Electronic Supplementary Information

Coke Tolerance of Ni/Al_2O_3 Nanosheet Catalyst for Dry Reforming of Methane

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Experimental Section

Catalyst preparation

Nickel alumina nanosheet catalyst was synthesized by solvent free hydrothermal method. Preparation method was modified from our previous method[16]. The ratio of deionized water and aluminum precursor was changed to 1.5:1. Brij®32 was used as a surfactant. Nickel nitrate hexahydrate was adjusted to obtain 10 wt% and 25wt% Ni-loaded alumina catalyst. All metal precursor and surfactant was mixed completely. Deionized water was added with mixing. Reaction was followed in autoclave for 3 days at 423K. Obtained powder was washed by ethanol. After drying, catalyst was directly used as the uncalcined catalyst. The calcined catalyst was heated in air at 1073K for 5 h. Common nickel alumina catalyst was prepared by co-precipitation method as a reference. Nickel nitrate hexahydrate and aluminum nitrate nonahydrate were dissolved in deionized water, and K_2CO_3 solution was added as precipitating agent. Aging step was followed at 333 K for 1 h. Aged sample was filtered and washed by hot water to remove potassium ion. Filtrated sample was dried at 373 K overnight.

Catalyst evaluation

Dry reforming of methane was carried out by a quartz reactor with 8 mm of inner diameter. 100mg of catalyst was loaded on quartz wool. Every catalyst was reduced at 973 K right before the dry reforming reaction at 1073K. Composition of reactant gases was CH_4:CO_2:N_2=1:1.05:1. Total gas flow was 180 sccm.

Catalyst characterization

Temperature-programmed reduction (TPR) was investigated with. U-type quartz reactor. Thermocouple was positioned to touch the top of the samples. Before TPR test, the sample was pre-dried at 473K under nitrogen flow for 2 h. Upon cooling the sample to 423 K, temperature increase to 1173K with a heating rate of 10 K/min under the 60 sccm flow of 10% H_2/Ar gas. The amount of consumed hydrogen was determined by TCD detectors. Crystal structure was evaluated by X-ray diffractometer (Panlytical, Powedr-Xpro) with monochromatic Cu Kα radiation at 40 kV and 30mA. Porous structure of catalysts was characterized by mercury porosimetry (Autopore 9510). The N_2 adsorption-desorption isotherms were obtained at 77 K to obtain BET surface areas and BJH pore-size distribution. Thermo-gravimetric analysis (TGA) was carried out on Q500 (TA instruments). Temperature was raised from 303K to 1273K at 10K/min ramp. A flow of 40 sccm of N_2 and 60 sccm of air was used as a balance gas and sample gas, respectively.

Table S1. Textural properties derived from N_2 adsorption and mercury porosimetry for nanosheet catalysts and precipitation catalyst

	BET surface area (cm^2/g)	Permeability (mdarcy)	Total intrusion volume(ml/g)	Apparent density (g/ml)	Bulk density (g/ml)
Nanosheet	339.7	1520	1.868	1.098	0.360
Calcined-nanosheet	266.7	665	1.320	1.053	0.440
Precipitation	181	103	0.461	1.581	0.915

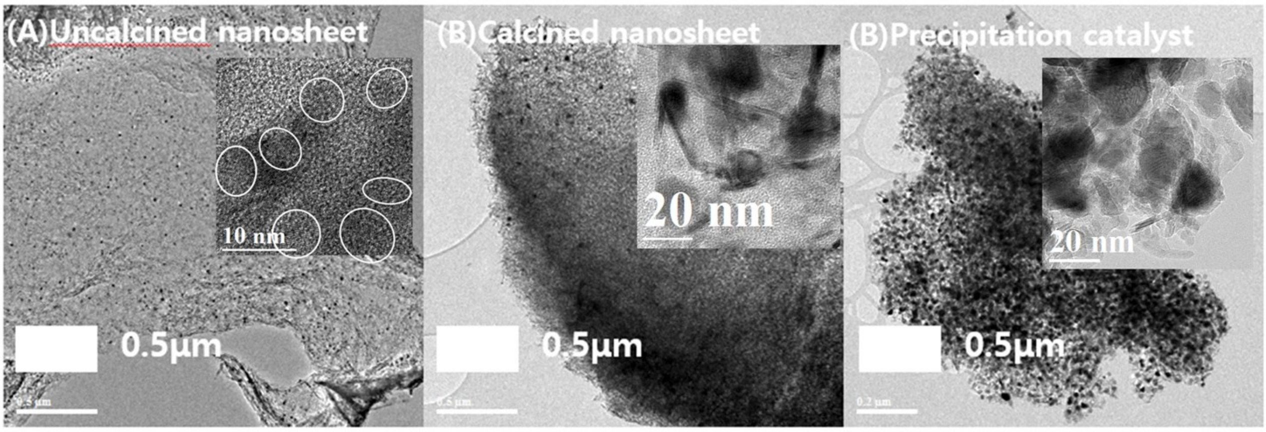

Figure S1. TEM images of reduced catalysts derived from different precursors. The highlighted circles in the inset A represent Ni particles.

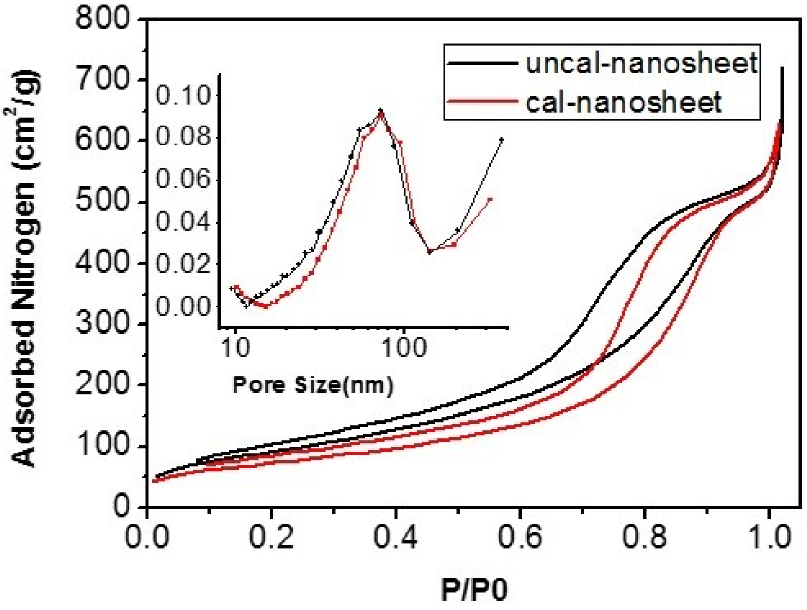

Figure S2. Nitrogen adsorption-desorption isotherms and BJH Pore size distribution from adsorption-desorption isotherms of calcined and uncalcined Ni/Al_2O_3 nanosheet catalysts before the DRM reaction

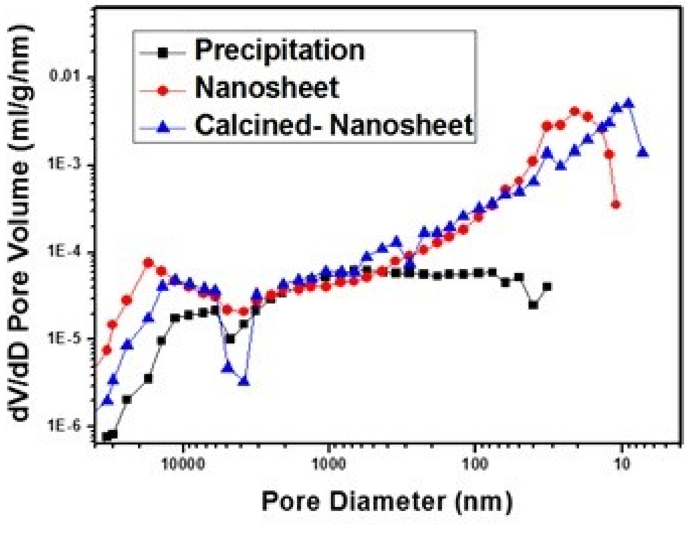

Figure S3. Pore size distribution from differential intrusion of mercury porosimetry

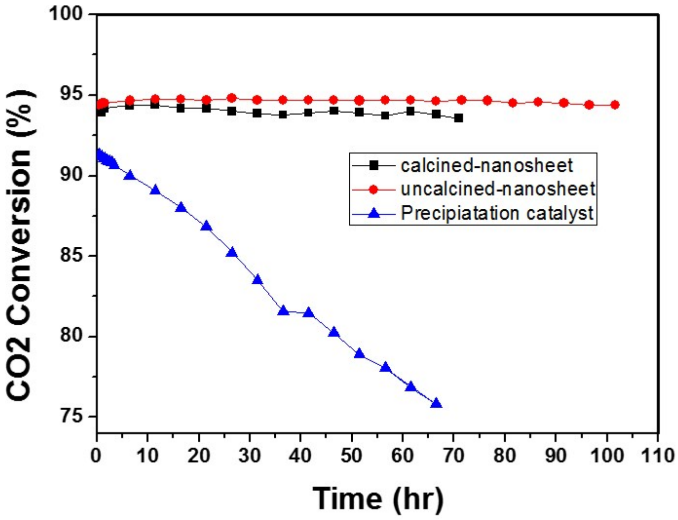

Figure S4. Conversion of carbon dioxide in dry reforming of methane at 1073 K over Ni/Al_2O_3 catalysts.

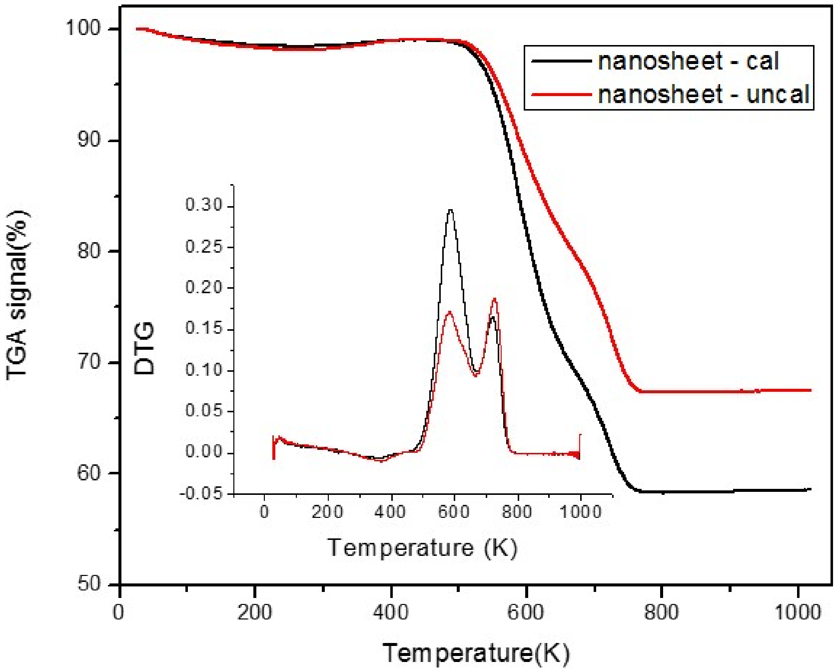

Figure S5. TGA data of calcined nanosheet and uncalcined nanosheet after the DRM reaction.

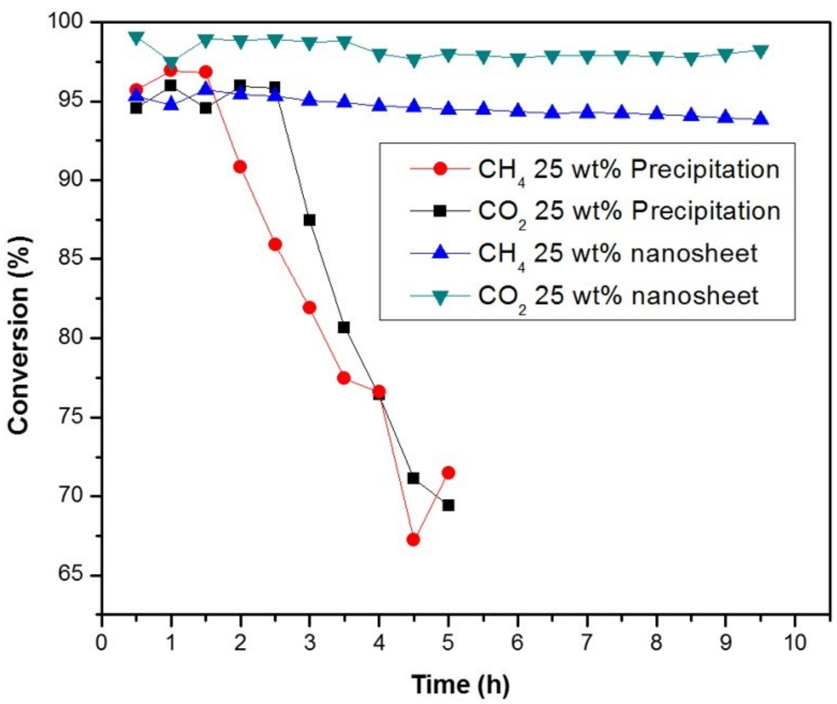

Figure S6. Stability test of 25 wt% nickel loading nanosheet and precipitation catalysts