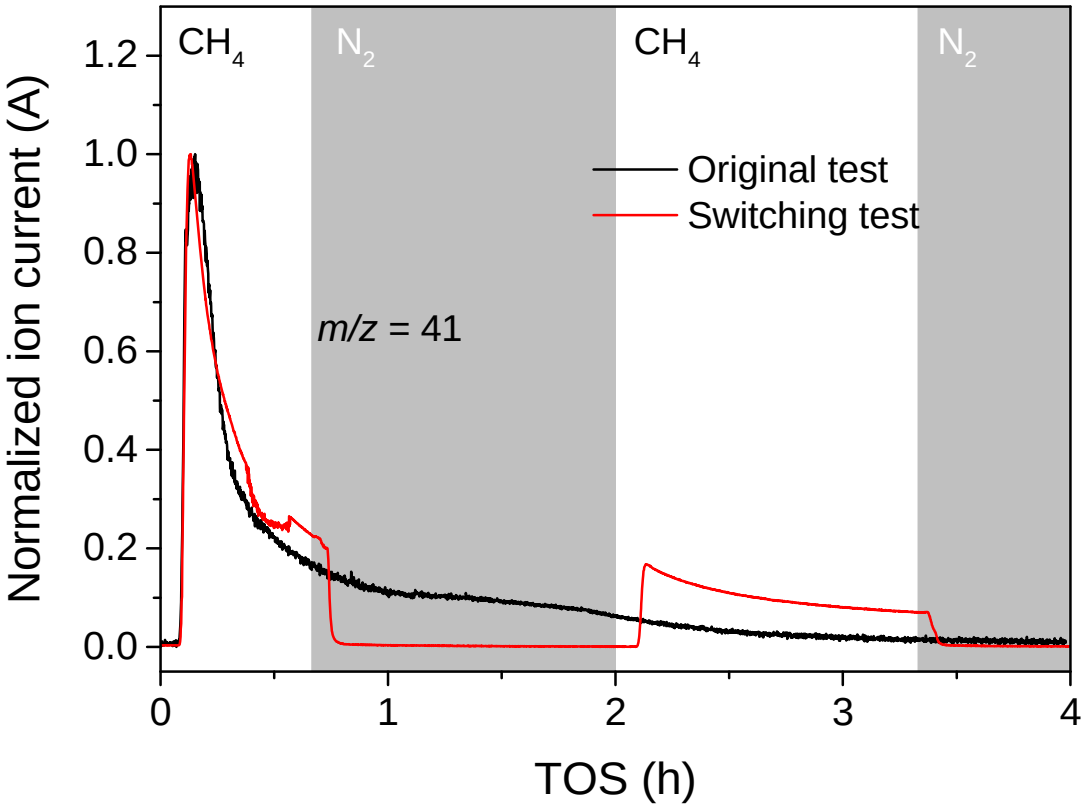

Figure S11. The AcCN MS signal (*m/z* = 41) of the alternating feeding test of CH_4-N_2-CH_4 using GaN-(C_3N_4)-(2) as the catalyst at 700 °C with a GHSV of 3000 $mL_{CH_4}/g_{cat}/h$. Reaction conditions: g_{cat} = 0.2 g and methane flow rate = 10 mL/min. After collecting the data for 40 min, the flow was switched to a N_2 flow (10 mL/min). The N_2 flow was maintained for 80 min, and was then switched back to methane.

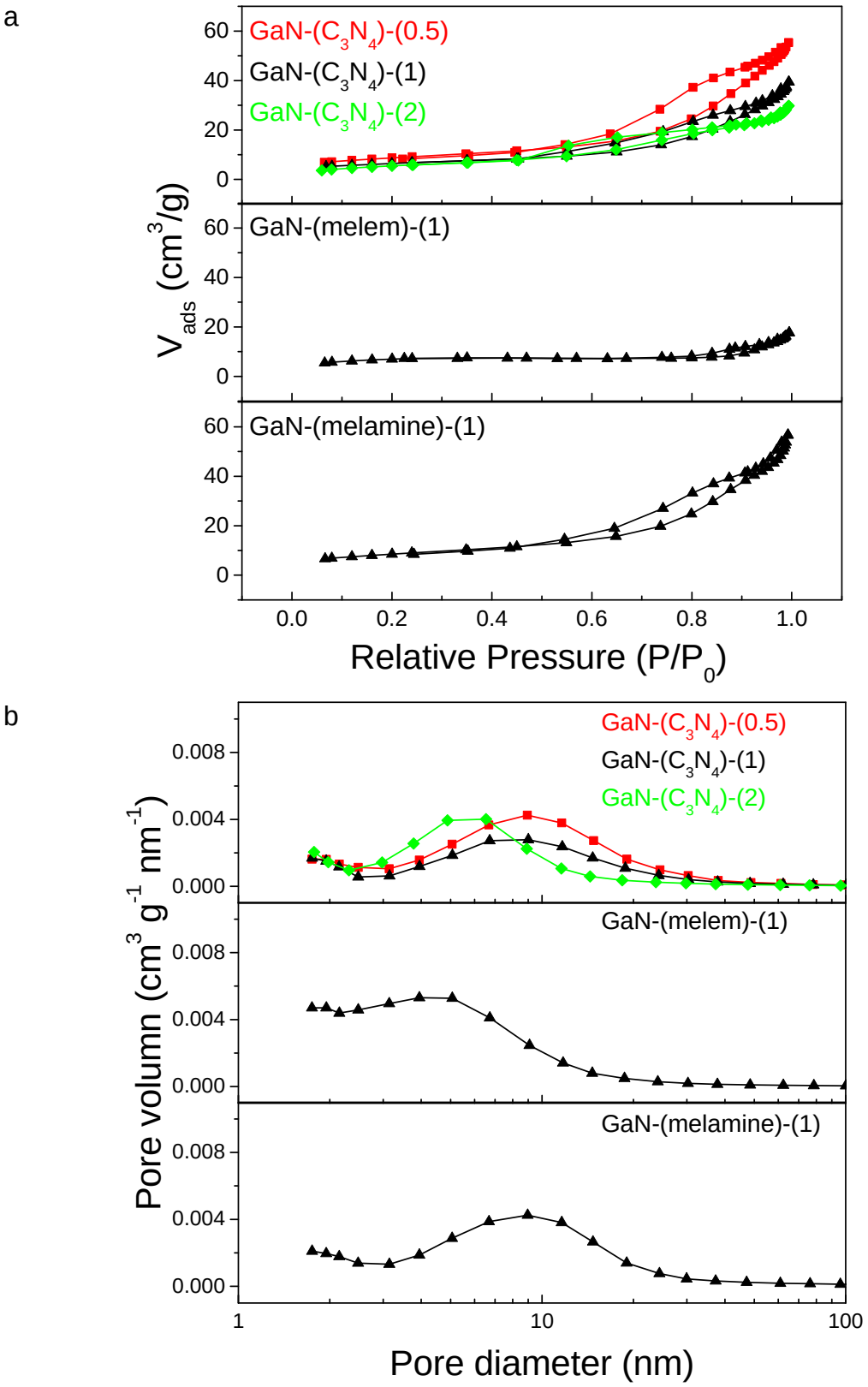

Figure S12. (a) The adsorption-desorption isotherms and (b) pore size distributions of tested catalysts.

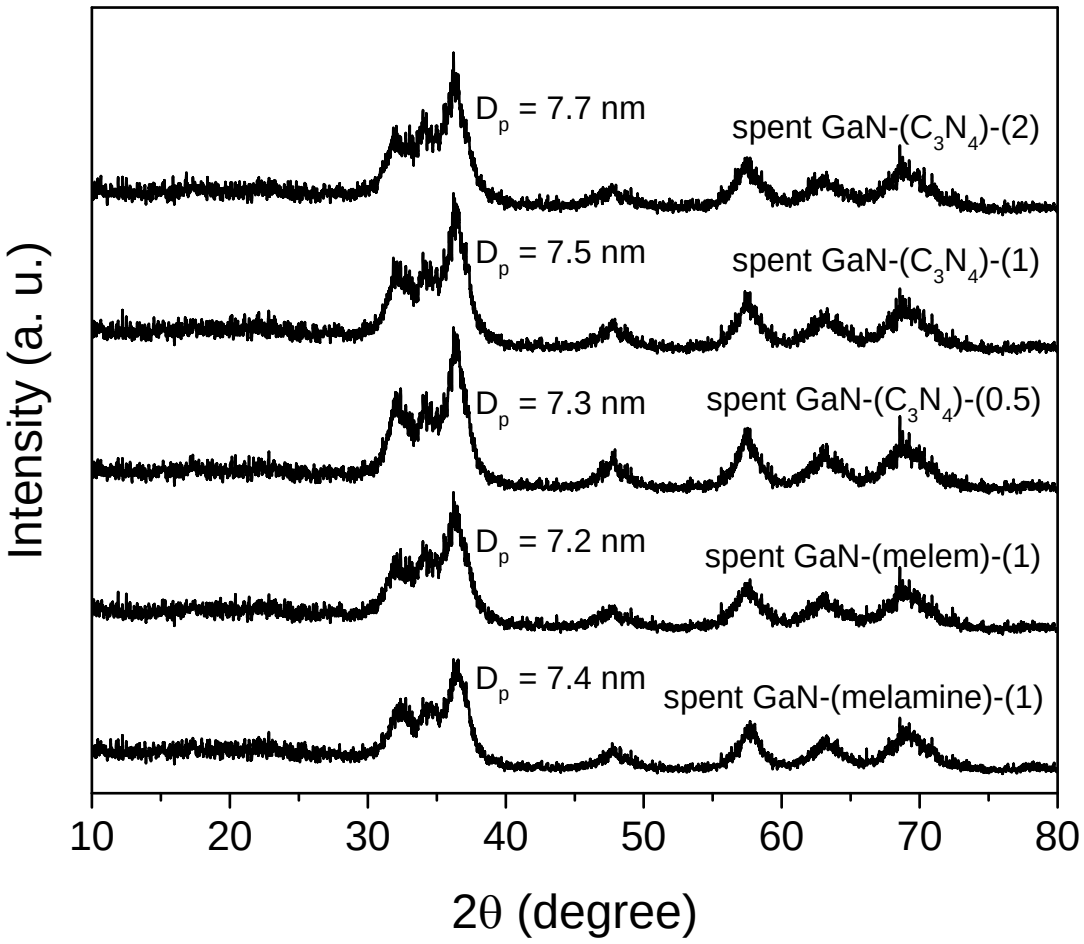

Figure S13. The XRD patterns of the post-reaction GaN catalysts.

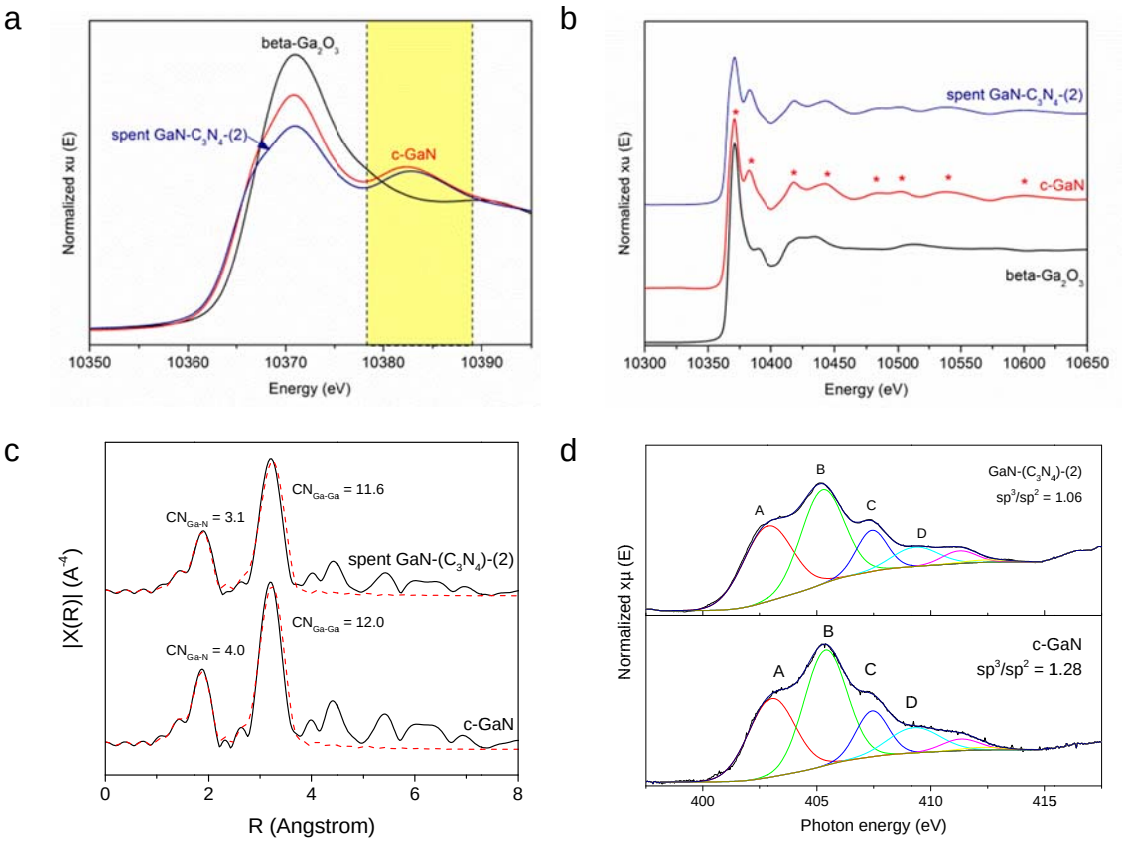

Figure S14. (a) Ga *K*-edge XANES and (b) the eight oscillation peaks (marked with asterisks) in the first 300 eV above the edge of spent GaN-(C_3N_4)-(2) and c-GaN. (c) Ga-N phase corrected RDFs of Ga *K*-edge for spent GaN-(C_3N_4)-(2) and c-GaN. The solid line represents the experimental data, and the dashed line represents the computer fit. (d) N *K*-edge XANES of spent GaN-(C_3N_4)-(2) and c-GaN. The fitted peaks of G_1 (red), G_2 (green), G_3 (blue), G_4 (cyan), G_5 (magenta), and G_6 (yellow) were included.

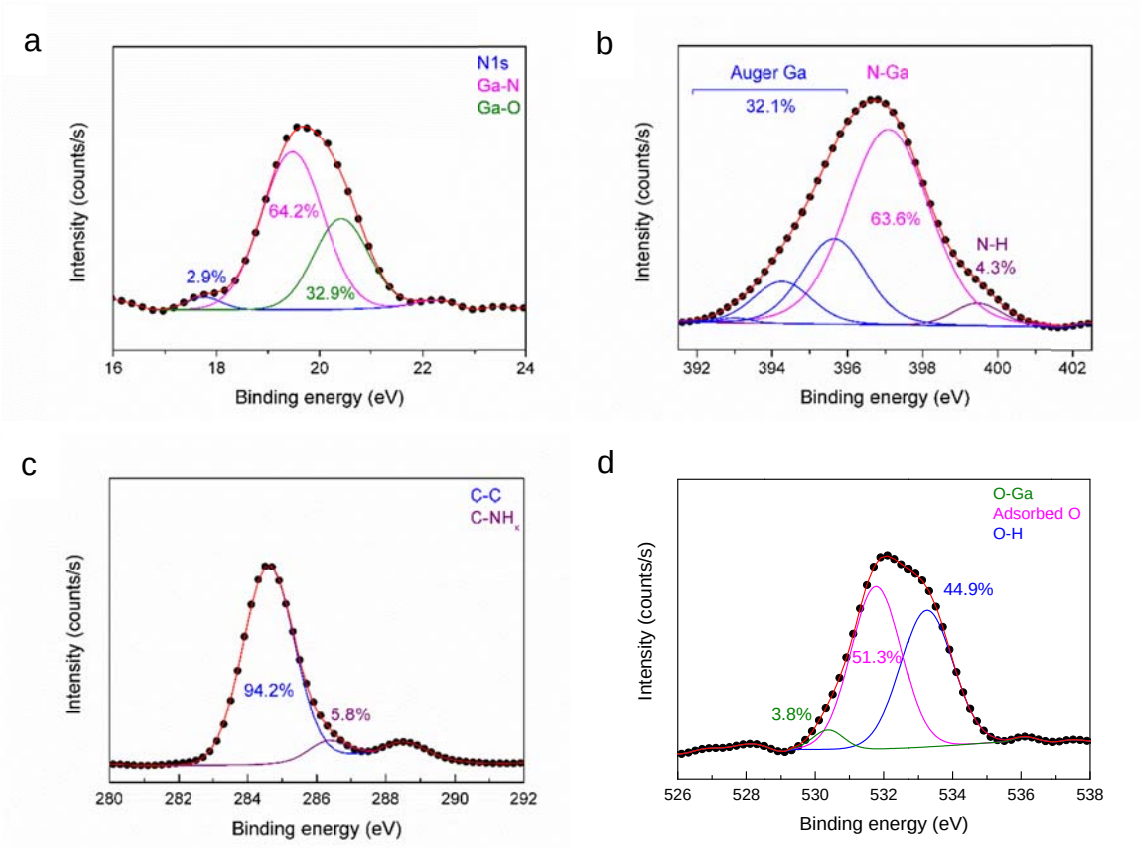

Figure S15. XPS spectra of (a) Ga 3d, (b) N 1s, (c) C 1s, and (d) O **1**s photolines of c-GaN.

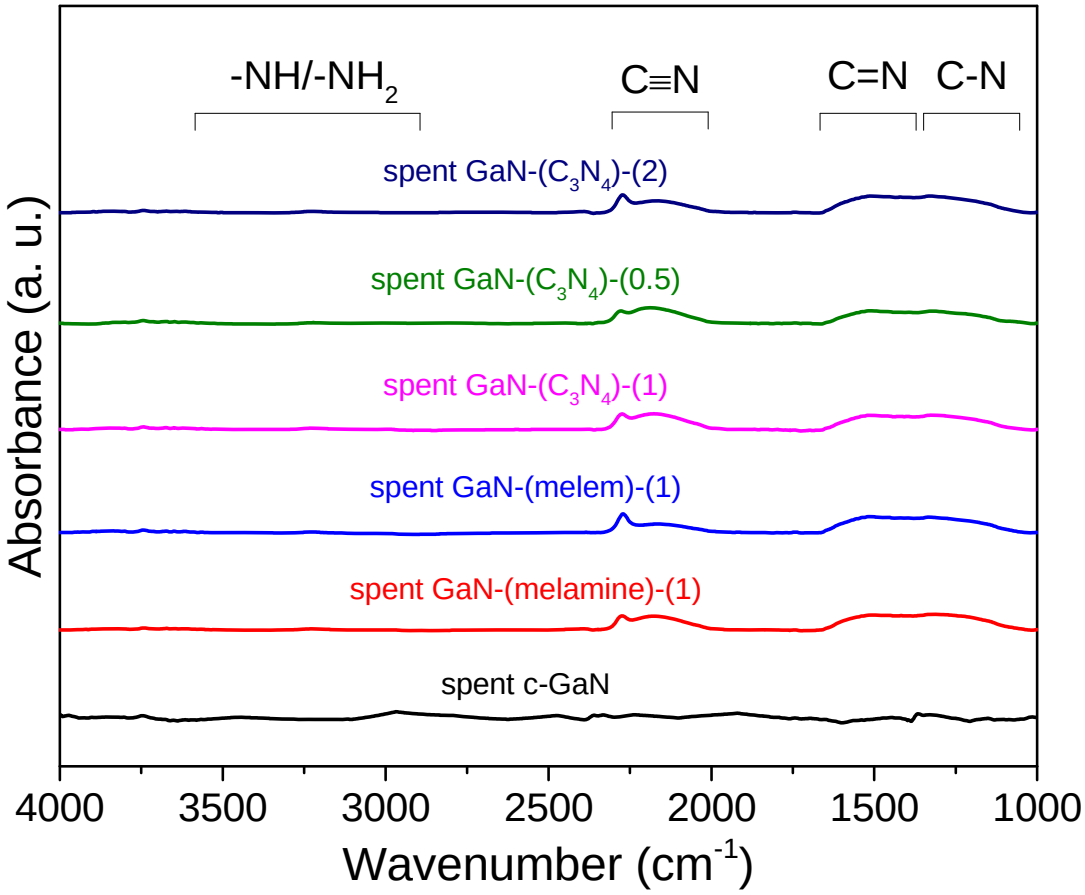

Figure S16. FTIR spectra of the post-reaction GaN catalysts.

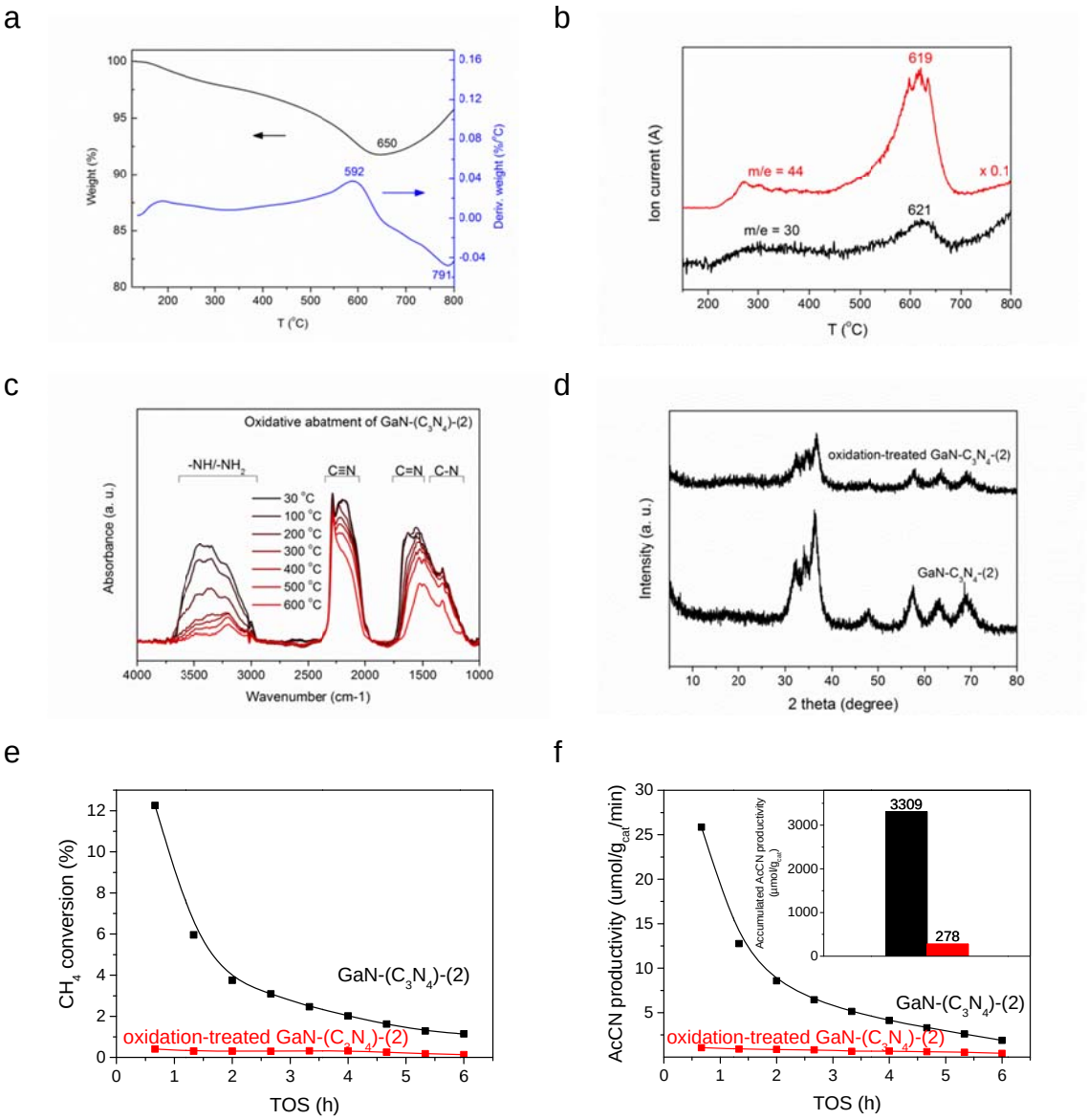

Figure S17. (a) TGA/DTA profiles, (b) the MS fragments (m/e = 30 and 44) of GaN-(C_3N_4)-(2) in an air stream (100 mL/min). (c) The temperature-resolved in-situ IR spectra of GaN-(C_3N_4)-(2) from 30 to 600 °C in a 10% O_2/N_2 stream (20 mL/min). (d) The XRD patterns of GaN-(C_3N_4)-(2) after subjecting to the oxidative abatement and its fresh counterpart. (e) Methane conversion and (f) AcCN productivity of GaN-(C_3N_4)-(2) after subjecting to the oxidative abetment at 700 °C.

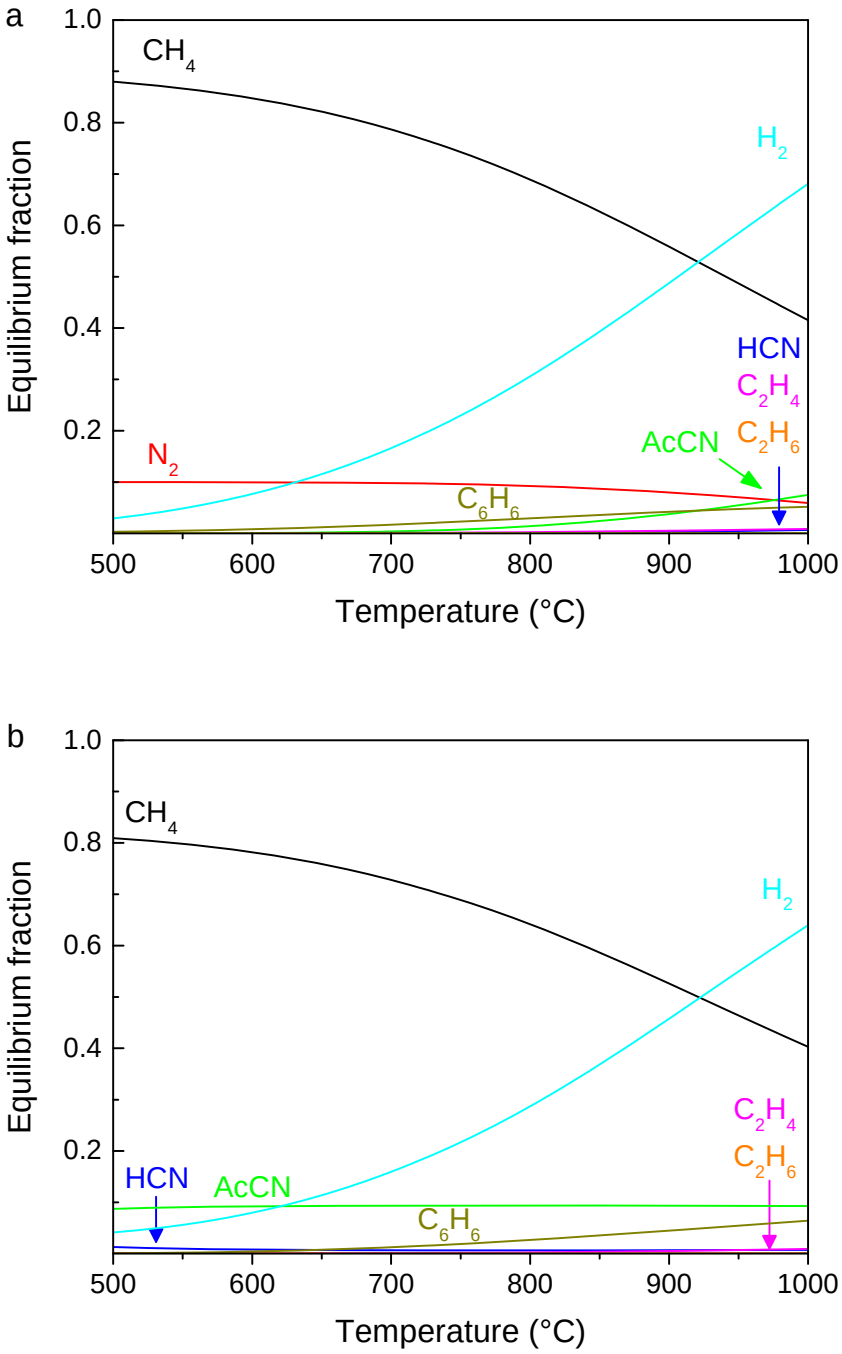

Figure S18. Calculated equilibrium compositions of AcCN, HCN, H_2, C_2H_4, C_2H_6, and C_6H_6 using (a) CH_4 and N_2 and (b) CH_4 and CN as the feeds (CH_4/N_2 or CH_4/CN = 9/1) in 500 to 1000 °C under ambient pressure.

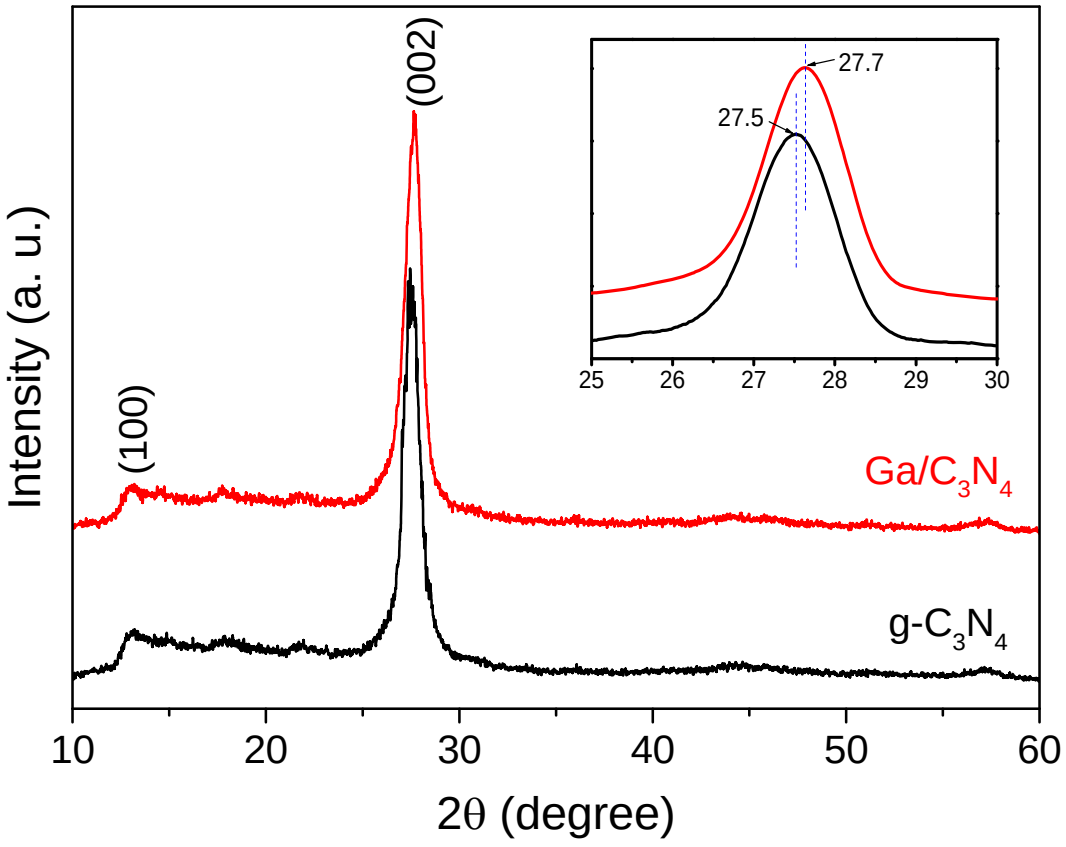

Figure S19. XRD patterns of g-C_3N_4 and 550 °C pyrolyzed precursor (Ga/C_3N_4).

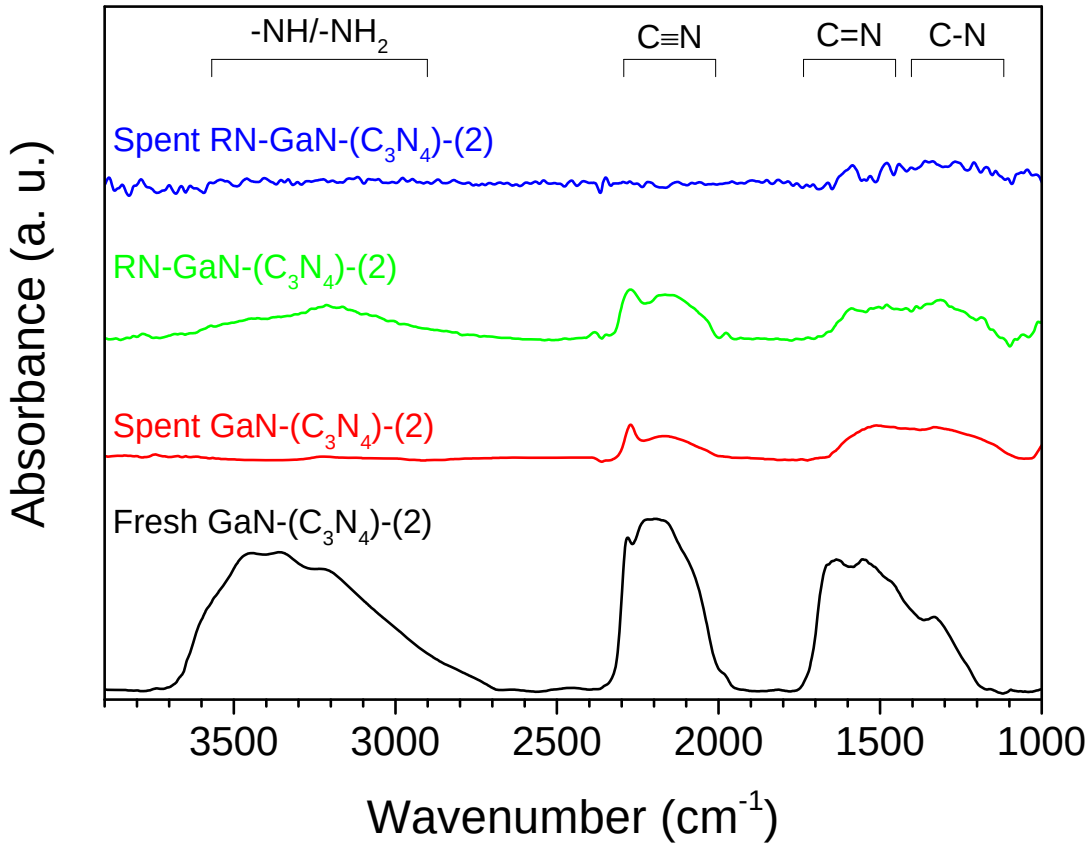

Figure S20. FTIR spectra of fresh GaN-(C_3N_4)-(2) (black), spent GaN-(C_3N_4)-(2) (red), regenerated GaN-(C_3N_4)-(2) (RN-GaN-(C_3N_4)-(2), before the 2nd on-stream test, green), and spent RN-GaN-(C_3N_4)-(2) (after the 2nd on-stream test, blue).

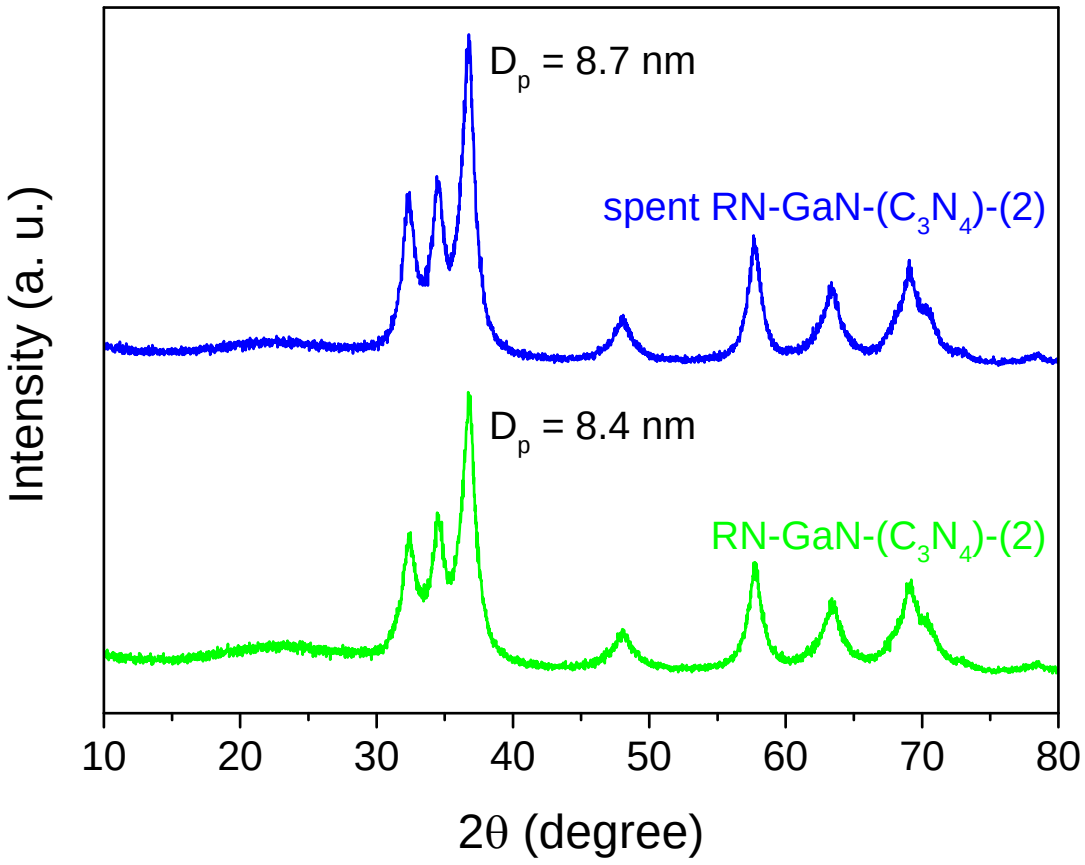

Figure S21. The XRD patterns of regenerated GaN-(C_3N_4)-(2) (RN-GaN-(C_3N_4)-(2), before the 2nd on-stream test, green) and spent RN-GaN-(C_3N_4)-(2) (after the 2nd on-stream test, blue).