Supplementary Information for

Catalytic dehydrochlorination of 1, 2-dichloroethane to produce vinyl chloride over N-doped cocoanut activated carbon

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Catalyst characterization

Elemental analyses was performed by vario EL CUBE elemental analyzer from ELEMENTAR in Germany.

Table S1

Bulk phase mass composition of catalysts tested by elemental analyses.

Samples	Element content of fresh catalysts (wt%)			Element content of used catalysts (wt%)		
	C	H	N	C	H	N
AC	93.68	2.39	0.48	92.43	2.52	0.41
700-AC	93.96	2.21	0.41	92.02	2.48	0.47
0.5:10-N-AC	93.17	2.17	1.84	90.16	2.93	1.88
1:10-N-AC	92.14	2.19	2.98	89.05	2.69	2.85
2:10-N-AC	91.09	1.91	4.23	88.35	2.88	4.35
5:10-N-AC	89.73	1.99	5.66	87.66	2.61	5.31
7:10-N-AC	89.34	1.94	6.08	87.15	2.73	5.54

Table S2

Desorption amount of the fresh catalysts, determined by TPD measurement.

Samples	Desorption area of EDC	Desorption area of HCl	Desorption area of VCM
Initial AC	4959	38	1749
700-AC	5301	47	2322
0.5:10-700-N-AC	6183	571	3038
1:10-700-N-AC	7229	943	3709
2:10-700-N-AC	7910	1290	4214
5:10-700-N-AC	8465	1836	5423
7:10-700-N-AC	8892	2137	6255

For the 1,2-DCE–TPD test, sample amount of AC, 700-AC, 0.5:10-N-AC, 1:10-N-AC, 2:10-N-AC, 5:10-N-AC, 7:10-N-AC: 180 mg, 169 mg, 144 mg, 123 mg, 114 mg, 106 mg, 100 mg.
For the HCl–TPD test, sample amount of AC, 700-AC, 0.5:10-N-AC, 1:10-N-AC, 2:10-N-AC, 5:10-N-AC, 7:10-N-AC: 370 mg, 250 mg, 19 mg, 11 mg, 8 mg, 6 mg, 5 mg.
For the VCM–TPD test, sample amount of AC, 700-AC, 0.5:10-N-AC, 1:10-N-AC, 2:10-N-AC, 5:10-N-AC, 7:10-N-AC: 179 mg, 136 mg, 102 mg, 83 mg, 74 mg, 58 mg, 50 mg.

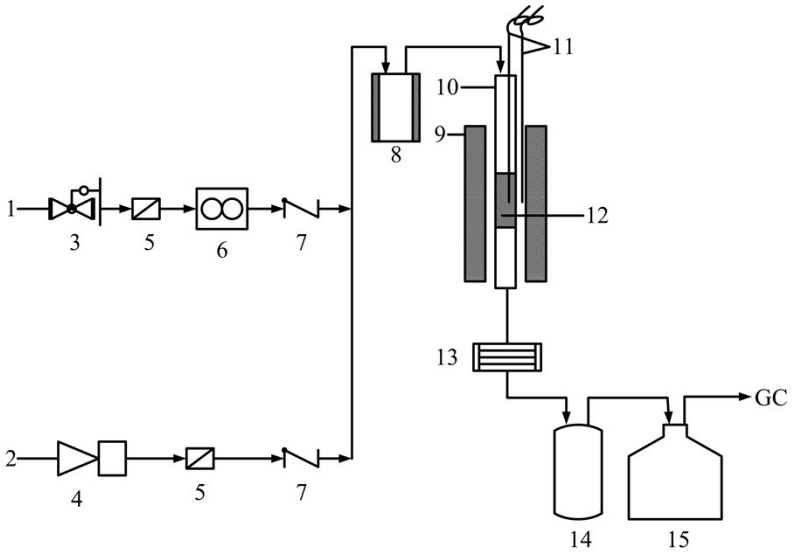

Fig. S1. Experimental catalyst testing setup.

1. Nitrogen, 2. EDC, 3. Pressure relief valve, 4. Micro-injection pump, 5. Filter, 6. Mass flowmeter, 7. One-way check valve, 8. Vaporizing chamber, 9. Furnace, 10. Reactor, 11. Thermocouple, 12. Catalyst, 13. Condenser, 14. Buffer tank, 15. Absorption bottle.

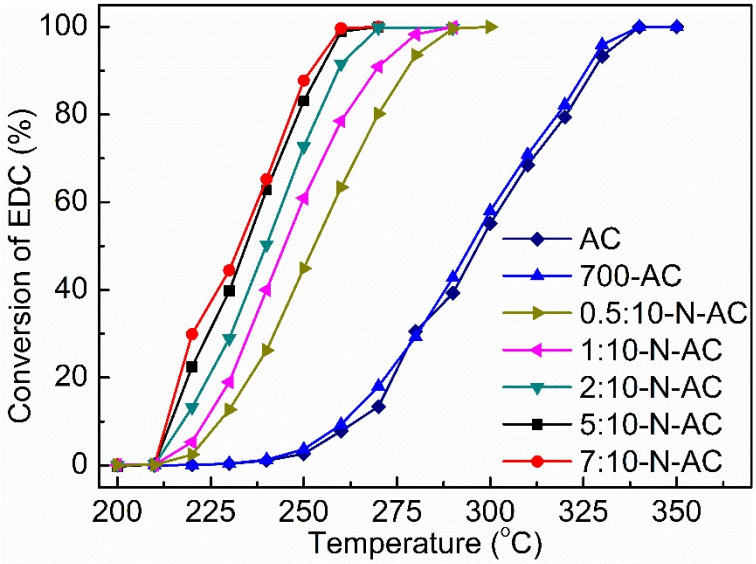

Fig. S2. Effect of temperature on catalytic performance. Reaction conditions: 0.1 MPa, LHSV (EDC) = 0.2 h^{-1}.

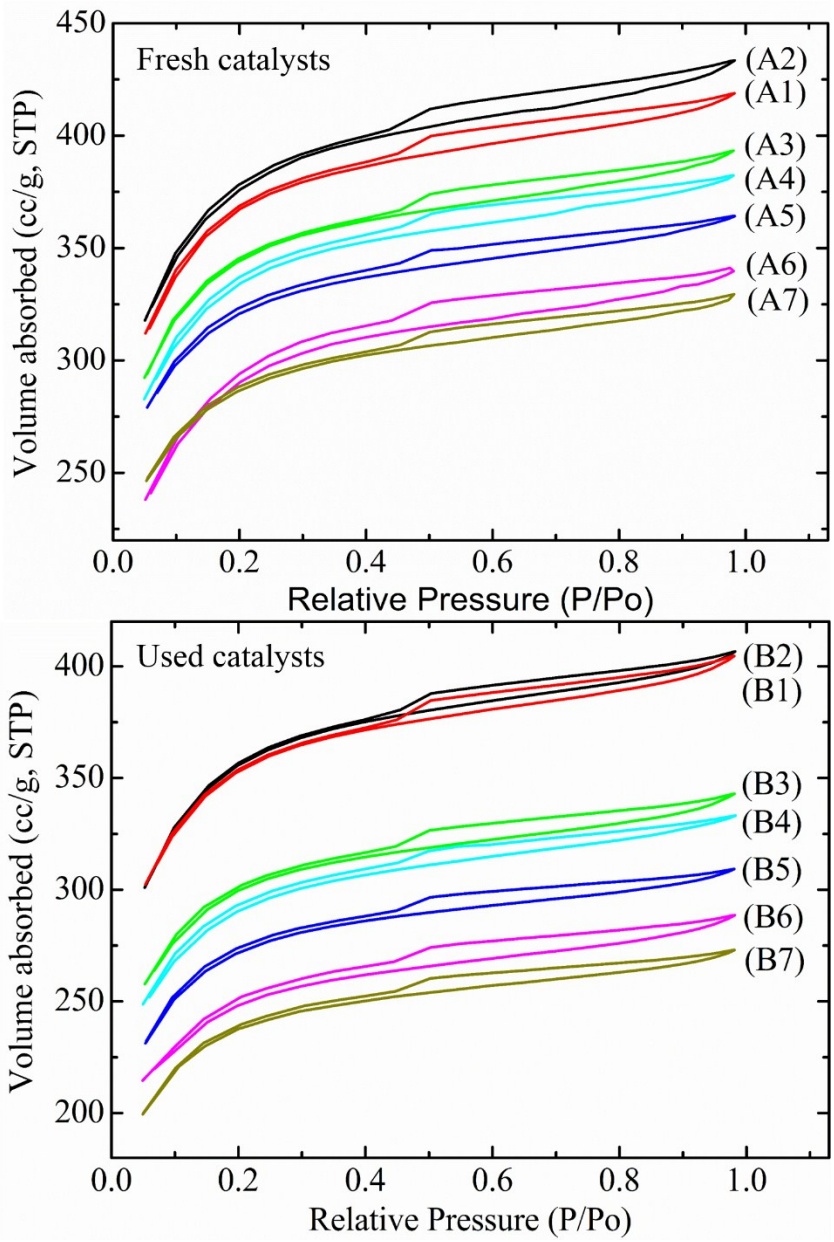

Fig. S3. Nitrogen adsorption-desorption isotherms of fresh and used catalysts. A1-A7: fresh AC, fresh 700-AC, fresh 0.5:10-N-AC, fresh 1:10-N-AC, fresh 2:10-N-AC, fresh 5:10-N-AC, fresh 7:10-N-AC; B1-B7: used AC, used 700-AC, used 0.5:10-N-AC, used 1:10-N-AC, used 2:10-N-AC, used 5:10-N-AC, used 7:10-N-AC. All the isotherms belonged to type I curves, and due to abundant micropore structure in activated carbon, the H4 adsorption–desorption hysteresis loop based on IUPAC nomenclature could be observed in the isotherms.

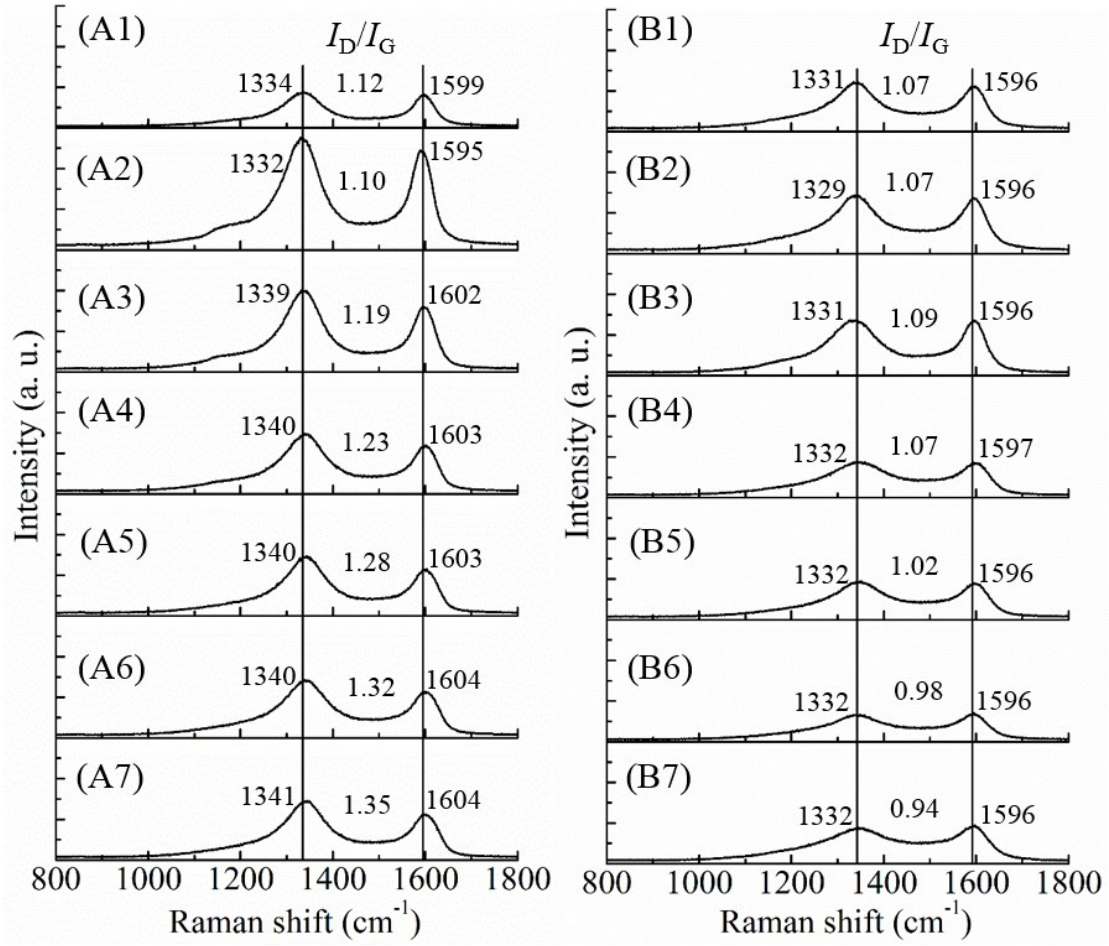

Fig. S4. Raman spectroscopy for fresh and used catalysts. A1-A7: fresh AC, fresh 700-AC, fresh 0.5:10-N-AC, fresh 1:10-N-AC, fresh 2:10-N-AC, fresh 5:10-N-AC, fresh 7:10-N-AC; B1-B7: used AC, used 700-AC, used 0.5:10-N-AC, used 1:10-N-AC, used 2:10-N-AC, used 5:10-N-AC, used 7:10-N-AC.

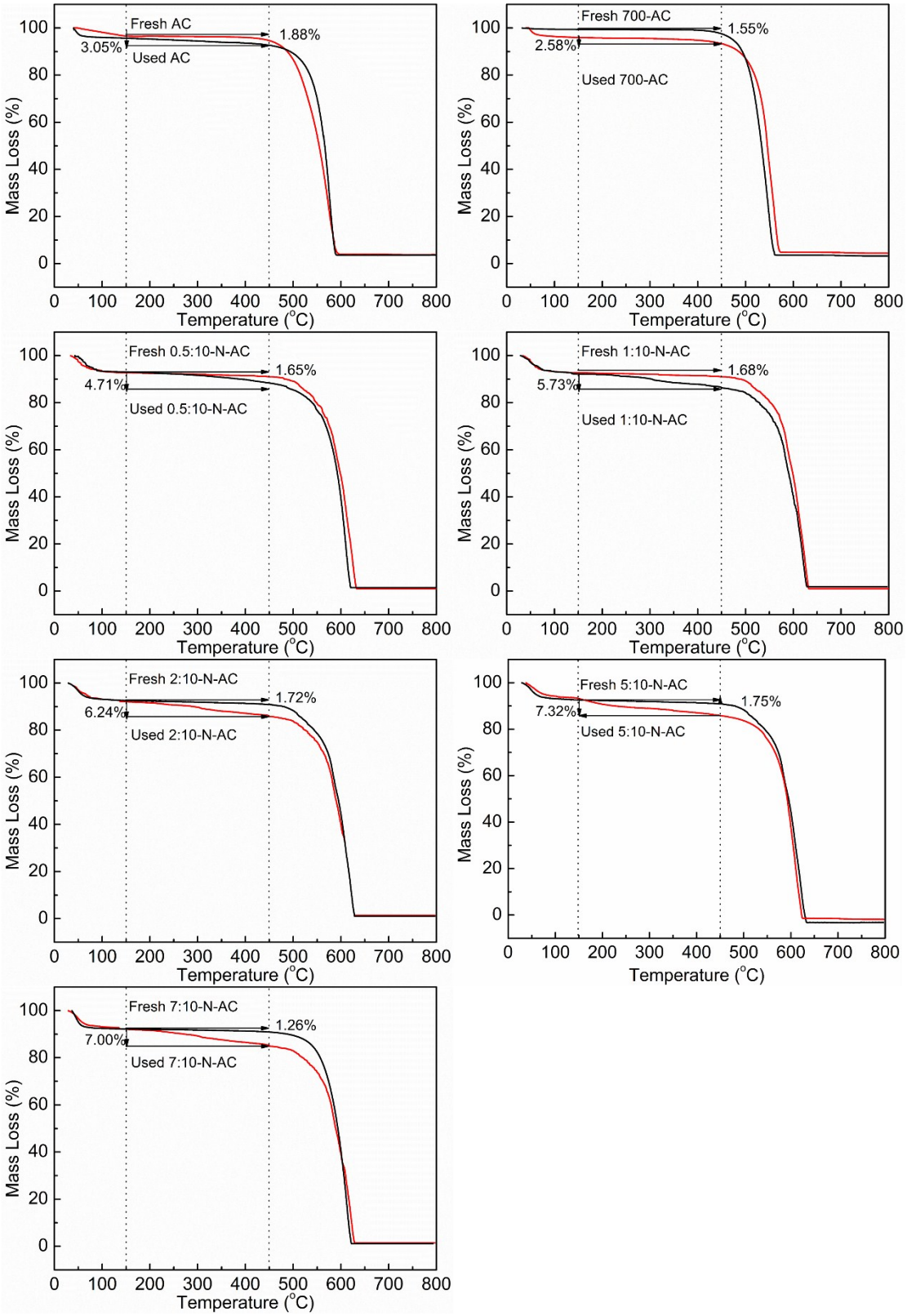

Fig. S5. Thermogravimetric analysis (TGA) curves recorded in air atmosphere of fresh and used catalysts.

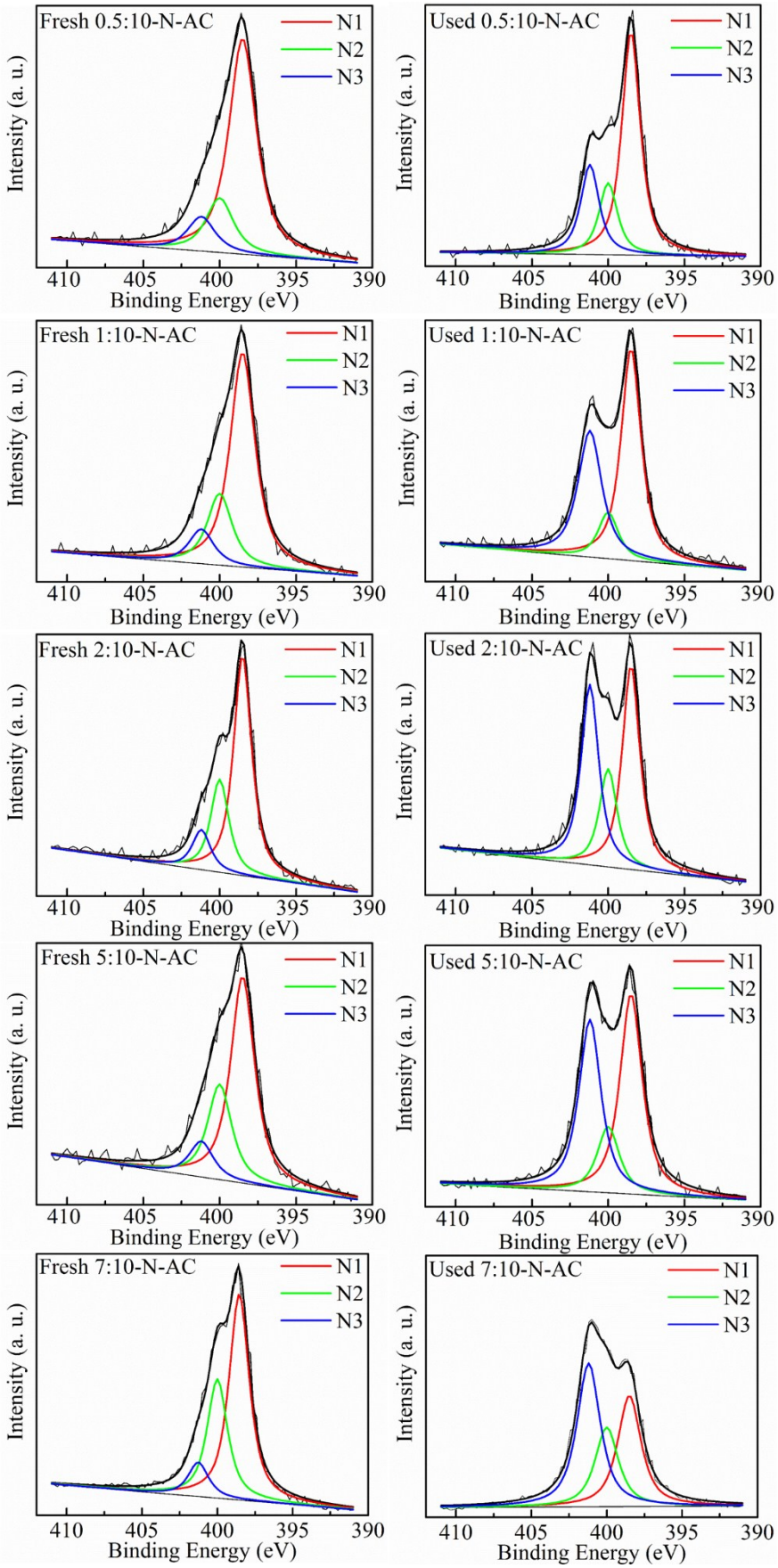

Fig. S6. High-resolution XPS spectra of N 1s for fresh and used catalyst.

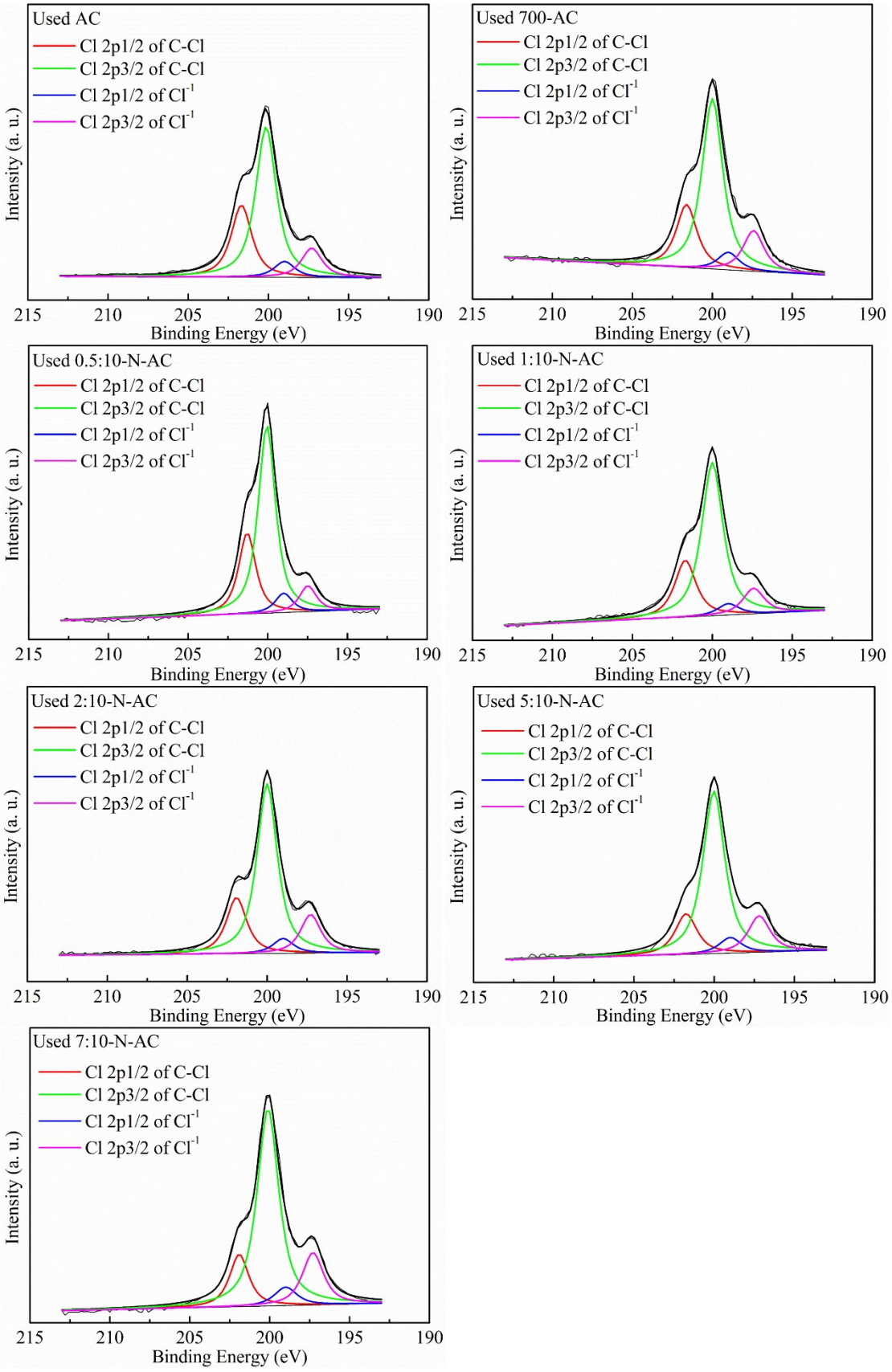

Fig. S7. High-resolution XPS spectra of Cl 2p for used catalysts.

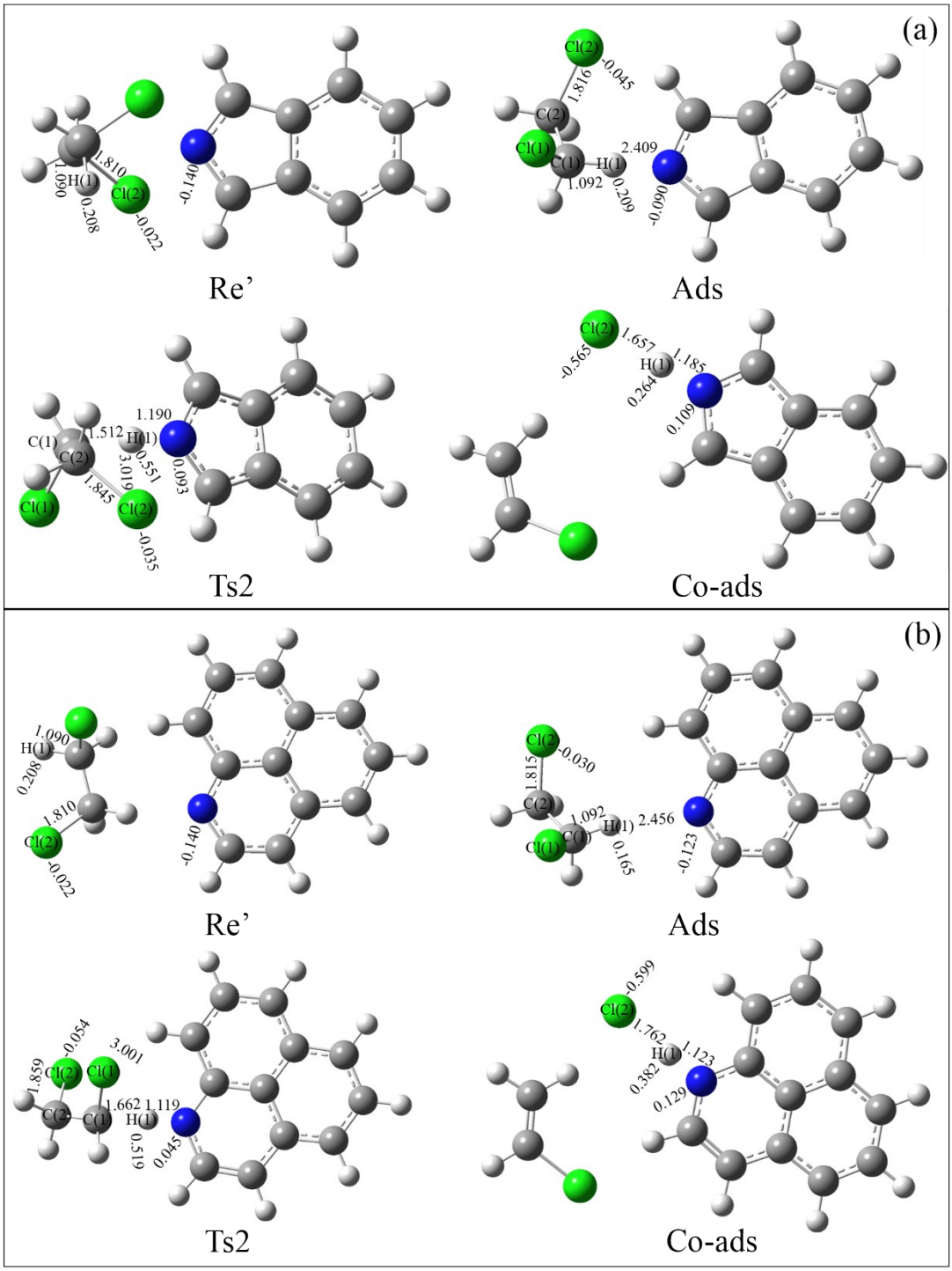

Fig. S8. The geometries of the substances involved in the reaction path. (a): for pyrrolic nitrogen structure; (b): for pyridinic nitrogen structure. The path contains: adsorbed reactants (Ads), transition state (Ts), intermediate product (Im). Chlorine, nitrogen, carbon, and hydrogen atoms are depicted in green, blue, gray and white, respectively.

Intrinsic Reaction Roordinate (IRC) calculations

The intrinsic reaction coordinate (IRC) calculations were used to indentify that each transition state links the correct product with reactant. In ts-IRC-forward and ts-IRC-reverse, the total energy of the cluster were calculated by 100 steps. The configurations at the last step were optimized and got all corresponding stable substances. It indicates that the reaction is continuous and complete.

Additional Experiments

We have prepared other N-AC catalysts, including 500-N-AC, 700-N-AC and 900-N-AC, at different calcination temperature, which was named according to the calcination temperature, e.g., 500-N-AC indicates the N-AC calcined at 500 ^{o}C. Table R4 lists the pore structure parameters of these catalysts. It is indicated that the surface area and the total pore volume increase as the calcination temperature increases.

The total N contents and relative contents of different nitrogen species were list in Table R2 and Table R3, and the N 1s XPS spectra were shown in Fig R2. As shown in Table R2, the total N contents decreases as the calcination temperature increases. As listed in Table R3, the contents of the pyridinic nitrogen (N1) and the pyrrolic nitrogen (N2) are decreased but the content of quaternary nitrogen (N3) is increased at high calcination temperature. Considering the variation of the total N content in these N-AC, the individual nitrogen species of N1 and N2 is respectively 3.68% (3.68%=5.8%*63.57%) and 1.73% (1.73%=5.8%*29.95%) for 500-N-AC, 2.63% (2.63%=4.3%*61.21%) and 1.21% (1.21%=4.3%*28.21%) for 700-N-AC, 1.02% (1.02%=1.9%*53.92%) and 0.52% (0.52%=1.9%*27.28%) for 900-N-AC.

Fig R3 shows the catalytic performance of these catalysts. As shown in Fig R3, 700-N-AC exhibits the best catalytic activity. The total N content of 700-N-AC is

higher than 900-N-AC, so the catalytic activity of 700-N-AC is higher than 900-N-AC. The total N content of 500-N-AC is higher than 700-N-AC, but the S_{BET} of 500-N-AC is much lower than 700-N-AC, so the catalytic activity of 700-N-AC is higher than 500-N-AC.

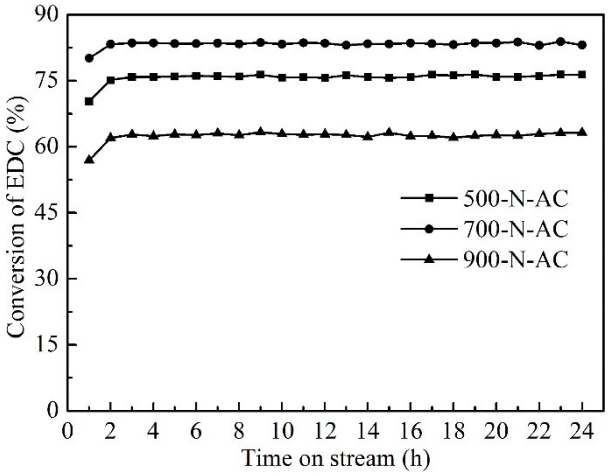

Fig. S9. Conversion of 1,2-DCE over different catalysts.

Reaction conditions: temperature = 250 ^{o}C, 0.1 MPa, LHSV (1,2-DCE) = 0.2 h^{-1}.

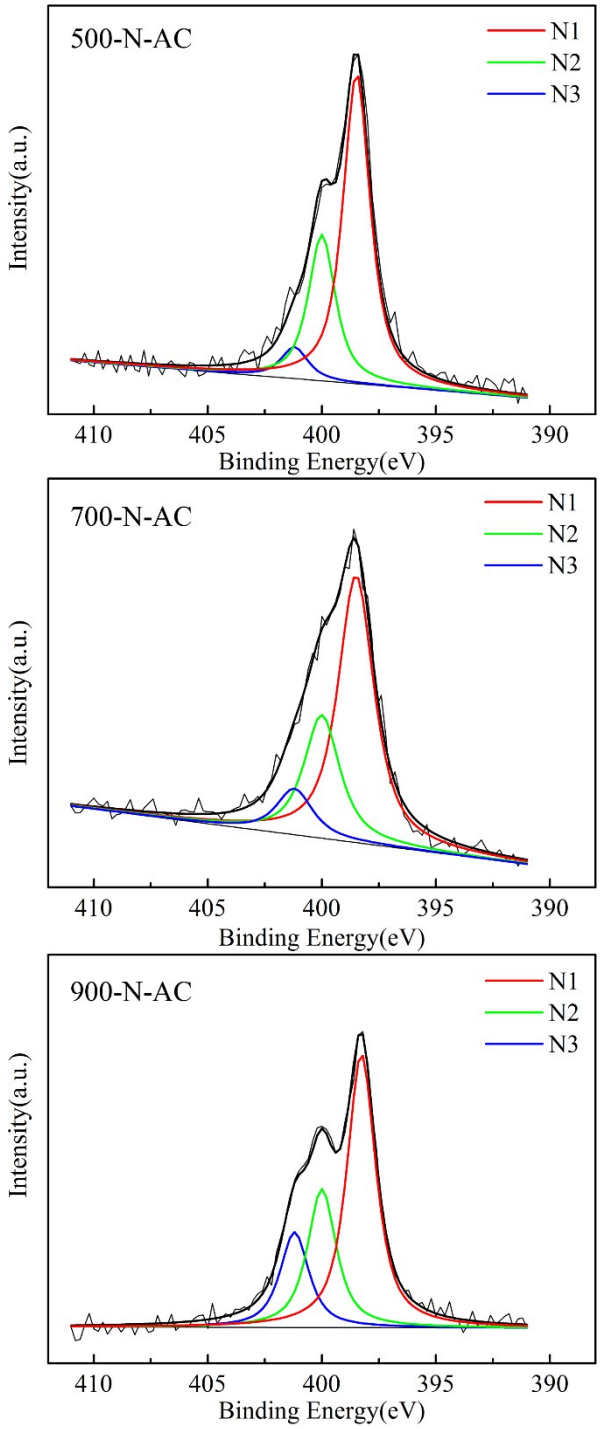

Fig. S10. High-resolution XPS spectra of N 1s for the catalysts.

Table S3

Surface element content of the catalysts determined by XPS.

Samples	Surface atomic composition of fresh catalysts (atom. %)			
	C 1s	O 1s	N 1s	Cl 2p
500-N-AC	88.8	5.3	5.8	0.1
700-N-AC	91.2	4.4	4.3	0.1
900-N-AC	94.9	3.1	1.9	0.1

Table S4

The relative contents and binding energies of nitrogen species in the catalysts.

Samples	Relative contents (Area%)		
	N1 (398.5 eV)	N2 (400.0 eV)	N3 (401.2 eV)
500-N-AC	63.57	29.95	6.48
700-N-AC	61.21	28.21	10.58
900-N-AC	53.92	27.28	18.80

Note: N1: pyridinic nitrogen, N2: pyrrolic nitrogen, N3: quaternary nitrogen.

Table S5

Pore structure parameters of the catalysts test by N_2 adsorption-desorption.

Samples	S_{BET}(m^2 g^{-1})	V (cm^3 g^{-1})
500-N-AC	741	0.39
700-N-AC	929	0.53
900-N-AC	1097	0.61

S_{BET}: surface area; V: total pore volume.