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Revised Electronic Supplementary Information

Hollow Zeolite encapsulated Ni-Pt bimetals for sintering and coking resistant dry reforming of methane

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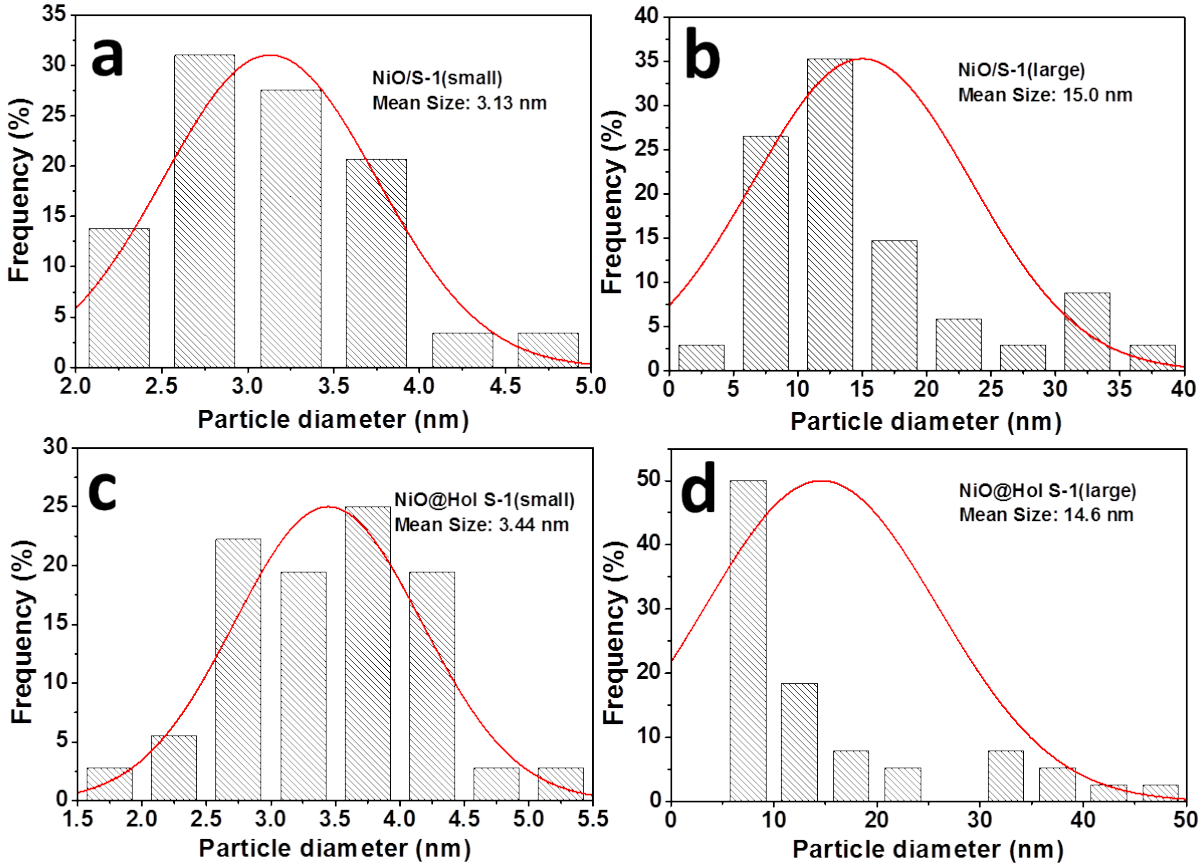

Fig. S1. Metal particle size distributions of prepared (a, b) 1.5NiO/S-1 and (c, d) 1.5NiO@Hol S-1 after reduction under H_2 at 800 ^oC for 30 min.

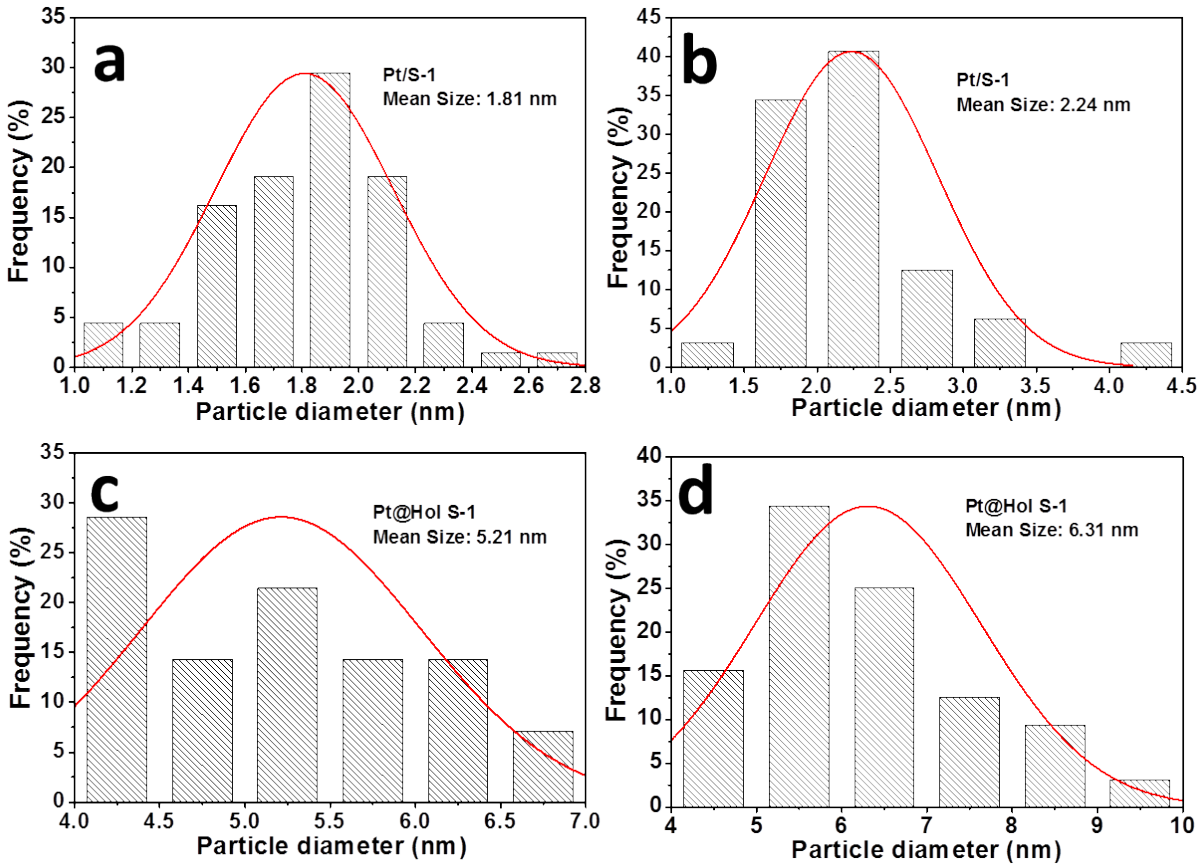

Fig. S2. Metal particle size distributions of prepared (a, b) 0.5Pt/S-1 and (c, d) 0.5Pt@Hol S-1 after calcination at 400 ^{o}C for 2 h (a, c) and reduction under H_2 at 800 ^{o}C for 30 min (b, d).

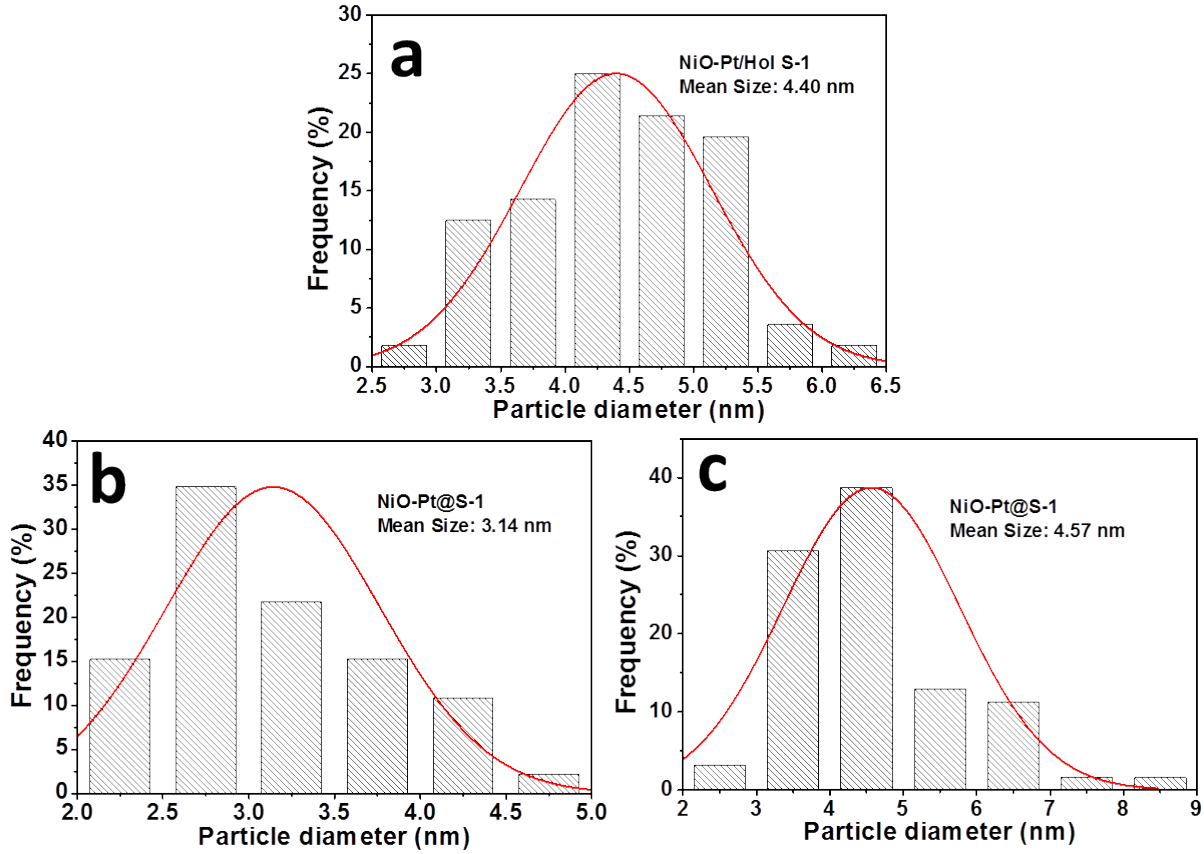

Fig. S3. Metal particle size distributions of prepared (a) 1.5NiO-0.5Pt/S-1 and (b, c) 1.5NiO-0.5Pt@Hol S-1 after calcination in air at 400 °C for 2 h (b) and reduction under H_2 at 800 °C for 30 min (a, c).

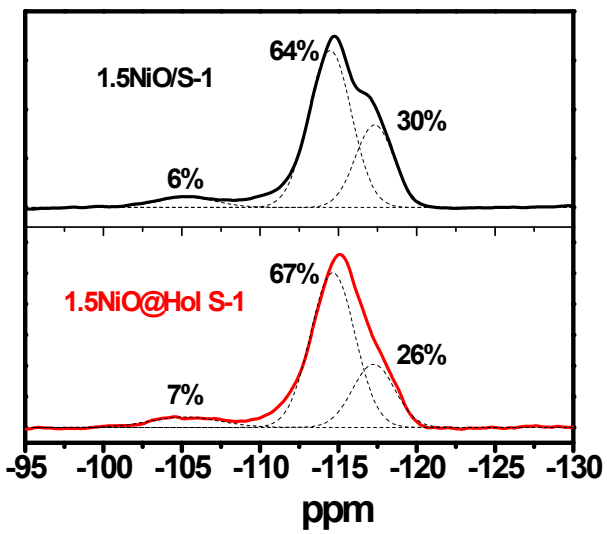

Fig. S4. ^{29}Si MAR NMR spectra of 1.5NiO/S-1 and 1.5NiO@Hol S-1.

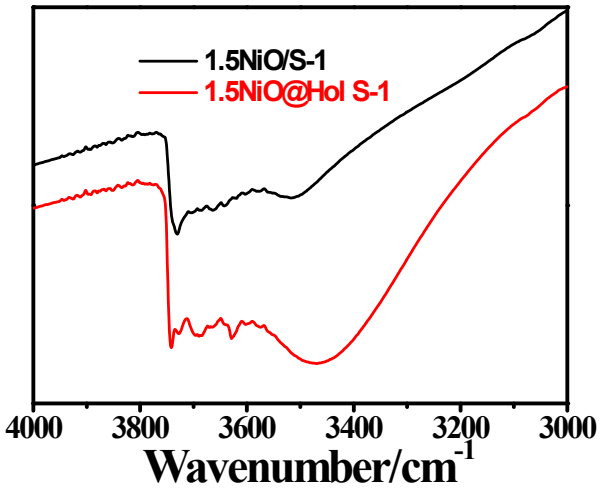

Fig. S5. FT-IR spectra in the hydroxyl range of 1.5NiO/S-1 and 1.5NiO@Hol S-1.

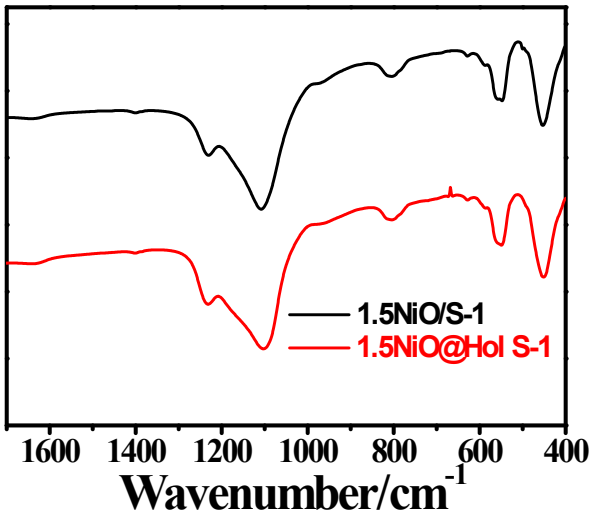

Fig.S6. FT-IR spectra of 1.5NiO/S-1 and 1.5NiO@Hol S-1.

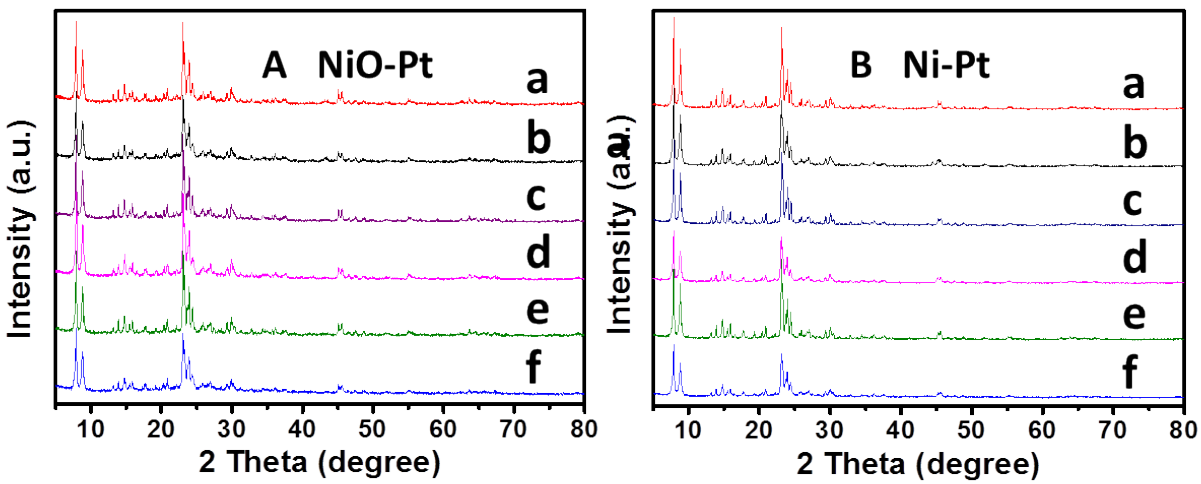

Fig. S7. XRD patterns of prepared (a) 1.5NiO/S-1, (b) 1.5NiO@Hol S-1, (c) 0.5Pt/S-1, (d) 0.5Pt@Hol S-1, (e) 1.5NiO-0.5Pt/S-1, (f) 1.5NiO-0.5Pt@Hol S-1 after calcination in air at 400 °C for 2 h (A) and reduction under H_2 at 800 °C for 30 min (B).

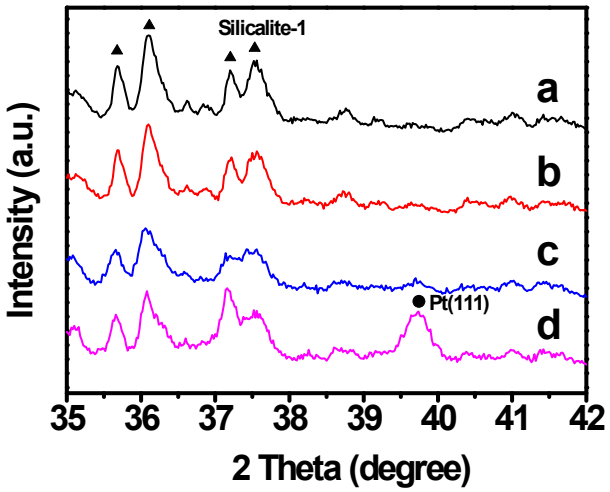

Fig. S8. XRD patterns of prepared (a) Silicalite-1, (b) 0.5Pt/S-1, (c) 0.5Pt@Hol S-1 after calcination in air at 400 °C for 2 h and (d) 0.5Pt@Hol S-1 after reduction under H_2 at 800 °C for 30 min.

Table S1. H_2 consumption of samples calculated from H_2-TPR

Sample	H_2 consumption (μmol/g)
1.5NiO/S-1	94.8
1.5NiO@Hol S-1	109
0.5Pt/S-1	11.7
0.5Pt@Hol S-1	0
1.5NiO-0.5Pt/S-1	198
1.5NiO-0.5Pt@Hol S-1	100

The conversions of CH_4 and CO_2 over the catalysts with different metal content were shown in **Fig. S9**. With the nickel increasing, the conversions of CH_4 and CO_2 didn't improve and the sample of 1.5Ni@Hol S-1 showed the best performance. With the Pt content increasing, the conversions of CH_4 and CO_2 improve obviously (**Fig. S10**). Due to the high price of Pt, the amount of platinum kept within 0.5%. According to **Fig. S9** and **Fig. S10**, this loading (1.5%Ni and 0.5%Pt) is optimal. The real Ni and Pt contents of the samples were listed in Table S2.

Table S2 Ni and Pt contents of the samples before reduction

Sample	Real composition[a]	
	Ni (wt%)	Pt (wt%)
1.5NiO@Hol S-1	1.96	/
3NiO@Hol S-1	3.99	/
5NiO@Hol S-1	6.44	/
1.5NiO-0.1Pt@Hol S-1	1.76	0.14
1.5NiO-0.3Pt@Hol S-1	2.07	0.45
1.5NiO-0.5Pt@Hol S-1	1.58	0.54

a ICP analysis

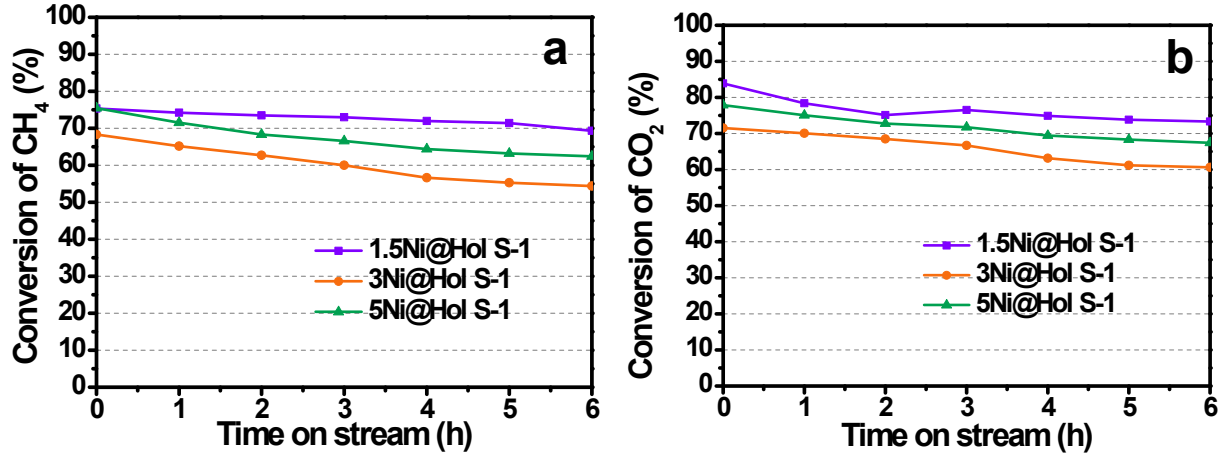

Fig. S9. (a) CH_4 and (b) CO_2 conversions over Ni@Hol S-1 with different nickel contents (F/W=72000 ml/g·h, 800 °C, atmospheric pressure).

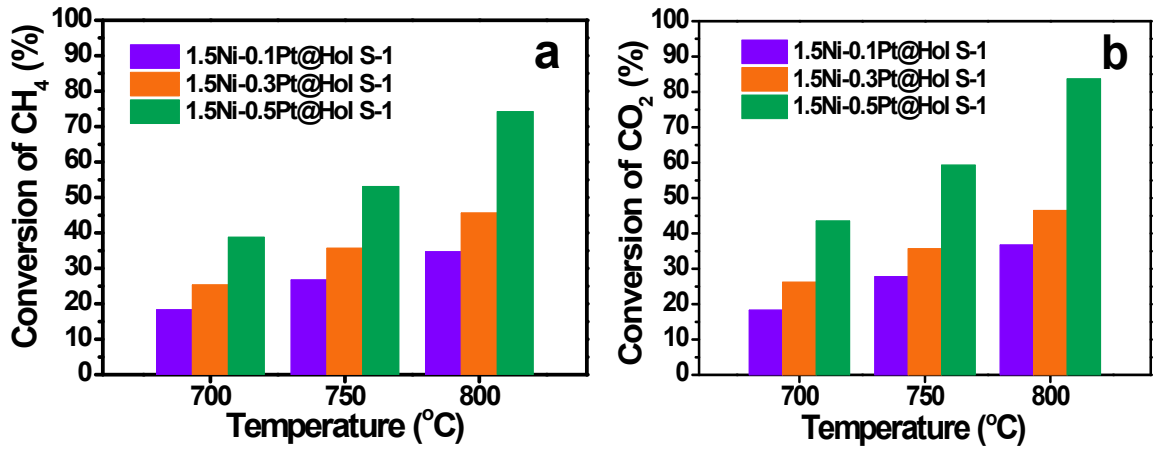

Fig. S10. (a) CH_4 and (b) CO_2 conversions over the catalysts at different reaction temperatures (F/W=72000 ml/g·h, atmospheric pressure), time on stream 2 h.

The effect of reaction temperature on catalytic activity of catalysts was compared and the results were shown in **Fig. S11**. Over the two catalysts, there is an increase of CH_4 and CO_2 conversions with the rise of temperature. The conversions of CH_4 and CO_2 are low at 700 °C. With increasing temperature to 750 °C, CH_4 conversion is about 40% over 1.5Ni@Hol S-1, which is lower than that over 1.5Ni-0.5Pt@Hol S-1 (>50%). At 800 °C, the two catalysts are rather similar in performance.

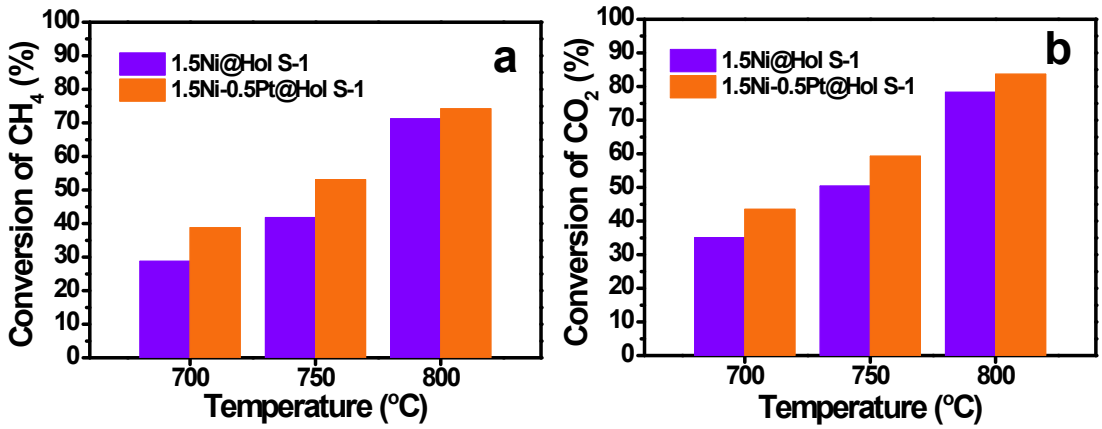

Fig. S11. (a) CH_4 and (b) CO_2 conversions over the catalysts at different temperatures (F/W=72000 ml/g·h, atmospheric pressure), time on stream 2 h.

The distributions of the products were shown in **Fig. S12c, d**. As showed in Fig. S12c, the selectivities of H_2 were ca. 80% over the 1.5Ni@Hol S-1 and 1.5Ni-0.5Pt@Hol S-1 catalysts under the adopted reaction conditions. The higher CO_2 conversion compared with that of CH_4 (**Fig. S12a, b**) and the H_2/CO (n/n, Fig. S12d) is smaller than 1 are results of reversed-water-gas-shift reaction.

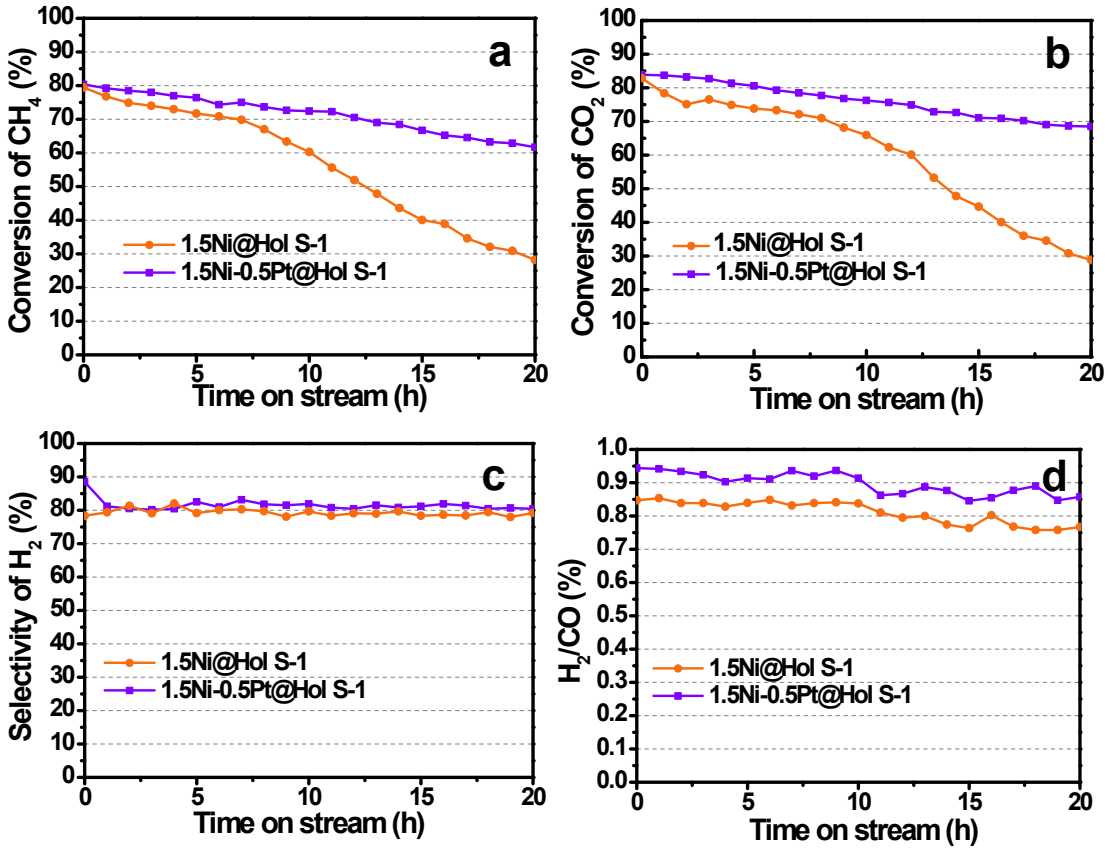

Fig. S12. (a) CH_4 and (b) CO_2 conversions, (c) H_2 selectivity and (d) H_2/CO (n/n) over the 1.5Ni@Hol S-1 and 1.5Ni-0.5Pt@Hol S-1 catalysts (F/W=72000 ml/g·h, 800 °C, atmospheric pressure).