Supporting Information

Producing hexamethylenediamine from caprolactam via 6-aminocapronitrile: A green production technology of the monomer of Nylon-66

Kaiyu Geng,[a] Hui Li,[a] Dianzi Zhang,[b] Baowei Yu,[b] Hongqin Hu,[b] Jiao Geng*,[a] Youting Wu*,[a] Xingbang Hu* [a]

[a] School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China.

[b] Shenma Corporation, Pingdingshan 467000, China.

* Corresponding authors

E-mail: gengjiao@nju.edu.cn, ytwu@nju.edu.cn, huxb@nju.edu.cn

Chemical reagents

Caprolactam (99%), Raney Ni (Ni≥90%), and vanadium pentoxide (98%) were supplied by Beijing Innochem Technology Co., Ltd. Ethanol (AR), toluene (AR), and barium triphosphate (CP) were supplied by Nanjing reagent Co., Ltd. Alumina (AR), sodium hydroxide (95%), USY zeolite (Si/Al=20), magnesium phosphate (99%), and calcium metasilicate (AR) were supplied by Shanghai Macklin Biochemical Co., Ltd. Hexadecyl trimethyl ammonium Bromide (99%), adiponitrile (99%), cerium oxide (99.99%), potassium polymetaphosphate (99%), magnesium oxide (99%), and cobalt sesquioxide (AR) were supplied by Meryer Biochemical Technology Co., Ltd. 6-aminocapronitrile (95%), calcium phosphate (98%), zinc phosphate (99%), and aluminium phosphate (99%) were supplied by Bidpharm Technology Co., Ltd. Aluminum tri-sec-butoxide (95%), titanium dioxide (AR), tungsten trioxide (95%), zinc oxide (97%), ferric oxide (99%), niobium pentoxide (99%), and silicon dioxide (99%) were supplied by Tianjin Heowns Biochemical Technology Co., Ltd. HY zeolite (Si/Al=5), NaY zeolite (Si/Al=5) were supplied by Beike Nanomedicine Technology Co., Ltd. N_2 (99.99%), and NH_3 (99.999%) were supplied by Nanjing Tianze Gas Center.

Characterization

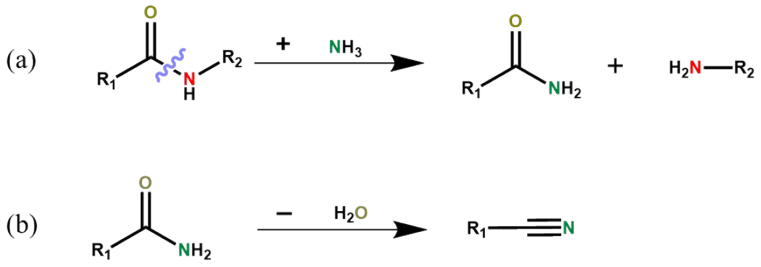
The specific surface areas, pore volumes, and pore sizes were determined by analyzing nitrogen (N_2) adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method. Surface area was determined by BET multi-point method. Average pore width was determined by the BJH desorption. Pore volume was determined at P/P_0 = 0.99. Crystallinity and particle size were obtained by Powder X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu Kα radiation (λ = 1.5406 Å). Morphological characteristics of the catalyst surface were examined through scanning electron microscope (SEM JEOL JSM-7800F).

All products were analyzed offline by a Shimadzu 2014C gas chromatograph (GC) equipped with an ZB-5 capillary column (30m×0.25mm×0.32um) and a flame

ionization detector (FID). The GC temperature program was from 50℃ to 280℃ with 10℃/min heating rate. Composition of effluents was identified offline by a QP2010 gas chromatography-mass spectrometry (GC-MS) equipped with an InertCap 17MS capillary column (30m×0.25mm×0.25um). The GC-MS temperature program was set to rise steadily from 50℃ to 280℃ in 23 minutes. All tests were repeated by three times.

Theoretical calculation

Theoretical calculation was performed by Gaussian 09 program. Structures were optimized using the B3LYP method, grounded in Density Functional Theory (DFT). Stationary points were differentiated into minima or transition states (TS) through the Hessian matrix diagonalization and vibrational normal modes inspection. The distinctive features of the TSs were identified by exploring the motions defined by the eigenvector associated with the imaginary frequency.



Scheme S1. (a) Ammoniation of amide and (b) amide dehydration to nitrile

Table S1: Comparison between the main industrial HMDA route (BD hydrocyanation) and this work (CTH process)

	BD hydrocyanation		CTH process	
Factor: index	BD	HCN	CPL	NH_3
Ecotoxicity: LC_{50} (rat, inhalation)	129042 ppm for 4h	524 ppm for 1h	1860 ppm for 4h	2000 ppm for 4h
Human toxicity: LD_{50} (rat, oral)	5480 mg/kg	1.52 mg/kg	1210 mg/kg	350 mg/kg
IDLH	2000 ppm	50 ppm	-	300 ppm
Bio-accumulation: $logK_{ow}$	Moderate risk (1.99)	Low risk (0.66)	Low risk (-0.29)	No risk (-1.44)
Eutrophication	No risk	No risk	No risk	Medium risk
Flammability	Highly flammable	Highly flammable	Not flammable	Flammable
Human carcinogenicity	Carcinogenic (Group 1)	Not carcinogenic (Group 4)	Not carcinogenic (Group 4)	Not carcinogenic (Group 4)
Persistence	Low	Mediun	Medium	Low
Process flow	Primary cyanidation, isomerization, secondary cyanidation, hydrogenation		Ammoniation, hydrogenation	
Catalytic system	Homogeneous		Hetergeneous	
Hydrogenation	Two nitrile groups hydrogenation		One nitrile group hydrogenation	
Energy usage	Moderate energy usage in reaction process (complex process and high energy usage in separation due to substances with similar boiling point)		Moderate energy usage in reaction process (320°C reaction temperature, but relatively low energy usage in separation)	
Waste treatment	Waste involving HCN requires careful handling and neutralization		Waste involving water and small amounts of by-products	
Life cycle	Butadiene is typically derived from petrochemical processes, which have significant environmental footprints.		Caprolactam production from benzene or cyclohexane has associated environmental impacts	

Reference:

1. Green Chem., 2020,22, 13-15.

2. Registration Dossier - ECHA (europa.eu)

3. TOXICOLOGICAL PROFILE FOR CYANIDE (cdc.gov)

4. Stanford Environmental Health & Safety

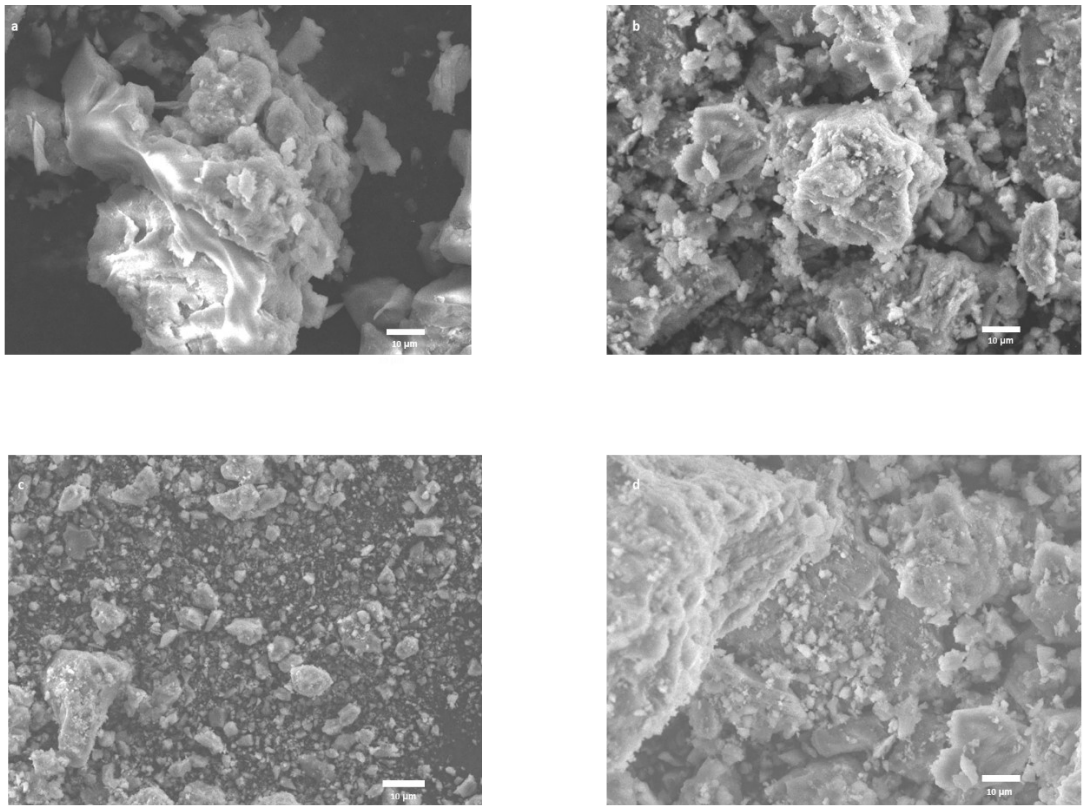


Fig. S1 (a) SEM images of Meso-Al_2O_3(0). (b) SEM images of Meso-Al_2O_3(7). (c) SEM images of Meso-Al_2O_3(14). (d) SEM images of Meso-Al_2O_3(21)

Table S2. Stability test for CPL

Entry	Carrier gas	Catalyst	CPL Conversion (%)	ACN Selectivity (%)
1	N_2	Blank	0	-
2	N_2	Al_2O_3	0	-

Reaction conditions: 4g catalyst loading; 320℃ reaction temperature; NH_3/CPL molar ratio=30; 25wt.% CPL in toluene; WHSV=0.8h^{-1}; atmospheric reaction pressure

Table S3. Influence of water content on catalytic performance of CPL ammoniation

Entry	Water content (wt. %)	CPL Conversion (%)	ACN Selectivity (%)
1	0	57.8	98.3
2	1	53.4	98.0
3	2	49.9	98.1
4	3	47.5	97.9
5	4	45.4	98.2

Reaction conditions: 4g catalyst loading; 320℃ reaction temperature; NH_3/CPL molar

ratio=30; 25wt.% CPL in toluene; WHSV=0.8h^{-1}; atmospheric reaction pressure

Cartesians coordinates of the optimized structures

CPL

6	0	-0.628157	-1.170179	-0.571504
6	0	0.609235	-1.572162	0.257194
6	0	1.859228	-0.714643	0.016261
6	0	1.722182	0.770422	0.374010
6	0	0.628996	1.511791	-0.407429
7	0	-0.735263	1.220982	0.027731
6	0	-1.396901	0.024497	-0.021671
8	0	-2.550144	-0.075435	0.373392
1	0	-1.347260	-1.988744	-0.595392
1	0	-0.328388	-0.967800	-1.607684
1	0	0.855574	-2.609740	0.010941
1	0	0.347463	-1.565932	1.321627
1	0	2.143214	-0.797007	-1.041434
1	0	2.692052	-1.138603	0.587356
1	0	2.677385	1.267804	0.170584
1	0	1.526960	0.887257	1.446159
1	0	0.737053	1.307202	-1.480488
1	0	0.763207	2.588267	-0.284595
1	0	-1.286761	1.975543	0.410506

Cat

13	0	-2.445481	-1.085468	1.493942
13	0	0.385918	-0.524827	1.216980
8	0	-2.514777	-2.552725	0.561210
8	0	-3.510011	0.170255	1.046342
13	0	-3.432668	1.145728	-0.357617
13	0	1.278977	2.609118	0.603894
8	0	0.294297	1.160732	0.453170
8	0	-0.940879	-0.832503	2.279176
8	0	-2.041194	0.973749	-1.343227
13	0	-1.277528	-2.608867	-0.604111
13	0	3.431700	-1.146263	0.358064
8	0	2.040627	-0.974527	1.344295
8	0	-0.293494	-1.160217	-0.453172
8	0	0.939884	0.833822	-2.279511
13	0	-0.386031	0.525602	-1.216265
13	0	2.445074	1.084705	-1.494700
8	0	2.516049	2.551689	-0.561532
8	0	3.507962	-0.172379	-1.047073
8	0	0.883722	3.746602	1.793061

8	0	-4.713347	2.206799	-0.734763
8	0	4.713793	-2.205394	0.735698
8	0	-0.882764	-3.745891	-1.794132
1	0	1.338004	4.563846	1.997859
1	0	-4.733042	2.770312	-1.508496
1	0	4.735132	-2.768140	1.509927
1	0	-1.338531	-4.562576	-1.998056

Rea

13	0	-1.445796	-1.573079	-1.641810
13	0	0.530629	-0.463633	0.166851
8	0	-0.617429	-0.984231	-3.118558
8	0	-2.990463	-2.248268	-1.281444
13	0	-3.911539	-1.716054	0.056848
13	0	0.112890	1.403267	2.743644
8	0	-0.462382	0.492140	1.360849
8	0	-0.167933	-1.892704	-0.446912
8	0	-3.413984	-0.279347	0.864748
13	0	-0.279945	0.532941	-2.389822
13	0	1.348667	2.527972	-1.388500
8	0	1.074856	0.730002	-1.089421
8	0	-1.586651	0.350921	-1.179204
8	0	-2.233710	2.587400	0.618762
13	0	-2.211224	0.862268	0.404457
13	0	-0.710564	3.295772	0.910618
8	0	-0.151741	3.062195	2.553727
8	0	0.471391	3.523822	-0.290465
8	0	1.199444	0.507418	3.711807
8	0	-5.295740	-2.583741	0.573662
8	0	2.951483	3.009892	-1.782380
8	0	0.255976	2.176010	-2.924796
6	0	1.862291	-2.619153	1.520085
8	0	1.298232	-2.935665	2.528539
6	0	2.381890	-3.622603	0.515491
6	0	2.848639	-3.185362	-0.875423
6	0	4.132942	-2.348243	-0.901227
6	0	3.955382	-0.900216	-0.436308
6	0	3.494855	-0.720216	1.005832
7	0	2.073982	-1.152657	1.310316
1	0	1.631838	0.785999	4.520412
1	0	-5.834311	-2.289624	1.308909
1	0	3.505880	2.596170	-2.442766
1	0	-0.124797	2.799915	-3.546364
1	0	3.189749	-4.153578	1.037864

1	0	1.565797	-4.343248	0.426845
1	0	2.031035	-2.667991	-1.384145
1	0	3.022906	-4.104609	-1.442529
1	0	4.517988	-2.327558	-1.925297
1	0	4.906313	-2.839778	-0.295789
1	0	4.913917	-0.375877	-0.516147
1	0	3.262858	-0.375202	-1.099451
1	0	3.535247	0.338744	1.269390
1	0	4.159118	-1.249435	1.697093
1	0	1.861284	-0.780226	2.248026

TS1

13	0	1.472041	1.305571	-1.584223
13	0	-0.542138	0.424234	0.480553
8	0	0.249423	1.324612	-2.881213
8	0	3.167602	1.482936	-1.397710
13	0	4.075385	0.449103	-0.373675
13	0	-0.056441	-1.908182	2.666309
8	0	0.371873	-0.938009	1.254369
8	0	0.510644	1.721654	-0.091072
8	0	3.275464	-0.934611	0.258336
13	0	-0.434542	-0.162544	-2.341927
13	0	-2.446058	-1.786803	-1.350693
8	0	-1.562952	-0.243421	-0.851076
8	0	1.046810	-0.565425	-1.401970
8	0	1.190207	-3.224077	-0.138142
13	0	1.712454	-1.570570	-0.082068
13	0	-0.416525	-3.483927	0.393115
8	0	-0.578490	-3.430824	2.129903
8	0	-1.773967	-3.169150	-0.581257
8	0	-0.083159	-1.118655	4.167024
8	0	5.717018	0.788107	-0.035691
8	0	-4.147934	-1.709997	-1.546727
8	0	-1.498774	-1.458176	-2.999551
6	0	0.140013	2.860272	1.233338
8	0	0.992982	2.873188	2.060081
6	0	-0.480877	4.053678	0.544917
6	0	-1.593980	3.877983	-0.493607
6	0	-3.020240	3.732771	0.058168
6	0	-3.376508	2.402653	0.736102
6	0	-2.604609	2.079066	2.014692
7	0	-1.214906	1.620224	1.784007
1	0	-0.296898	-1.494145	5.021574
1	0	6.256640	0.230998	0.525875

1	0	-4.639903	-0.998503	-1.953863
1	0	-1.451589	-2.004368	-3.786854
1	0	-0.803577	4.722785	1.351107
1	0	0.382310	4.540751	0.079006
1	0	-1.345863	3.054271	-1.166953
1	0	-1.579080	4.778800	-1.115458
1	0	-3.717488	3.877975	-0.773872
1	0	-3.217619	4.553782	0.760165
1	0	-4.439182	2.430586	1.000155
1	0	-3.264002	1.576253	0.024997
1	0	-3.138530	1.294199	2.563054
1	0	-2.585113	2.958402	2.670419
1	0	-0.786821	1.443418	2.692433

Int1

13	0	-2.559489	-1.285249	-0.018340
13	0	0.783082	-0.155508	0.947364
8	0	-1.623356	-2.736064	-0.322779
8	0	-2.544844	-0.142221	-1.322164
13	0	-1.772181	0.480941	-2.696060
13	0	2.003618	2.716994	-0.053479
8	0	1.074475	1.232441	-0.219730
8	0	-1.150186	-0.434934	1.173964
8	0	-0.071126	0.337063	-2.839218
13	0	-0.019519	-2.771152	-0.833560
13	0	3.827185	-1.052014	1.661699
8	0	2.160189	-0.708823	1.823017
8	0	0.821590	-1.255654	-0.582880
8	0	2.933798	0.213951	-2.084092
13	0	1.239658	0.095510	-1.761190
13	0	3.938414	0.734513	-0.797778
8	0	3.648512	2.384999	-0.328989
8	0	4.639046	-0.321520	0.343114
8	0	1.182292	4.158088	0.295522
8	0	-2.696594	1.261235	-3.908441
8	0	4.688387	-2.037418	2.756894
8	0	0.900187	-4.016993	-1.535455
1	0	1.569600	5.026897	0.404219
1	0	-2.303069	1.634031	-4.698132
1	0	4.296188	-2.459428	3.521302
1	0	0.582524	-4.888624	-1.771967
6	0	-1.215947	0.499371	2.106308
8	0	-0.100272	0.979952	2.389392
6	0	-2.528634	0.910588	2.660763

6	0	-3.261051	1.852911	1.654553
6	0	-4.793711	1.693805	1.640808
6	0	-5.366856	0.637981	0.671159
6	0	-5.324060	-0.838020	1.088166
7	0	-3.995062	-1.458421	1.066739
1	0	-3.118045	-0.000007	2.789319
1	0	-2.370342	1.406671	3.618090
1	0	-2.890380	1.683323	0.639734
1	0	-2.992027	2.880849	1.909281
1	0	-5.212122	2.661456	1.344015
1	0	-5.161784	1.509840	2.658186
1	0	-6.425130	0.880699	0.521366
1	0	-4.890222	0.751601	-0.309166
1	0	-6.019640	-1.375650	0.425926
1	0	-5.749275	-0.919173	2.099876
1	0	-4.036051	-2.368609	1.512469

TS2

13	0	2.436745	-0.875708	0.948498
13	0	-0.747029	-0.673079	-0.625596
8	0	1.526066	-1.849099	2.101654
8	0	2.517391	0.801652	1.392335
13	0	1.734553	2.238213	1.837005
13	0	-2.076333	2.069592	-1.852877
8	0	-1.130462	1.129414	-0.713064
8	0	1.165229	-0.910059	-0.482887
8	0	0.026705	2.319121	1.818242
13	0	-0.060624	-1.409605	2.486709
13	0	-3.779118	-1.866314	-0.350332
8	0	-2.123667	-1.734788	-0.738966
8	0	-0.817252	-0.396527	1.285335
8	0	-2.955576	1.685845	1.360125
13	0	-1.260878	1.373180	1.189263
13	0	-3.958852	1.141256	0.083905
8	0	-3.718426	2.005921	-1.407702
8	0	-4.627244	-0.427122	0.022424
8	0	-1.296464	2.878800	-3.125109
8	0	2.676897	3.599651	2.284249
8	0	-4.618870	-3.356695	-0.356728
8	0	-1.012877	-1.832367	3.833983
6	0	1.271196	-1.156184	-1.839852
8	0	0.081637	-1.009025	-2.341324
6	0	2.494771	-0.633850	-2.586998
6	0	2.970905	0.776529	-2.166521

6	0	4.499974	0.853567	-1.990706
6	0	5.104594	0.292968	-0.683970
6	0	5.087157	-1.226740	-0.412578
7	0	3.838189	-1.782755	0.161377
1	0	-1.720627	3.418771	-3.792394
1	0	2.276665	4.430602	2.543224
1	0	-4.212420	-4.194959	-0.575315
1	0	-0.717183	-2.339078	4.590494
1	0	3.321845	-1.326047	-2.436928
1	0	2.235194	-0.659487	-3.647904
1	0	2.489214	1.080494	-1.235070
1	0	2.655060	1.501079	-2.920779
1	0	4.787050	1.909582	-2.037795
1	0	4.986167	0.376807	-2.852828
1	0	6.161645	0.582690	-0.695053
1	0	4.660467	0.810587	0.171838
1	0	5.914592	-1.426076	0.279054
1	0	5.348909	-1.753085	-1.345157
1	0	4.077734	-2.609904	0.700271
7	0	1.674296	-2.906225	-1.769374
1	0	0.898521	-3.408071	-1.342771
1	0	1.873839	-3.303583	-2.683869
1	0	2.509635	-2.910921	-1.155293

AHA

13	0	2.048014	1.255113	0.695036
13	0	-0.259708	-0.736234	-0.077471
8	0	1.524961	1.637193	2.330146
8	0	2.150418	2.581685	-0.421810
13	0	0.917532	3.502079	-1.157840
13	0	-2.461741	-0.644022	-2.396379
8	0	-1.306016	0.165443	-1.372360
8	0	1.410171	-0.248148	0.122119
8	0	-0.714378	3.058081	-0.938897
13	0	-0.120680	1.267845	2.542565
13	0	-2.784346	-1.849161	1.660900
8	0	-1.304175	-1.842998	0.805472
8	0	-0.906320	0.912152	1.039784
8	0	-3.405739	1.739916	-0.218292
13	0	-1.672264	1.747069	-0.362816
13	0	-4.080572	0.171127	-0.242679
8	0	-4.059665	-0.540392	-1.838991
8	0	-4.095847	-0.911661	1.073345
8	0	-1.801198	-1.626327	-3.634707

8	0	1.360837	4.850683	-2.122672
8	0	-3.059013	-2.872253	3.007373
8	0	-1.039377	1.126055	3.971196
1	0	-2.321343	-2.120017	-4.270925
1	0	0.704826	5.406554	-2.544882
1	0	-2.365553	-3.398540	3.405642
1	0	-0.722643	1.265258	4.863610
6	0	4.467248	-0.510022	0.749126
8	0	4.564535	-1.254712	1.683511
6	0	4.751072	-0.843443	-0.697818
6	0	4.795187	-2.345068	-1.035326
7	0	4.064201	0.871436	0.978759
6	0	3.453263	-2.941415	-1.497008
6	0	2.414425	-3.172250	-0.386145
6	0	1.000398	-3.425203	-0.916676
7	0	0.379506	-2.182016	-1.481521
1	0	4.033281	-0.311861	-1.330233
1	0	5.729822	-0.388983	-0.907240
1	0	5.179588	-2.895387	-0.171691
1	0	5.522771	-2.480167	-1.840580
1	0	4.241898	1.123182	1.951425
1	0	4.510780	1.538778	0.349516
1	0	3.653188	-3.895520	-1.998090
1	0	3.046609	-2.282096	-2.275430
1	0	2.715625	-4.040320	0.209198
1	0	2.376049	-2.316102	0.286868
1	0	0.346618	-3.761742	-0.110793
1	0	1.019627	-4.204918	-1.687156
1	0	-0.325051	-2.442933	-2.171697
1	0	1.083797	-1.674071	-2.013991