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Electronic Supplementary Information (ESI)

In situ preparation of Ni nanoparticles in cerium–modified silica aerogels for coking- and sintering-resistant dry reforming of methane†

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Preparation details of Ni/SiO_2-I catalyst

All chemicals were used without any further purification. Nickel nitrate ($Ni(NO_3)_3 \cdot 6H_2O$, 98%), were produced by Sinopharm Chemical Reagent Company, Chin. The commercial SiO_2 were purchased from Tai Yang Chemical Co., Ltd. Deionized water was used throughout the experiment.

The Ni/SiO_2–I catalyst was prepared by an wetness impregnation method. In a typical synthesis, SiO_2 (1.0g) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.56g) were added into deionized water (60ml). After stirring for 6 h, the solution was dried in hot air at 70 °C for two days. Powder obtained after the drying was heated to 600 °C at a heating rate of 1 °C /min. It was then calcined at the same temperature (600 °C) in air for 3 h. Ni/ SiO_2–I catalyst was obtained by reduction in a H_2/N_2 flow (having 10% H_2 in N_2 gas with a flow rate of 40 ml/min) at 900 °C for 1 h.

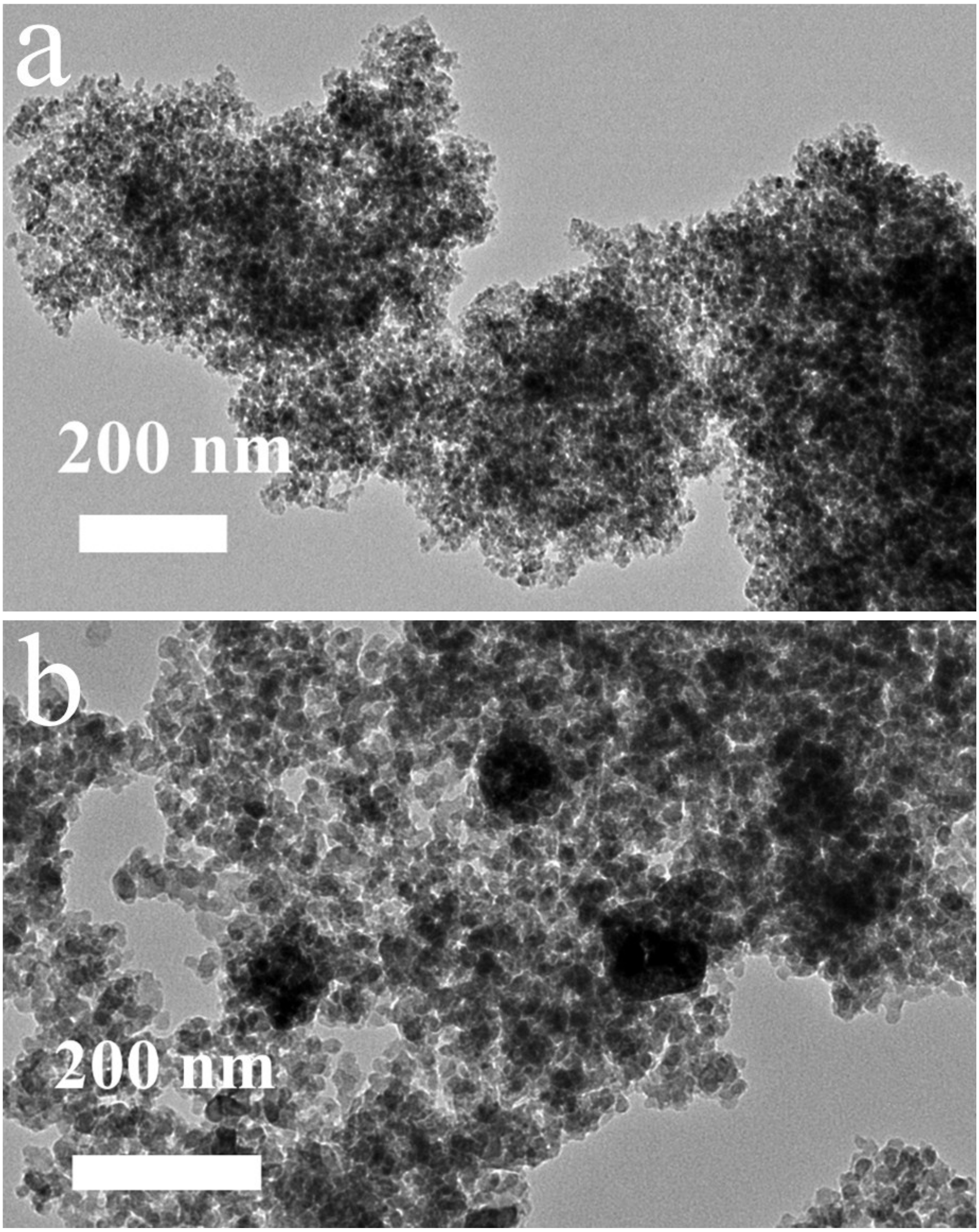

Fig. S1 TEM images of (a) Ni/SiO_2-A and (b) Ni/SiO_2-I catalysts.

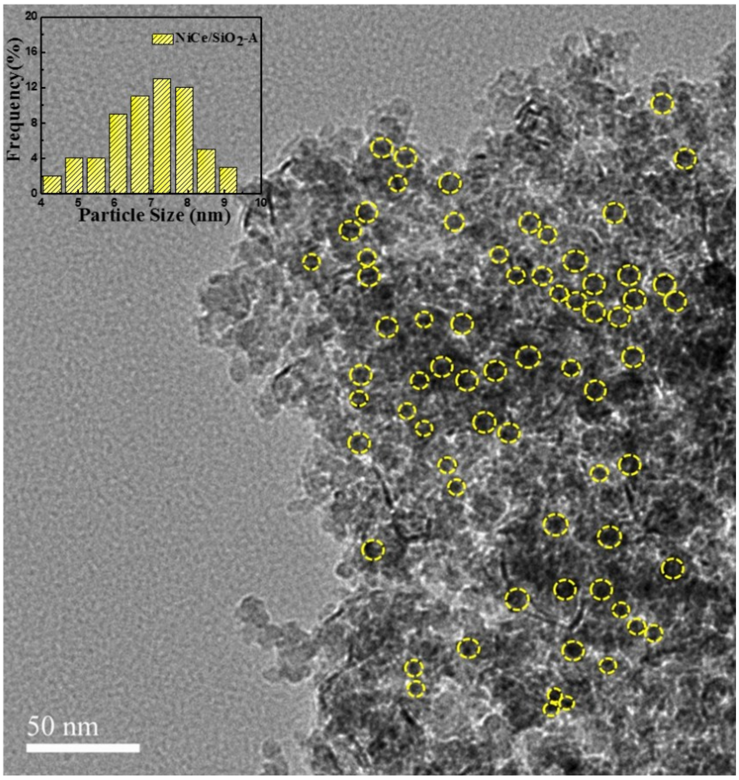

Fig. S2 TEM images of NiCe/SiO$_2$-A catalysts.

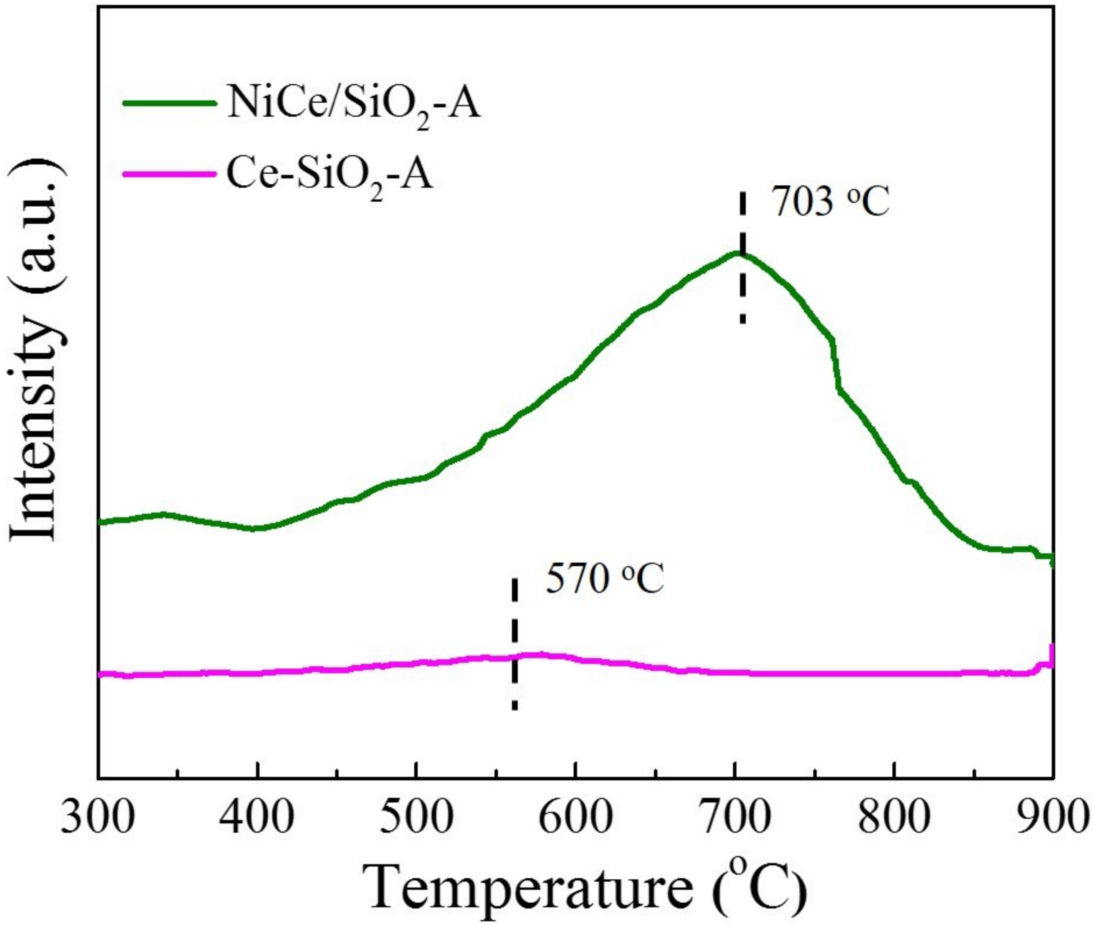

Fig. S3 H_2-TPR profiles of Ce-SiO_2-A catalyst and NiCe/SiO_2-A catalyst.

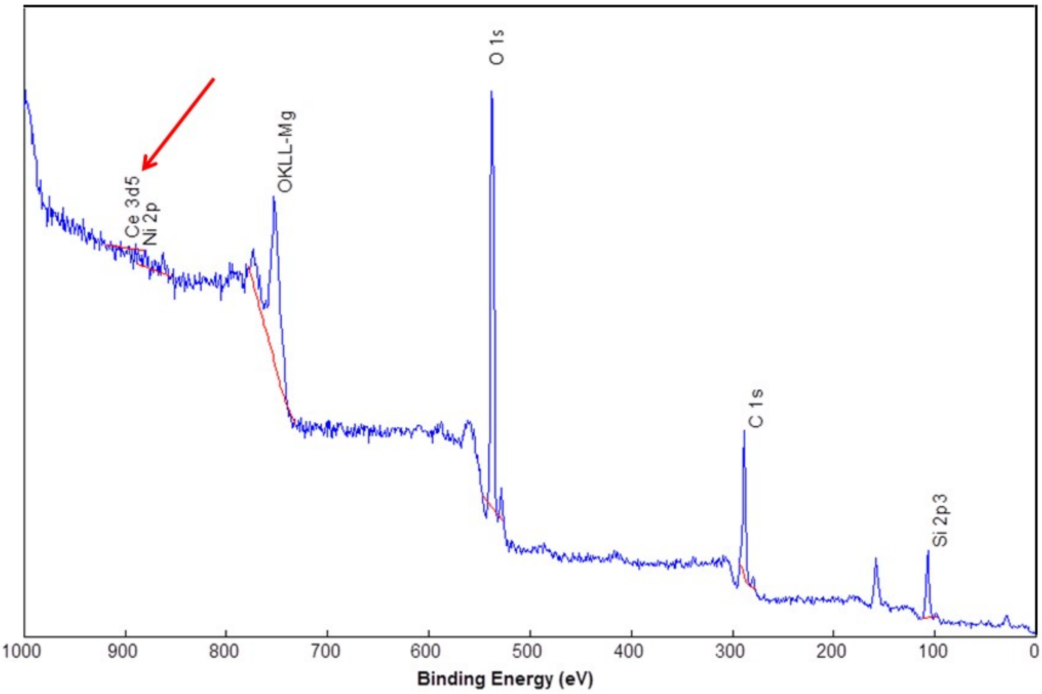

Fig. S4 XPS whole spectra of NiCe/SiO$_2$-A catalysts.

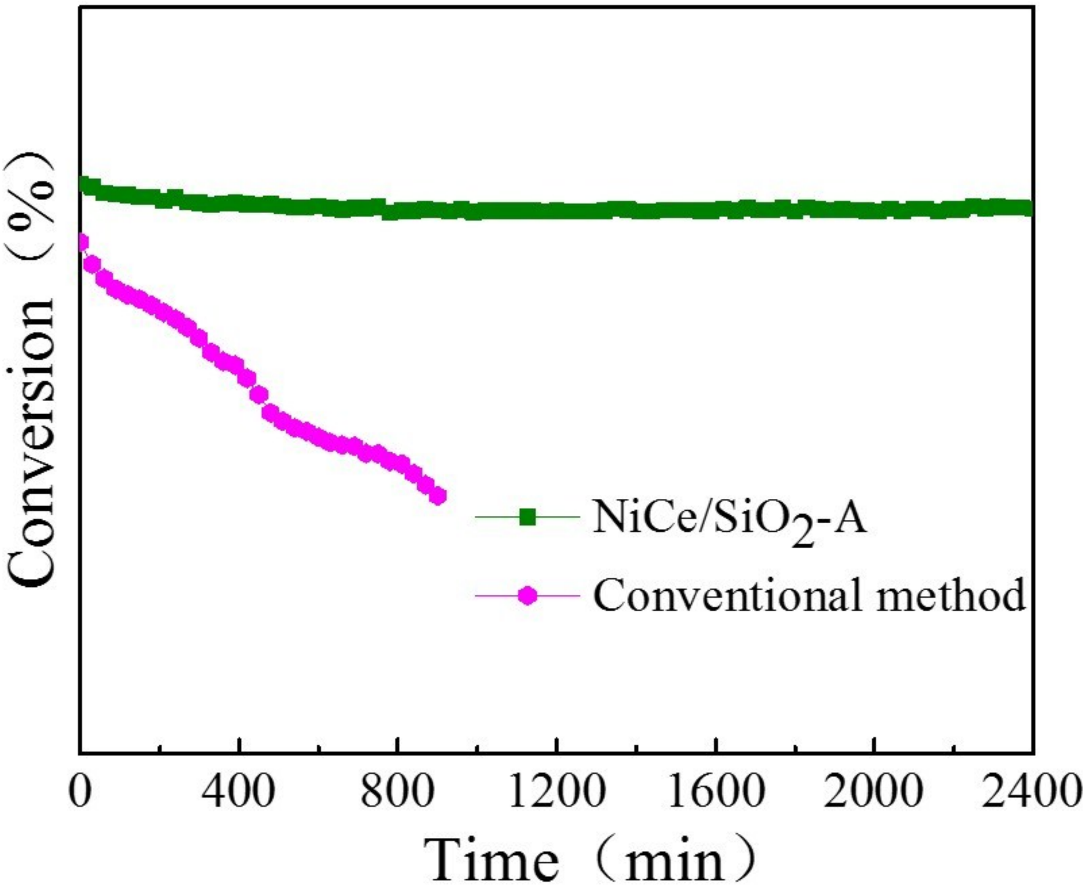

Fig. S5 Catalytic stability of catalysts prepared by conventional method and in situ method.

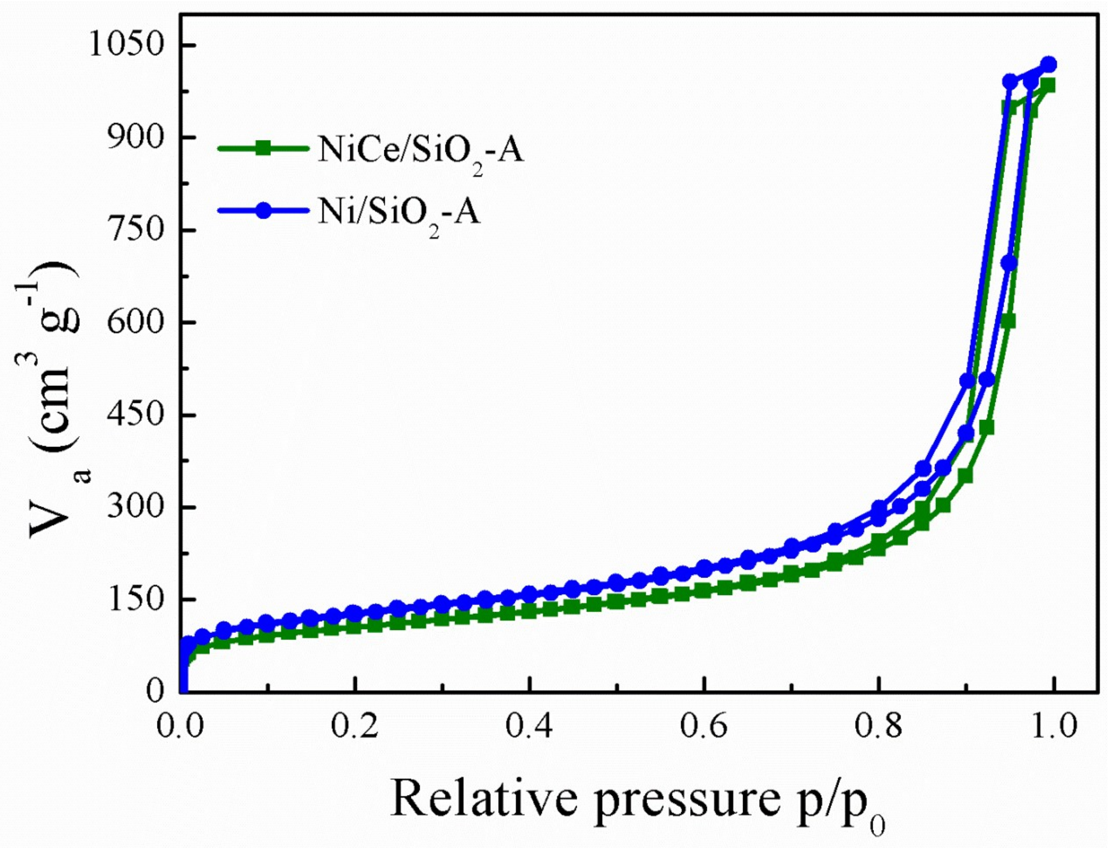

Fig. S6 Nitrogen adsorption-desorption isotherms of used NiCe/SiO_2-A and Ni/SiO_2-A catalysts after removing the carbon deposition by O_2-TPO.

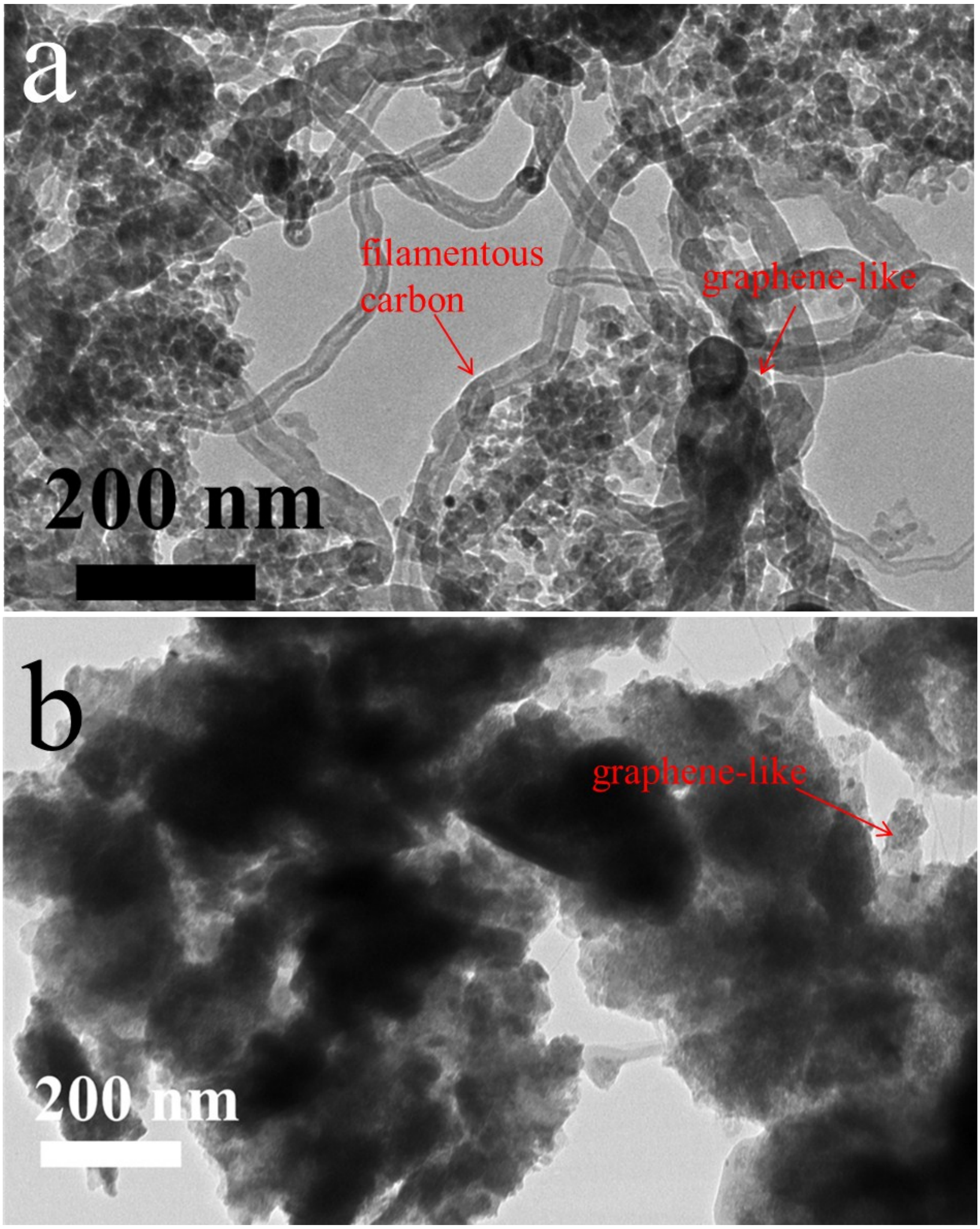

Fig. S7 TEM images of (a) Ni/SiO$_2$-I and (b) Ni/SiO$_2$-A catalysts after 2400 min stability tests.

Table S1. Summary of stabilities of Ni-based catalysts in DRM reaction

Catalysts	Temp. (^oC)	Time X (h)	X_{CH4} (%) T=0h	X_{CH4} (%) T=Xh	Stability loss(%)	Ref
Ni/SBA-15	750	20	86	82	4	1
Ni/mSiO$_2$	750	20	88	80	8	2
Ni/Al$_2$O$_3$–A	750	30	91	77	16	3
Ni/SiO$_2$–F	700	6	62	56	6	4
Ni-MgO-Al$_2$O$_3$@m-SiO$_2$	750	8	80	77	3	5
NiMg/SBA-15-C	700	100	66	52	14	6
NiCe/SiO$_2$-A	750	40	86	84	2	This work

Reference

1. T. Xie, L. Y. Shi, J. P. Zhang, D. S. Zhang, Chem. Commun., 2014, 50, 7250-7253.

2. T. Xie, X. Y. Zhao, J. P. Zhang, L. Y. Shi, D. S. Zhang, International journal of hydrogen energy, 2015, 40, 9685-9695.

3. X. Y. Zhao, Y. Cao, H. R. Li, J. P. Zhang, L. Y. Shi, D. S. Zhang, RSC Adv., 2017, 7, 4735–4745.

4. S. Wen, M. Liang, J. Zou, S. Wang, X. Zhu, L. Liu and Z.-j. Wang, J. Mater. Chem. A, 2015, 3, 13299-13307.

5. X. Du, D. Zhang, R. Gao, L. Huang, L. Shi, J. Zhang, Chem. Commun., 2013, 49, 6770-6772.

6. N. Wang, K. Shen, X. Yu, W. Qian, W. Chu, Catal. Sci. Technol. 2013, 3, 2278-2287.