

## **Supporting Information**

### **Embedding uniform Ni nanoparticles into Silicalite-1 zeolite for dry reforming of methane**

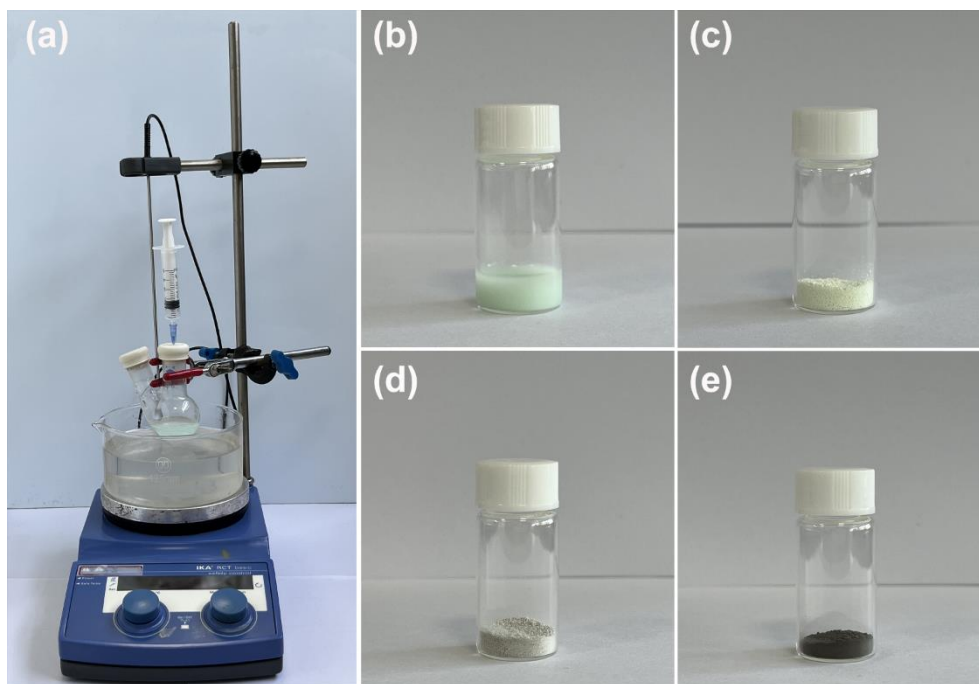
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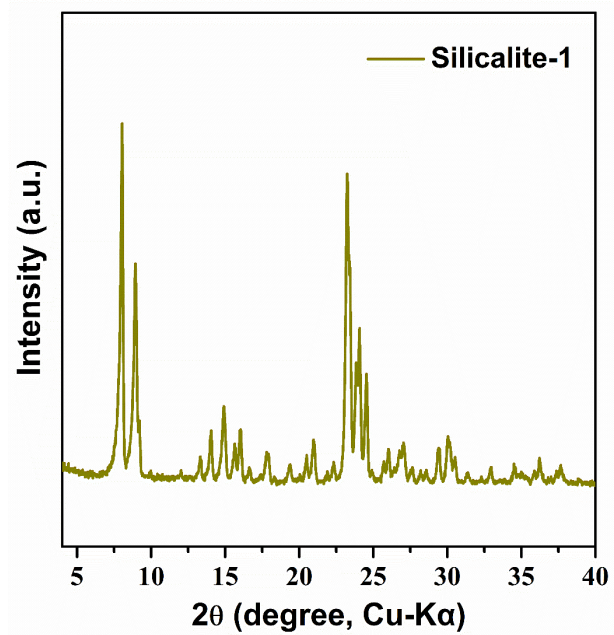
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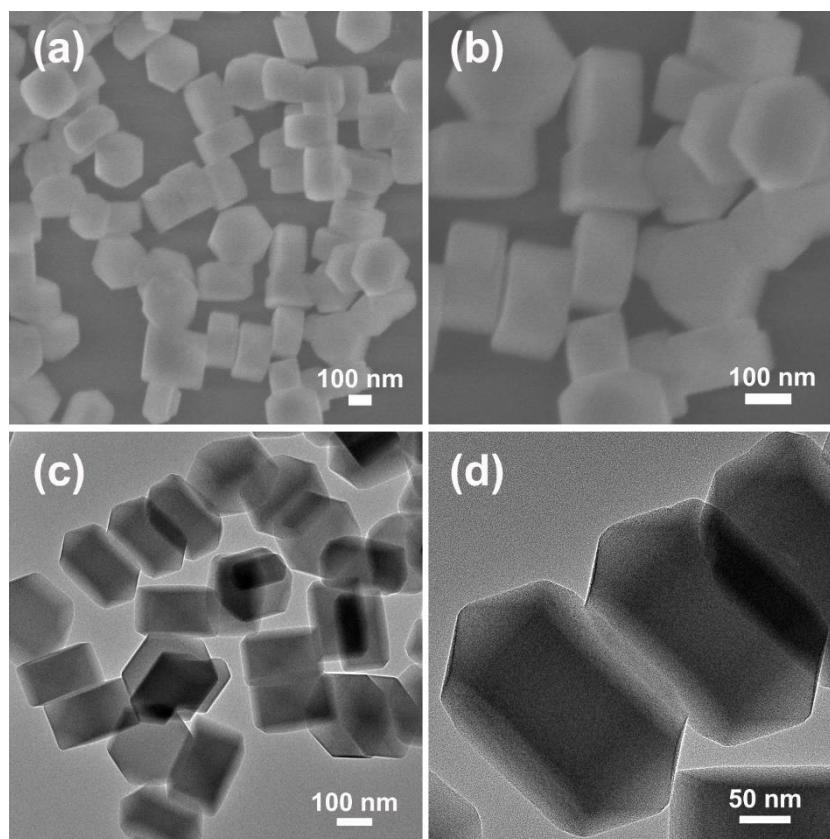
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**Figure S1.** Ni-based Silicalite-1 catalysts prepared via deposition-precipitation and wet impregnation methods: (a) Ni/S-1-DP catalyst obtained by deposition-precipitation method; (b-e) Ni@S-1-WI catalyst prepared through wet impregnation method; (c) sample after drying; (d) sample after calcination; (e) sample after hydrogen reduction.



**Figure S2.** PXRD patterns of parent nanosized silicalite-1 zeolites.



**Figure S3.** SEM images (a, b) and TEM images (c, d) of parent nanosized silicalite-1 zeolites.

**Table S1.** Data including binding energies and peak fitting areas from XPS analysis before and after H<sub>2</sub> reduction.

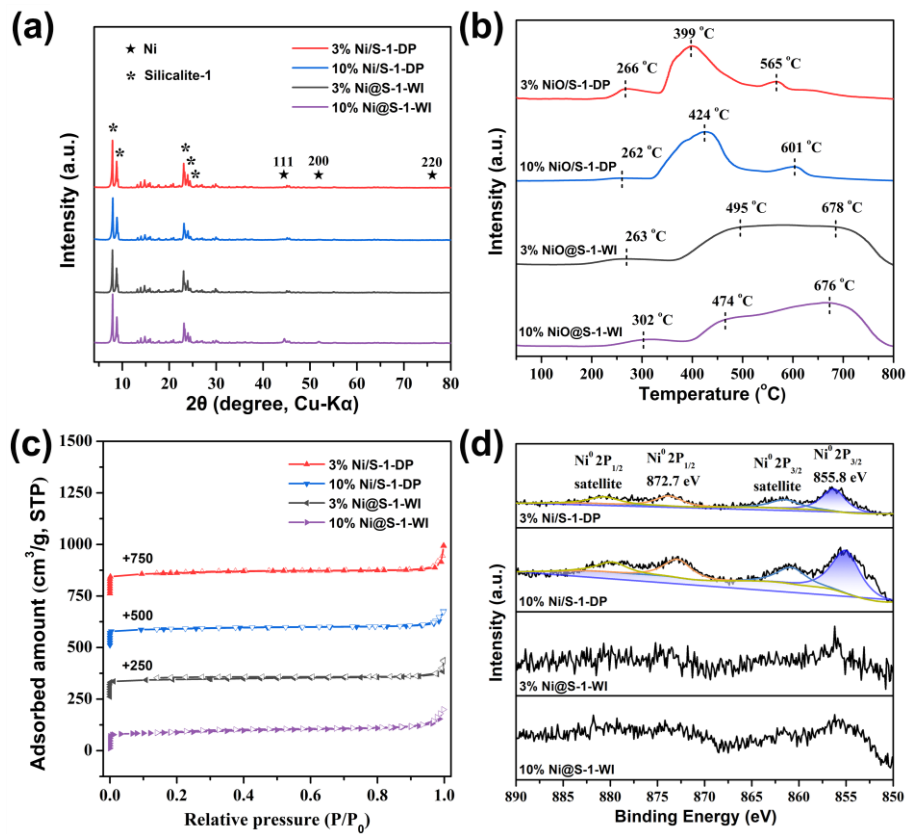
Sample	Ni 2P <sub>3/2</sub>			Ni 2P <sub>1/2</sub>		
	Binding Energy/eV	Raw area <sup>a</sup>	FWHM <sup>a</sup>	Binding energy/eV	Raw area <sup>a</sup>	FWHM <sup>a</sup>
5% NiO@S-1-WI	856.6	3208	3.6	874.3	1631	3.6
5% NiO/S-1-DP	856.1	23177	3.2	873.7	11732	3.2
5% Ni@S-1-WI	855.6	3496	3.4	872.5	1778	3.4
5% Ni/S-1-DP	855.7	12599	3.6	872.5	6314	3.6

<sup>a</sup> obtained by Gaussian fitting method.

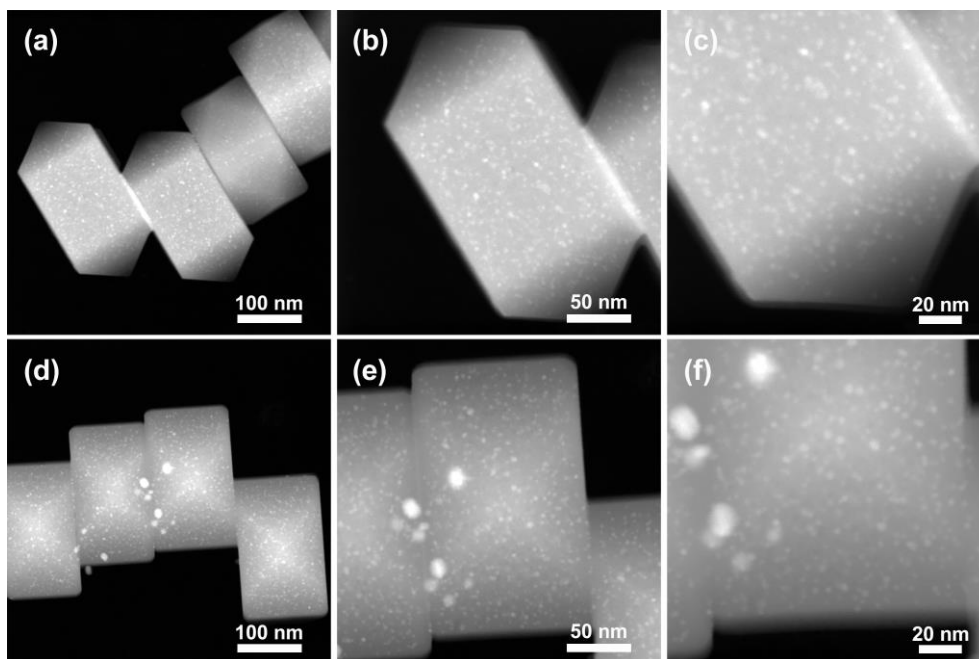
**Table S2.** Metal loading and porous properties of two Ni-based zeolite catalysts.

Samples	Ni <sup>a</sup> (wt%)	S <sub>BET</sub> <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>micro</sub> <sup>c</sup> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>ext</sub> <sup>c</sup> (m <sup>2</sup> g <sup>-1</sup> )
Silicalite-1	/	391	242	149
3% Ni@S-1-WI	2.32	298	210	88
5% Ni@S-1-WI	4.78	284	195	89
10% Ni@S-1-WI	9.26	266	183	83
3% Ni/S-1-DP	1.92	340	235	105
5% Ni/S-1-DP	4.11	333	214	119
10% Ni/S-1-DP	8.04	291	194	97

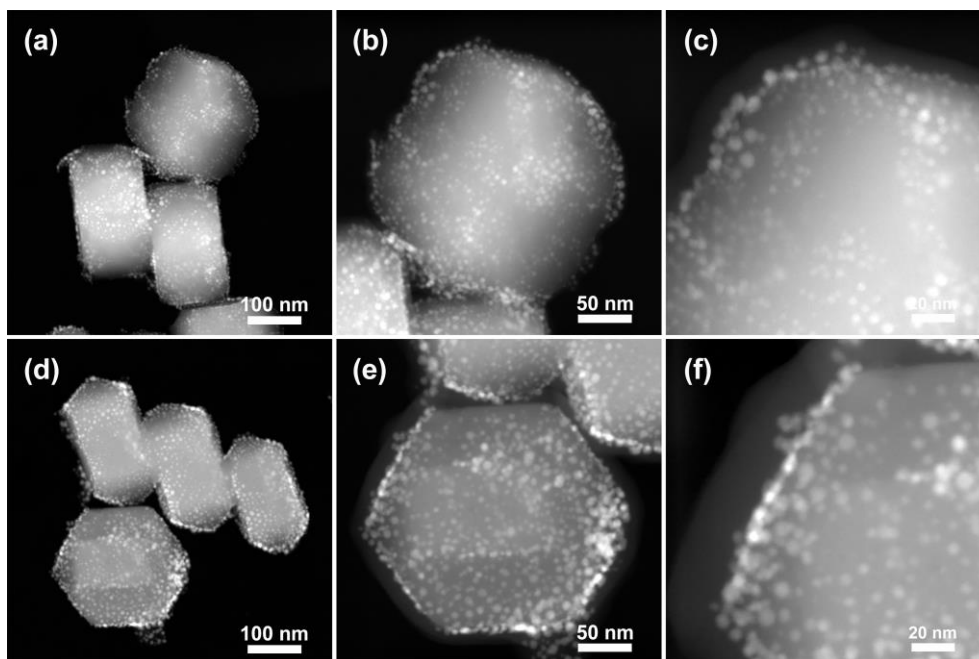
<sup>a</sup> obtained by ICP-AES. <sup>b</sup> S<sub>BET</sub>: total surface area, calculated by the BET method. <sup>c</sup> S<sub>micro</sub>: micropore surface area and S<sub>ext</sub>: mesopore surface area, calculated by the t-plot method.



**Figure S4.** Characterization of the Ni@S-1-WI and Ni/S-1-DP with different Ni loadings. (a) PXRD patterns. (b) H<sub>2</sub>-TPR profiles. (c) N<sub>2</sub> adsorption/desorption isotherm. (d) XPS spectra.



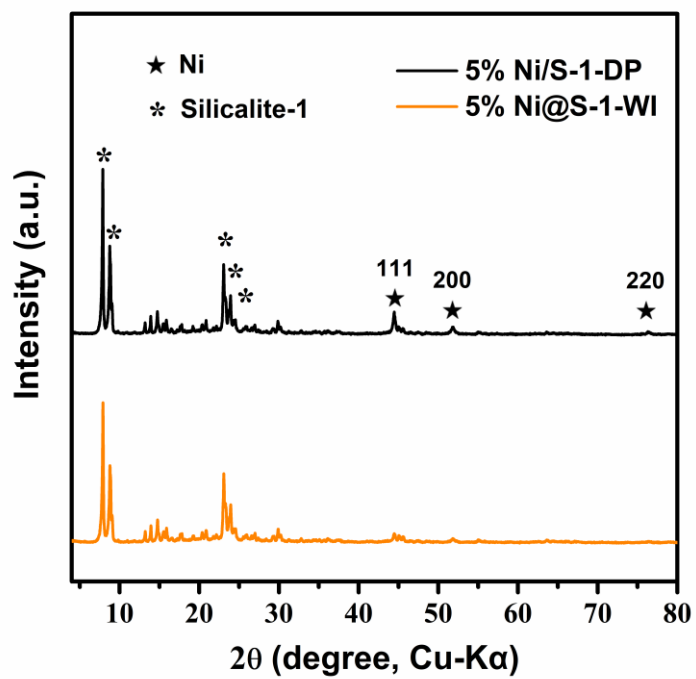
**Figure S5.** The HAADF-STEM images of catalysts 3% Ni@S-1-WI (a, b, c) and 10% Ni@S-1-WI (d, e, f).



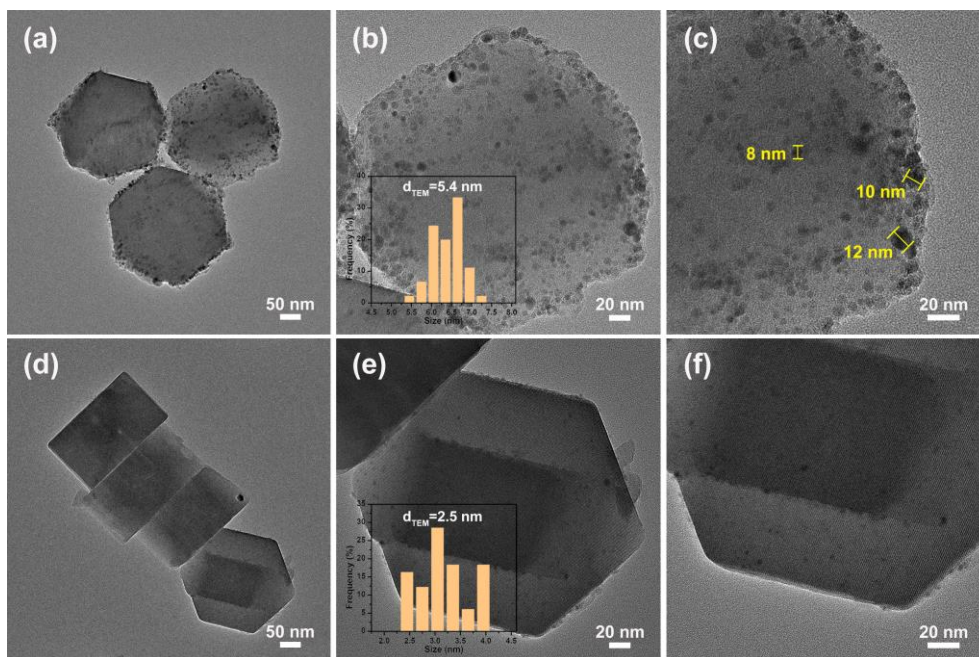
**Figure S6.** The HAADF-STEM images of catalysts 3% Ni/S-1-DP (a, b, c) and 10% Ni/S-1-DP (d, e, f).

**Table S3.** Comparative catalytic performance of representative DRM catalysts reported in literature versus the present work.

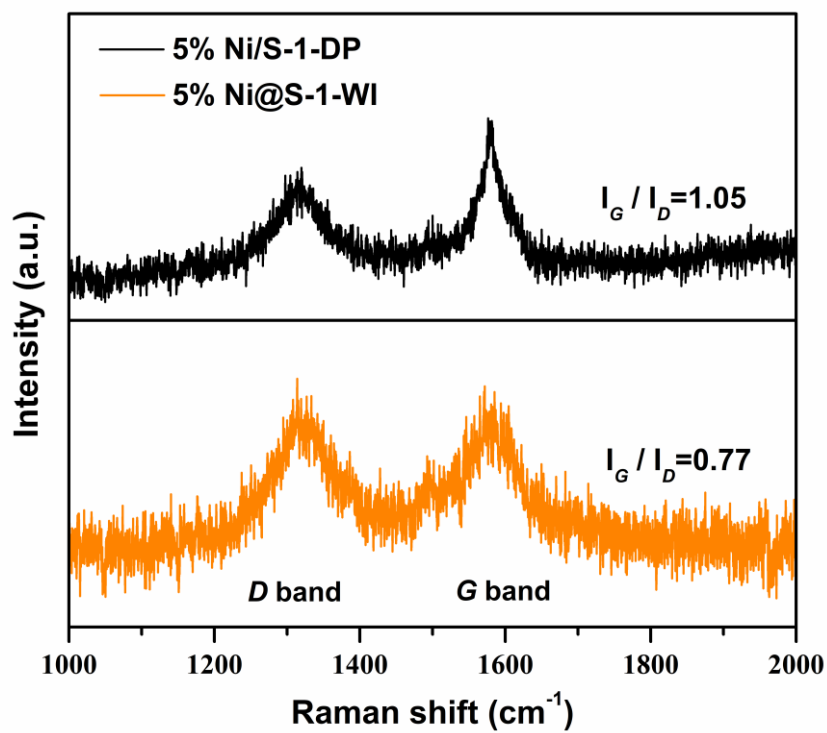
Catalysts	Reaction conditions			CH <sub>4</sub> Cov. %	CO <sub>2</sub> Cov. %	Reference
	Temperature (°C)	WHSV (L·g <sup>-1</sup> ·h <sup>-1</sup> )	Lifetime (h)			
5% Ni@S-1-WI	800	30	200	88	94	This work
Ni/ZSM-5	800	30	30	70	74	[1]
Ni-Ta/ZSM-5	784	33	60	80	90	[2]
Ni-Mo/ZSM-5	750	25	100	88	94	[3]
Ni-HAP-Ce	750	60	100	84	92	[4]
Ni/SiO <sub>2</sub>	700	40	200	70	80	[5]
Ni-MCM-41	700	45	200	70	80	[6]
0.5Ni/CeNi <sub>x</sub> O <sub>y</sub>	800	36	140	80	87	[7]
Ni@Al <sub>2</sub> O <sub>3</sub>	800	36	50	79	82	[8]
NiMo-MgO	800	60	200	100	100	[9]



**Figure S7.** PXRd patterns of the spent 5% Ni@S-1-WI and 5% Ni/S-1-DP.



**Figure S8.** TEM images of the spent 5% Ni/S-1-DP (a, b, c) and 5% Ni@S-1-WI (d, e, f).



**Figure S9.** Raman spectra of the spent 5% Ni@S-1-WI and 5% Ni/S-1-DP.

## References

1. H. U. Hambali, A. A. Jalil, A. A. Abdulrasheed, T. J. Siang and D.-V. N. Vo, *J. Energy Inst.*, 2020, **93**, 1535–1543.
2. H. U. Hambali, A. A. Jalil, A. A. Abdulrasheed, T. J. Siang, A. H. K. Owgi and F. F. A. Aziz, *Chem. Eng. Sci.*, 2021, **231**, 116320.
3. X. Zhang, J. Deng, M. Pupucevski, S. Impeng, B. Yang, G. Chen, S. Kuboon, Q. Zhong, K. Faungnawakij, L. Zheng, G. Wu and D. Zhang, *ACS Catal.*, 2021, **11**, 12087–12095.
4. M. Akri, S. Zhao, X. Li, K. Zang, A. F. Lee, M. A. Isaacs, W. Xi, Y. Gangarajula, J. Luo, Y. Ren, Y.-T. Cui, L. Li, Y. Su, X. Pan, W. Wen, Y. Pan, K. Wilson, L. Li, B. Qiao, H. Ishii, Y.-F. Liao, A. Wang, X. Wang and T. Zhang, *Nat. Commun.*, 2019, **10**, 1–10.
5. J. Tian, B. Ma, S. Bu, Q. Yuan and C. Zhao, *Chem. Commun.*, 2018, **54**, 13993–13996.
6. J. Tian, H. Li, X. Zeng, Z. Wang, J. Huang and C. Zhao, *Chinese J. Catal.*, 2019, **40**, 1395–1404.
7. J. Dou, Z. Bao and F. Yu, *ChemCatChem*, 2018, **10**, 250–258.
8. Q. Huang, X. Fang, Q. Cheng, Q. Li, X. Xu, L. Xu, W. Liu, Z. Gao, W. Zhou and X. Wang, *ChemCatChem*, 2017, **9**, 3563–3571.
9. Y. Song, E. Ozdemir, S. Ramesh, A. Adishev, S. Subramanian, A. Harale, M. Albuali, B. A. Fadhel, A. Jamal, D. Moon, S. H. Choi and C. T. Yavuz, *Science*, 2020, **367**, 777–781.