Supporting information

NiO-MgO prepared by the complex-decomposition method as a catalyst for carbon dioxide reforming of methane

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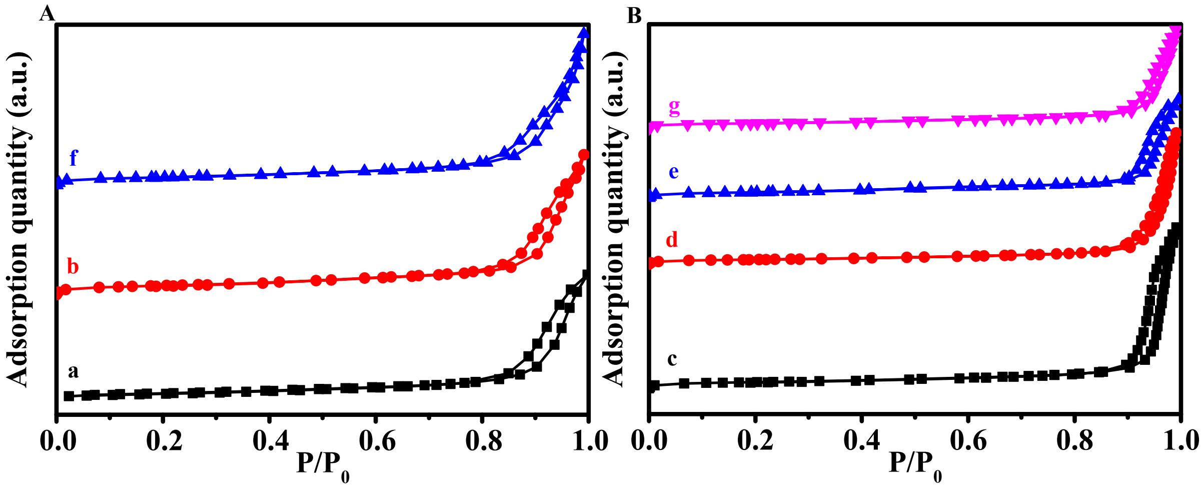

Figure S1. N_2 adsorption-desorption isotherms of the fresh catalysts of $Ni_{0.1}Mg_{0.9}O$-800-Gly (a), $Ni_{0.1}Mg_{0.9}O$-800-Gla (b), $Ni_{0.1}Mg_{0.9}O$-800-Oxa (c), $Ni_{0.1}Mg_{0.9}O$-800-Pro (d), $Ni_{0.1}Mg_{0.9}O$-800-Ser (e), $Ni_{0.1}Mg_{0.9}O$-800-Urea (f), and $Ni_{0.1}Mg_{0.9}O$-800-Ala (g).

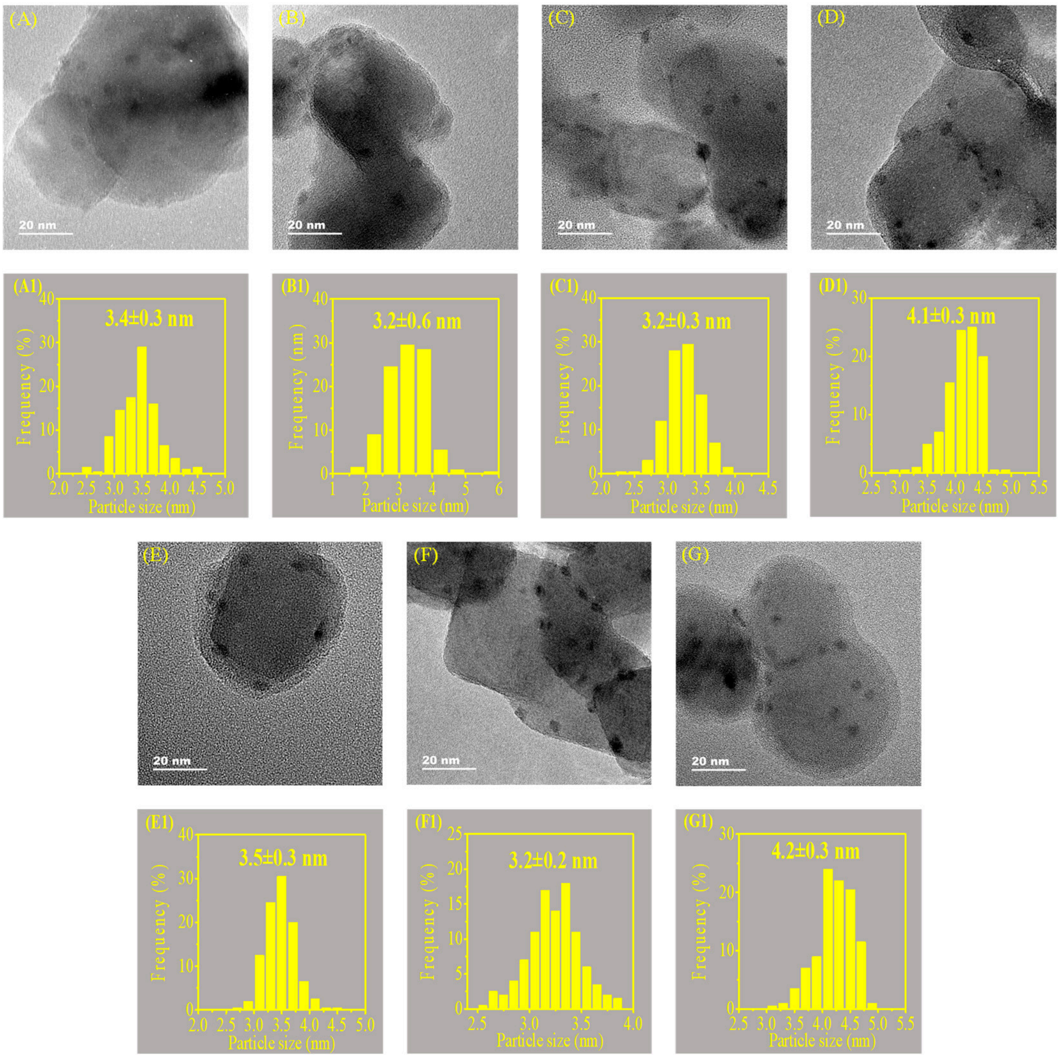

Figure S2. TEM images and the corresponding particle-size distributions for the reduced catalysts of $Ni_{0.1}Mg_{0.9}O$-800-Gly (A, A1), $Ni_{0.1}Mg_{0.9}O$-800-Gla (B, B1), $Ni_{0.1}Mg_{0.9}O$-800-Oxa (C, C1), $Ni_{0.1}Mg_{0.9}O$-800-Pro (D, D1), $Ni_{0.1}Mg_{0.9}O$-800-Ser (E, E1), $Ni_{0.1}Mg_{0.9}O$-800-Urea (F, F1), $Ni_{0.1}Mg_{0.9}O$-800-Ala (G, G1).

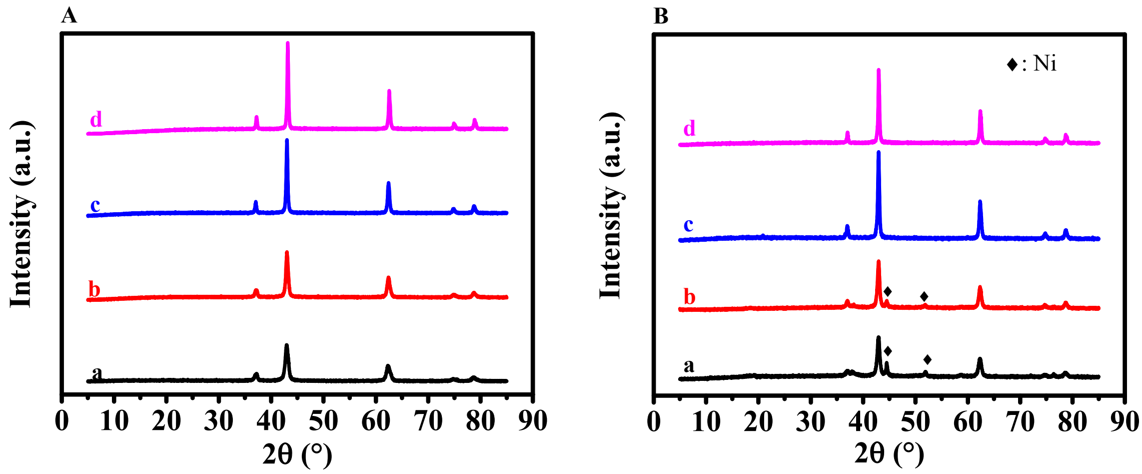

Figure S3. XRD patterns for the fresh (A) and reduced (B) catalysts of $Ni_{0.1}Mg_{0.9}O$-Gly-600 (a), $Ni_{0.1}Mg_{0.9}O$-Gly-700 (b), $Ni_{0.1}Mg_{0.9}O$-Gly-800 (c), $Ni_{0.1}Mg_{0.9}O$-Gly-900 (d).

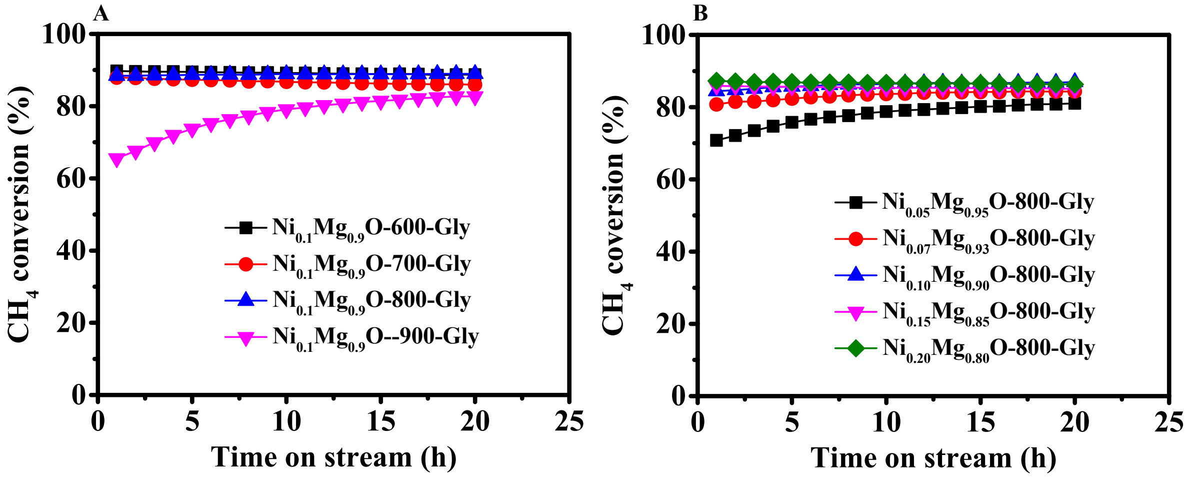

Figure S4. The time-on-stream conversions of CH_4 for $Ni_{0.1}Mg_{0.9}O$-T-Gly (A) and $Ni_xMg_{1-x}O$-800-Gly (B) catalyzed CRM under the conditions of $CH_4/CO_2 = 1$, 750 ºC, 0.1 MPa and GHSV of 60000 $mL \cdot g^{-1} \cdot h^{-1}$

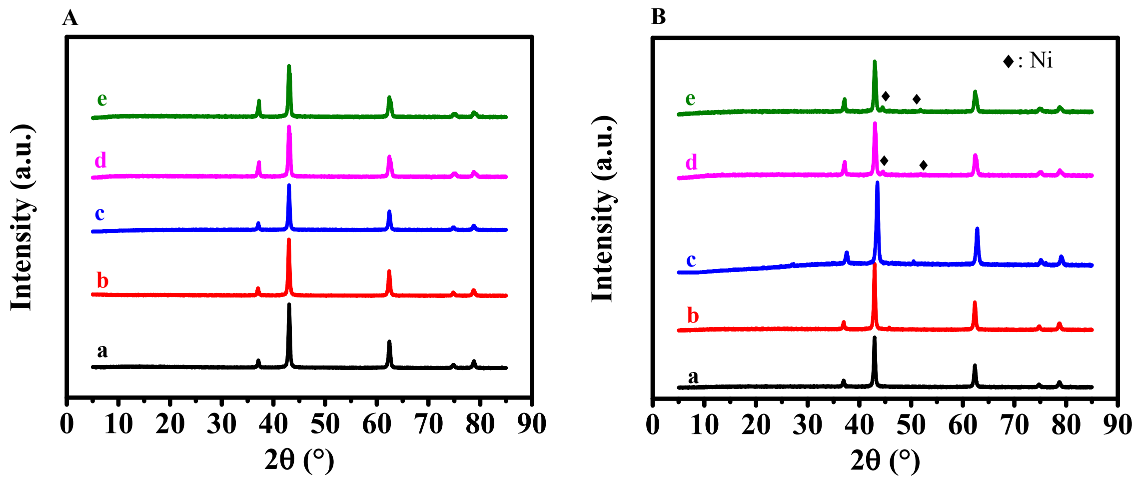

Figure S5. XRD patterns of fresh (A) and reduced (B) catalysts of $Ni_{0.05}Mg_{0.95}O$-800-Gly (a), $Ni_{0.07}Mg_{0.93}O$-800-Gly (b), $Ni_{0.10}Mg_{0.90}O$-800-Gly (c), $Ni_{0.15}Mg_{0.85}O$-800-Gly (d), $Ni_{0.20}Mg_{0.80}O$-800-Gly (e).

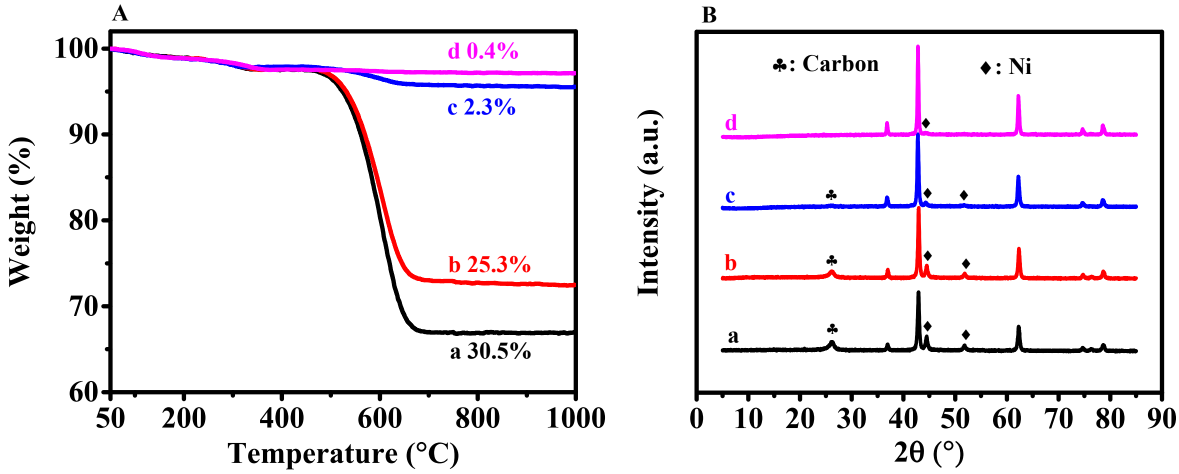

Figure S6. TG curves (A) and XRD patterns (B) for the spent catalysts of $Ni_{0.1}Mg_{0.9}O$-Gly-600 (a), $Ni_{0.1}Mg_{0.9}O$-Gly-700 (b), $Ni_{0.1}Mg_{0.9}O$-Gly-800 (c), $Ni_{0.1}Mg_{0.9}O$-Gly-900 (d).

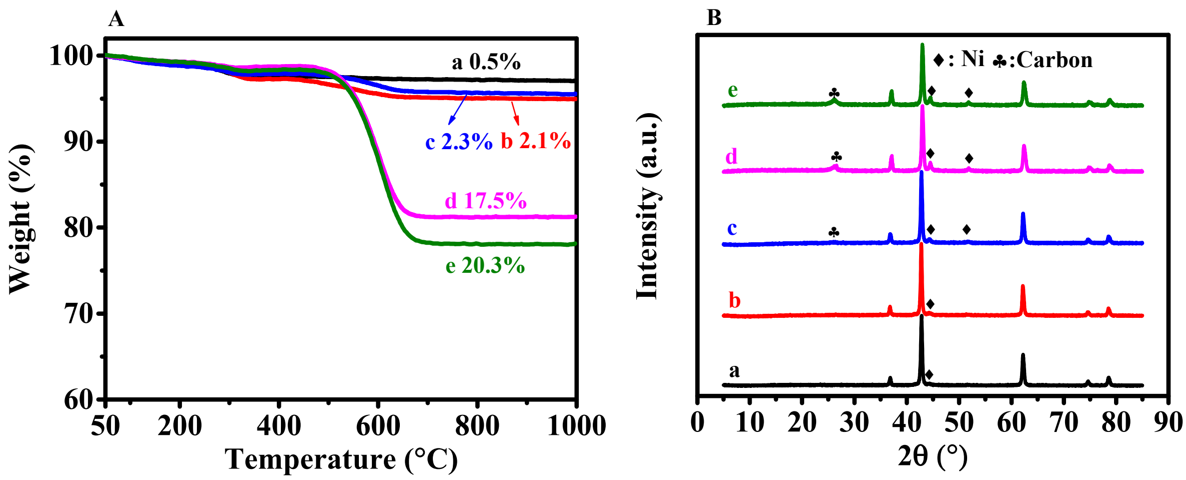

Figure S7. TG curves (A) and XRD patterns (B) for the spent catalysts of $Ni_{0.05}Mg_{0.95}O$-800-Gly (a), $Ni_{0.07}Mg_{0.93}O$-800-Gly (b), $Ni_{0.10}Mg_{0.90}O$-800-Gly (c), $Ni_{0.15}Mg_{0.85}O$-800-Gly (d), $Ni_{0.20}Mg_{0.80}O$-800-Gly (e).

Table S1 Summarized reaction conditions and the typical CRM results of the optimal NiO-MgO and the representatively reported Ni-based catalysts.

Catalysts	**Temperature (°C)**	**Feed molar ratio**	**GHSV ($\times 10^4$ mL·h^{-1}·g^{-1})**	**Activity (mol·g^{-1}·h^{-1})***	**Stability (%/h)***	**References**
$Ni_{0.1}Mg_{0.9}O$-800-Gly	750	CH_4/CO_2 = 1/1	6.0	11.5	0	This work
Ni/MOR zeolite	650	CH_4/CO_2 = 1/1	7.2	7.4	0.58	S1
Ni/SBA-15	750	$CH_4/CO_2/N_2$ = 1/1/2	1.2	11.4	0	S2
Ni/Al_2O_3-Ole	800	$CH_4/CO_2/N_2$ = 1/1/1	2.4	~ 3.2	0	S3
Pt-12Ni/hydrotalcite	700	CH_4/CO_2/Ar = 2/2/1	18	~ 42.2	0.13	S4
Ni/$La_2O_2CO_3$-Al_2O_3	650	$CH_4/CO_2/N_2$ = 3/3/14	24	~ 20.9	0	S5
Ni/Al_2O_3	700	CH_4/CO_2 = 1/1	3.0	8.1	0	S6

*: The specific activity is defined as CH_4 converted per gram of Ni over the loaded catalyst per hour, and the stability is estimated by the average rate for the decrease of CH_4 conversion with increasing the time on stream.

References

S1 Bacariza, C.; Karam, L.; Hassan, N.E.; Lopes, J.M.; Henriques, C. Carbon dioxide reforming of methane over nickel-supported zeolites: a screening study. *Processes*. **2022,** 10, 1331

S2 Park, K.S.; Cho, J.M.; Park, Y.M.; Kwon, J.H.; Yu, J.S.; Jeong, H.E.; Choung, J.W.; Bae J.W., Enhanced thermal stability of Ni nanoparticles in ordered mesoporous supports for dry reforming of methane with CO_2. *Catal. Today* **2022,** 388-389, 224-230.

S3 Seo, J.-C.; Kim, H.; Lee, Y.-L.; Nam, S.; Roh, H.-S. Lee, K.; Park, S.B., One-pot synthesis of full-featured mesoporous Ni/Al_2O_3 catalysts via pyrolysis-assisted evaporation-induced self-assembly method for dry reforming of methane. *ACS Sustainable Chem. Eng.* **2021,** 9, 894-904.

S4 Niu, J.; Wang, Y.; Liland, S.E.; Regli, S.K.; Yang, J.; Rout, K.R.; Luo, J.; Ronning, M.; Ran, J.; Chen D. Unraveling enhanced activity, selectivity, and coke resistance of Pt-Ni bimetallic clusters in dry reforming. *ACS Catal.* **2021,** 11, 2398-2411.

S5 Li, K.; Pei, C. Li, X.; Chen, S.; Zhang, X.; Liu, R.; Gong, J. Dry reforming of methane over $La_2O_2CO_3$-modified Ni/Al_2O_3 catalysts with moderate metal support interaction. *Appl. Catal. B-Environ.* **2020,** 264, 118448.

S6 Ma, Q.; Han, Y.; Wei, Q.; Makpal S.; Gao, X.; Zhang, J.; Zhao, T.-S., Stabilizing Ni on bimodal mesoporous-macroporous alumina with enhanced coke tolerance in dry reforming of methane to syngas. *J. CO_2 Util.* **2020,** 35, 288-297.