

Supporting information for

Sustainable Syngas Generation from Methane: Enhanced Catalysis with Metal-Promoted Nickel on Silica-Alumina Composites

Ahmed S. Al-Fatesh^{*1}, Ahmed A. Ibrahim^{1*}, Mohammed O. Bayazed¹, Ahmed E. Abasaheed¹, Maher M. Alrashed¹, Mohammed F. Alotibi², Anis H. Fakeeha¹, Ahmed I. Osman^{3*}

¹Chemical Engineering Department, College of Engineering, King Saud University P.O. Box 800, Riyadh 11421, Saudi Arabia.

²Institute of Refining and Petrochemicals Technologies King Abdulaziz City for Science and Technology (KACST) P.O. Box 60, Saudi Arabia.

³School of Chemistry and Chemical Engineering, Queen's University Belfast, Northern Ireland, Belfast, UK

*Correspondence: aalfaesh@ksu.edu.sa (A.S.A-F): aidid@ksu.edu.sa (A.A.I)

and aosmanahmed01@qub.ac.uk (A. I. O)

Selection of 1 wt.% promoter loading S1

Promoters have a significant impact on the interaction between the active metal and the support material, which improves the performance of catalysts. By altering the catalyst's surface characteristics, promoters can enhance the stability, selectivity, and activity of the catalyst in catalytic processes. A 1% loading of a promoter in catalysts is a well-founded choice that combines real-world knowledge with ideas from literature verification ^{1,2,3}.

This strategic decision is especially important when dealing with noble metals, which are valued for their rare qualities and high cost. The performance of the catalyst can be greatly increased by adding a small amount of promoter, such as noble metals like rhodium, platinum, and palladium. Furthermore, improved dispersion and control over the catalytic effects on the catalyst surface are made possible by the exact addition of a small percentage of promoter material, guaranteeing excellent performance free from needless complications. All things considered, the decision to load a promoter at 1% is a well-rounded strategy that draws on both real-world knowledge and academic research to produce a catalyst design that is both efficient and profitable.

Catalyst Characterization S2

The study involved analyzing promoted Ni-based catalysts through various techniques. X-ray diffraction (XRD) patterns were obtained using a Miniflex Rigaku diffractometer, utilizing Cu-K X-ray radiation with an operating voltage of 40 kV and a current of 40 mA. Nitrogen sorption isotherms were determined at -196 °C using a Micromeritics Tristar II 3020 surface area and porosity analyzer after outgassing the samples at 250 °C for 3 hours to eliminate any adsorbed gases or vapors. The pore size distributions of the samples were assessed based on the adsorption profiles of isotherms, employing the Barrett–Joyner–Halenda (BJH) model. Hydrogen temperature-programmed reduction (H₂-TPR) was conducted on the freshly synthesized catalysts. This analysis covered a temperature range of 50–800 °C and utilized a mixture of 10% H₂/Ar with a flow rate of 40 mL/min in the TPR analysis. The formation of coke and the amount of carbon deposits on the catalyst surfaces were quantified using a thermogravimetric analyzer (Shimadzu-TGA). The

samples were heated up to 1000 °C while ramping up the temperature at 10 °C/min, and weight losses were recorded. To assess the extent of graphitization of the carbon deposits on the used catalysts, laser Raman spectroscopy with an NMR-4500 instrument was employed. This measurement utilized a 5x magnification objective lens and a beam excitation wavelength of 532 nm, with spectra recorded within the 1350–1600 cm^{-1} range. To determine how much carbon had been deposited on the catalyst sample that was being used, a thermogravimetric analysis was performed at the end of the reaction. A Shimadzu TGA thermogravimetric/differential analyzer was used for the analysis. Ten milligrams of the samples were heated at a rate of twenty degrees Celsius per minute from room temperature to 1000 degrees Celsius, and the weight change was noted as the temperature increased⁴.

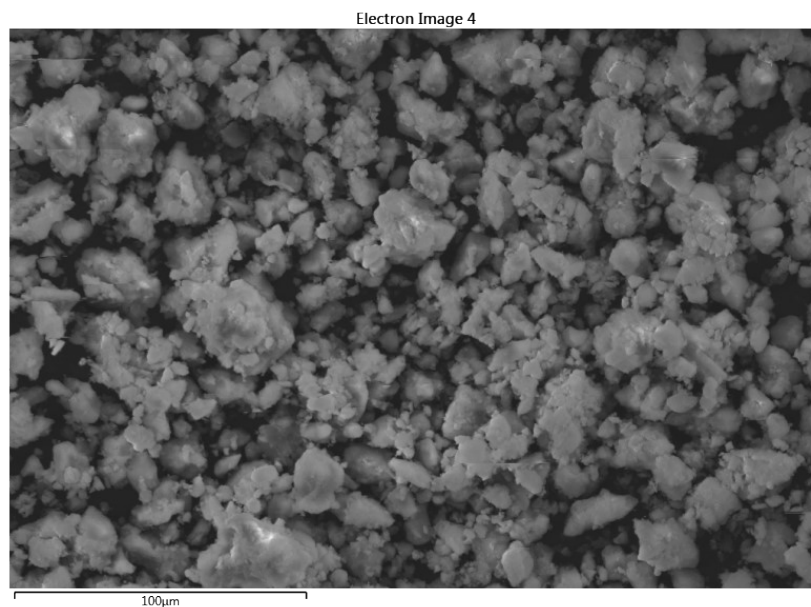


Figure S1 SEM of the fresh NiRh/SiAl catalyst

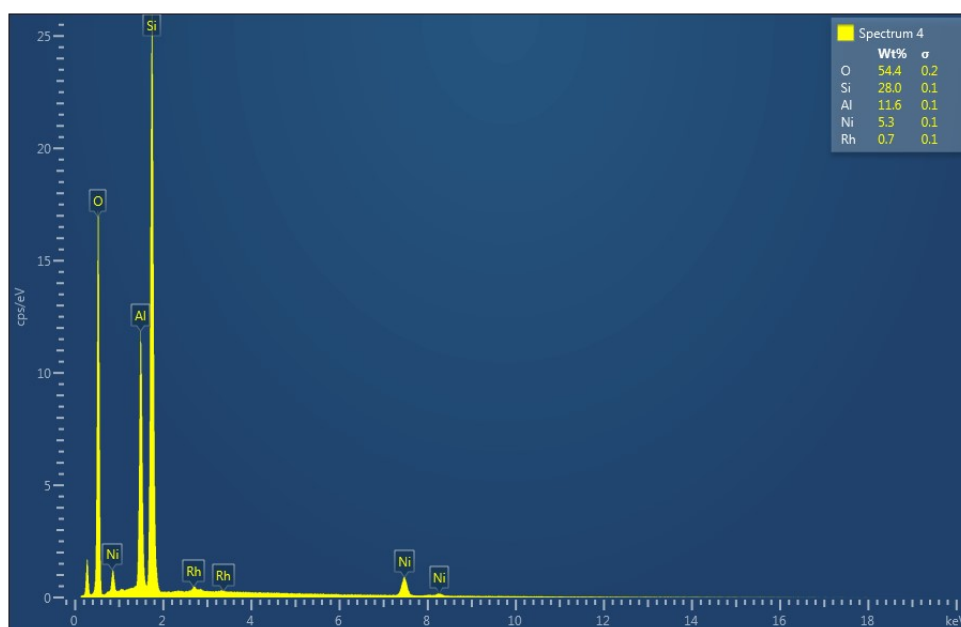


Figure S2 Composition of NiRh/SiAl catalyst as per EDX analysis

Table S1 is provided showing the various % average conversion of the investigated catalysts in this work operated at 700°C.

Catalyst Sample	% Conversion ^a	
	CH ₄	CO ₂
NiIr/SiAl	38.8	44.3
NiPd/SiAl	39.2	43.7
NiPt/SiAl	43.2	50.6
NiRh/SiAl	65.2	71.5
NiRu/SiAl	46.3	57.5

Table S2 Compares the findings of this study with those previously published for Ni-based catalyst systems promoted by noble and non-noble metals.

Catalyst	CA (mg)	F	Cg	RT (°C)	TOS (h.)	C(CH ₄) %	Ref.
5Ni1Cu/Al	100	3:3	1	700	7	80	[1]

5 Ni-Na/MCM-41	60	1:1	1	700	4	40	[5]
5Ni1Zn/Al	100	3:3	1	700	7	79	[1]
5Ni1Gd/Al	100	3:3	1	700	7	76	[1]
10Ni1Mn/ ZrO ₂	30	1:1	6	650	3.5	20	[6]
1Ni1Mn/Al ₂ O ₃	10	1:1	2	650	3.5	38	[3]
1Ni1Mn/Al ₂ O ₃	10	1:1	2	650	6	34	[3]
1Ni1Fe/ Al ₂ O ₃	10	1:1	2	650	12	30	[3]
Ce-NiCu/EXVTM-SiO ₂	120	1.3:1.3	1	750	2.5	50	[7]
	100	1:1	0.5	700	7.5	65	This work
NiRh/SiAl	100	1:1	0.5	800	7.5	87	This work

References

- (1) Fakeeha, A. H.; Bagabas, A. A.; Lanre, M. S.; Osman, A. I.; Kasim, S. O.; Ibrahim, A. A.; Arasheed, R.; Alkhalifa, A.; Elnour, A. Y.; Abasaeed, A. E.; Al-Fatesh, A. S. Catalytic Performance of Metal Oxides Promoted Nickel Catalysts Supported on Mesoporous γ -Alumina in Dry Reforming of Methane. *Process. 2020, Vol. 8, Page 522* **2020**, 8 (5), 522. <https://doi.org/10.3390/PR8050522>.
- (2) Franz, R.; Franz, R.; Kühlewind, T.; Shterk, G.; Abou-Hamad, E.; Parastaev, A.; Uslamin, E.; Hensen, E. J. M.; Kapteijn, F.; Gascon, J.; Pidko, E. A. Impact of Small Promoter Amounts on Coke Structure in Dry Reforming of Methane over Ni/ZrO₂. *Catal. Sci. Technol.* **2020**, 10 (12), 3965–3974. <https://doi.org/10.1039/d0cy00817f>.
- (3) Franz, R.; Pinto, D.; Uslamin, E. A.; Urakawa, A.; Pidko, E. A. Impact of Promoter Addition on the Regeneration of Ni/Al₂O₃ Dry Reforming Catalysts. *ChemCatChem* **2021**, 13 (23), 5034–5046. <https://doi.org/10.1002/cctc.202101080>.
- (4) Al-Fatesh, A. S.; Arafat, Y.; Kasim, S. O.; Ibrahim, A. A.; Abasaeed, A. E.; Fakeeha, A. H. In Situ Auto-Gasification of Coke Deposits over a Novel Ni-Ce/W-Zr Catalyst by Sequential Generation of Oxygen Vacancies for Remarkably Stable Syngas Production via CO₂-Reforming of Methane. *Appl. Catal. B Environ.* **2021**, 280 (August 2020), 119445. <https://doi.org/10.1016/j.apcatb.2020.119445>.
- (5) Nisa, K. S.; Suendo, V.; Sophiana, I. C.; Susanto, H.; Kusumaatmaja, A.; Nishiyama, N.; Budhi, Y. W. Effect of Base Promoter on Activity of MCM-41-Supported Nickel Catalyst for Hydrogen Production via Dry Reforming of Methane. *Int. J. Hydrogen Energy* **2022**, 47 (55), 23201–23212. <https://doi.org/10.1016/j.ijhydene.2022.05.081>.

- (6) Franz, R.; Franz, R.; Kühlewind, T.; Shterk, G.; Abou-Hamad, E.; Parastaev, A.; Uslamin, E.; Hensen, E. J. M.; Kapteijn, F.; Gascon, J.; Pidko, E. A. Impact of Small Promoter Amounts on Coke Structure in Dry Reforming of Methane over Ni/ZrO₂. *Catal. Sci. Technol.* **2020**, *10* (12), 3965–3974. <https://doi.org/10.1039/D0CY00817F>.
- (7) Meng, Z.; Wang, Z. The Effect of Different Promoters (La₂O₃, CeO₂, and ZrO₂) on the Catalytic Activity of the Modified Vermiculite-Based Bimetallic NiCu/EXVTM-SiO₂Catalyst in Methane Dry Reforming. *ACS Omega* **2021**, *6* (44), 29651–29658. <https://doi.org/10.1021/acsomega.1c03959>.