

Table S1. Compositions of different pure catalysts.

Catalyst	Metal content (wt%)				
	Mn	Na	W	La	Mg
La/MgO	--	--	--	3.02	40.80
MnNaWSi	1.28	0.62	2.09	--	--

Table S2. Expected catalytic performance of stacked 10 wt% catalyst based on performance of single components and their mass composition.

	La ₂ O ₃	MgO	MnNaWSi	La/MgO-MnNaWSi_0.1s
Composition of stacked catalyst [mg]	0.18	4.82	45	-
Measured CH ₄ conversion [%]	22.5	14	6	21
Measured C ₂ selectivity [%]	37	14.6	48	50
Predicted CH ₄ conversion based on stacked catalyst [%] composition				6.8
Predicted C ₂ selectivity based on stacked catalyst [%] composition				45

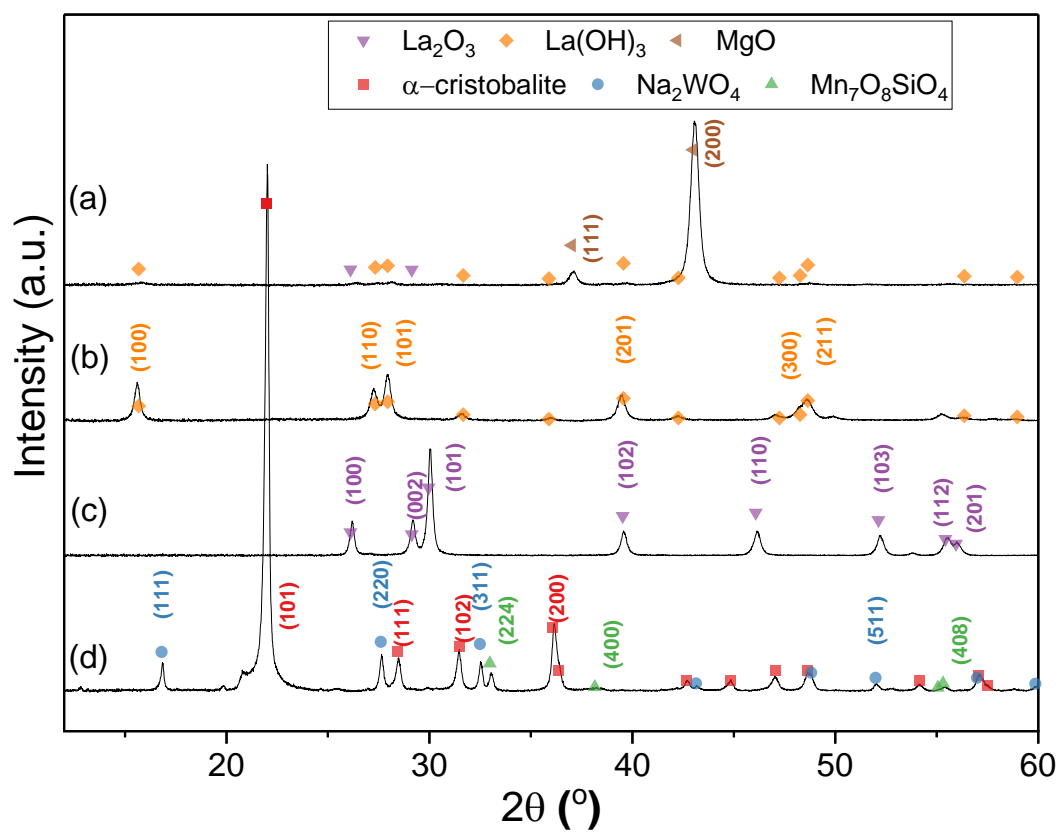


Figure S1. XRD patterns for the original catalysts, (a) La/MgO; (b) La_2O_3 (after exposure to ambient air); (c) La_2O_3 (fresh); (d) MnNaWSi.

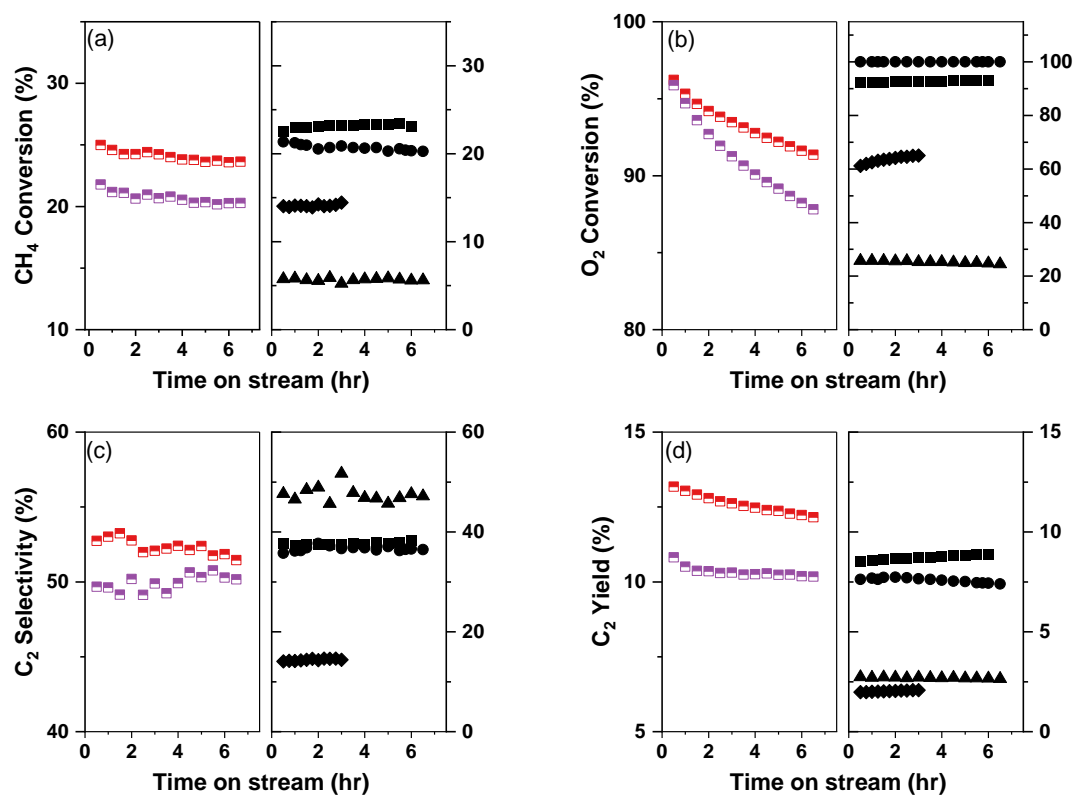


Figure S2. Catalytic performance of La₂O₃ or La/MgO bed stacking over MnNaWSi bed at 725°C.

■ La₂O₃-MnNaWSi_0.1s ■ La/MgO-MnNaWSi_0.1s ● La/MgO ■ La₂O₃ ▲ MnNaWSi ◆ MgO

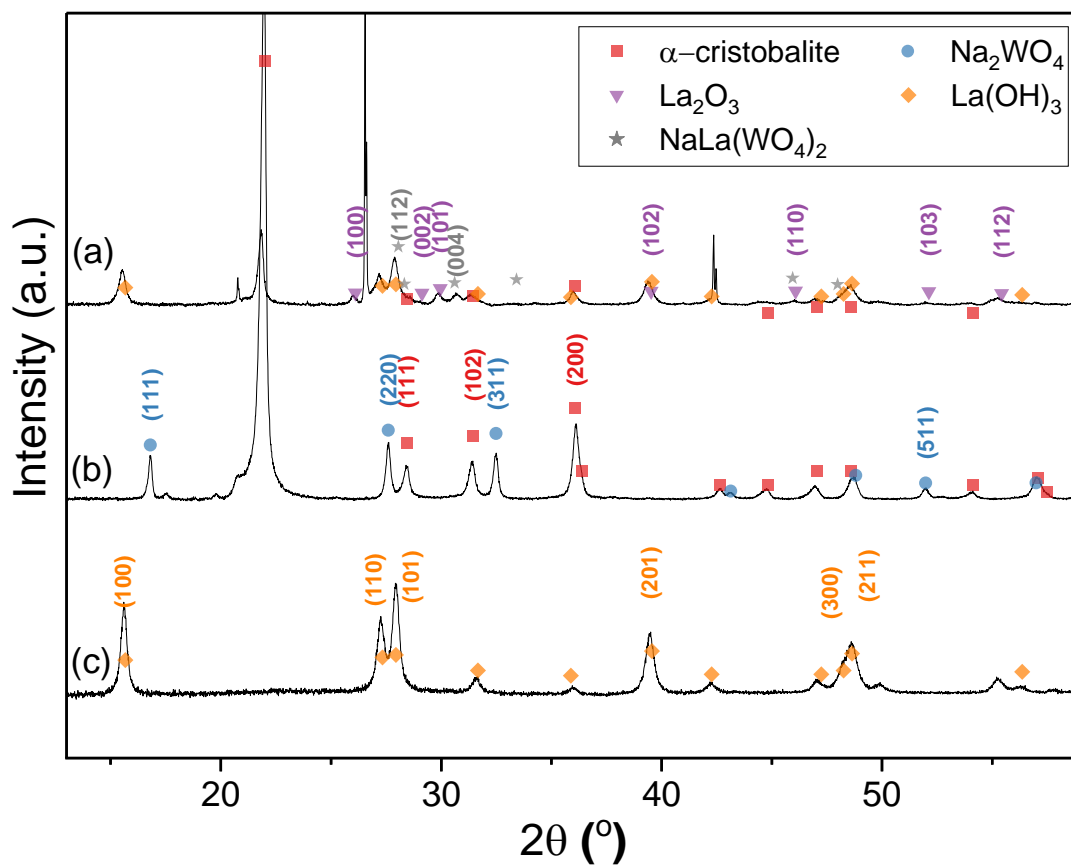


Figure S3. XRD patterns: (a) Spent $\text{La}_2\text{O}_3\text{-NaWSi}_{0.8\text{m}}$ bed reacted for 14 hours at 675 - 725 °C; (b) Fresh NaWSi catalyst; (c) Fresh La_2O_3 catalyst.

* The sharp peaks at 20.76°, 26.53° and 42.36° are assigned to the inert quartz sand in the mixture.

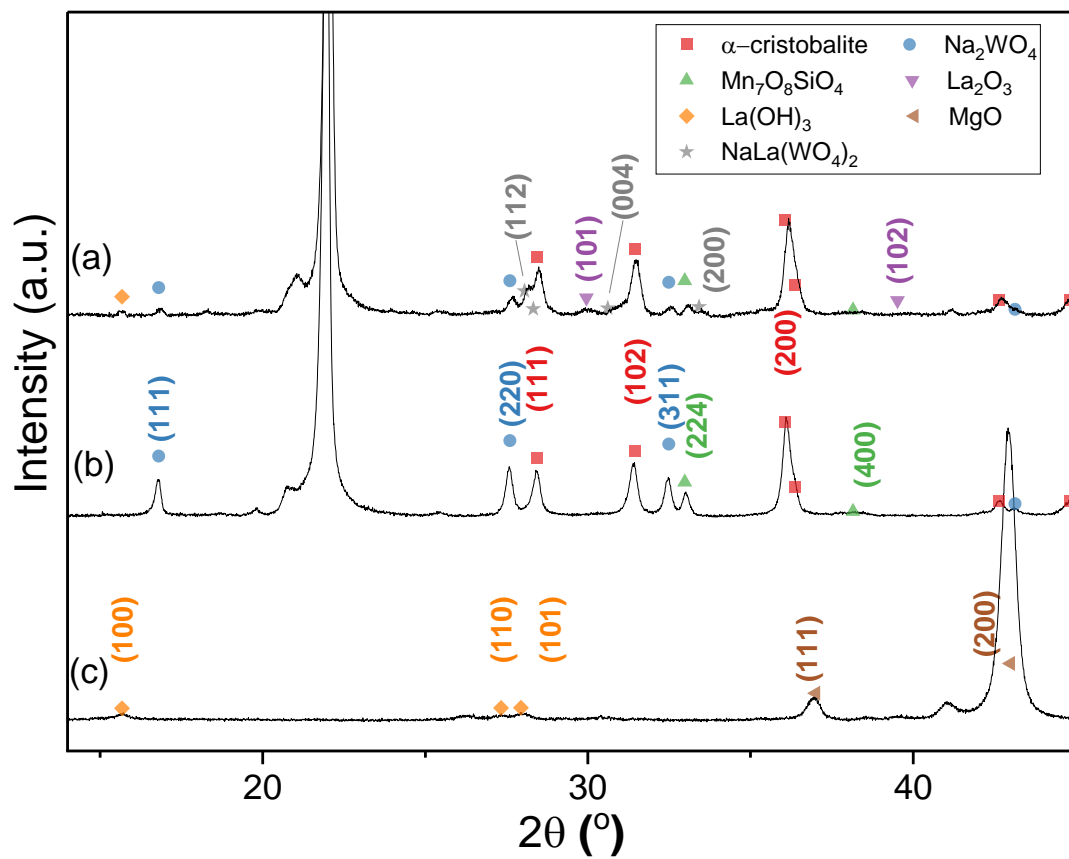


Figure S4. XRD patterns: (a) Spent La/MgO-MnNaWSi_{0.1m} bed, reacted for 14 hours at 725-750 °C; (b) Fresh MnNaWSi catalyst; (c) Fresh La/MgO catalyst.

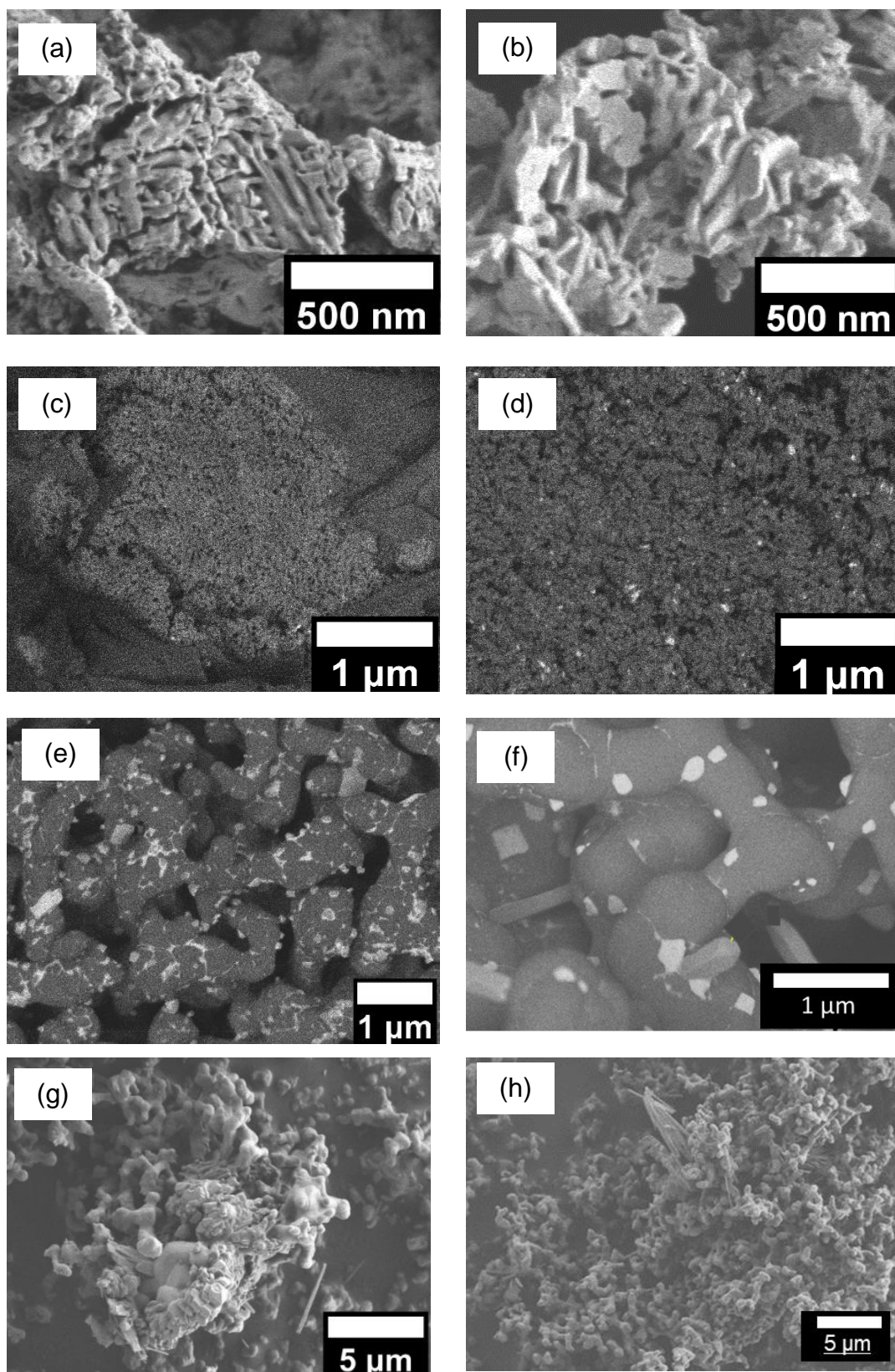


Figure S5. HR-SEM images of fresh and spent catalysts: (a) fresh bulk La_2O_3 ; (b) Spent La_2O_3 ; (c) fresh La/MgO ; (d) Spent La/MgO ; (e) fresh MnNaWSi ; (f) spent MnNaWSi ; (g) spent $\text{La/MgO-MnNaWSi}_{0.1s}$; (h) spent $\text{La/MgO-MnNaWSi}_{0.1m}$. The images for the spent catalysts were taken after 14-20 h of reaction at 725-750 °C.

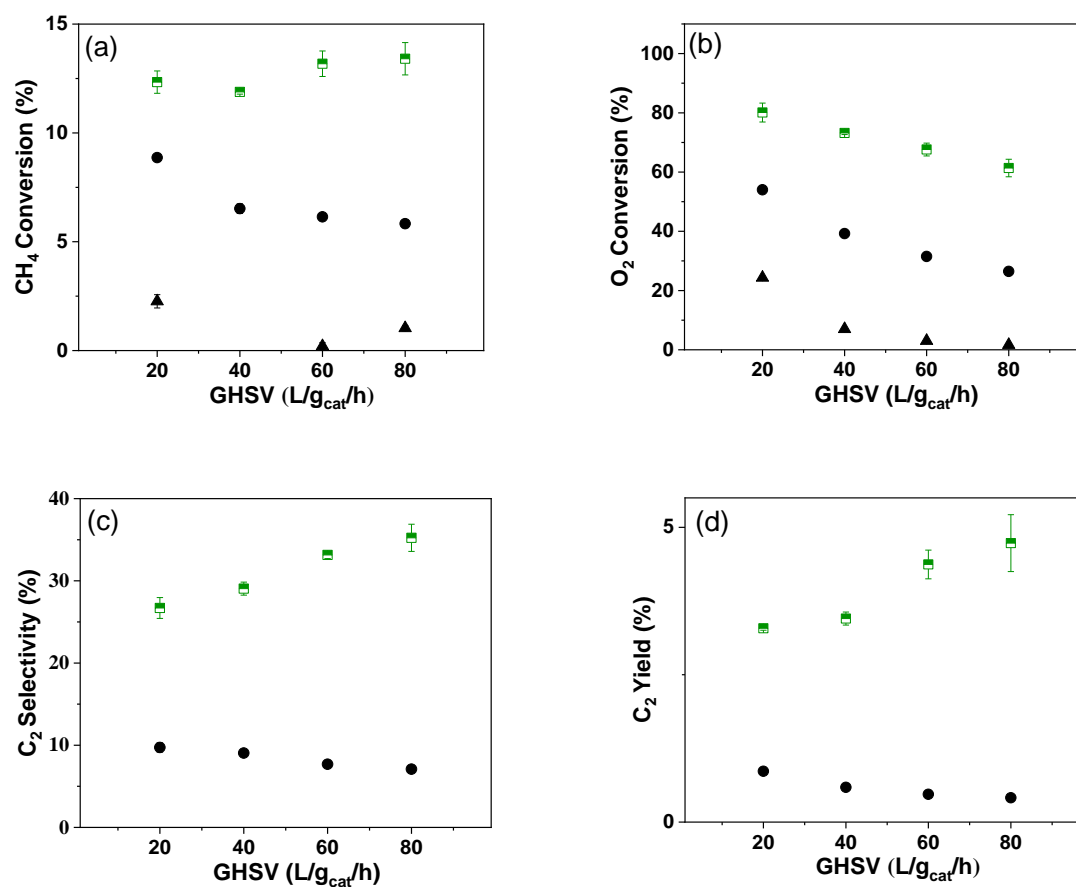


Figure S6. Catalytic performance over a range of GHSV (20-80 L g⁻¹ h⁻¹) at T = 675 °C; 50 mg catalyst; Catalyst bed 5 mm; molar ratio of CH₄:O₂:N₂:Ar = 4:1:1:4 and ~1.3 bar. To retain the same bed size we replaced part of the domains with quartz particles.

(La/MgO-MnNaWSi_{0.1}s, La/MgO and 7MnNaWSi

* Note, the 7MnNaWSi did not show measurable C₂ selectivity and yield under the current reaction condition.