

Single Ni Sites Distributing on N-doped Carbon for Selective Hydrogenation of Acetylene

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1. Materials and Methods:

Synthesis Ni SAs/N-C

In a typical procedure, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3g) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3g) was dissolved in methanol (15mL) to form a clear solution. Then the solution was injected into 15mL of methanol containing 1g 2-methylimidazole (MeIM) under ultrasound for 20min at room temperature. The precipitates were washed with ethanol three times and dried in vacuum at 80°C for overnight. The powder was placed in a furnace and then heated to the desired temperature (700 °C) at the rate of 5 °C /min for 3 h under N_2 gas and then cooled to room temperature to get the representative samples.

Synthesis Ni SAs/N-C 700, Ni SAs/N-C 800, and Ni SAs/N-C 900

In a typical procedure, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3g) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3g) was dissolved in methanol (15mL) to form a clear solution. Then the solution was injected into 15mL of methanol containing 1g 2-methylimidazole (MeIM) under ultrasound for 20min at room temperature. The precipitates were washed with ethanol three times and dried in vacuum at 80°C for overnight. The powder was placed in a furnace and then heated to the desired temperature (700, 800 and 900 °C) at the rate of 5 °C /min for 3 h under N_2 gas and then cooled to room temperature to get the representative samples.

Synthesis of Ni NPs/N-C

In a typical procedure, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.53g) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06g) was dissolved in methanol (15mL) to form a clear solution. Then the solution was injected into 15mL of methanol containing 1g 2-methylimidazole (MeIM) under ultrasound for 20min at room temperature. The precipitates were washed with ethanol three times and dried in vacuum at 80°C for overnight. The powder was placed in a furnace and then heated to the 1000 °C at the rate of 5 °C /min for 3 h under N_2 gas and then cooled to room temperature to get the representative samples.

The selective hydrogenation of acetylene.

Catalyst was loaded in a microreactor. The feedstock was introduced into the reactor after it was cooled to room temperature. Acetylene (0.5%) was hydrogenated in admixture with ethylene (50%) and hydrogen (5%) over the catalyst. Aliquots were taken at specific time for determination of component concentrations by GC.

Characterization:

Powder X-ray diffraction patterns of samples were recorded on a Rigaku Miniflex-600 operating at 40 kV voltage and 15 mA current with CuK α radiation ($\lambda=0.15406\text{nm}$). Transmission electron microscopy (TEM) was carried out by a JEM-2100F FETEM equipped with energy dispersive X-ray spectrometer (EDX) analyses at 100 kV, and the high-angle annular dark-field scanning TEM (HAADF-STEM), EDX elemental mapping were operated at 200 kV. The scanning electron microscope (SEM) was performed on JSM-6700F SEM. Fourier-transformed infrared resonance (FT-IR) spectra were obtained in transmission mode on a Nicolet 8700 FT-IR. Thermogravimetric analyses (TG and DTA) were carried out on a TA SDT Q600 thermal analyzer heating from room temperature to 1000 °C at the rate of 10 °C min⁻¹. The obtained adsorption-desorption isotherms were evaluated to give the pore parameters including Brunauer-Emmett-Teller (BET) specific surface area and pore size. These were all performed on a Micromeritics Tristar II 3020M.

2. Supplementary Figures and Tables.

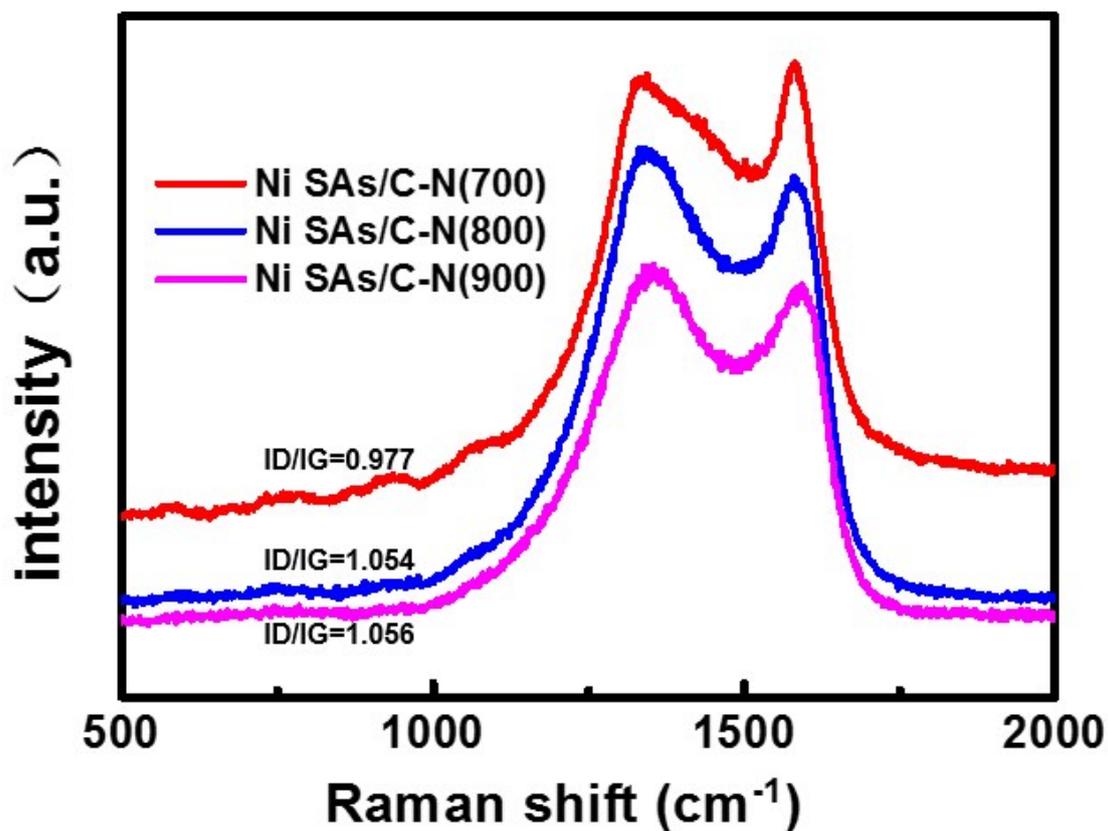


Fig. S1. Raman spectra for the pyrolyzed ZnNi-ZIF at 700, 800 and 900 °C, respectively.

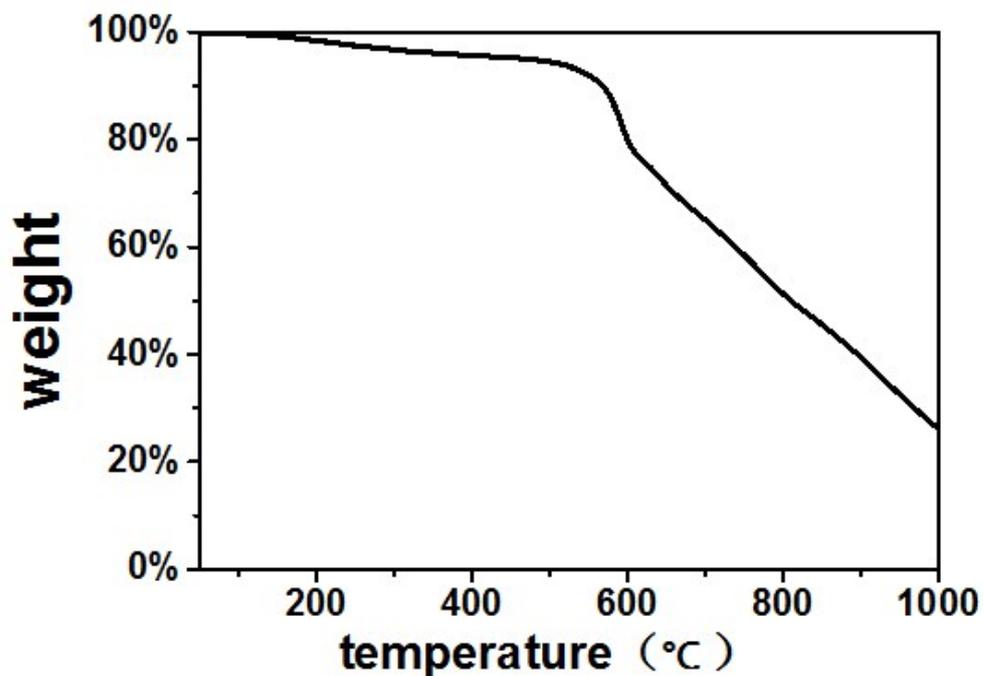


Fig. S2. TGA pattern of ZnNi-ZIF.

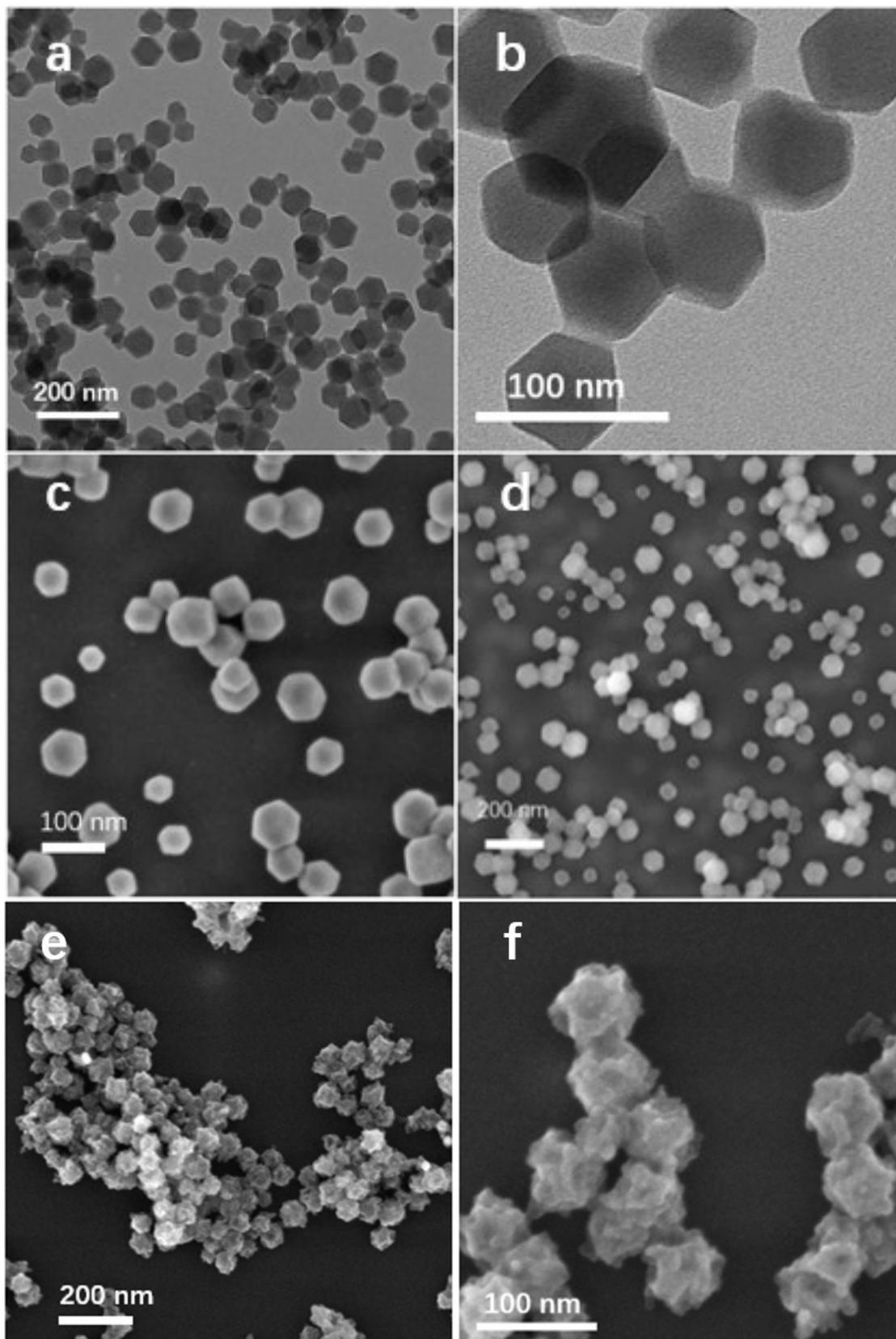


Fig. S3 a,b) TEM image of ZnNi-ZIF, c,d) SEM image of ZnNi-ZIF ,e,f) SEM images of Ni SAs/N-C..

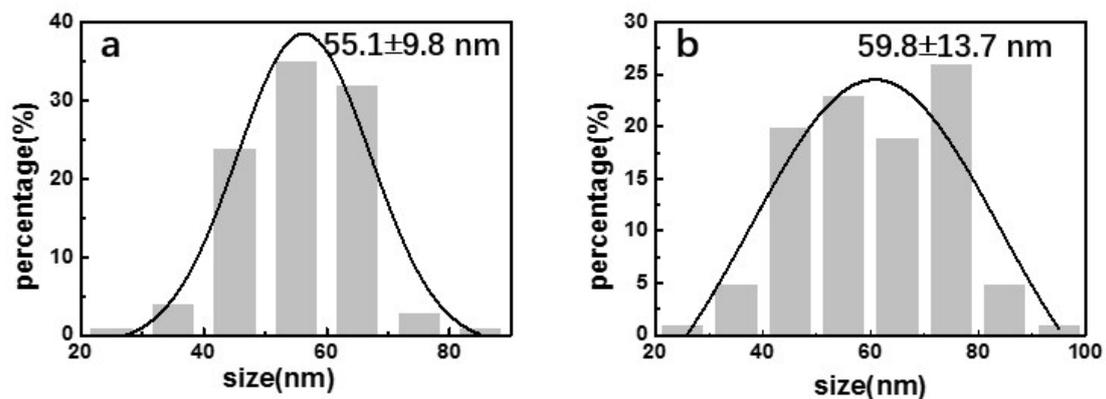


Fig. S4 The histograms of size distribution of (a) Ni SAs/N-C and (b) ZnNi-ZIF.

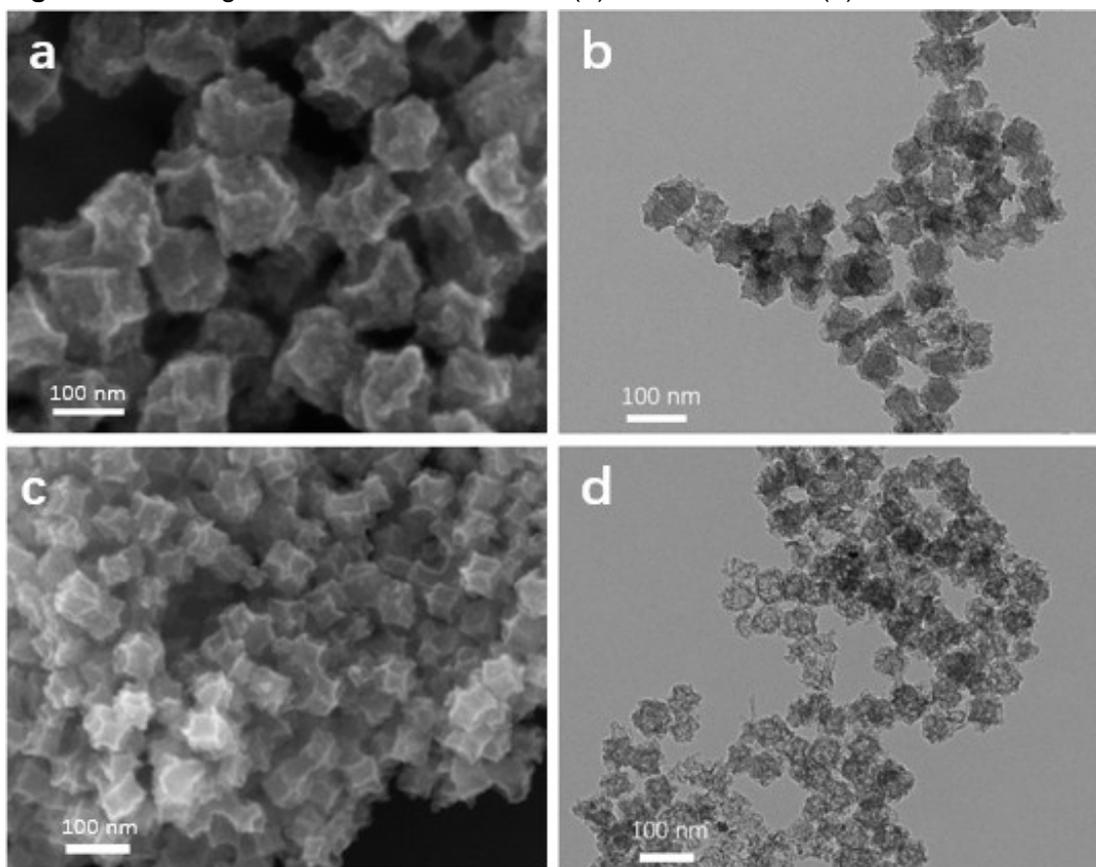


Fig. S5. a) SEM image, b) TEM image of Ni SAs/N-C 800, c) SEM image, d) TEM image of Ni SAs/N-C 900.

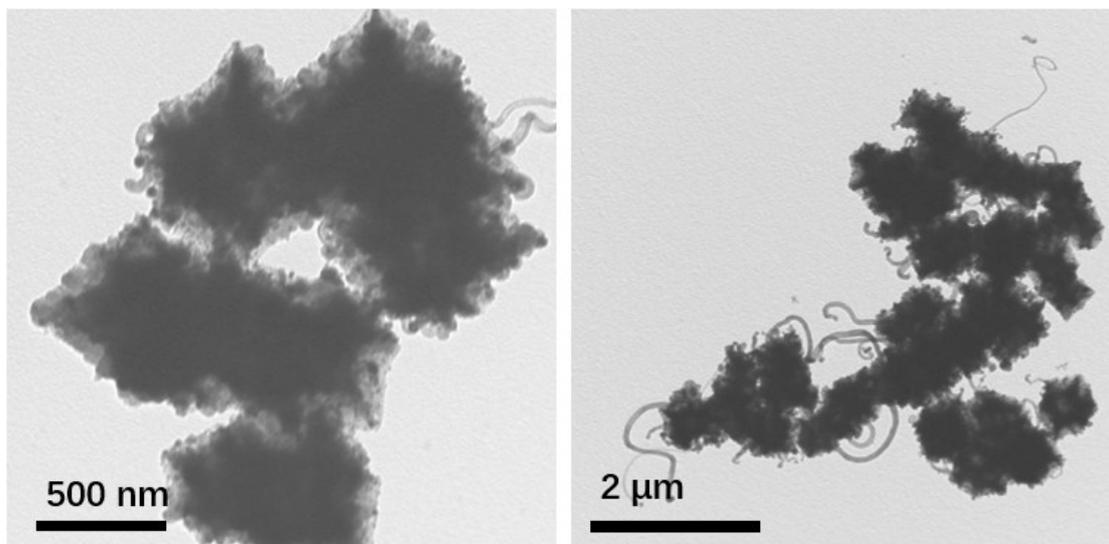


Fig. S6. TEM images of Ni NPs/N-C at different scale.

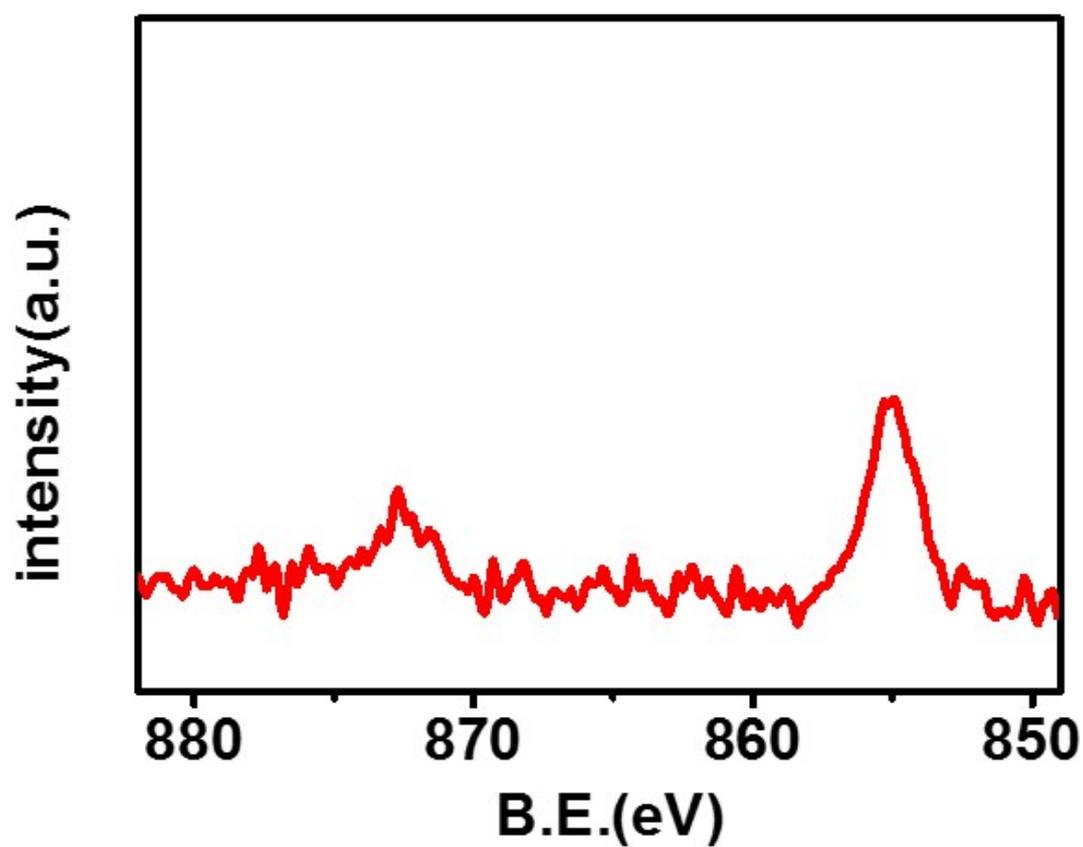


Fig. S7. Evolution of Ni 2p XPS of the Ni SAs/N-C.

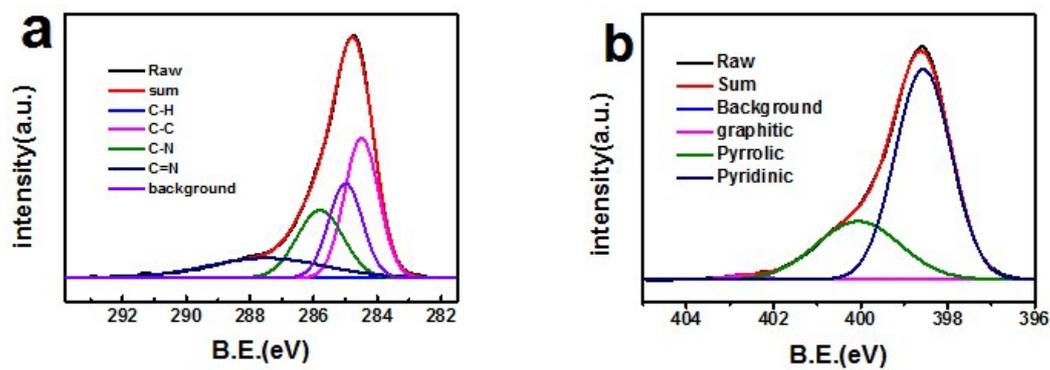


Fig. S8. XPS spectra for the (a) C 1s, (b) N 1s regions of Ni SAs/N-C.

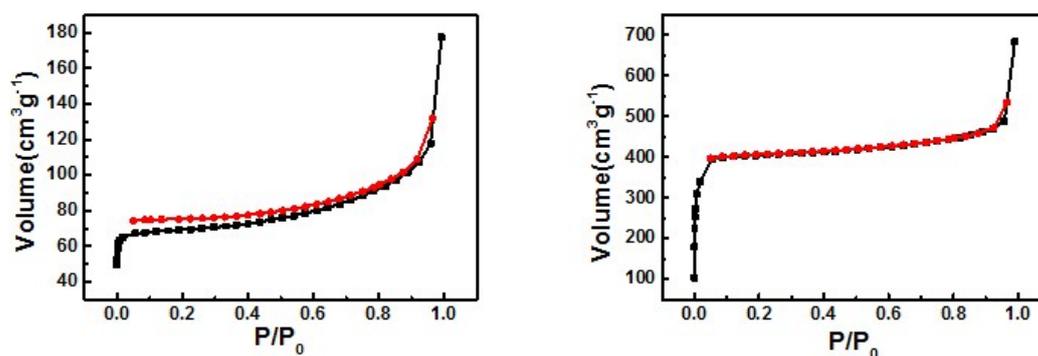


Figure S9: Nitrogen adsorption isotherm and desorption isotherm of Ni SAs/N-C and ZnNi-ZIF measured at 77 K.

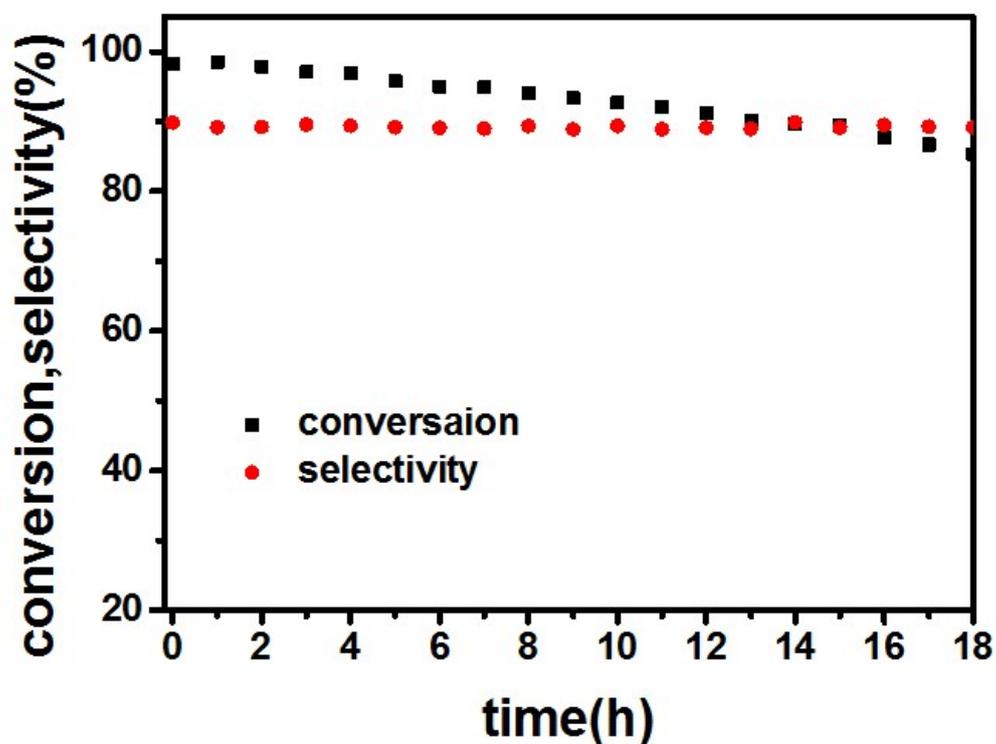


Fig. S10: Conversion and selectivity as a function of time on stream at 200 °C catalyzed by SAs/N-C.

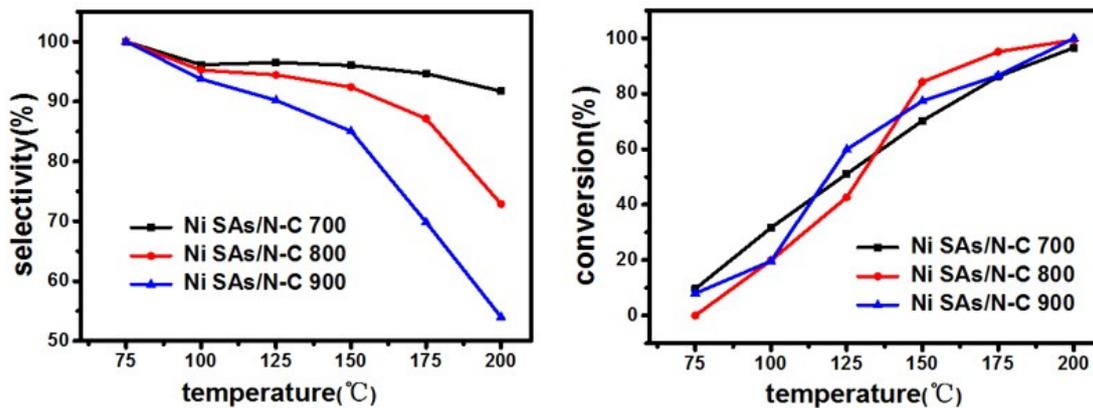


Figure S11: The selectivity and conversion to ethylene by Ni SAs/N-C with different pyrolysis temperature

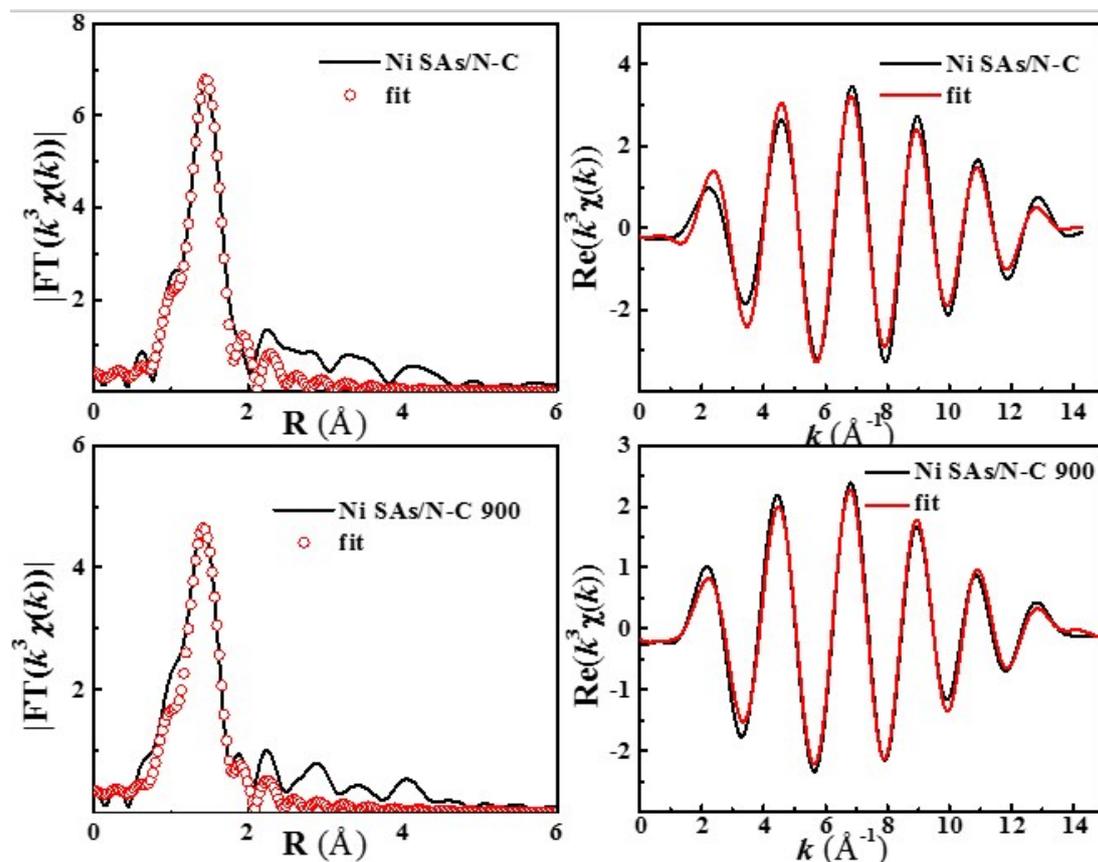


Fig. S12: The corresponding XAFS fitting curves of Ni SAs/N-C and Ni SAs/N-C 900.

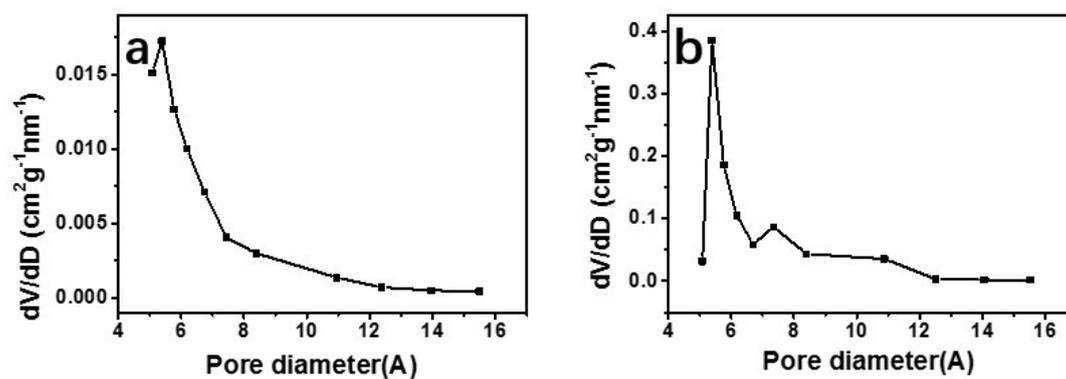


Figure S13: Pore diameter distribution for (a) Ni SAs/N-C and (b) ZnNi ZIF-8.

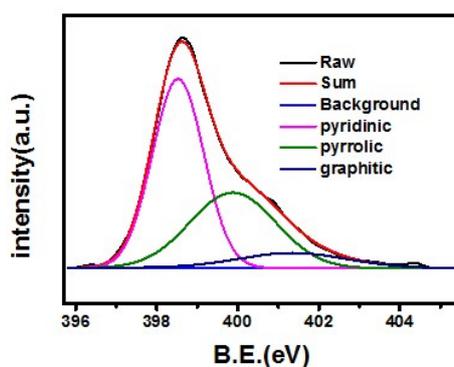


Figure S14: XPS spectra for the N 1s regions of Ni SAs/N-C 800.

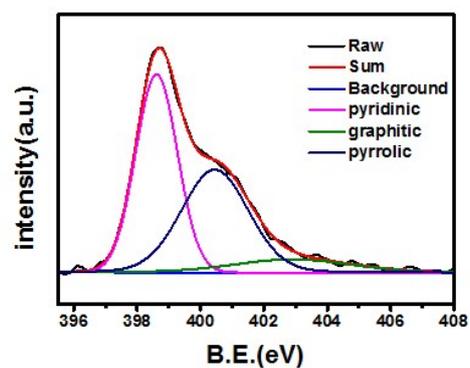


Figure S15: XPS spectra for the N 1s regions of Ni SAs/N-C 900.

Table S1. The BET Surface Area and Pore Diameter of Ni SAs/N-C and ZnNi-ZIF

sample	BET Surface Area(m ² •g ⁻¹)	Average pore diameter(Å)
Ni SAs/N-C	228.2903	6.48
ZnNi-ZIF	1227.7030	6.21

Table S2. XAFS data fitting results of Ni SAs/N-C.

Sample	Path	N	R (Å)	σ^2 (10 ⁻³ Å ²)	ΔE_0 (eV)
Ni SAs/N-C	Ni-N	4.0	1.88	4.2	-1.4
Ni SAs/N-C 900	Ni-N	3.0	1.87	4.4	-6.0

N, coordination number; R, distance between absorber and backscatter atoms; σ^2 , the Debye-Waller factor value; ΔE_0 (eV), inner potential correction to account for the difference in the inner potential between the sample and the reference compound.