Electronic Supplementary Information

NiRu Catalysts Supported on η-Al_2O_3 for Selective Methanation of CO in H_2-rich Gases

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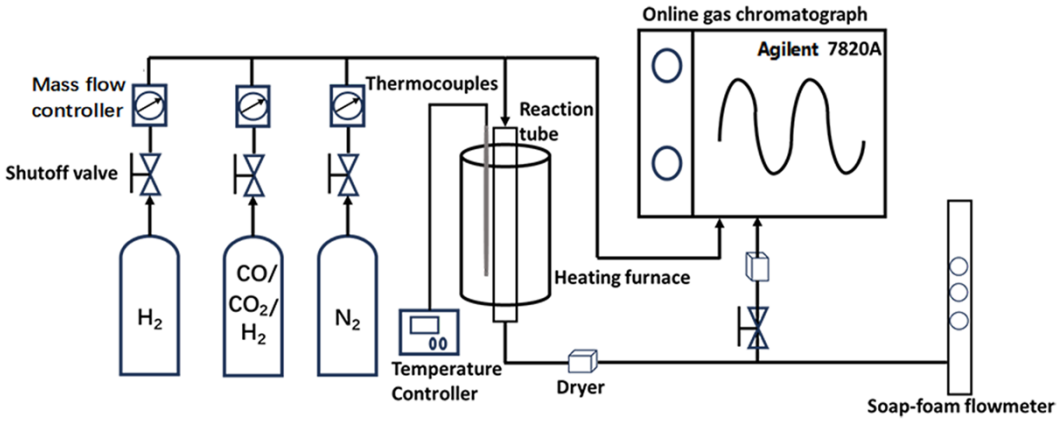

Figure S1 Overall experimental set-up diagram.

Table S1 The actual metal loading of NiRu/η-Al_2O_3 and NiRu/γ-Al_2O_3 confirmed by ICP-OES measurement.

Sample	**Ni loading (wt%)**	**Ru loading (wt%)**
NiRu/η-Al_2O_3	8.47	0.13
NiRu/γ-Al_2O_3	8.39	0.15

Table S2 Results from XRD, TEM and hydrogen chemisorption for the NiRu/η-Al_2O_3 and NiRu/γ-Al_2O_3.

Sample	d_{XRD}[a] (nm)	d_{TEM}[b] (nm)	H_2 take[c] (μmol/g)	D_{Ni}[d] (%)
NiRu/η-Al_2O_3	3.60	3.59	16.51	4.33
NiRu/γ-Al_2O_3	4.01	3.93	12.86	4.23

[a] Ni crystallite size was characterized using the Scherrer equation.

[b] Ni crystallite size was characterized using TEM.

[c] Determined by H_2 chemisorption experiment.

[d] The dispersion of Ni was quantified based on H_2 chemisorption experiment, assuming a 1:1 H:Ni stoichiometric ratio.

Table S3 Textural properties of η-Al_2O_3, γ-Al_2O_3, NiRu/η-Al_2O_3 and NiRu/γ-Al_2O_3.

Sample	**Specific surface area (m^2/g)**	**Average pore size (nm)**
η-Al_2O_3	200.84	3.97
γ-Al_2O_3	175.57	5.02
NiRu/η-Al_2O_3	136.74	4.73
NiRu/γ-Al_2O_3	119.41	7.42

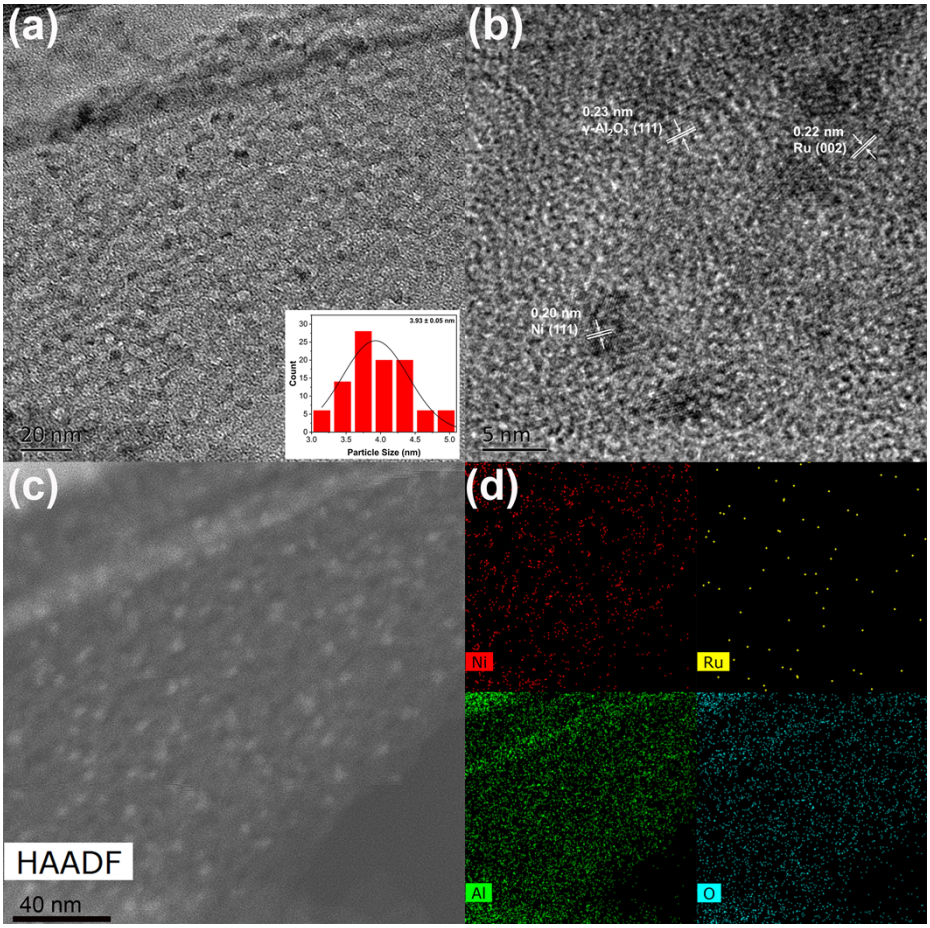

Figure S2 The TEM, HRTEM (along with its inset showing particle size distribution), HAADF-STEM, and EDX elementary mapping images of NiRu/γ-Al_2O_3 are presented in (a), (b), (c), and (d) respectively.

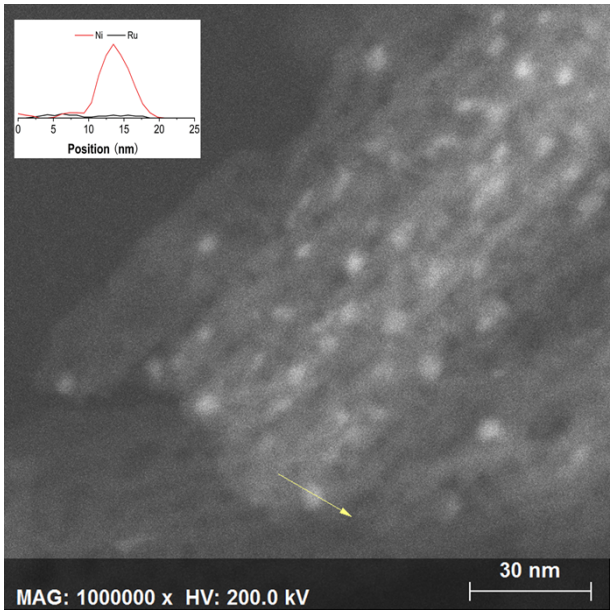

Figure S3 The elemental line-scanning image of NiRu/γ-Al_2O_3.

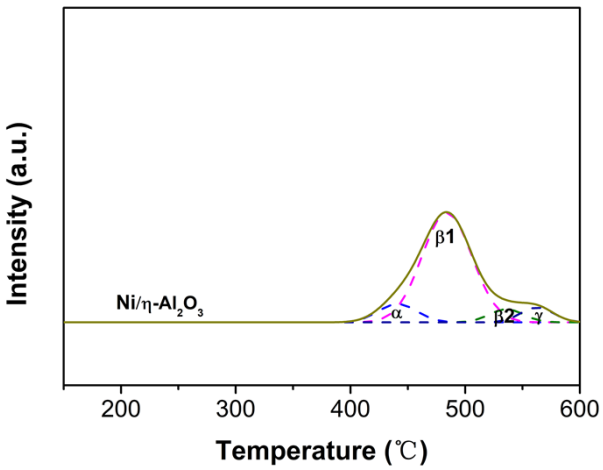

Figure S4 Profile of H_2-TPR for the Ni/η-Al_2O_3.

Table S4 The XPS analysis results of $Ni2p_{3/2}$ over the reduced $NiRu/Al_2O_3$ catalysts.

Sample	Ni^0 (eV)	Area (%)	Ni^{2+} (eV)	Area (%)	Satellite (eV)	Area (%)
NiRu/η-Al_2O_3	852.56	8.13	855.93	65.49	861.75	26.38
NiRu/γ-Al_2O_3	852.82	7.33	856.12	62.89	861.96	29.78

Table S5 The XPS analysis results of O 1s spectra of reduced NiRu/Al_2O_3 catalysts.

Catalyst	O_L (eV)	The area (%)	O_D (eV)	The area (%)	O_H (eV)	The area (%)
NiRu/η-Al_2O_3	531.01	15.46	532.13	66.32	533.54	18.22
NiRu/γ-Al_2O_3	531.12	21.84	532.04	62.12	533.43	16.04

Table S6 Summary has been conducted to compare the CO-SMET activities between the catalysts used in this work and those reported in previous studies.

Catalyst	WHSV [a] (ml/h/g)	SOTW [b]	CO (ppm)	Stability (h)	Reference
NiRu/η-Al_2O_3	6000	215-300	<10	120	This work
NiRu/γ-Al_2O_3	6000	-	40	-	This work
Ru-Ni/Al_2O_3	-	-	11	80	[1]
RuNi/GA-MMO	4000	220-300	<10	120	[2]
Ru-Ni/TiO_2	11000	-	50	-	[3]
Ni-Al_2O_3-Na	6000	240-320	-	-	[4]
Ni@Ru-La_2O_3/SiO_2	90000	-	-	350	[5]
Ni-Ru/HZSM-5		-	<50	72	[6]
Ni-Ru/SiO_2 (EG)	40000	-	-	50	[7]
MRNAT-30Ni	4800	-	<50	200	[8]
Ru/NiAl	2400	-	13	-	[9]
Ru/ $NiAl_xO_y$	-	-	13	-	[10]

[a] A total weight hourly space velocity.

[b] The suitable operating temperature window, in which the effluent CO concentration lower than 10 ppm and a CO selectivity greater than 50%.

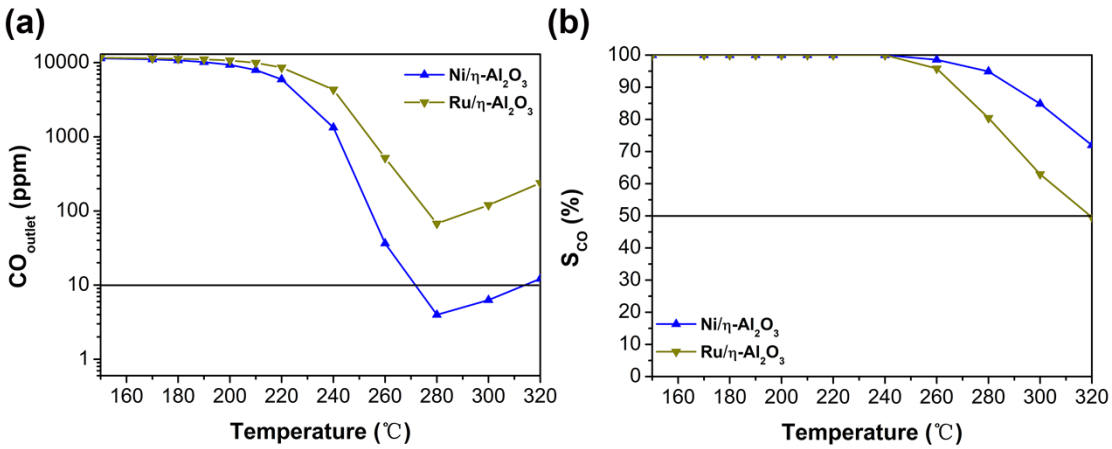

Figure S5 The CO outlet concentration (a) and the selectivity of CO methanation (b) of Ni/η-Al_2O_3 and Ru/η-Al_2O_3 catalysts.

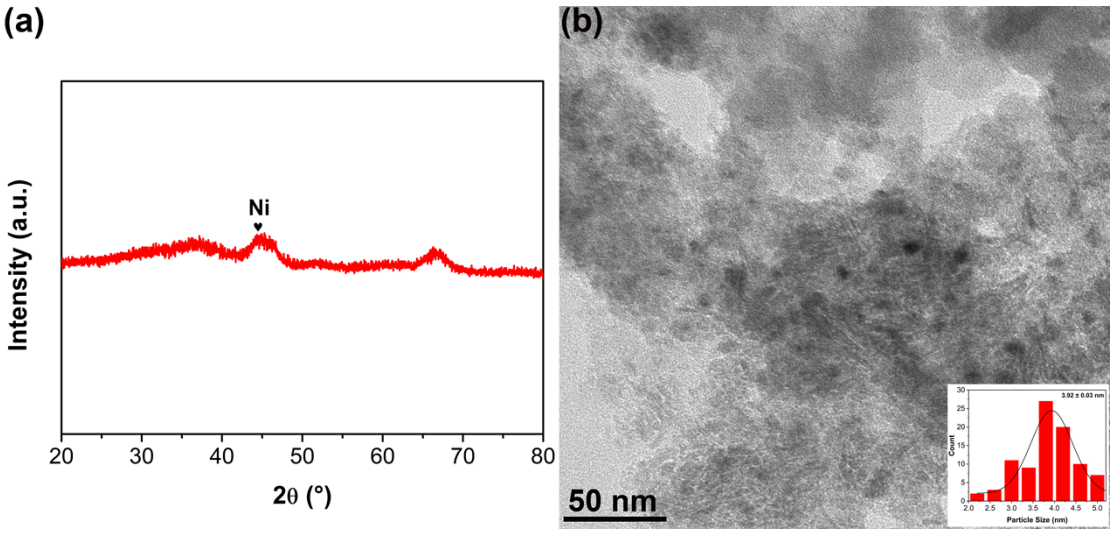

Figure S6 (a) The XRD profile and (b) TEM image of spent NiRu/η-Al_2O_3 after 120 hours stability test at 240 °C.

References

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