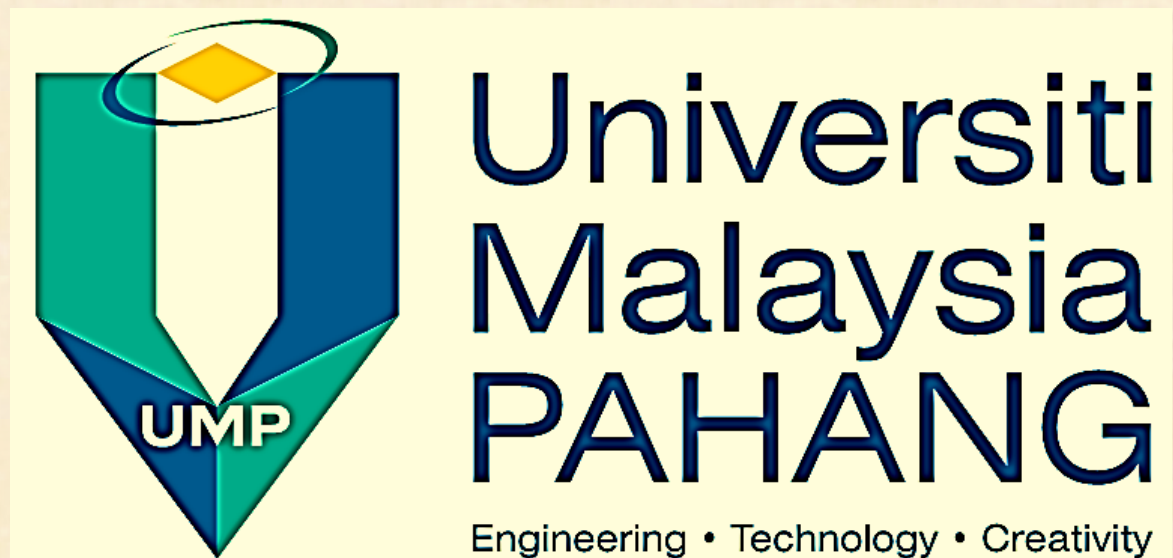


Influence of Promoter Type on Bimetallic Co-Ni/Al₂O₃ Catalyst for Steam Reforming of Glycerol

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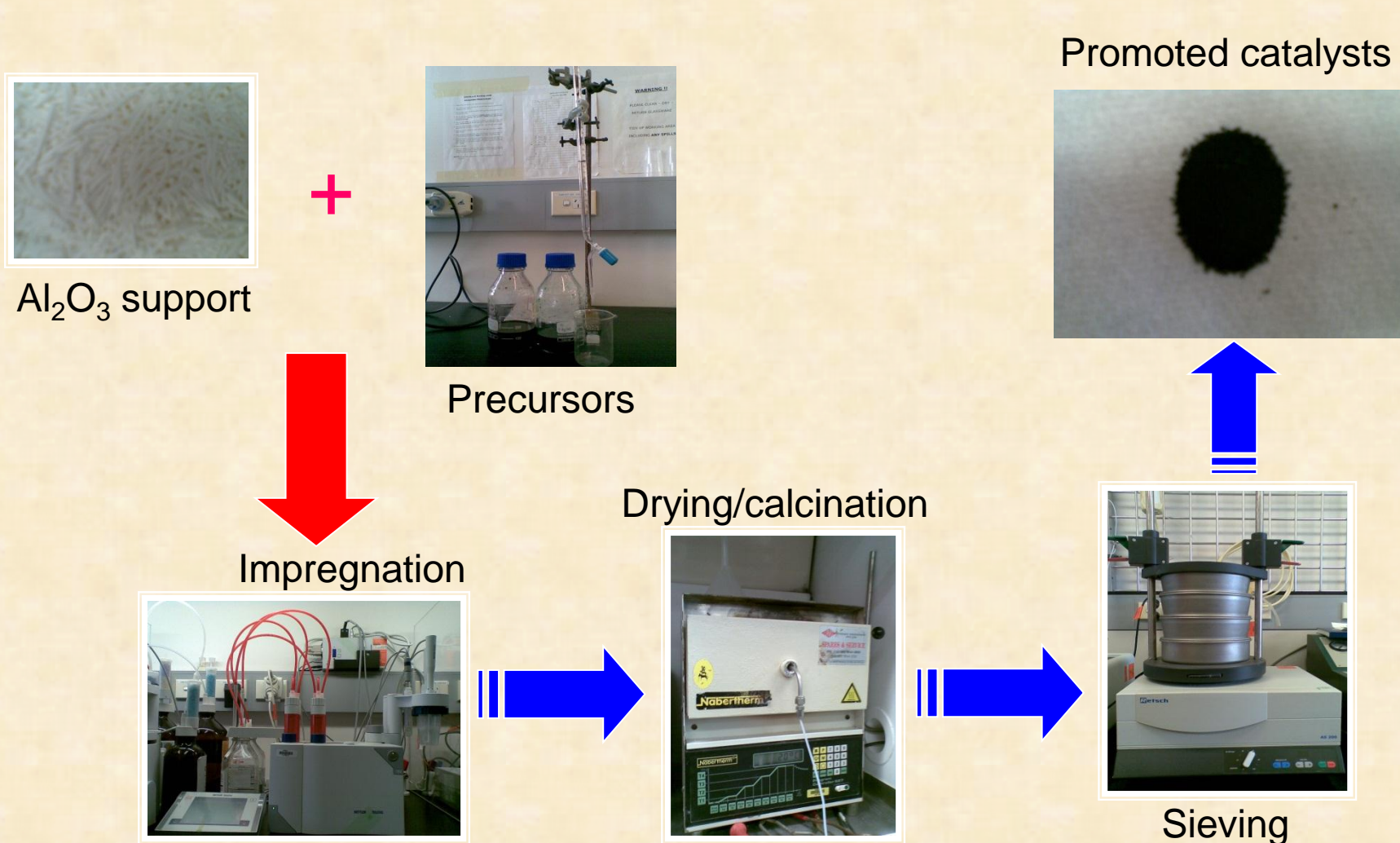


Introduction

Biodiesel is produced from a variety of renewable sources including waste cooking oil. However, its production has led to a glut of glycerol (a by-product, in the amount of 1 mol of glycerol for every three of fatty acid methyl esters). Glycerol presently has low-level and limited use in pharmaceuticals production. The present work deals with steam reforming of glycerol over a bimetallic Co-Ni/Al₂O₃ catalyst system promoted by 2.5wt% alkaline earth oxides (AEO) and lanthanide oxides (LO). The addition of metal oxide from these two groups reportedly minimizes carbon deposition with possible improvement in product selectivity and syngas production rate. Our objective was to provide a systematic correlation between physicochemical properties of the promoted catalyst and reaction metrics.

Experimental Work

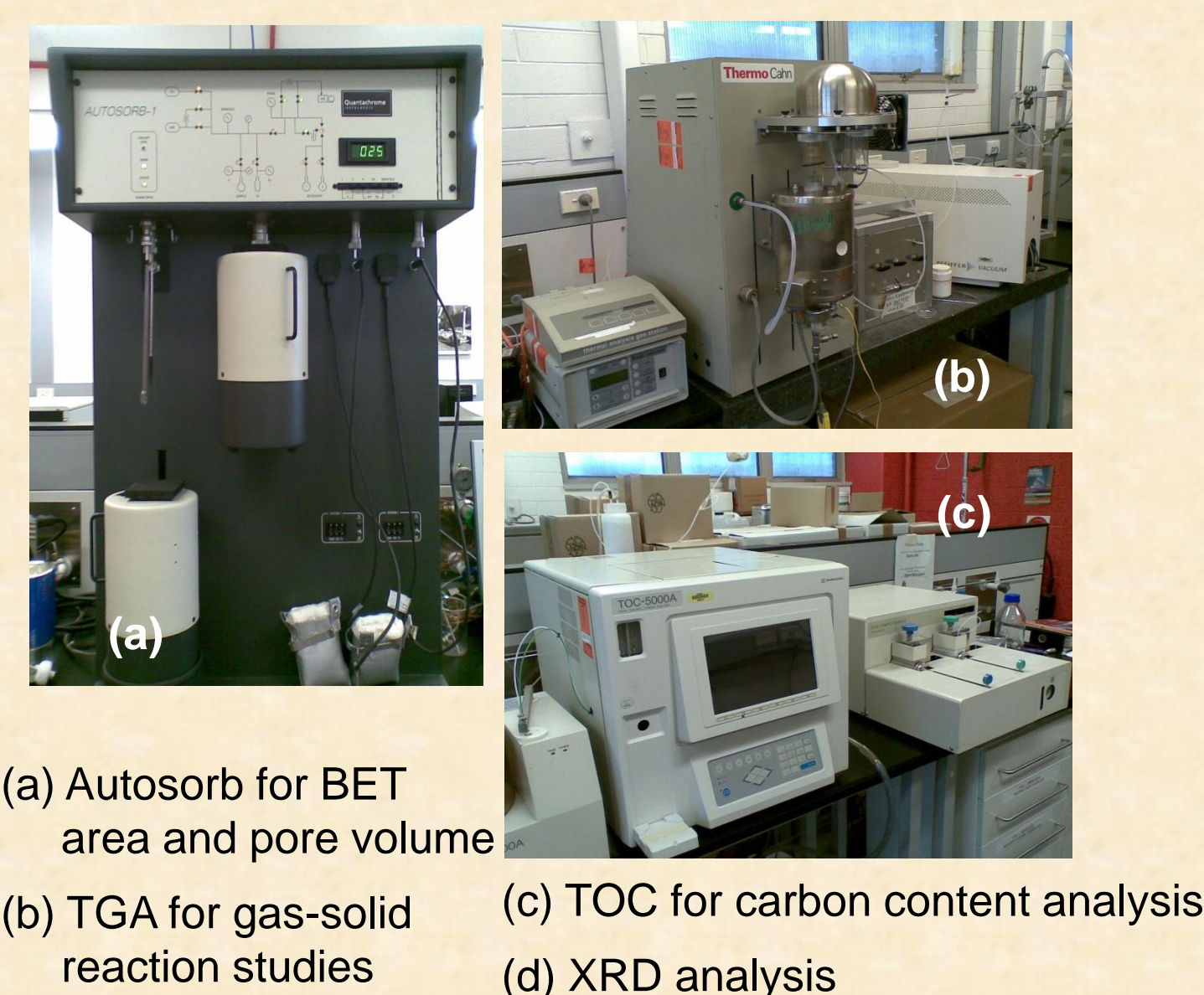
Catalyst Preparation



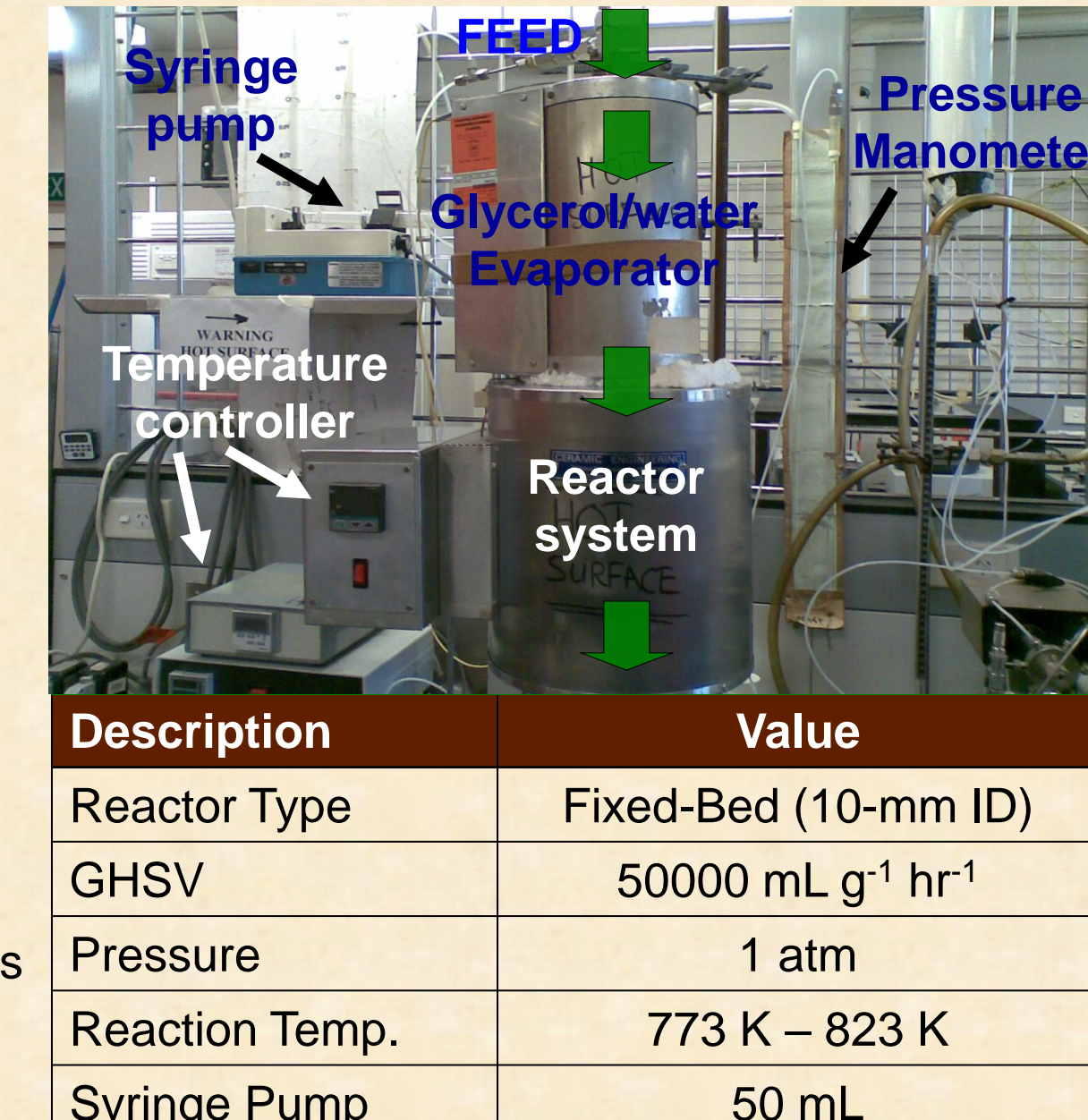
Procedure

- 1) Alumina pellets crushed into 90-425µm particle and air-calcined at 873K for 6 hr.
- 2) Alumina particle was mixed with pre-determined loading of metal precursors solution.
- 3) Impregnation was carried out at room temperature for 3 hr using an auto-titrator.
- 4) Subsequently, the slurry was dried at 403K for 12 hr followed by calcination under the flowing air at 873K for 4 hr.
- 5) Finally, catalyst was sieved to 90-140µm for reaction study.

Catalyst Characterization



Reforming Reaction



Procedure

- 1) Accurately weighed catalysts were loaded into a stainless-steel reactor supported by quartz wool.
- 2) Catalysts were reduced at 873K for 2 hr, then cooled to T_{reaction}.
- 3) Glycerol/water mixture was syringe-pumped as feed to evaporator.
- 4) The glycerol/steam mixture was fed to the reactor.
- 5) Pressure drop was measured using U-tube manometer (<3 kPa).

Results – Catalyst Characterization

(i) Physicochemical Properties

Properties	Co-Ni	MgO	CaO	SrO	BaO	CeO ₂	Pr ₂ O ₃	Sm ₂ O ₃
BET surface area (m ² g ⁻¹)	166.0	152.6	159.2	159.8	160.2	161.2	165.2	162.9
Pore volume (ml g ⁻¹)	0.58	0.52	0.52	0.55	0.57	0.54	0.54	0.53
Pore diameter (Å)	130.7	136.9	131.2	135.5	141.3	134.6	131.8	130.9
Dispersion (%)	0.74	0.77	1.08	1.09	1.10	0.82	0.83	0.95
Metal surface area (m ² g ⁻¹)	0.74	0.77	1.08	1.09	1.10	0.82	0.84	0.95
Active particle diameter (nm)	136.0	131.2	93.4	92.8	91.8	123.3	120.8	106.3

• Addition of promoters reduced the BET surface area by 0.5% to 8.0%. In addition, pore volume also dropped suggesting deeper pore penetration of promoted metals.

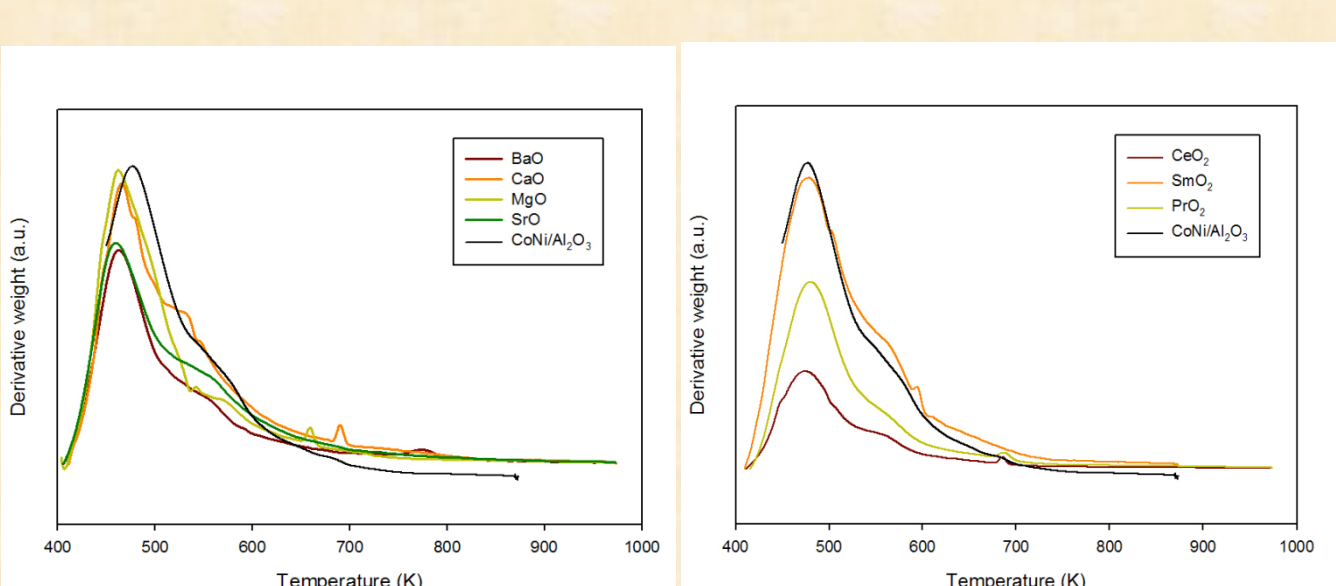
• Metal dispersion improved with addition of both promoters suggesting stronger metal-support interaction.

(ii) Basicity and Acidity Properties

Properties		Co-Ni	MgO	CaO	SrO	BaO	CeO ₂	Pr ₂ O ₃	Sm ₂ O ₃
Acid site conc. (µmol m ⁻²)	Peak I	1.50	1.51	1.57	1.33	1.37	1.49	1.51	1.41
	Peak II	2.90	2.43	2.21	2.08	2.03	2.23	2.36	2.46
Basic site conc. (µmol m ⁻²)	Peak I	0.21	0.23	0.26	0.23	0.26	0.24	0.25	0.26
	Peak II	0.42	0.43	0.43	0.45	0.46	0.31	0.30	0.42
Acid : Basic site ratio	Peak I	7.33	6.56	6.03	5.78	5.26	6.21	6.04	5.42
	Peak II	6.98	5.65	5.13	4.62	4.41	7.19	7.86	5.86

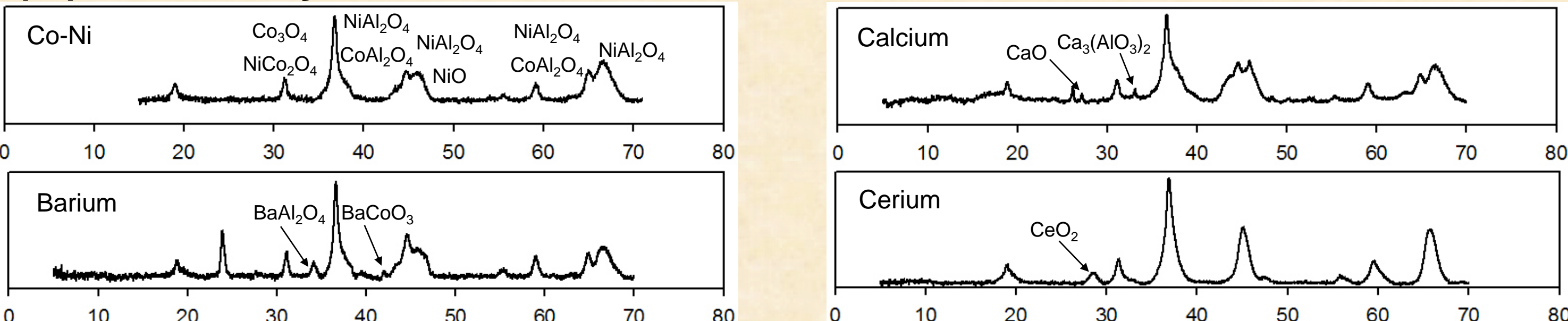
• LO promoters showed no apparent effect on acid:basic ratio for site II. However, addition of AEO decrease acid:basic ratio by increasing the basicity of Co-Ni/Al₂O₃.

(iii) Calcination Profiles



• 1st peak shifted due to promoter-CoNi interaction. 2nd peak is attributed to metal oxidized.

(iv) XRD Analysis

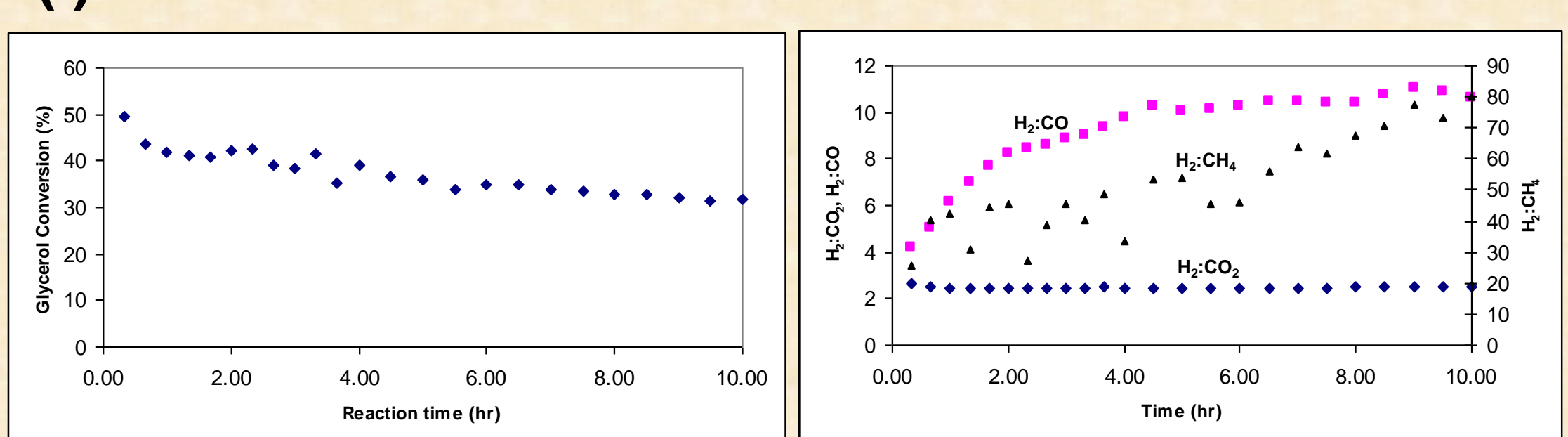


Catalyst	Actual weight changes (%) [‡]	Theoretical weight changes (%)
CoNi/Al ₂ O ₃	23.32	20.94
Mg-CoNi/Al ₂ O ₃	21.82	19.09
Ca-CoNi/Al ₂ O ₃	21.92	19.80
Sr-CoNi/Al ₂ O ₃	23.39	20.40
Ba-CoNi/Al ₂ O ₃	22.12	20.58
Ce-CoNi/Al ₂ O ₃	22.85	20.42
Pr-CoNi/Al ₂ O ₃	22.60	20.60
Sm-CoNi/Al ₂ O ₃	22.45	20.95

[‡] average values of weight changes captured at 3 different heating rates (5, 10, 20 K min⁻¹)

Results – Reaction Study

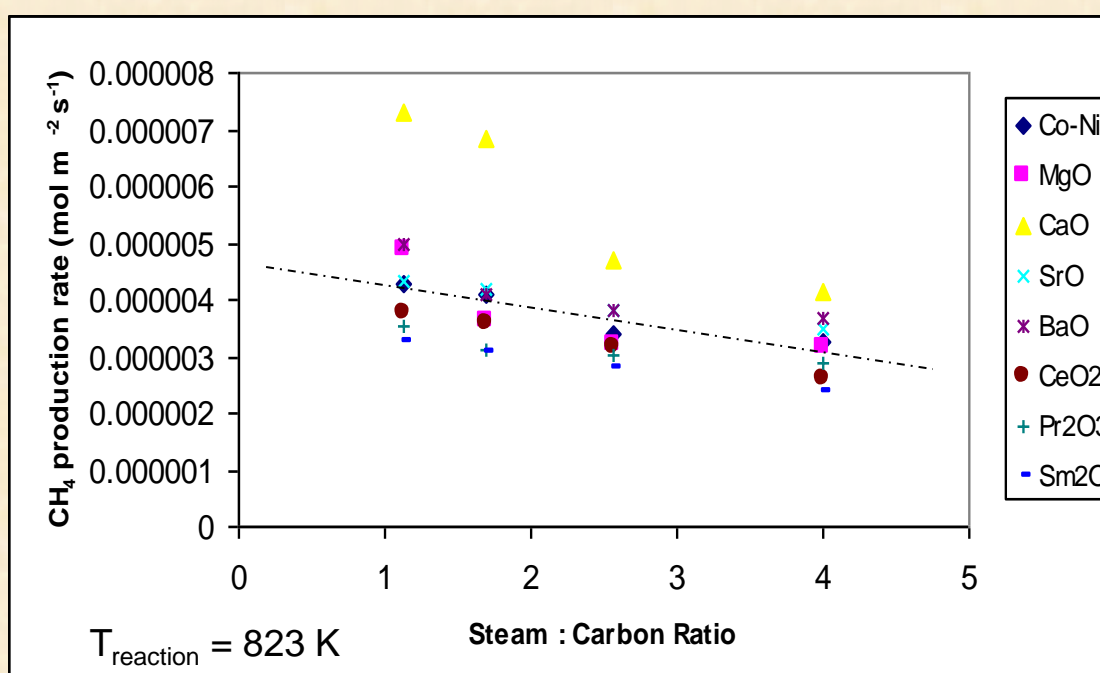
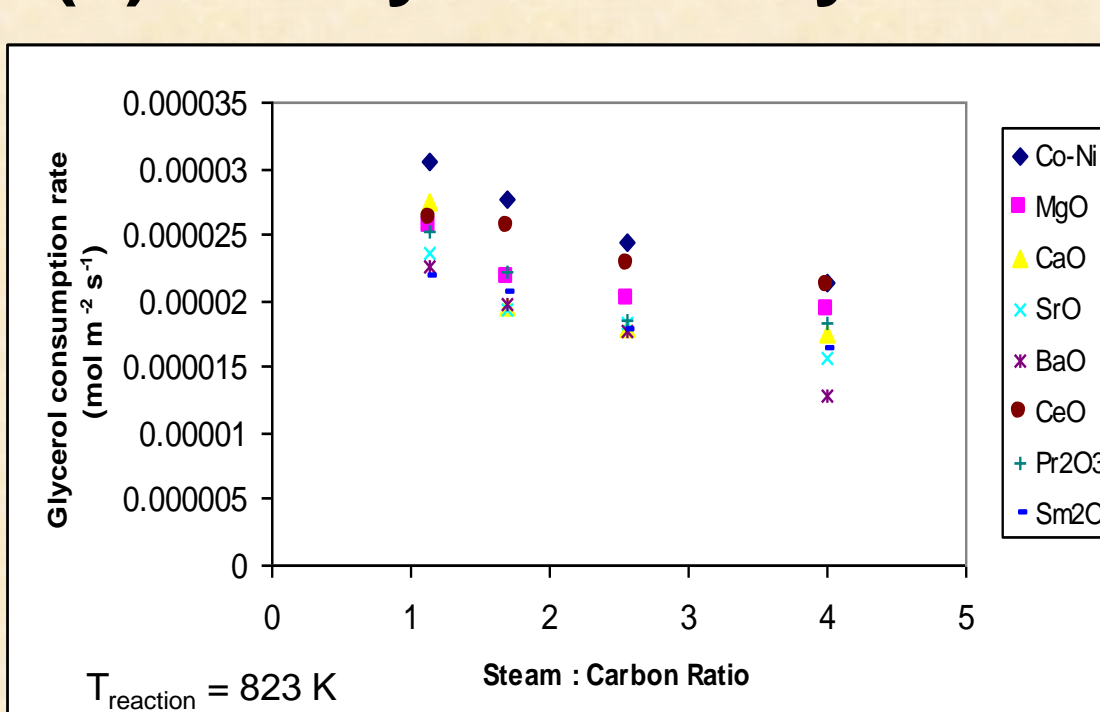
(i) Transient Profiles



Based on 10-hr runs at 823 K with P_{glycerol} = 7.40 kPa and P_{steam} = 25.2 kPa using CeO₂ promoted catalyst.

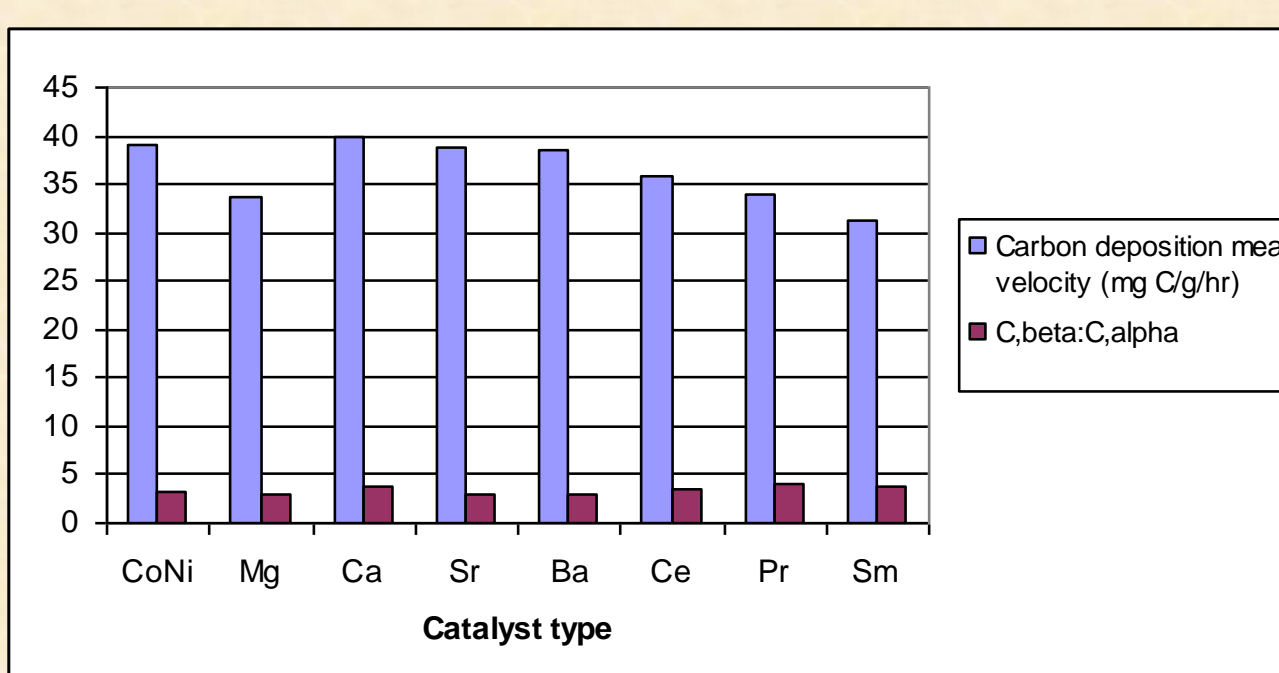
• Transient profile shows an initial overshoot in glycerol conversion followed by a gradual drop to steady-state value after about 6 h. The sluggish decay may be due top build-up of carbonaceous deposit.
• H₂:CO and H₂:CH₄ ratios experienced a gradual increment indicative of time-on-stream reduction in both CO and CH₄ formation rates.

(ii) Catalytic Activity

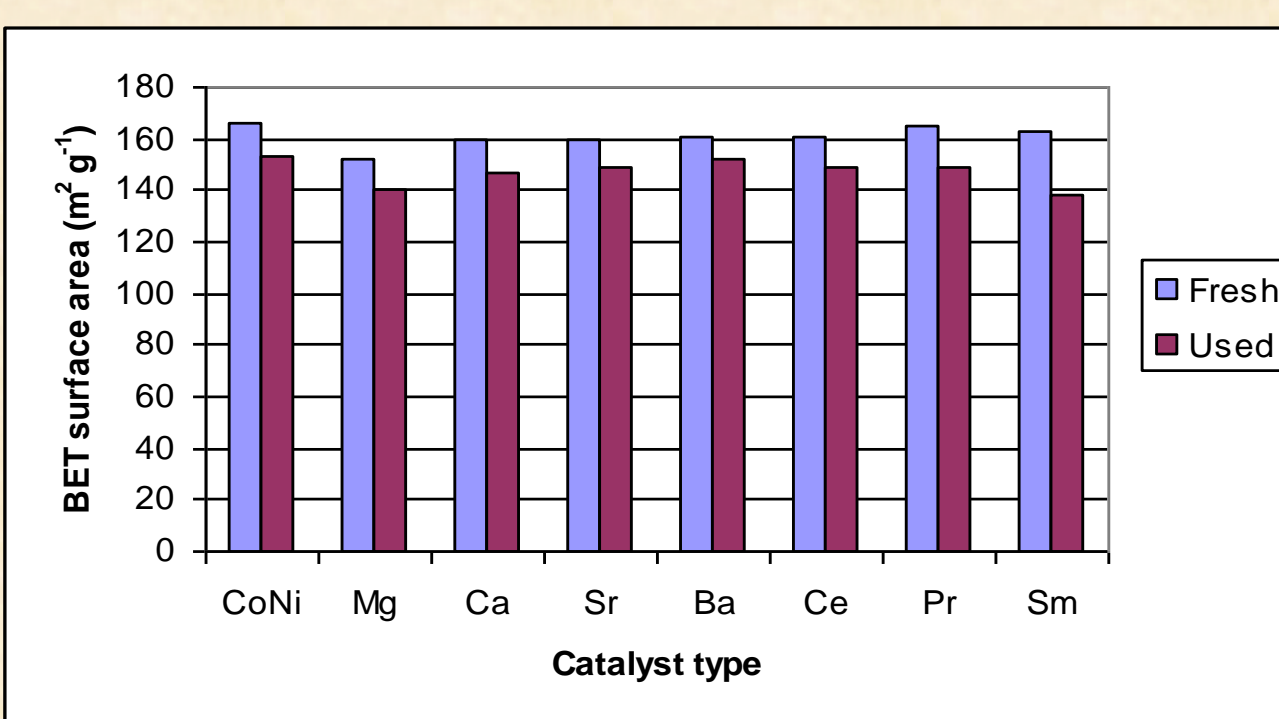


• Bimetallic Co-Ni/Al₂O₃ catalyst generally showed the highest specific glycerol consumption rate.
• The introduction of 2.5wt% of AEO- and LO-promoters reduced the consumption rate of glycerol.
• Addition of AEO results in increase of CH₄ production rate compared to base catalyst. However, addition of LO promoter reduced the CH₄ production rate.
• The suppression of CH₄ production by LO may be attributed to the flexibility in multiple stable oxidation states as distinct from the single oxidation state possessed by the AEO.
• Lower carbon deposition was recorded for LO-promoters.

Results – Post Reaction Analysis



• Addition of LO reduced the coking velocity by ~20%. However, AEO show little inhibition effect.
• AEO promoters tend to decrease C_β:C_α ratio (except CaO) while LO metals increased C_β:C_α weight ratio.



• The regenerated “used” catalysts were subjected to surface area analysis.
• The thermal stability of catalyst was improved by the AEO promoter but LO-addition seemed to have a detrimental effect.

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