

Electronic Supplementary Information for

A new automated synthesis of a coke-resistant Cs-promoted Ni-supported nanocatalyst for sustainable dry reforming of methane

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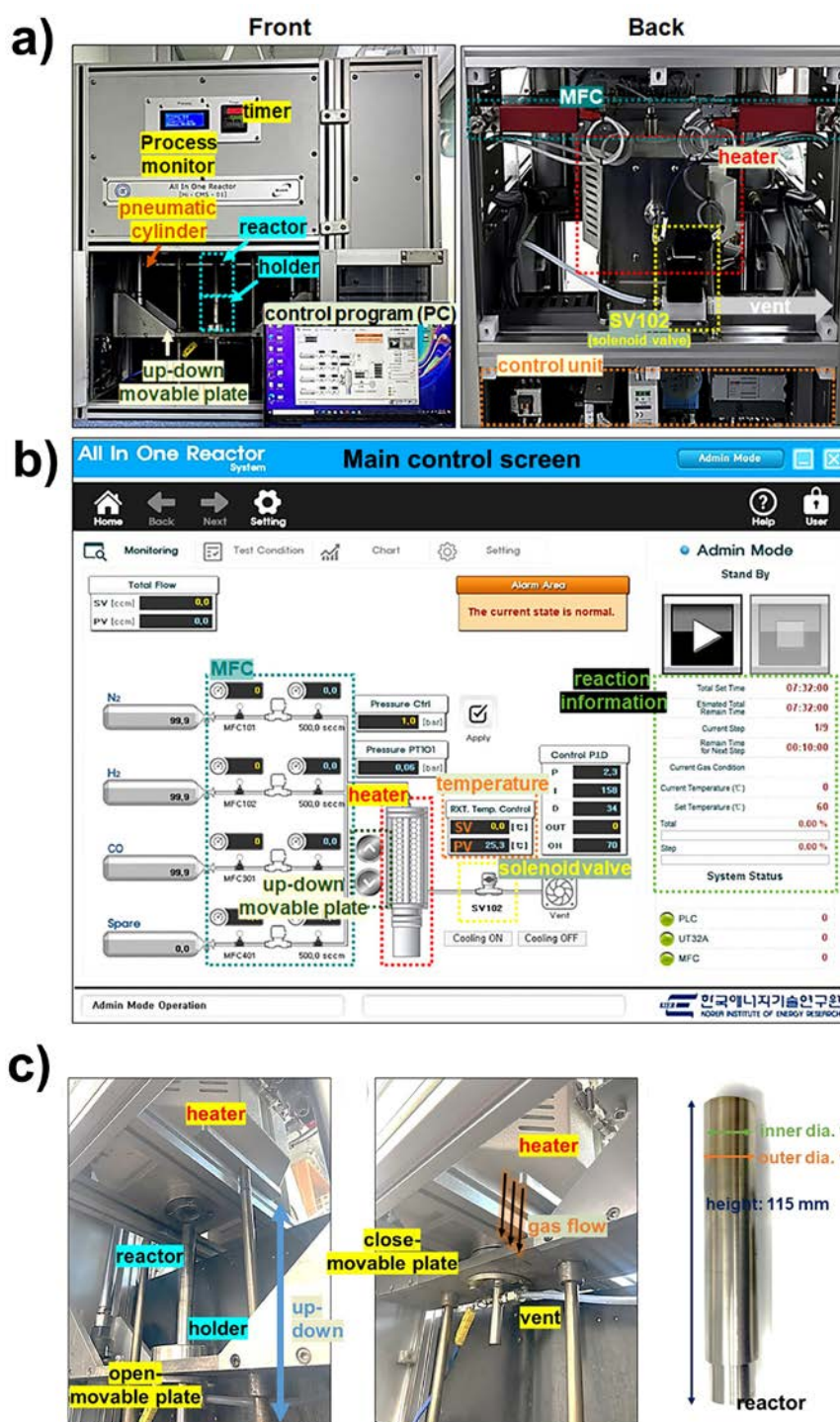


Figure S1. (a) Photographs of the AIO apparatus, (b) control program, and (c) the reactor and the loading system by a movable plate with a stainless steel reactor used for catalyst synthesis.

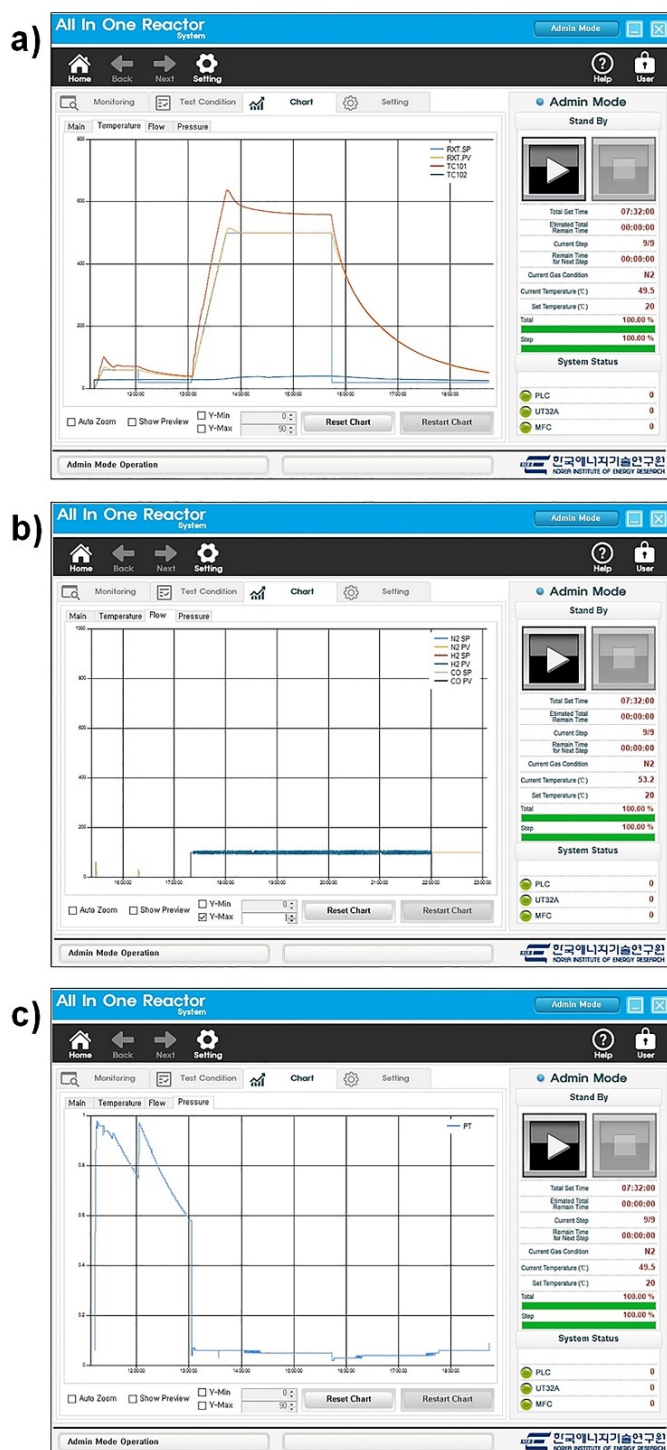


Figure S2. Screenshots in the control program for the real-time data (a: temperature, b: gas flow, c: pressure).

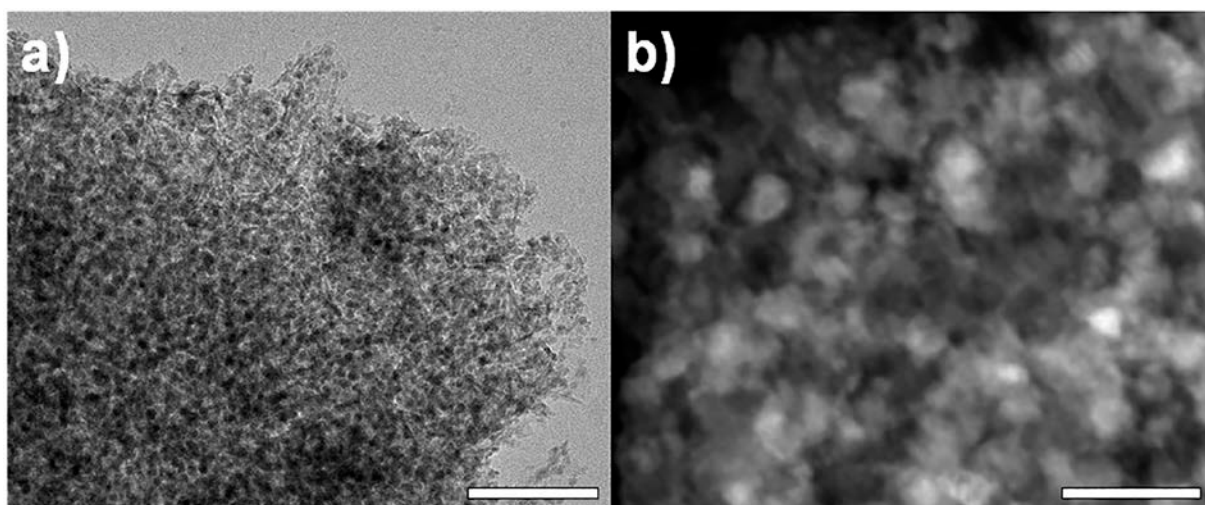


Figure S3. (a) Low-resolution TEM and (b) HAADF-STEM images of the U-(Cs)Ni/Al₂O₃ nanocatalyst. The bars represent 100 nm (a) and 20 nm (b).

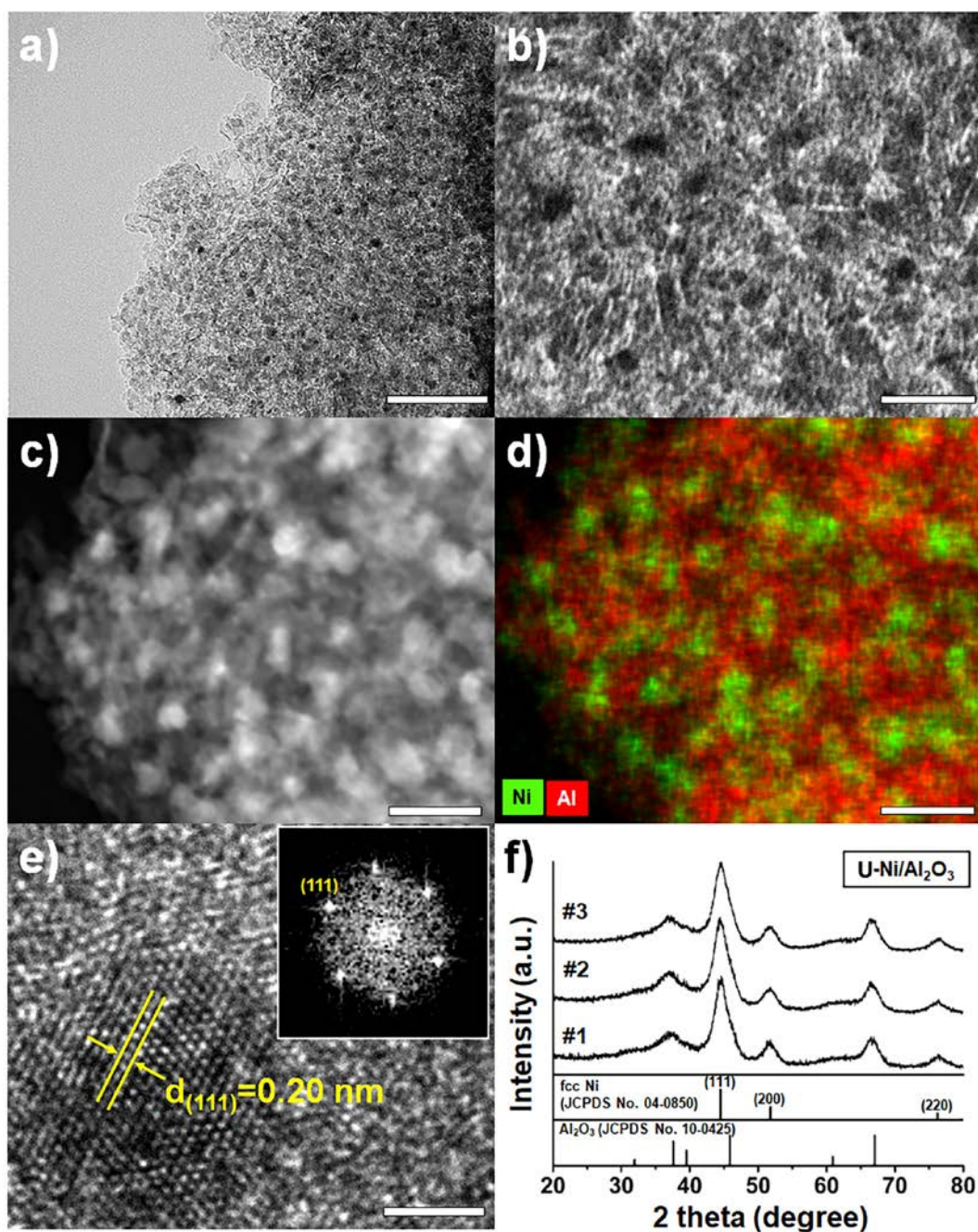


Figure S4. (a) Low-resolution and (b) magnified TEM images, (c) HAADF-STEM image, (d) elemental mapping image, and (e) HR-TEM image with corresponding FT pattern (inset of e) of U-Ni/Al₂O₃ nanocatalyst. (f) XRD spectra of the U-Ni/Al₂O₃ nanocatalysts in three different batches. The bars represent 100 nm (a), 20 nm (b-d), and 2 nm (e).

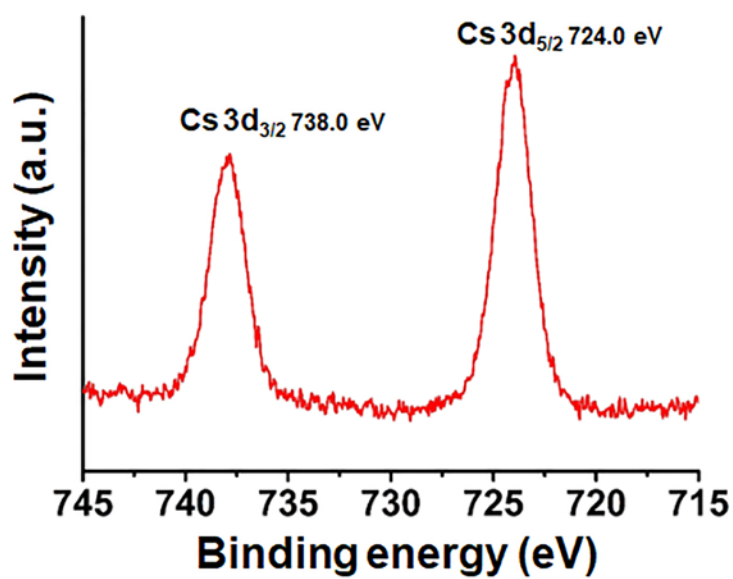


Figure S5. XPS spectrum in the energy region of the Cs 3d in U-(Cs)Ni/Al₂O₃ nanocatalyst.

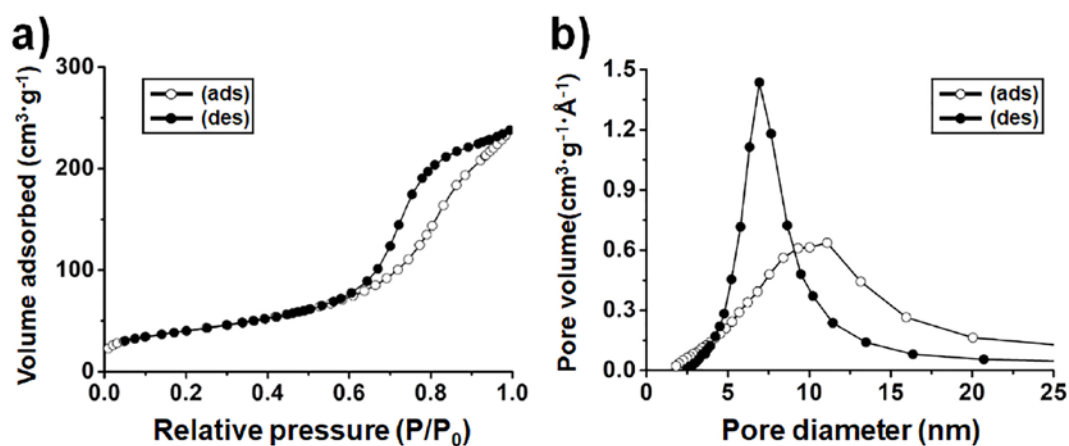


Figure S6. (a) N₂ sorption isotherms and (b) Pore size distribution diagram of the U-Ni/Al₂O₃ nanocatalyst.

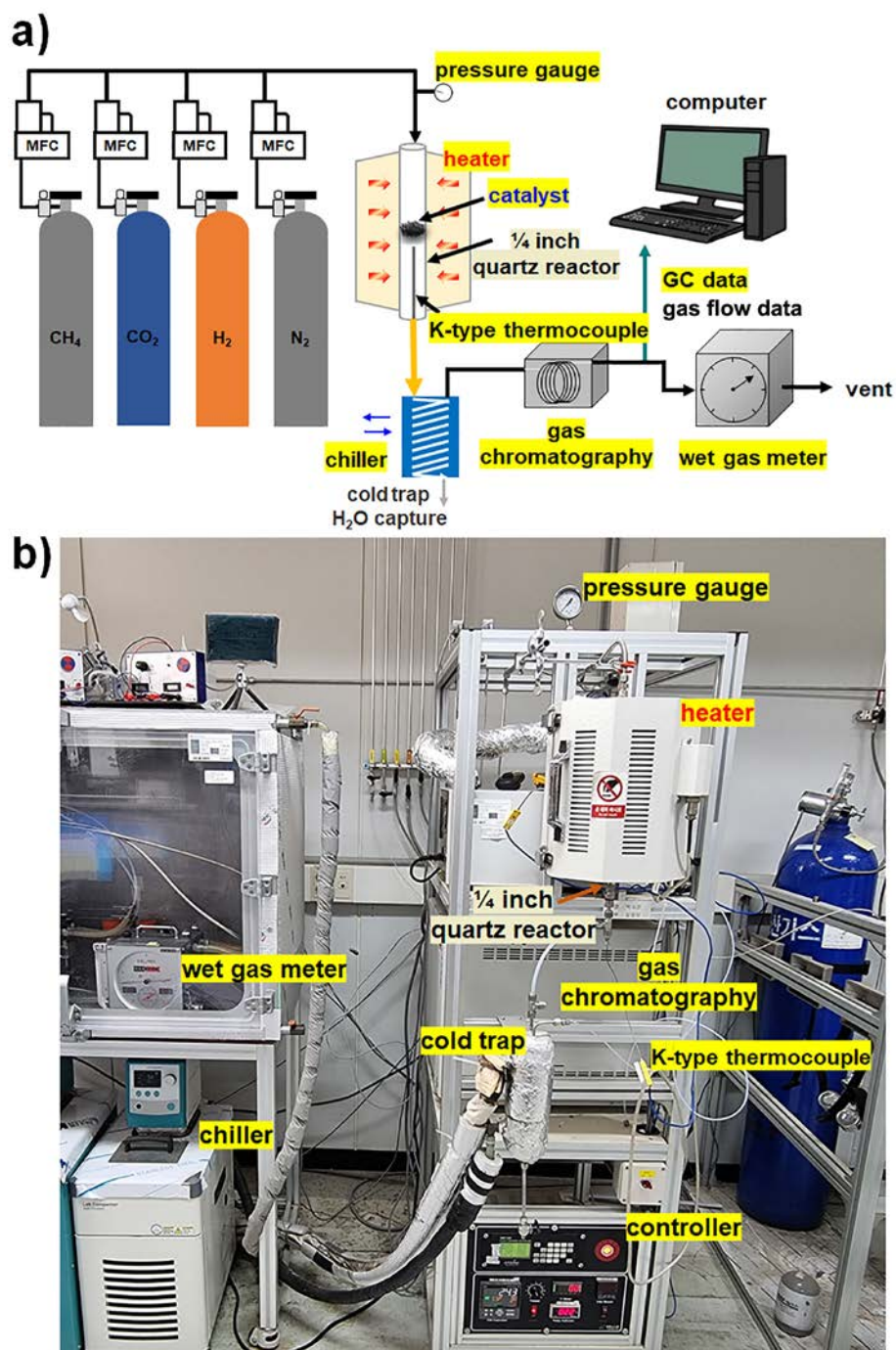


Figure S7. (a) Schematic diagram and (b) Picture of the DRM reaction system.

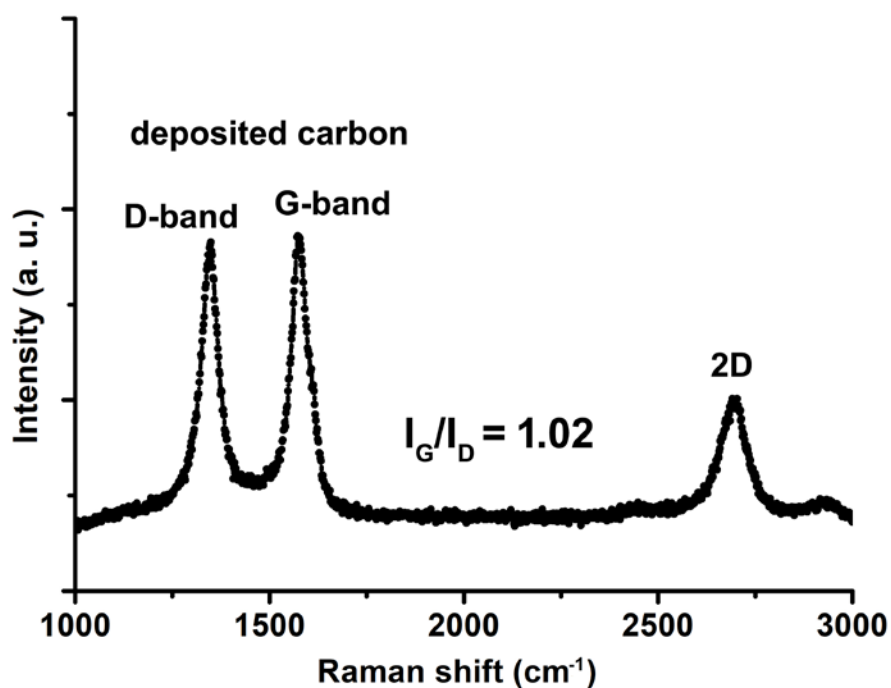


Figure S8. Raman spectrum of Cs-free U-Ni/Al₂O₃ nanocatalyst recovered after the DRM reaction under GHSV=72 NL·g_{cat}⁻¹·h⁻¹ at 800 °C.

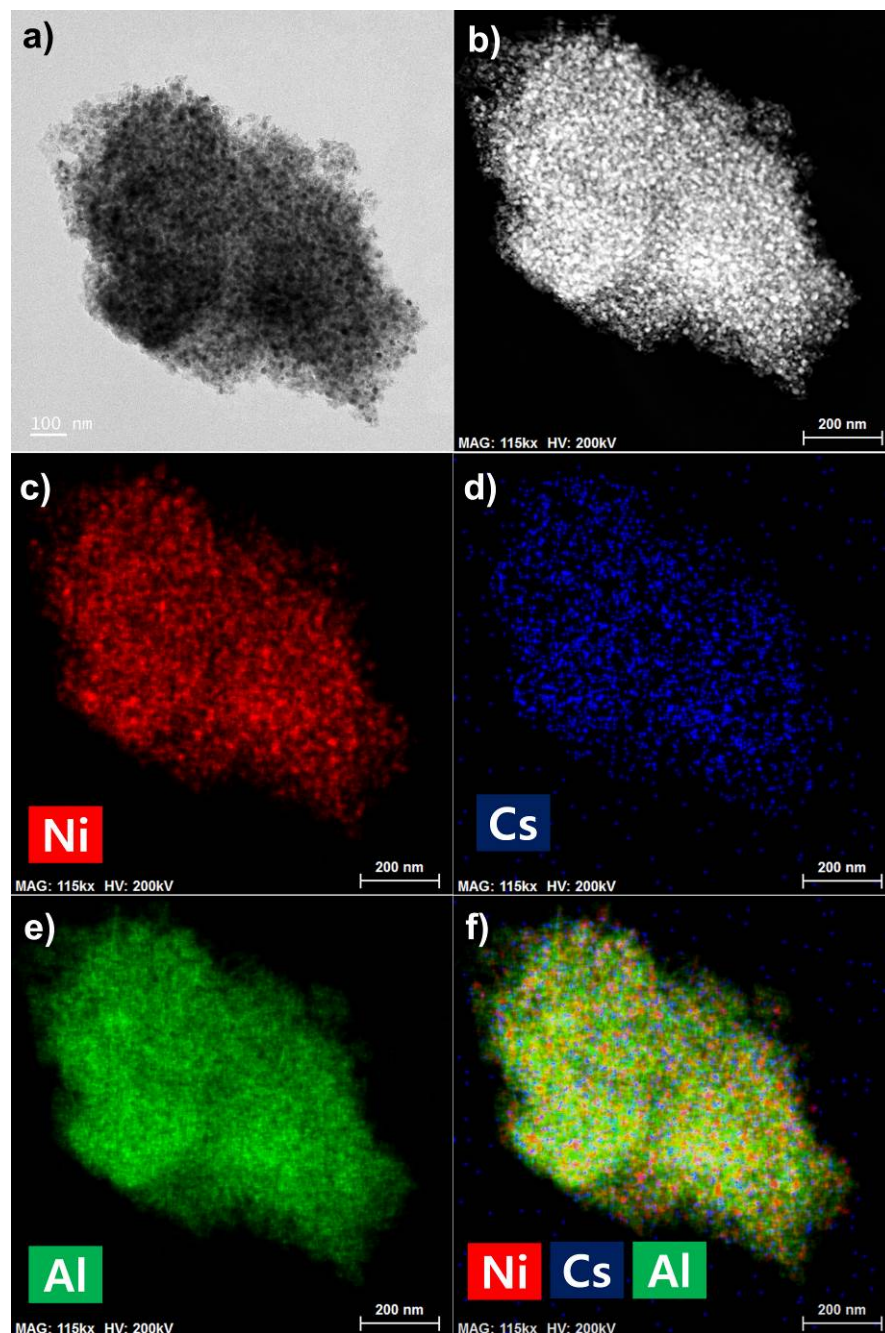


Figure S9. (a) TEM image, (b) HAADF-STEM image, and (c-f) elemental mapping images of the spent U-(Cs)Ni/Al₂O₃ nanocatalyst recovered after the DRM reaction under GHSV=72 NL·g_{cat}⁻¹·h⁻¹ at 800 °C.

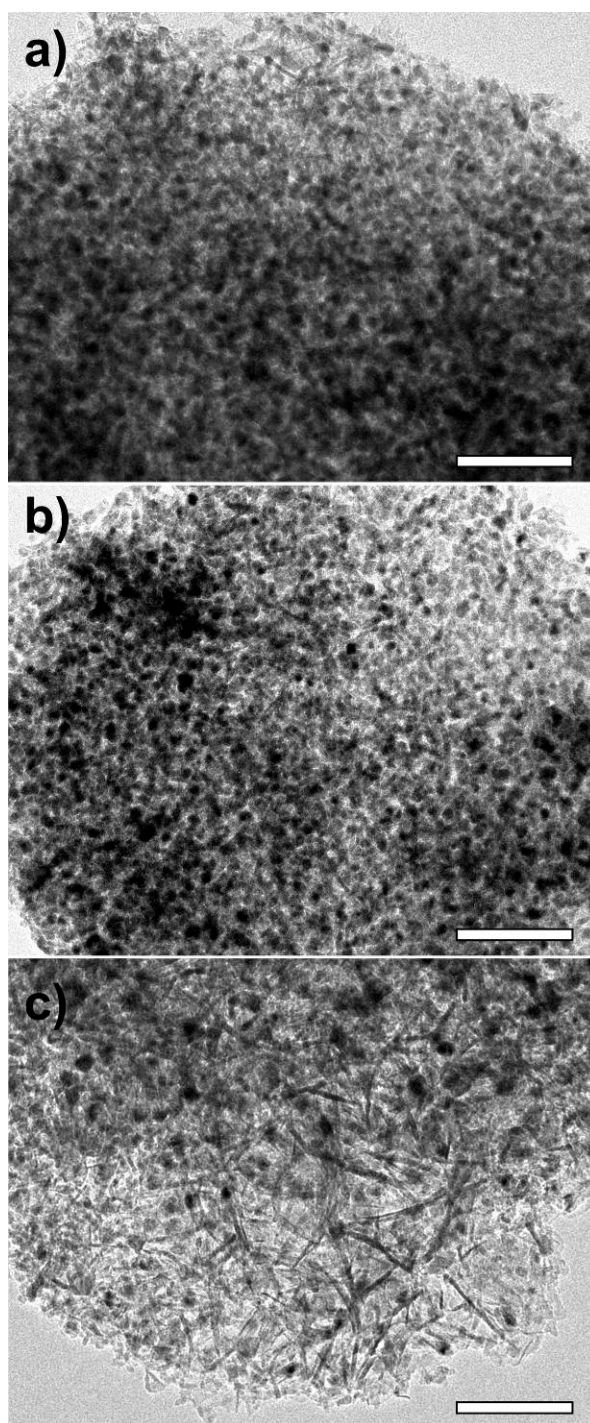


Figure S10. Low-resolution TEM images of (a) fresh U-(Cs)Ni/Al₂O₃ nanocatalyst, (b) U-(Cs)Ni/Al₂O₃ after thermal treatment under a H₂ flow at the reaction temperature (800 °C), and (c) recovered U-(Cs)Ni/Al₂O₃ after the DRM reaction under GHSV=72 NL·g_{cat}⁻¹·h⁻¹ at 800 °C. All bars represent 100 nm.

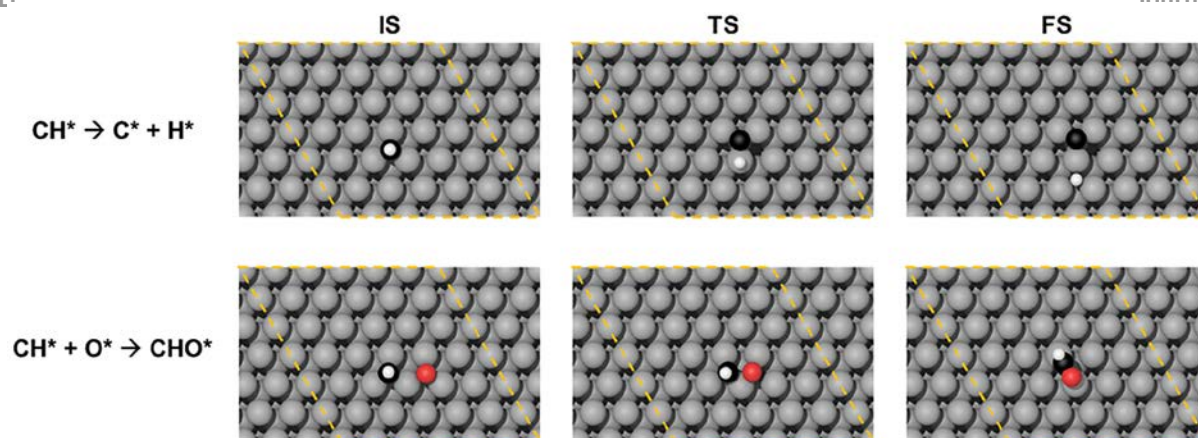


Figure S11. Geometry optimized structures of the CH^* dehydrogenation and oxidation steps for the bare Ni (111) surface. Grey, black, red, and white balls represent Ni, C, O, and H atoms, respectively. Yellow dashed lines in the atomic structures indicate the supercell used in this work.

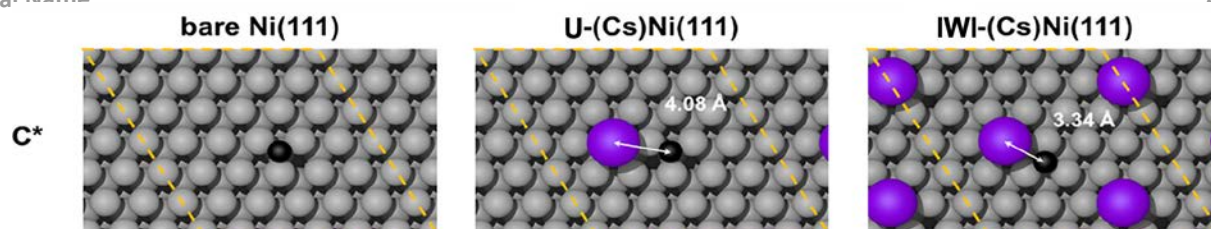


Figure S12. Geometry optimized structures for the most stable adsorption site of C on bare Ni (111), U-(Cs)Ni (111), and IWI-(Cs)Ni (111).

Table S1. An optimized sequence data for the synthesis of U-(Cs)Ni/Al₂O₃ nanocatalysts.^{a)}

Step conditions	1	2	3	4	5	6	7	8	9
Set Reaction Temp. (°C)	60	60	20	20	500	500	20	20	20
Time (min)	10	40	1	60	40	120	1	120	60
N ₂ flow (mL·min ⁻¹)	0	0	0	0	0	0	0	0	100
H ₂ flow (mL·min ⁻¹)	0	0	0	0	100	100	100	100	0
Stage	Aging			Heating		Calcination	Cooling		Purge

^{a)} The trend data with real-time monitoring during the whole synthesis procedure are shown in the attached movie S1.

Table S2. Comparison of Ni-based catalysts for dry reforming of methane at a reaction temperature of 800 °C.

Catalyst	GHSV (NL·g _{cat} ⁻¹ ·h ⁻¹)	CH ₄ /CO ₂ /inert gas	CH ₄ Conv. (%) ^a	CO ₂ Conv. (%) ^a	carbon deposition rate (mg _{carbon} ·g _{cat} ⁻¹ ·h ⁻¹)	ref.
U-(Cs)Ni/Al ₂ O ₃		1/1	89.8	91.8	4.7 (1.87 wt % loss in TGA)	
U-Ni/Al ₂ O ₃	72	1/1	86.9	88.5	30 (12.0 wt % loss in TGA)	This work
commercial Ni cat.		1/1	67.3	77.6	78.1 (31.2 wt % loss in TGA)	
Ni@Al ₂ O ₃ (Ni: 12 wt%)	36	1/1	86	82	3.0 (15.0 wt % loss in TGA)	[1]
Ni-Ca-4	14.4	1:1	52	96.7	42.9 (18.0 wt% loss in TGA)	[2]
La-Ni-1 (Ni: 9.6 wt%)	14.4	1:1	94.3	96.6	7.0 (5.6 wt% loss in TGA)	[3]
Ni@SiO ₂ (Ni: 18.6 wt%)	36	1/1/1	90	95	No carbon in TGA	[4]
Ni/Al ₂ O ₃ nanosheet-uncal (Ni: 10wt%)	108	1/1.05/1	92	95	280 (35 wt % loss in TGA)	[5]
0.5Ni/CeNi _x O _y (Ni: 15.1 wt%)	36	1/1/1	86.2	87.7	45 (47.1 wt% loss in TGA)	[6]
Ni@SiO ₂ /Al ₂ O ₃ /FeCrAl- fiber (Ni: 32.68 wt%)	5	1/1.1	90.8	89.9	No carbon in TGA	[7]
Ni/Al ₂ O ₃ -Y ₂ O ₃ -3%Nd ₂ O ₃ (Ni: 10.22wt%)	27	1/1/0.6	88.5	92.2	10.8 (6.47 wt% loss in TGA)	[8]

^a The conversion rates are obtained from the final data point of each reaction.

References

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Table S3. Calculated adsorption energy of each adsorbate and its corresponding most stable adsorption site during the DRM process for bare Ni (111), U-(Cs)Ni (111), and IWI-(Cs)Ni (111).

Adsorbate	Adsorption energy (eV) / Adsorption site		
	bare Ni (111)	U-(Cs)Ni (111)	IWI-(Cs)Ni (111)
CH ₃	−2.28 / <i>fcc</i> hollow	−2.21 / <i>fcc</i> hollow	−2.14 / <i>fcc</i> hollow
CH ₂	−4.31 / <i>fcc</i> hollow	−4.37 / <i>fcc</i> hollow	−4.34 / <i>fcc</i> hollow
CH	−6.74 / <i>fcc</i> hollow	−6.83 / <i>fcc</i> hollow	−6.81 / <i>fcc</i> hollow
C	−7.11 / <i>hcp</i> hollow	−7.18 / <i>hcp</i> hollow	−7.31 / <i>fcc</i> hollow
CHO	−2.38 / bridge	−2.47 / <i>hcp</i> hollow	−2.45 / atop
CO	−2.13 / <i>hcp</i>	−2.28 / <i>hcp</i> hollow	−2.47 / <i>fcc</i> hollow
CO ₂	−0.01 / bridge	−0.38 / bridge	−0.81 / bridge
O	−5.60 / <i>fcc</i> hollow	−6.03 / <i>fcc</i> hollow	−6.06 / <i>fcc</i> hollow
H	−2.95 / <i>fcc</i> hollow	−3.00 / <i>fcc</i> hollow	−3.01 / <i>fcc</i> hollow

Captions for Movie

Movie S1. In situ synthesis monitoring by the automated AIO reaction system from start to end.