Active and Stable Ru and Ni-based Catalysts for CO_2 Reforming of Glycerol to Syngas

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Motivation and Aim

- Utilization of glycerol (G) and carbon dioxide (CO_2)
- **Glycerol:** Continuously accumulating side product of biodiesel synthesis
- **CO_2:** Global warming effects due to its accumulation
- Dry reforming of glycerol to produce synthesis gas (H_2/CO) at ratios ≈ 1
- Ru-based catalysts: High activity and stability in dry reforming conditions of various hydrocarbons, one of the cheapest precious metals
- Ni-based catalysts: High activity in hydrocarbon reforming and cheaper than precious metals

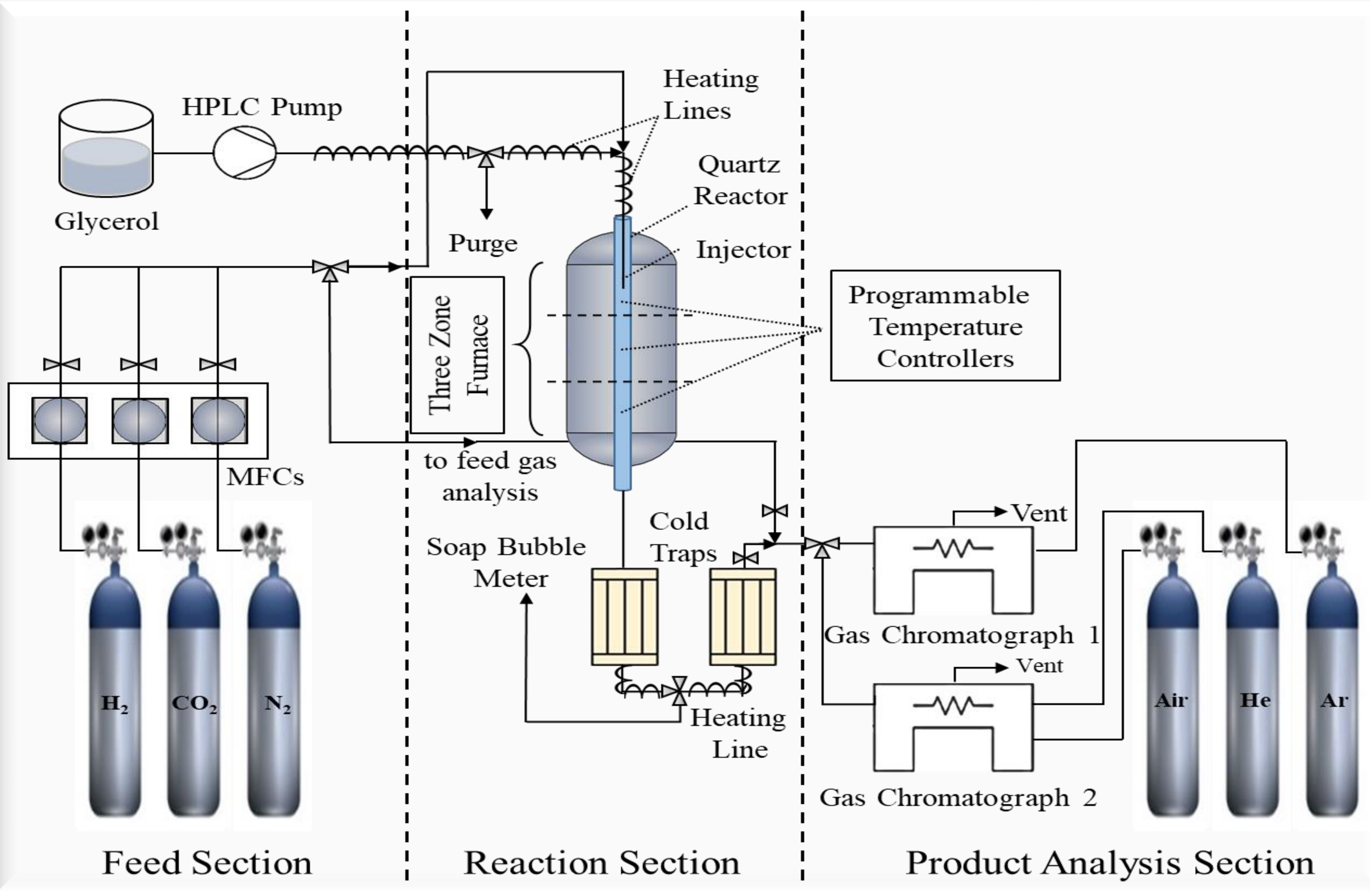
Possible Reaction Network

Reaction		ΔH° (kJ/mol)
Glycerol Dry Reforming	$C_3H_8O_3 + CO_2 \rightarrow 4CO + 3H_2 + H_2O$	292
Glycerol Decomposition	$C_3H_8O_3 \rightarrow 3CO + 4H_2$	251
Reverse Water Gas Shift	$CO_2 + H_2 \rightarrow CO + H_2O$	41
Methane Steam Reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	206
Methane Dry Reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247
Coke Gasification	$C_{(s)} + H_2O \rightarrow CO + H_2$	131
Coke Gasification	$C_{(s)} + 2H_2O \rightarrow CO_2 + 2H_2$	90
Reverse Boudouard Reaction	$C_{(s)} + CO_2 \rightarrow 2CO$	172

Catalyst Preparation

- Supports: ZrO_2 (Z, Alfa Aesar, >99% purity), La_2O_3 (L, Sigma-Aldrich, 99.99% purity), La_2O_3-ZrO_2 (LZ, Daiichi Kigenso, 9 wt.% La_2O_3)
- Preparation of the 1 wt.% Ru-based (Ru/L, Ru/Z, Ru/LZ) and 5 wt.% Ni-based (Ni/L, Ni/Z, Ni/LZ) catalysts by incipient wetness impregnation method followed by calcination at 800 °C under air for 4 h
- Prior to reaction tests, *in-situ* reduction under pure H_2 flow at 800 °C for 2h

Catalyst Preparation



Reaction Conditions

Temperature: 750 °C

Molar Feed Composition (CO_2/G): 1–4

Total Feed Flow: 40 Nml/min (N_2 as balance gas)

Residence Time (W/F)

- Activity tests, 0.25 mg_{cat}.min/Nml
  10 mg active catalyst + 710 mg α-Al_2O_3
- Stability tests, 3.75 mg_{cat}.min/Nml
  150 mg active catalyst

Activity Tests

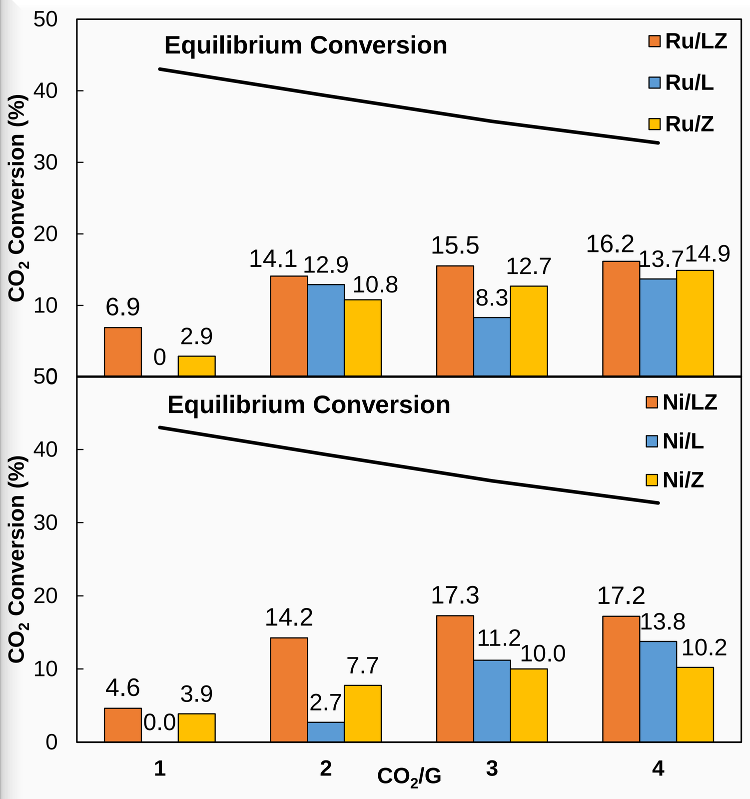


Figure 1. Effect of feed ratio on CO_2 conversion of (a) Ru-based catalysts, (b) Ni-based catalysts.

- Use of LZ improved activities of both Ru and Ni-based catalysts at all CO_2/G ratios
- Ru-based catalysts promote H_2 production, whereas Ni promote CO formation
- Ni-based catalysts produce more CH_4 than Ru-based catalysts

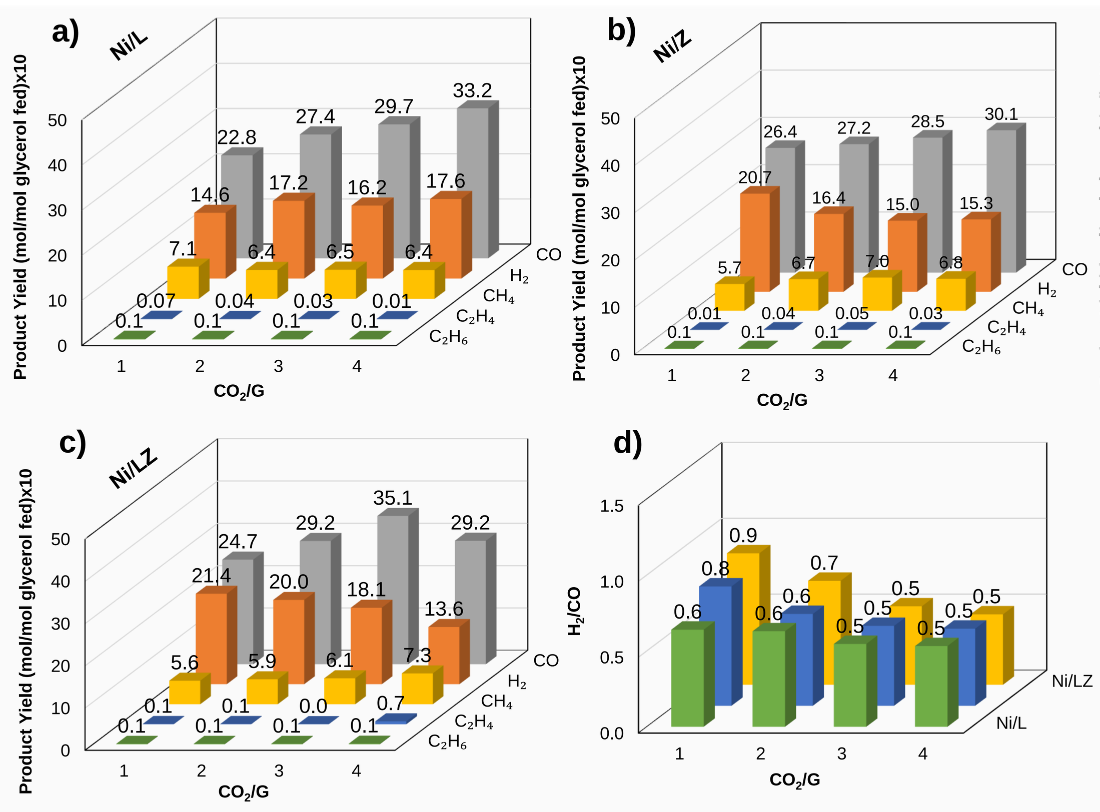


Figure 2. Effect of feed ratio on GDR product yields obtained in Ni/L (a), Ni/Z (b) and Ni/LZ experiments (c), and on the composition of the generated syngas (d).

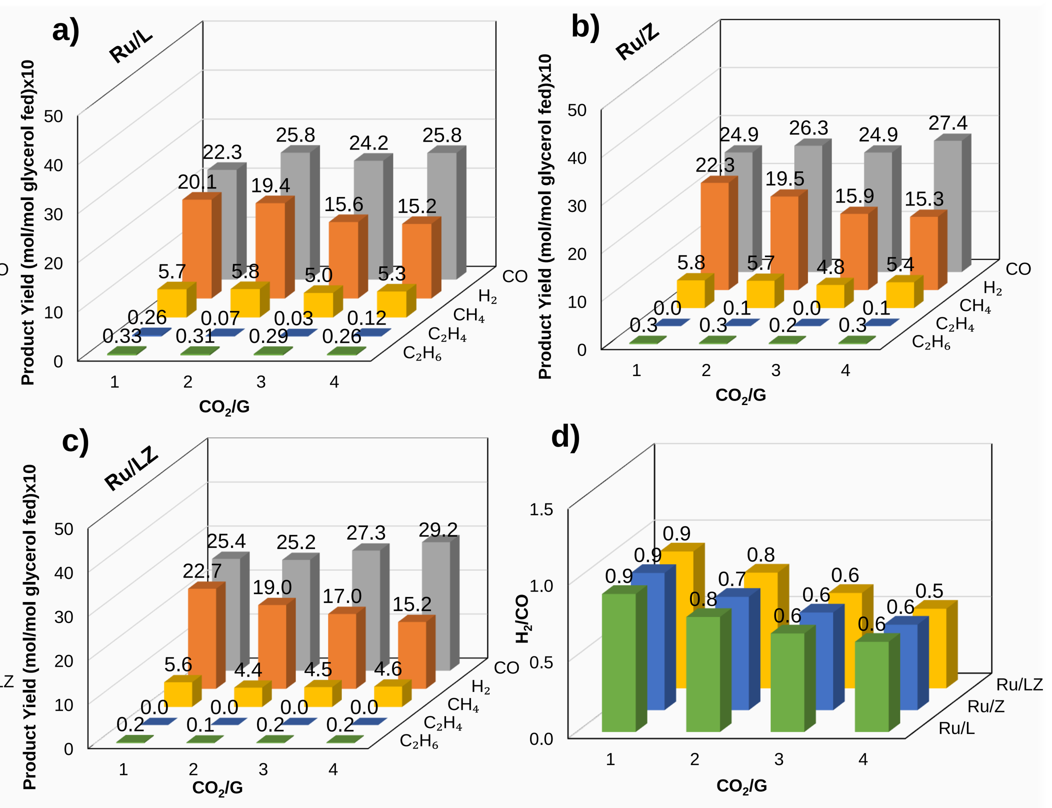


Figure 3. Effect of feed ratio on GDR product yields obtained in Ru/L (a), Ru/Z (b) and Ru/LZ experiments (c), and on the composition of the generated syngas (d).

Stability Tests

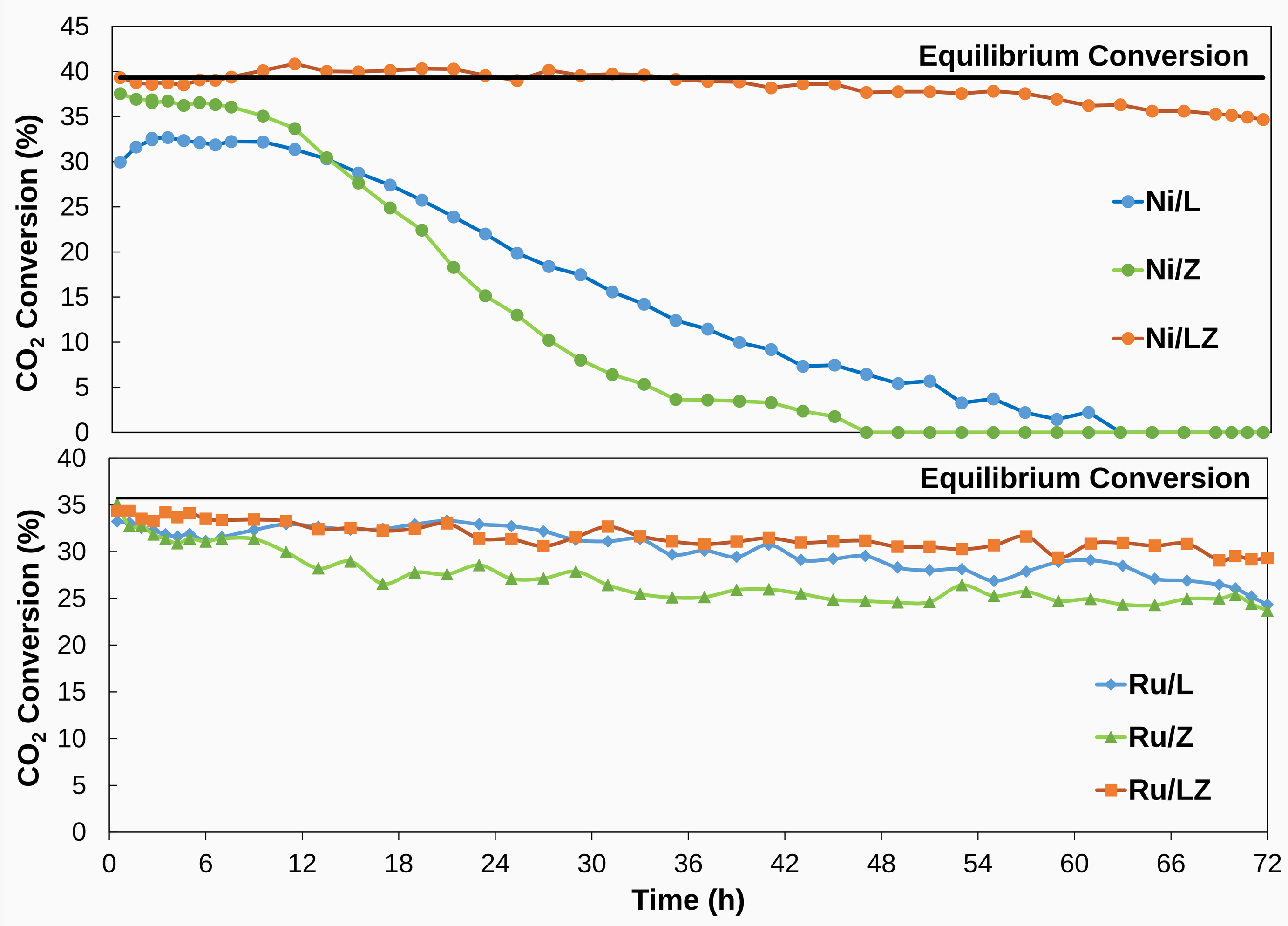


Figure 5. CO_2 conversions obtained in stability tests.

Activity loss:

- Ni/L: 100%
- Ni/Z: 100%
- **Ni/LZ: 12%**
- Ru/L: 20%
- Ru/Z: 28%
- **Ru/LZ: 13%**

Catalyst Characterization

Average Ru nanoparticle (NP) size on: (Characterization are ongoing for Ni-based catalysts)

Ru/L Fresh: 5-8 nm
After 30h coke overlayer

Ru/LZ Fresh: <1 nm
Spent: 1-2 nm

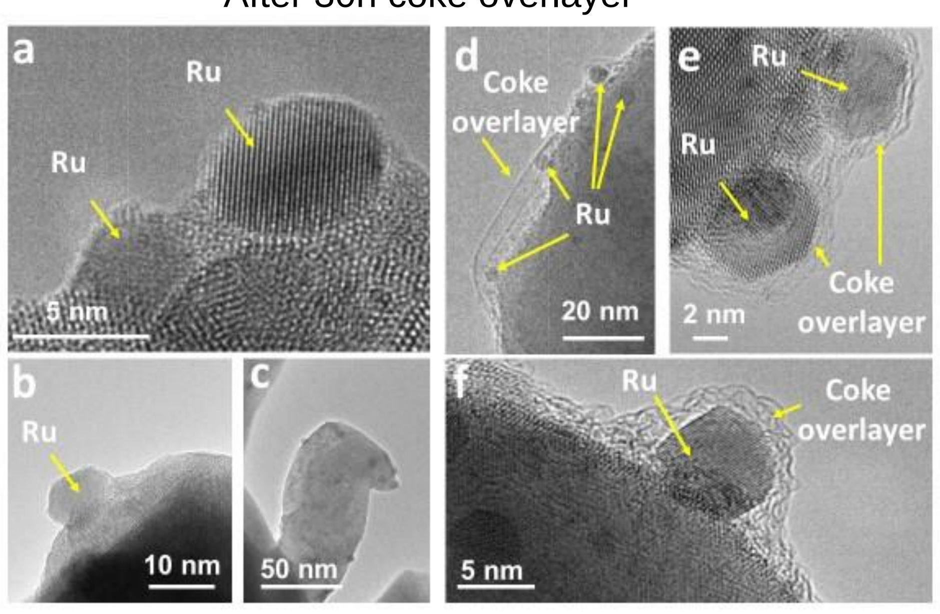


Figure 6. TEM images of the fresh(a–b) and spent(c–d) Ru/L

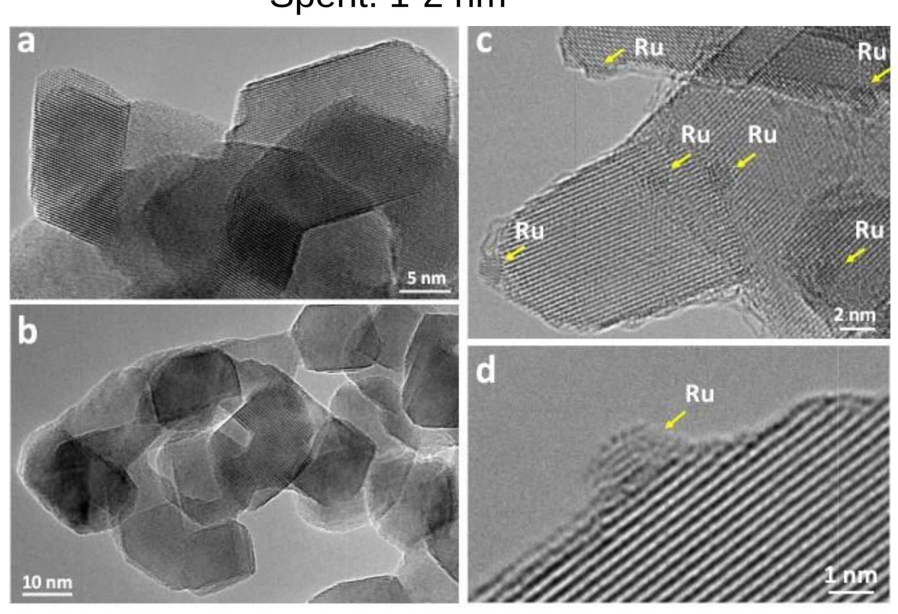


Figure 7. TEM images of the fresh(a–b) and spent(c–d) Ru/LZ

Concluding Remarks

- At higher CO_2/G, Ni/LZ was more active than Ru/LZ.
- Increasing CO_2/G improved CO_2 conversion but reduced H_2/CO ratio for all catalysts. This was attributed to increasing effect of RWGS.
- Ni/LZ and Ru/LZ showed exceptional stability with the activity loss of only 12 and 13%, respectively.
- Activity loss in Ru/L was associated mainly with coking, and very small NP growth after 72 h ToS justified stable nature of Ru/LZ.

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