Supporting Information

Sintering-resistant Ni-based Reforming Catalysts via the Nanoconfinement Effect

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1 Catalysts preparation

1.1 Synthesis of Ni/PS$_n$: The controllable synthesis of Ni/PS$_n$ involves an alkalinity-tuned hydrothermal method. In a typical procedure, 2.375 g of $NiCl_2 \cdot 6H_2O$ (this precursor was chosen according to the requirements for nanotube synthesis) was dissolved in 150 mL of deionized water, and 40 mL of 0.5 mol/L Na_2SiO_3 was added to form a light-green precipitate on magnetic stirring for 10 min. Then 29 g of NaOH was added, and after 10 min further stirring, the mixture was sealed in an autoclave, heated to 210 °C and maintained the temperature for 24 h. The autoclave was naturally cooled to room temperature; the obtained precipitates were first centrifuged, washed several times to remove ions remaining in the product, and then dried at 80 °C in air. The resultant solid was calcined at 700 ºC for 4 h, the calcined catalysts are called Ni/PS$_n$. The nickel loading is 36 wt%, and this loading is fixed according to the nickel content in pure phyllosilicates nanotube. The catalysts were reduced online at 400, 500, 600, and 700 ºC for 1 h under 10% H_2/N_2, and were respectively denoted as Ni/PS$_n$-400, Ni/PS$_n$-500, Ni/PS$_n$-600, and Ni/PS$_n$-700.

1.2 Synthesis of Ni/SiO$_{2P}$: Ni/SiO$_{2P}$ powder was prepared by the ammonia evaporation method as follows. A certain amount of $Ni(NO_3)_2 \cdot 3H_2O$ and a 25 wt.% ammonia aqueous solution (NH_3/Ni molar ratio = 8) dissolved in deionized water were mixed and stirred for 10 min. Silica sol (Qingdao Yurui chemical Co., LTD. SiO_2 content, 30 wt%; viscosity, 7.0 mPa·s; density, 1.19-1.21 g/cm^3; average particle size of 10 - 20 nm) was then added to the nickel ammonia complex solution and stirred for 6 h. The initial pH of the suspension was 11~12. All the above operations were performed at room temperature. The suspension was heated in a water bath preheated to 80 ºC to allow for the evaporation of ammonia, the decrease of pH, and the consequent deposition of nickel species on silica. When the pH value of the suspension decreased to 6-7, the evaporation process was terminated. The resultant precipitate was then filtered and washed thoroughly with deionized water to remove the residual ammonium ions. Then the solid was dried at 80 ºC for 12 h in a vacuum drying oven and was calcined at 700 ºC for 4 h in a muffle furnace. Catalyst was in situ reduced at 700 ºC under 10% H_2/N_2 for 1 h. The nickel loading is 20 wt%, which is nearly equal to those used in reforming reactions industrially.

1.3 Synthesis of Ni/SiO$_{2I}$: Commercial SiO$_2$ (Qingdao Yurui chemical Co., LTD) was calcined at 700 °C for 2 h. Ni/SiO$_{2I}$ was prepared by the incipient wetness impregnation method. SiO$_2$ was impregnated in a Ni(NO$_3$)$_2$•6H$_2$O aqueous solutions by mechanical agitation at 50 °C for 12 h, followed by evaporated at 60 °C using vacuum rotary until the ethanol was removed. The resultant solid was dried at 100 °C for 12 h, and then calcined at 700 °C for 4 h. Catalyst was in situ reduced at 700 ºC under 10% H$_2$/N$_2$ for 1 h. The amount of Ni loading was fixed to 20 wt%, equal to Ni/SiO$_{2P}$.

2 Activity test

Catalytic tests were conducted at the atmospheric pressure in a quartz fixed-bed reactor (Φ10 × 30 mm) loaded with 0.05 g catalysts (20-40 mesh) mixed with 1 ml of quartz particles. Prior to the test, the catalysts were reduced at 600 °C on line for 1 h in a flow of 10 vol% H$_2$/N$_2$ (50 ml/min). The liquid solution with a specific water/ethanol molar ratio was fed through an HPLC pump into a heated chamber (150 °C) to evaporate the solution completely in the stream of N$_2$ (60 ml/min). The products were analyzed online by two gas chromatographs. One is equipped with a FID, and a Porapak-Q column with N$_2$ as a carrier gas to analyze the organic species such as ethanol and methane. The other one is integrated with a TCD and a TDX-01 column using He as a carrier gas to monitor the incondensable gas species including hydrogen, carbon dioxide, carbon monoxide and methane.

3 Characterization

BET surface areas and pore structure of catalysts were measured using a Micromeritics Tristar 3000 analyzer by nitrogen adsorption at −196 ºC. The specific surface areas were calculated from the isotherms using the BET method, and the pore distribution and the cumulative volumes of pores were obtained by the BJH method from the desorption branches of the adsorption isotherms.

X-ray diffraction patterns (XRD) were recorded with a Bruker D8 Focus operated at 40 kV and 40 mA equipped with a nickel-filtered Cu Kα radiation (λ = 1.54056 Å) and a 2θ ranging from 10 to 80° at a scanning rate of 0.02°/step and 0.15 s/step.

IR spectra were recorded on a Thermo Nicolet 6700 spectrometer equipped with a DTGS detector. The samples were finely grounded, dispersed in KBr, pelletized, and dried. The spectral resolution was 4 cm^{-1} and 32 scans were recorded for each spectrum.

TEM images were obtained on a FEI Tecnai G2 F20 transmission electron microscope at 100 kV. The sample powder was dispersed in ethanol by sonification; drops of the suspension were applied onto a copper grid-supported transparent carbon foil and dried in air.

Temperature programmed profiles (TPR) was conducted to determine the reduction behavior of the catalysts. The experiments were performed on a Micromeritics AutoChem 2920 TPD/TPR apparatus using 0.1 g of catalyst and a temperature range from 50 to 900 ºC at a rate of 10 ºC/min. A flow rate of 30 mL/min of 10 vol% H_2/Ar was used for the reduction. A thermal conductivity detector (TCD) was employed to determine the amount of hydrogen consumed.

NH_3 temperature programmed desorption (NH_3-TPD) was conducted on a Micromeritics AutoChem 2920 TPD/TPR system. The sample (0.1 g) was first pretreated under flowing Ar (30 mL/min) at 400 ºC for ~30 min, then the sample was saturated with NH_3 by flowing 10%NH_3-N_2 at 120 ºC for 30 min, flushed with pure helium (30 mL/min) for 1 h before desorption analysis. NH_3-TPD analysis was carried out with a ramp of 10 ºC/min from 120 ºC to 800 ºC in a He flow of 30 mL/min.

XPS analysis was operated in a Perkin－Elmer PHI 1600 ESCA system with Mg *K*α 1253.6 eV radiation as the excitation source. The sample was mounted on the specimen holder by means of double-sided adhesive tape. Spectra were collected in steps of 0.15 eV.

Nickel active surface area was determined by H_2 pulse chemisorption (Micromeritics AUTOCHEM II 2920). After the catalyst was reduced at 700 °C for 1.0 h under 10% H_2/Ar flow, it was cooled down to room temperature under Ar, and then H_2 pulses were injected until the eluted peak area of consecutive pulses was constant. The active surface area of Ni was calculated from the volume of H_2 adsorbed by assuming a H/Ni_s (surface nickel atom) stoichiometry of 1 and a surface area of 6.5×10^{-20} m^2 per Ni atom.

Carbon deposition analysis was carried out using a thermal analysis system (STA449F3, NETZSCH Corp.). The experiments were performed in a flow of air (50 ml/min) with a heating rate of 10 °C/min and a final temperature of 800 °C.

Conversion, selectivity and yield calculations:

$$X_{EtOH} = \frac{F_{EtOH,in} - F_{EtOH,out}}{F_{EtOH,in}}$$

$$S_{H_2} = \frac{1}{6} \times \frac{moles(H_2)\,produced}{moles(EtOH)\mathrm{feed} \times X_{EtOH}} \times 100$$

$$S_j = \frac{(\%j) \times i}{\sum((\%j) \times i)}$$

where j represents the carbon containing species in the products, including CO, CO_2 CH_4, C_2H_4, C_2H_6, CH_3CHO, and CH_3COCH_3. i is the number of carbon atoms in the carbon-containing species.

TOF = mole flowrate of ethanol converted (at initial stable time, within 10 hours) / mole of the active nickel (calculation based on the result of H_2 pulse chemisorption before reaction) in the catalyst

The carbon balance was within ±5% for all catalytic runs. Data for the catalyst activity were collected when the reaction reached stable conditions, and repeated tests have been run to confirm the activity. It should be emphasized that according to the definitions, the sum of the selectivities of H_2 and the carbon-containing species does not lead to unity since they are calculated based on independent hydrogen and carbon balances, respectively.

Table S1 Temperatures of reduction peaks and integrated areas (normalized) obtained from peak fit profiles of TPR.

Catalyst	**Low temperature peak °C / %**		**Medium temperature peak °C / %**	**High temperature peak °C / %**
Ni/SiO_{2I}	**LT-1=362 19.5**	**LT-2=403 43.6**	**MT=508 36.9**	———
Ni/SiO_{2P}	**LT=439 28.0**		**MT=577 65.8**	**HT=650 6.2**
Ni/PS_n	**LT=384 27.6**		**MT=561 60.8**	**HT=698 11.6**

Table S2 Bind energies of Ni species and integrated areas (normalized) obtained from peak fit profiles of XPS data.

Binding energy	**852 eV**	**854 eV**	**Reduced nickel species**	**856 eV**
Nickel species	$\mathbf{Ni^0}$	**NiO**		$\mathbf{Ni(OH)_2}$
Ni/PS$_n$-400	**0**	**22.1**	**22.1**	**77.9**
Ni/PS$_n$-500	**4.8**	**18.3**	**23.1**	**76.9**
Ni/PS$_n$-600	**10.6**	**25.0**	**35.7**	**64.4**
Ni/PS$_n$-700	**27.7**	**30.3**	**58.0**	**42.0**

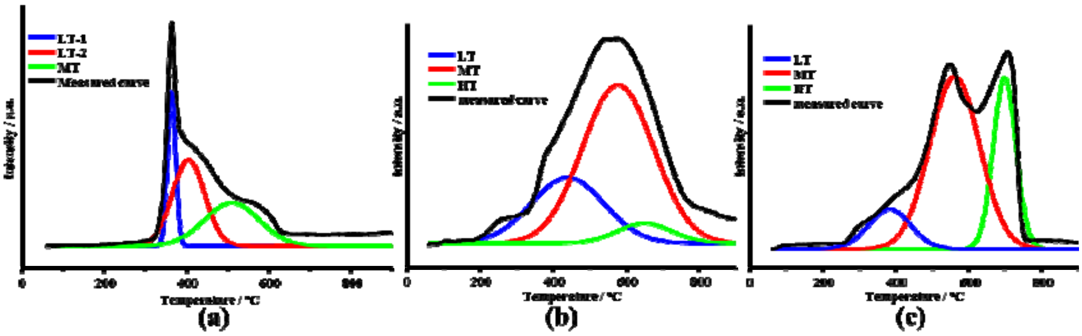

Figure S1. Peak fit profiles of TPR; (a) Ni/SiO$_{2I}$, (b) Ni/SiO$_{2P}$, (c) Ni/PS$_n$

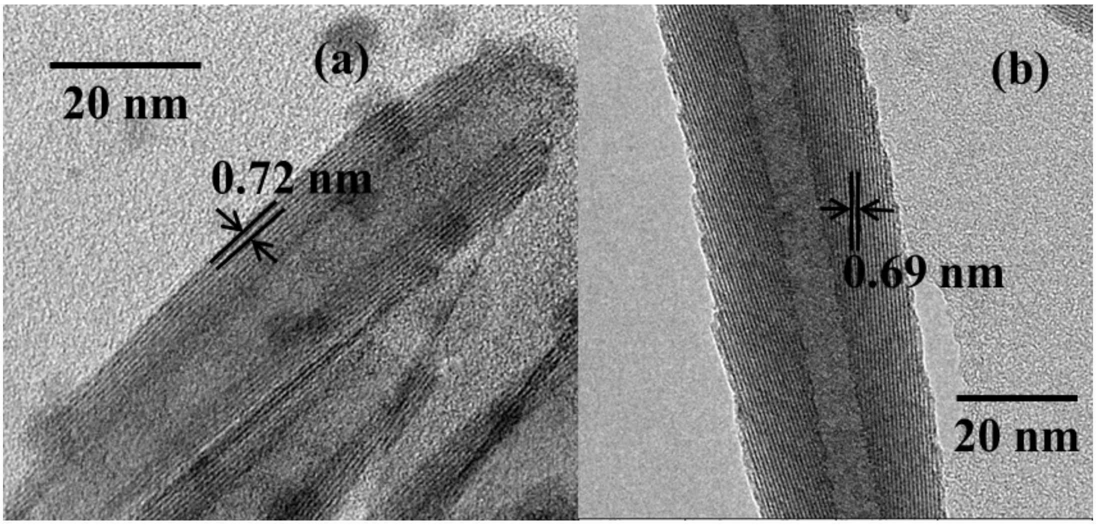

Figure S2. TEM images of Ni/PS$_n$ (a) before and (b) after calcination.

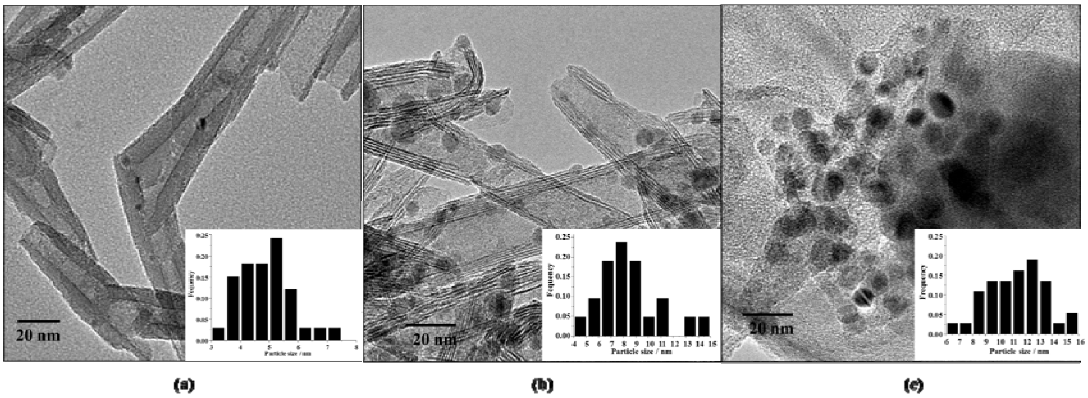

Figure S3. TEM images of Ni/PS$_n$ after reduction. (a): Ni/PS$_n$-400; (b): Ni/PS$_n$-500; (c): Ni/PS$_n$-700.

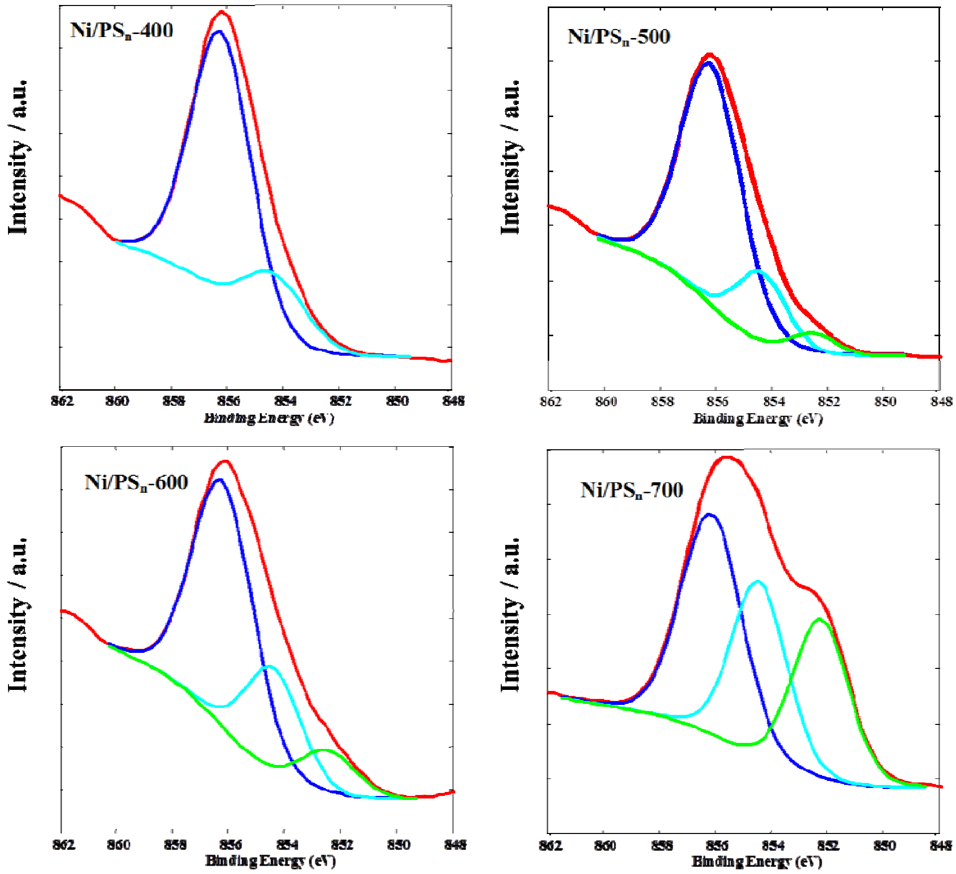

Figure S4. XPS profiles of the catalysts after reduction at different temperatures.

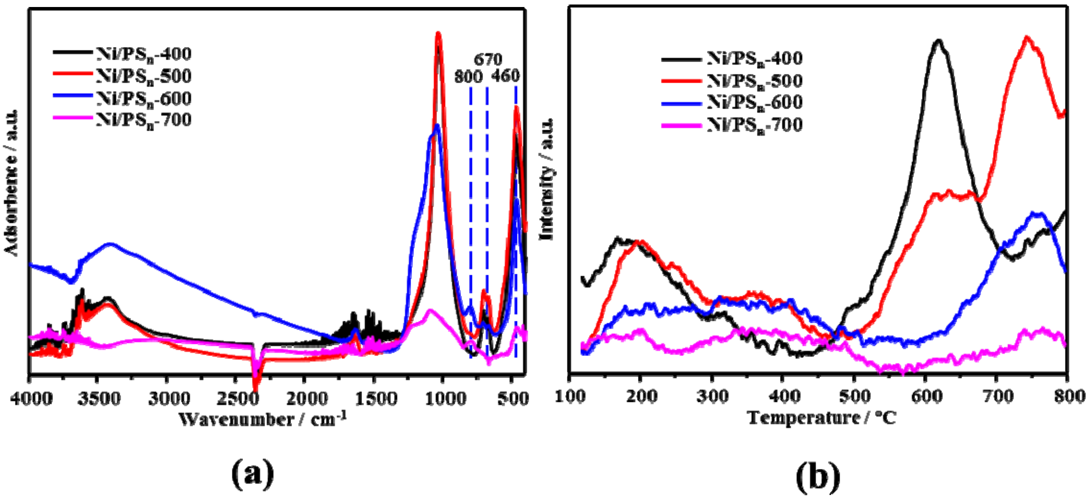

Figure S5. IR and NH_3-TPD profiles of the catalysts upon reduction at different temperatures.

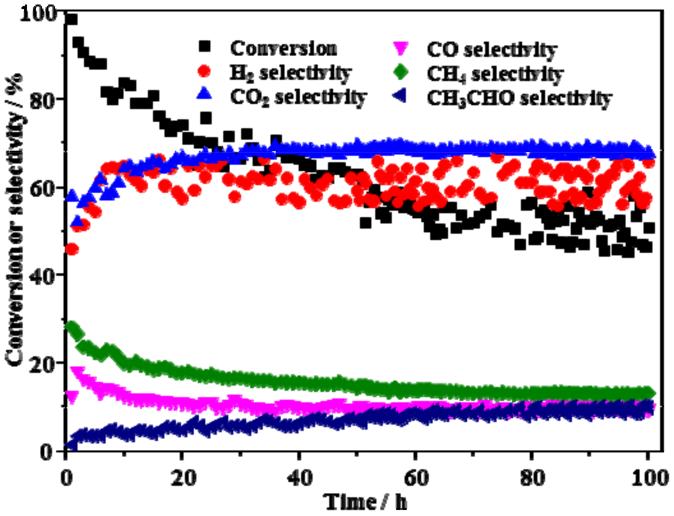

Figure S6. Stability test on Ni/SiO_{2P}, reaction conditions: 1 atm, 500 ºC, S/C=4, W/F=10 gh/mol, EtOH/gas=4.2 %.

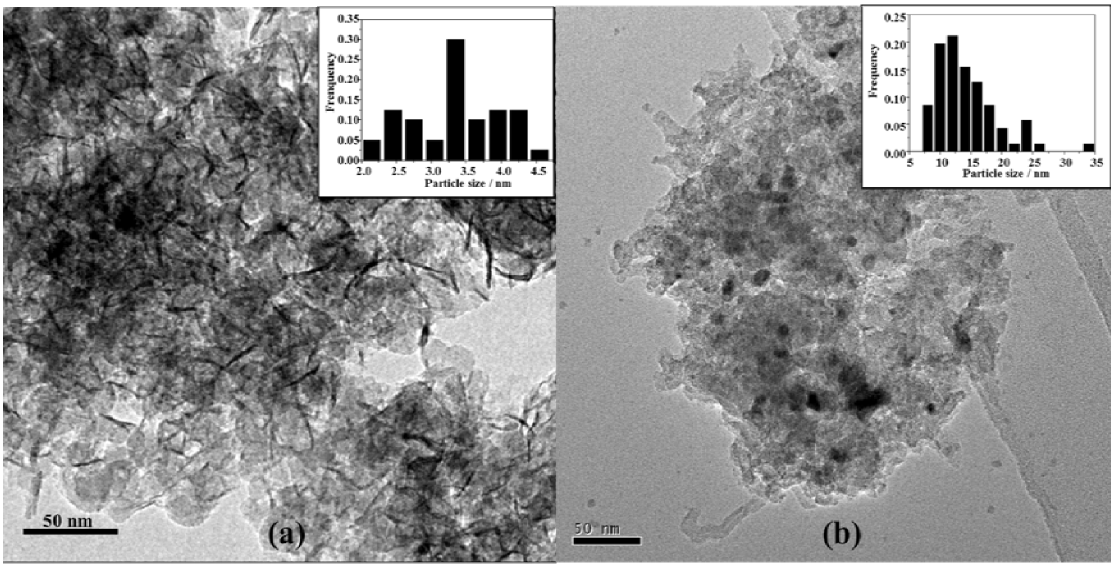

Figure S7. TEM images of Ni/SiO$_{2P}$ before and after 500 ºC stability test.

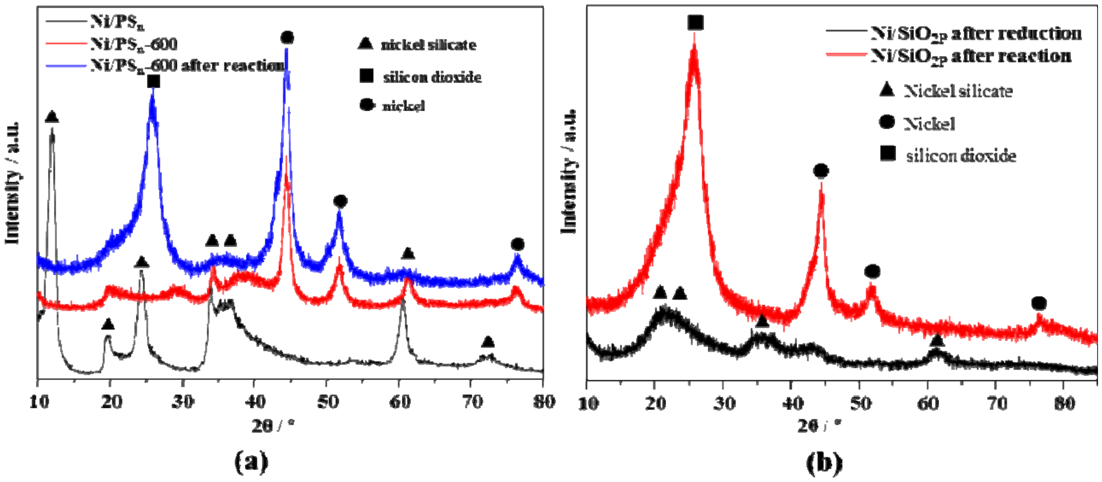

Figure S8. XRD patterns of the catalysts after 500 °C stability test: (a) Ni/PS$_n$-600; (b) Ni/SiO$_{2P}$.

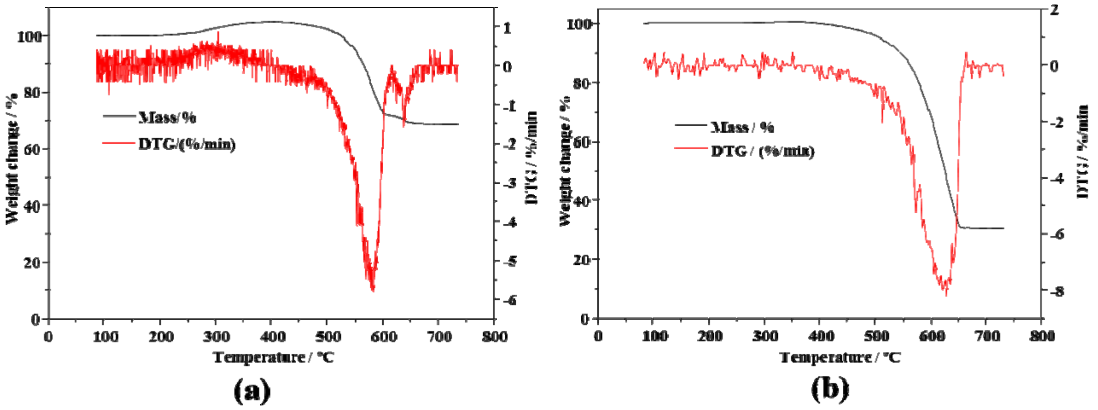

Figure S9. TG and DTG profiles of the catalysts after 500 ºC stability test, (a) Ni/PS$_n$-600; (b) Ni/SiO$_{2P}$. Carbon deposition rate : 3.6 mg/(g·h) for Ni/PS$_n$-600 and 7.2 mg/(g·h) for Ni/SiO$_{2P}$