Electronic Supplementary Material (ESI)

Coke-resistant defect-confined Ni-based nanosheet-like catalysts derived from halloysites for CO_2 reforming of methane

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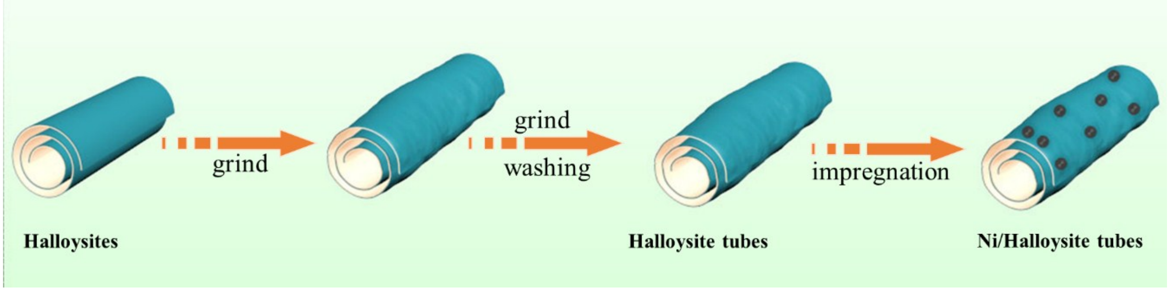

Scheme S1. Schematic illustration of the fabrication strategy of the Ni/HA tubes.

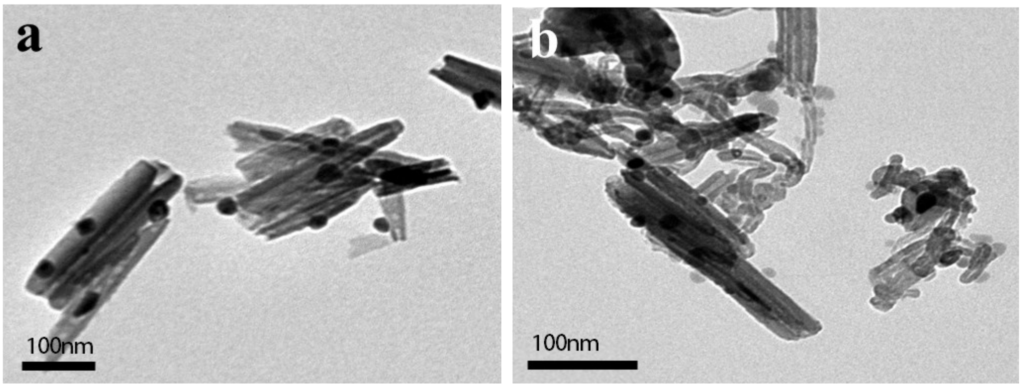

Fig. S1 TEM images of (a) Ni/HA tubes reduced at 750 ^{o}C for 1h b) Ni/HA tubes after the 20 h stability test.

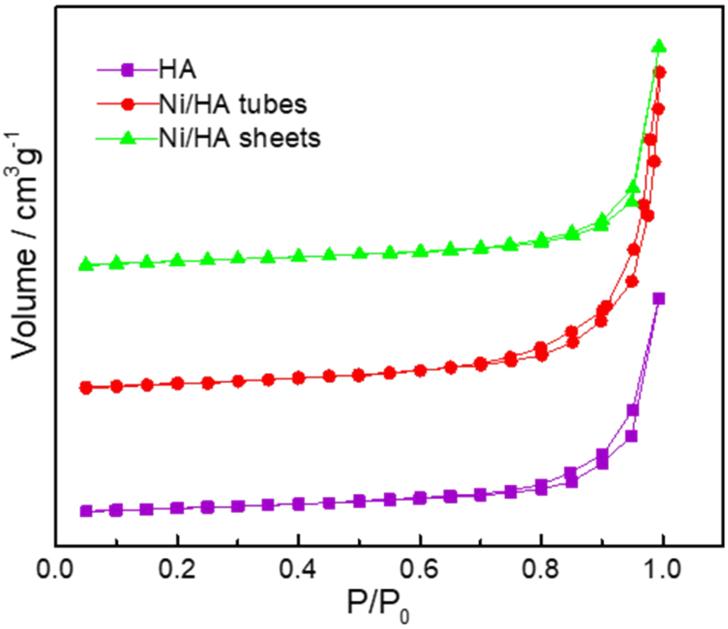

Fig. S2 N_2 sorption isotherms of HA, Ni/HA tubes and Ni/HA sheets.

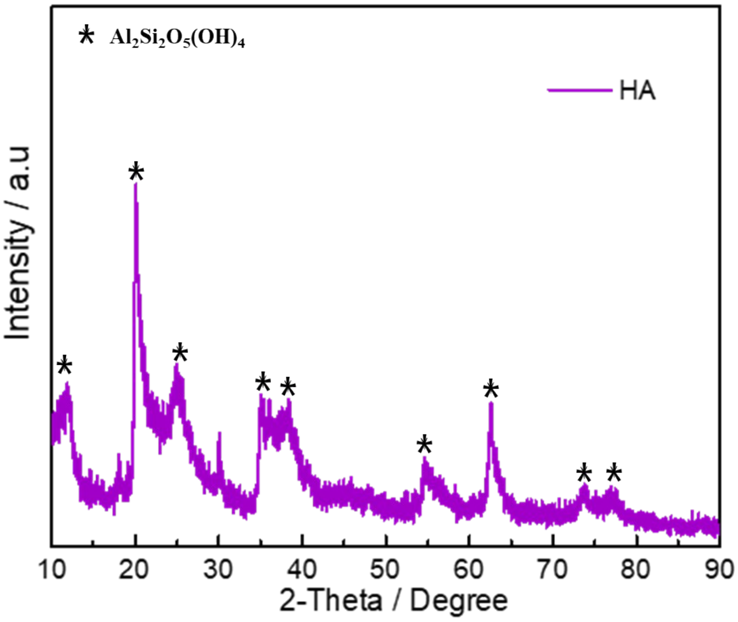

Fig. S3 XRD patterns of HA.

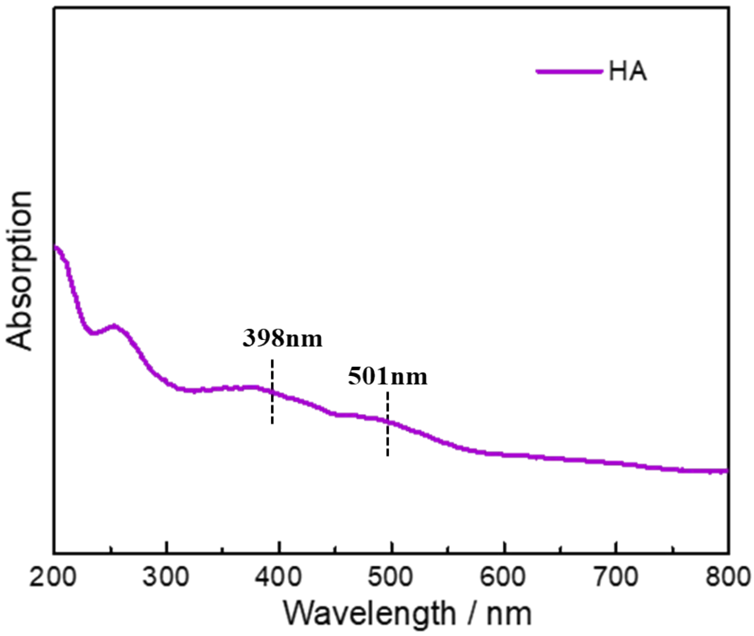

Fig. S4 UV-Vis spectra of HA.

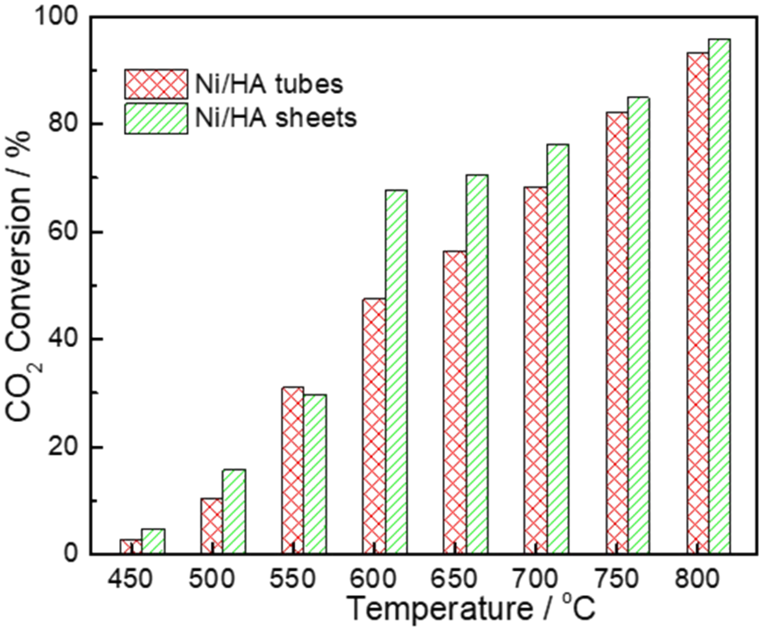

Fig. S5 Effects of reaction temperature on CO_2 conversion over the catalysts.

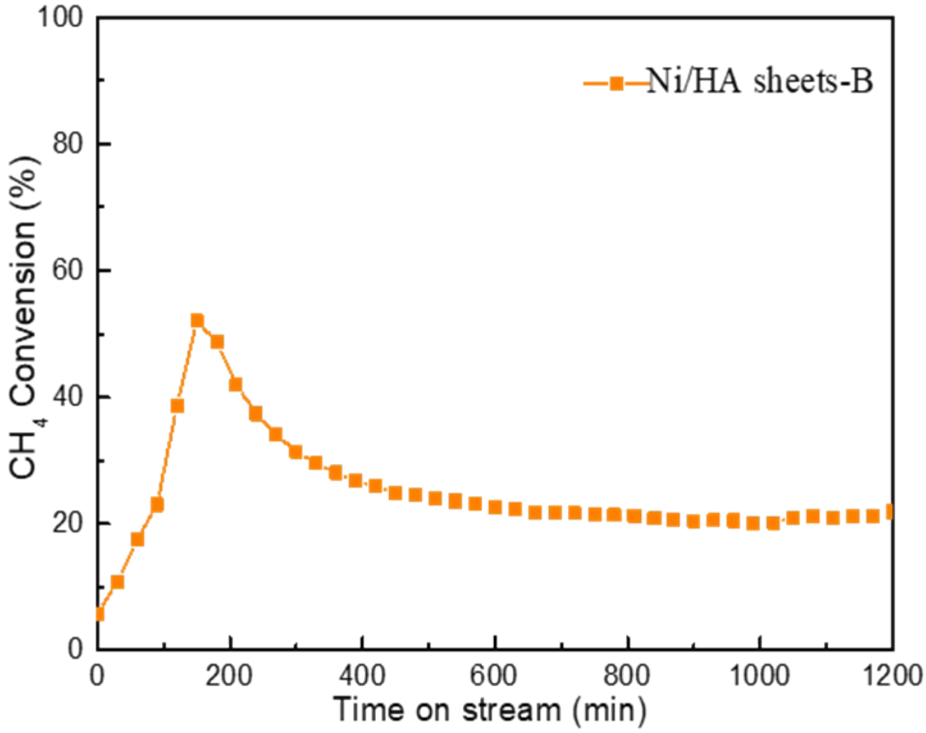

Fig. S6 CH$_4$ reforming of methane stability of the Ni/ HA sheets-B catalyst: CH$_4$ conversion as a function of reaction time (GHSV = 15,000 mL h^{-1}gcat^{-1}, 750 ^{o}C, 1 atm).

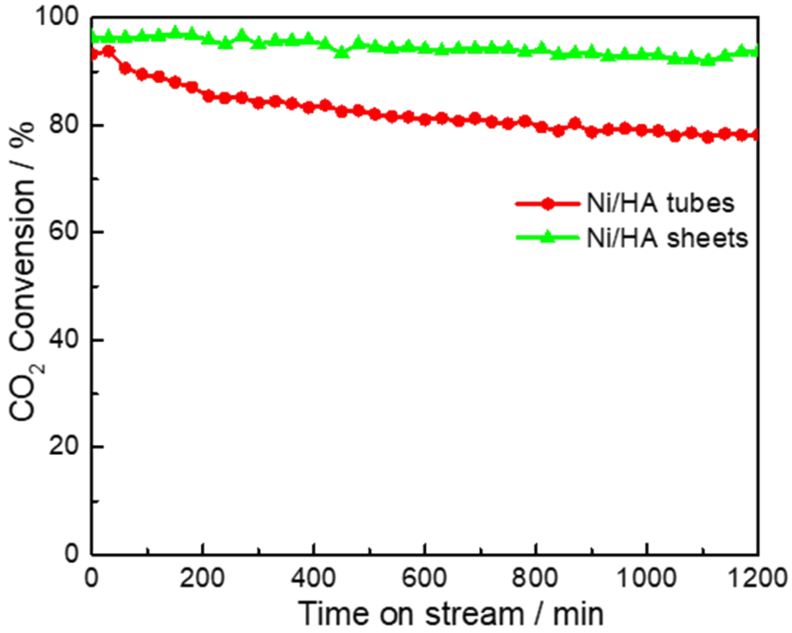

Fig. S7 CO_2 reforming of methane stability of the catalysts: CO_2 conversion as a function of reaction time (GHSV = 15,000 mL $h^{-1}gcat^{-1}$, 750 ^{o}C, 1 atm).

Table S1 Comparison of the previously reported Ni catalysts.

Catalysts	Temp. (^oC)	Time X (h)	CH_4 conv. (%) T=0h	CH_4 conv. (%) T=Xh	References
Ni/ZrO_2	750	12	53	33	ref. 1
10Ni15Ce/illite	800	4	88	84	ref. 2
Ni/SiO_2–F	700	6	62	56	ref. 3
$LaNi_{0.4}Ce_{0.6}O_3$	800	10	91	80	ref. 4
10Ni15La/illite	800	25	80	78	ref. 5
Ni/HA sheets	750	20	89	88	This work

Table S2 Comparison of TOF_{CH4} of the previously reported Ni catalysts.

Catalysts	Temp. (^{o}C)	Time X (h)	TOF_{CH4} ^{c} (h^{-1})	References
Ni/SBA-16	700	100	1728	ref. 6
Ni–MgO–ZrO_2	800	5	1577	ref. 7
Co/Al_2O_3	750	20	1584	ref. 8
Ni/HA sheets	750	20	2175	This work

Table S3 The TOF_{CH4} of the as-prepared catalysts during the DRM reaction at 500 ^{o}C and textural properties of the spent catalysts.

Catalysts	Temp. (^{o}C)	Time X (h)	Surface area [a] ($m^2 g^{-1}$)	Ni dispersion [b](%)		TOF_{CH4} [c](h^{-1})	
				t = 10 min	t = 360 min	t = 10min	t = 360min
Ni/HA tubes	550	6	51	0.98%	0.37%	790	624
Ni/HA sheets	550	6	55	0.33%	0.34%	2175	2169

[a] Specific surface area of the spent catalysts after the 20 h stability test determined by the BET method.

[b] Ni dispersion were measured by H_2 pulse chemisorption.

[c] The value of TOF was tested at 550^{o}C with CH_4 flowing of 45 ml/min.

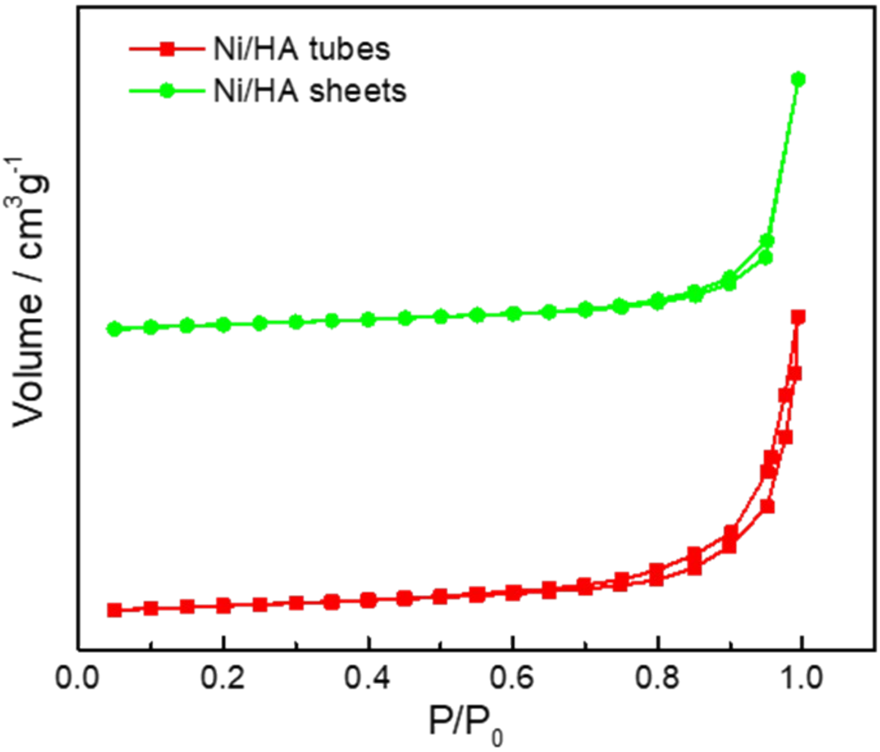

Fig. S8 N_2 sorption isotherms of the spent catalysts after the 20 h stability test.

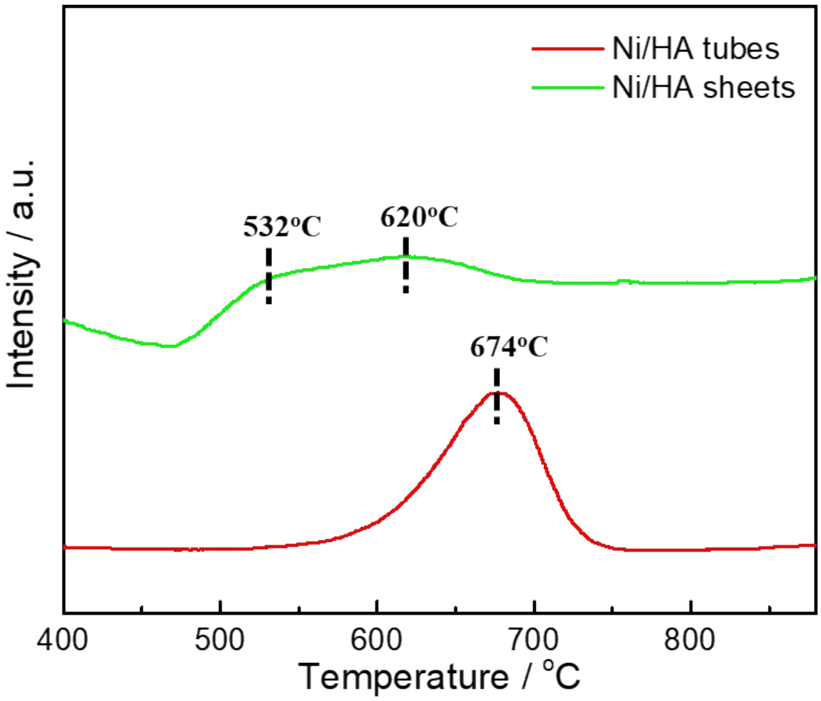

Fig. S9 O_2-TPO profiles of the spent catalysts after the 20 h stability test.

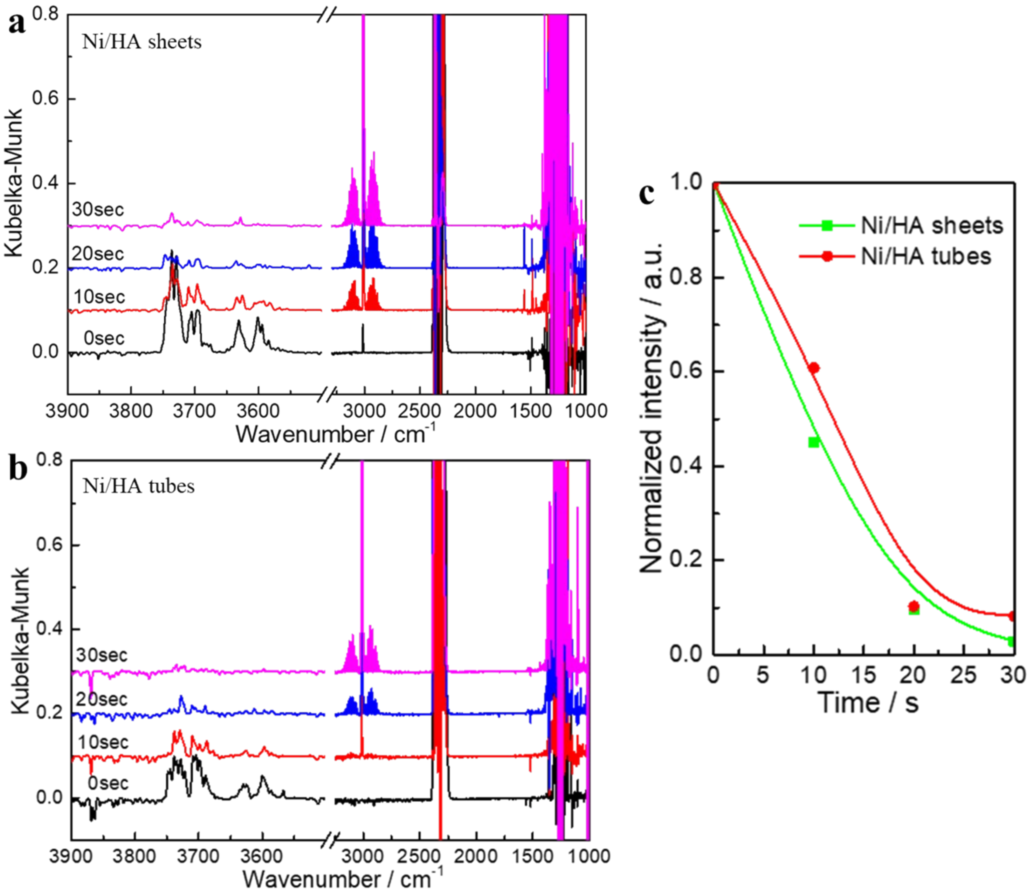

Fig. S10 *In situ* DRIFTs spectra of transient reactions over (a) Ni/HA sheets; (b) Ni/HA tubes catalysts after the CO_2 adsorption at 500 °C for 1 h and then exposed to CH_4; (c) consumption rate of Si-OH species over the Ni/HA sheets and Ni/HA tubes catalysts upon passing CH_4.

In situ DRIFTs of transient reactions over Ni/HA sheets and Ni/HA tubes catalysts was carried out to clarify the reaction mechanisms. First, the sample in the DRIFTs cell was pre-treated at 300 °C under a 50 ml/min N_2 atmosphere and kept at this temperature for 30 min. Then, the catalysts were pre-adsorbed by CO_2 at 500 °C for 1 h. After that, CH_4 introduced into the cell and spectra were obtained by collecting 16 scans with a resolution of 4 cm^{-1}. From the *in situ* DRIFTs spectra, the gas phase CH_4 can be easily discerned at wavenumbers 3015 and 1304 cm^{-1} and CO_2 peaks appeared at 2360 and 2340 cm^{-1}, respectively (Fig. S10a-b). The intensity of Si-OH peaks at 3694-3800 cm^{-1} over both the Ni/HA sheets and Ni/ HA tubes disappeared while exposing to CH_4. In addition, the intensity of Si-OH over Ni/HA sheets decreases rapidly than that of Ni/HA tubes with flowing CH_4 stream due to the strong interaction between Ni and HA sheets (Fig. S10c). We can also conclude that bidentate formate species at 2878 cm^{-1} dominate over bicarbonates detected at 1419 and 1224 cm^{-1} on the surface of the catalysts. It means that H* is produced via dissociation of CH_4 on Ni particles which accelerates the formation of transition from bicarbonate.

Reference

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