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Electronic Supplementary Information

Microemulsion prepared Ni88Pt12 for methane cracking

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Experimental

Catalyst preparation:
One microemulsion was prepared by mixing an aqueous solution of $Ni(NO_3)_2$ (0.45 M) and/or $PtCl_4$ (0.06 M) with Triton X-100 surfactant and cyclohexane. The molar ratio of water to surfactant (W_0) was fixed at 4.7. The other microemulsion consisting of an aqueous solution of N_2H_4, Triton X-100 and cyclohexane was also prepared with the same W_0 value. Both the microemulsions were left stirring for 30 min to obtain an optically clear homogeneous dispersion. The two microemulsions were then mixed with a stirrer for another 5 h. Nitrogen atmosphere was maintained throughout the reaction procedure to ensure the complete removal of oxygen. The precipitate of nanoparticles was separated from the solution by centrifugation. The sample was then washed with ethanol for twice and then dried in vacuum at 110°C overnight.

Characterization:
XRD: Both normal and in-situ XRD patterns were collected using a Bruker D8 Advanced A25 diffractometer in Bragg–Brentano geometry fitted with a copper tube operating at 40 kV and 40 mA and a linear position sensitive detector (opening 2.9°). The diffractometer was configured with a 0.36° diverging slit, 2.9° anti scattering slit, 2.5° Soller slits, and a Ni filter. The data sets were acquired in continuous scanning mode (0.008°/s) over the 2θ range 15–120°, using a step interval of 0.04° and a counting time of 5 s per step.
TGA: The amount of carbon deposited on the catalyst was also analyzed using thermos gravimetric analysis (TGA). The spent catalyst powder (20 mg) was placed in an alumina crucible and pretreated in flowing Ar (50 mL/min) for 0.5 h at 300°C, followed by cooling to room temperature. The temperature was then raised from room temperature to 1000°C at a rate of 10°C/min under air flow (50 mL/min). The sample remained heated at 1000°C for a time period until no weight change was detected. The deposited carbon amount was calculated based on the weight loss.
EM: TEM samples were prepared by the conventional method of dispersing a small amount of activated/spent catalyst in ethanol and stirring in an ultrasonic bath for 10 min, allowing the homogenized liquid to settle for 5 min and, taking a drop from the top of the vessel to a conventional TEM holder. The nature of the carbon deposit, size and properties were observed using high-resolution transmission electron microscopy (HRTEM) micrographs obtained from a Titan 60-300 TEM (FEI Co, Netherlands) equipped with an electron emission gun operating at 300 kV. Scanning electron microscope (SEM) images were taken by the 600 FEG environmental scanning electron microscope.
XPS: X-ray photoelectron spectroscopy (XPS) data were collected by an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum ($<10^{-8}$ torr) and by using a monochromatic Al Kα X-ray source operating at 150 W. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination which was set at 284.8 eV.

Catalyst activity test:
Activity measurements of the methane cracking process were conducted in a Microactivity Effi reactor from Process Integral Development Eng & Tech S.L. equipped with a long quartz tube reactor (internal diameter: 4 mm; length: 305 mm). A horizontal quartz frit (distributor) with holes of 100 µm was used to divide the reactor into two chambers. All of the variables affecting the process, including pressure, temperature and gas flow rate, were recorded continuously by an on-line PC. The reactor was heated to the desired reaction temperature using an electric furnace. Type K thermocouples were used for monitoring the reaction temperature (by placing the thermocouple into the quartz tube). Hydrogen, methane and nitrogen flow rates in the feeding gas were controlled by mass flow controllers (Bronkhorst). The carbon deposited during each run was determined by measuring the direct weight change of the sample. Pure methane gas was used as the feed. The methane flowed through a catalyst bed with 200-300 µm grain size. The sample was heated to reaction temperature under pure N_2, then switched to methane gas to start the reaction.

Characterization of ME-Ni and ME-Pt

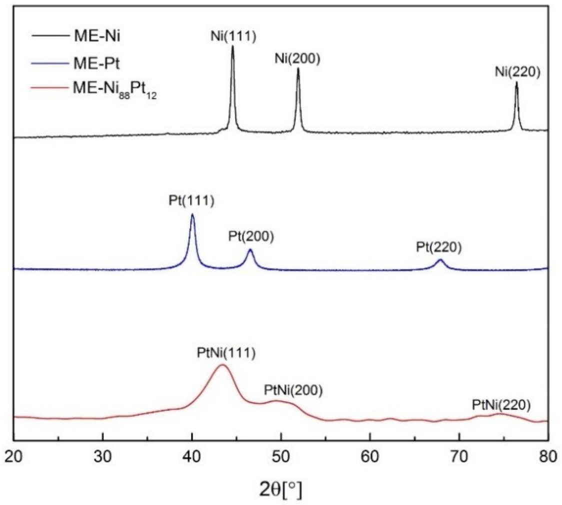

Figure S1 XRD patterns over fresh samples.

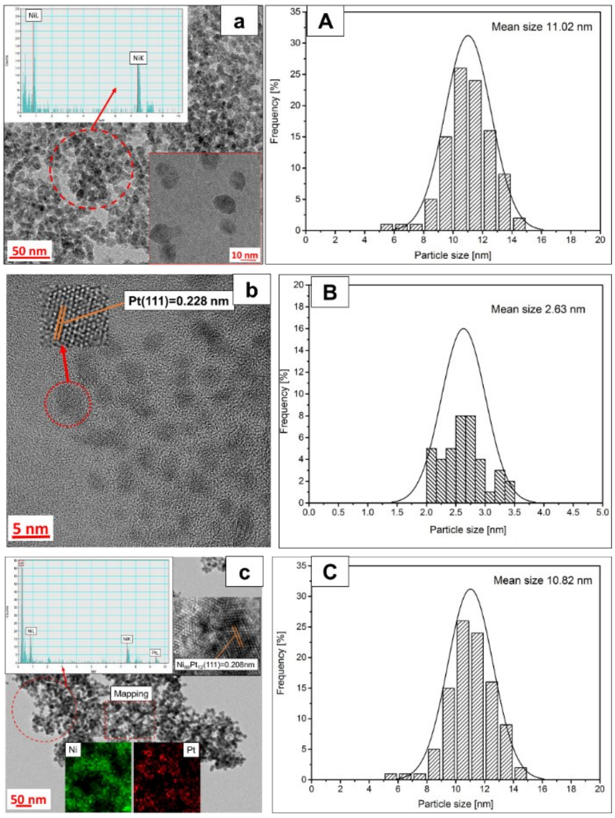

Figure S2 TEM and size distribution analyses over fresh samples. (a)(A) ME-Ni; (b)(B) ME-Pt; (c)(C) ME-$Ni_{88}Pt_{12}$

DFT study:

Total energy calculations of the various generated bimetallic Ni-Pt nanoalloy structures were performed using the spin-polarized density functional theory (DFT) within the plan wave (PW) approach as implemented in the Vienna Ab-initio Simulation Package (VASP) quantum simulation program [1-4]. The Perdew-Burke-Emzerhof (PBE) exchange-correlation functional [5] and the Projector-Augmented Plane Wave (PAW) approach [6] were employed to describe the electron-electron and electron-ion interactions, respectively. The convergence criterion for the electronic self-consistent-filed (SCF) cycles was fixed at 10^{-5} eV. To obtain reliable computed relative energies of the selected bimetallic Ni-Pt geometries, the atomic coordinates were fully optimized until the three components of the Hellmann-Feynman forces on each atom reached values below 0.01 eV $Å^{-1}$. Key geometrical configurations of Ni-rich bimetallic Ni-Pt nanoparticle were modeled starting from the initial 55-atom geometrical model of nickel (Ni_{55}) containing 42 atoms on the surface and 13 atoms in the core with the commonly observed FCC-derived icosahedral shape where 7 neutral Ni atoms were directly replaced by 7 neutral Pt atoms (Ni/Pt ratio very close to the experimental one) at different sites including core-shell and random alloy dispositions. The relative electronic energy was systematically computed for each structure in order to determine the most favorable structure at room temperature as well as the structural evolution during heating treatment.

References

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