Synthesis of Ni/γ-Al_2O_3 catalysts by the sol-gel method for the catalytic reforming of glycerol

Hugo Solís G, M.Sc.[1,2]; Jhonattan Manosalvas[1];Andrés De La Rosa, M.Sc. [1]; Carolina Montero, Ph.D.[1]; Pablo Araujo, Ph.D.[1]; C. Wolfs[2]; J. Mahy[2]; J. Geens[2]; R. Tilkin[2]; Stéphanie Lambert, Ph.D.[2]
[1]Central University of Ecuador – Faculty of Chemical Engineering.
[2]University of Liège – Department of Chemical Engineering. Nanomaterials, Catalysis and Electrochemistry.

Summary

Nickel supported gamma alumina catalysts have been developed for the use in glycerol reforming applications. The catalysts were developed using the sol-gel method and charaterized using TPR, BET, XRD, TEM and ICP techniques. The catalysts were prepared with different precursors of Ni, Al_2O_3, solvents and silicon precursors in order to determine the texture, morphology and crystallographic properties of each catalysis and select the best preparation route. It was developed a synthesis sol-gel procedure for the cogelation between the funtionalized silicon precursors and alumina precursors. From the results obtained, it was observed that the catalysts prepared with nickel acetate, 2-methoxyethanol and EDAS present a great stability in their structure, the presence of γ-Al_2O_3 was confirmed by XRD analysis, Ni metal particles doped in gamma alumina were noted using TEM analysis.

Introduction

Significant amount of glycerol is produced as a by-product during bio-diesel production by transesterification of vegetable oils, which are available at low cost in large supply from renewable raw materials.

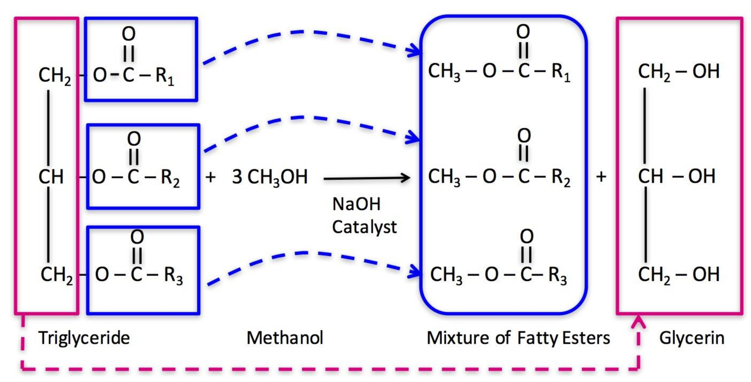

Figure 1. Transesterification reaction

Using glycerol as a source of producing hydrogen is a good possibility. Steam reforming is a promising way to utilize the diluted glycerol aqueous solution to produce hydrogen.

$$C_3H_8O_3(g) + 3H_2O(g) \rightarrow 7H_2(g) + 3CO_2(g) \quad [1]$$
$$\Delta H° = 128kJ/mol$$

Catalysis plays an important role for this proposal. Usually, nickel-based catalysts are used in the reforming of glycerol; however, the major problem associated with nickel catalysts is coke formation. The most common catalyst supports in the reforming of hydrocarbons to hydrogen are α-Al_2O_3, γ-Al_2O_3, MgO, $MgAl_2O_4$, SiO_2, ZrO_2, CeO_2 and TiO_2.

The sol–gel process provides a new approach to the preparation of functionalized silicon precursors and alumina precursors.

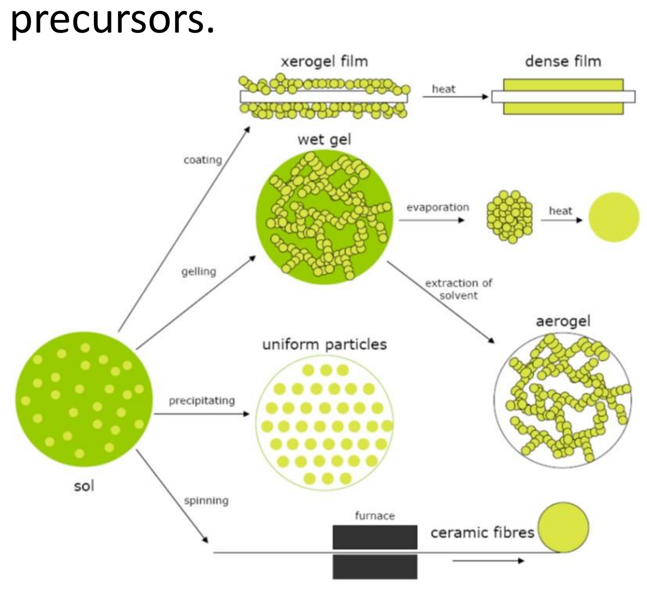

Figure 2. Sol-gel process.

Synthesis by the sol-gel method

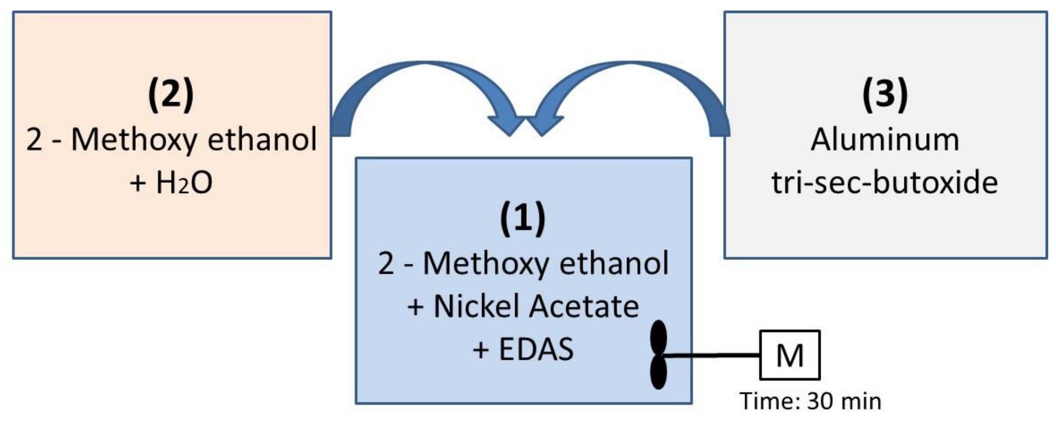

Figura 3. Synthesis by the sol-gel method

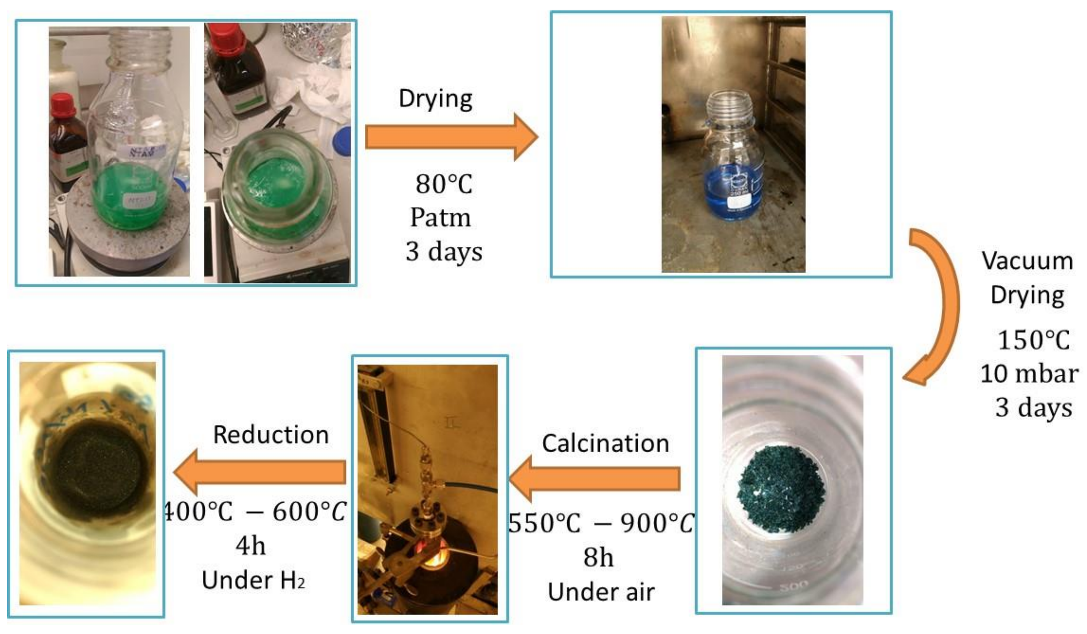

Figura 4. Preparation of catalysts

Characterization Results

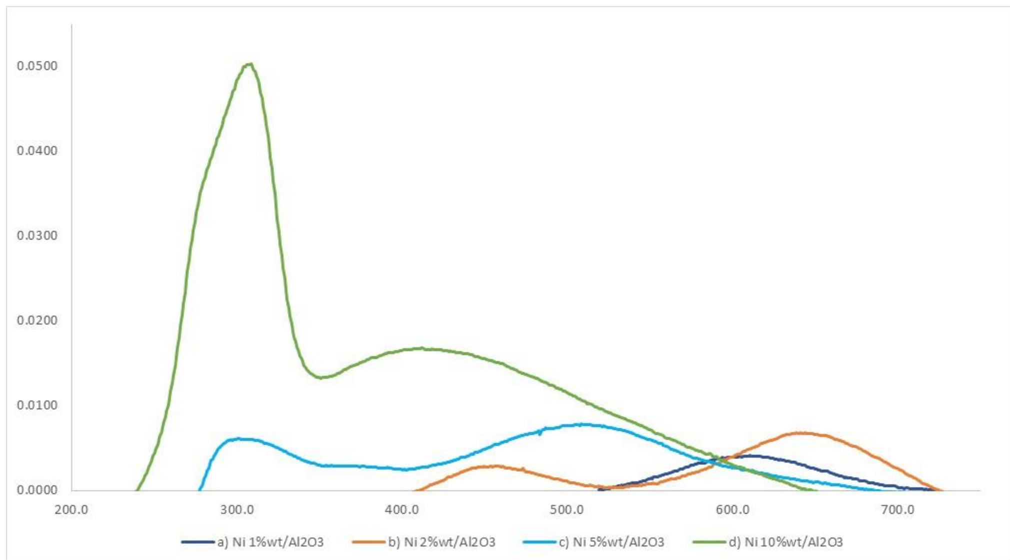

Figure 5. TPR for a) Ni(1%wt)/Al_2O_3 b) Ni(2%wt)/Al_2O_3 c) Ni(5%wt)/Al_2O_3 d) Ni(10%wt)/Al_2O_3. $T_{calcination}$ = 550°C

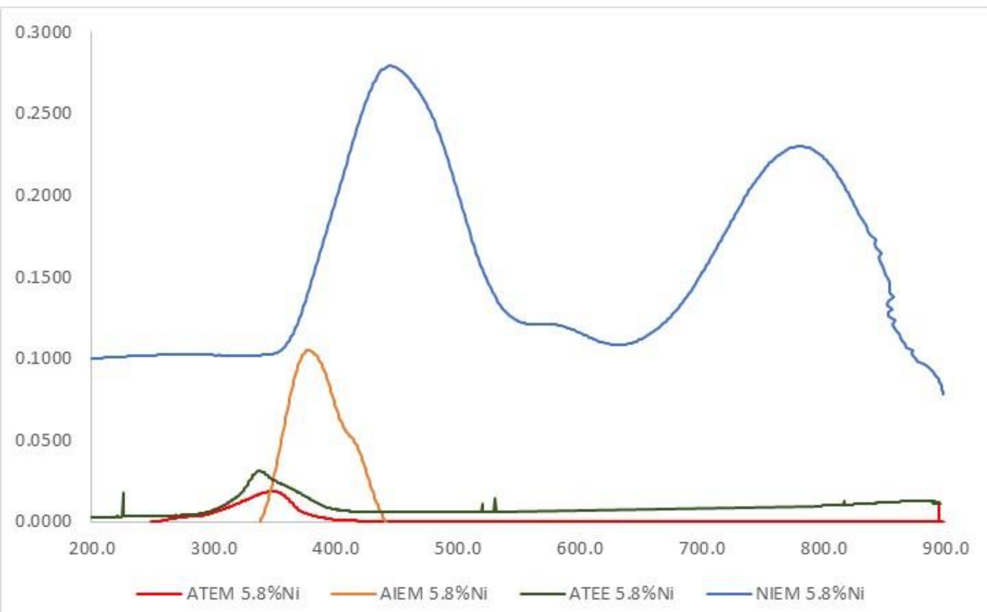

Figure 6. TPR for a) ATEM 5.8%Ni b) AIEM 5.8%Ni c) ATEE 5.8%Ni d) NIEM 5.8%Ni. $T_{calcination}$ = 900°C

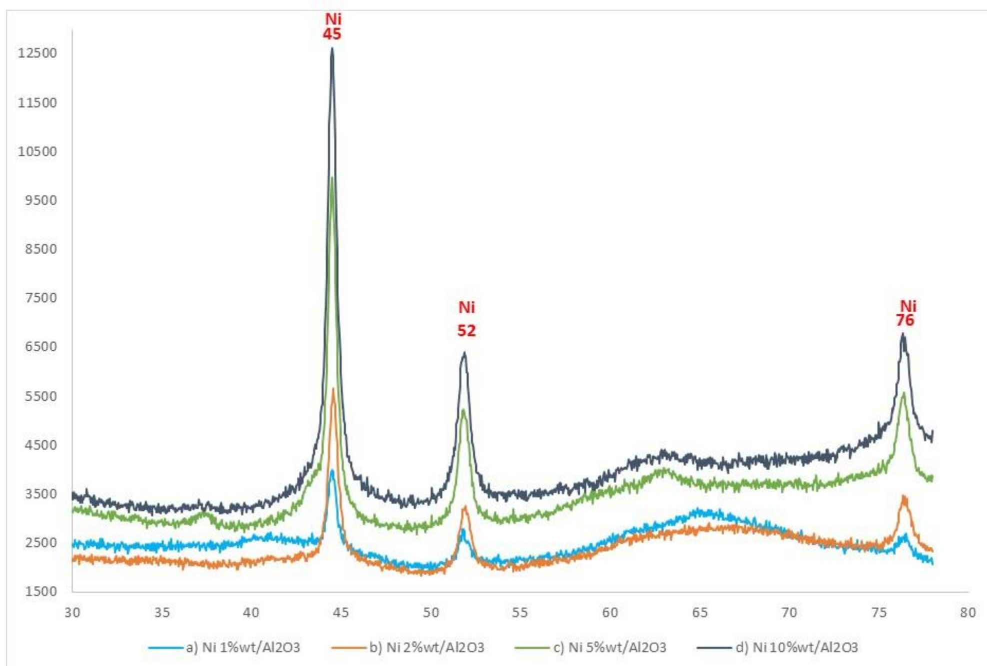

Figure 7. XRD Patterns for a) Ni(1%wt)/Al_2O_2 b) Ni(2%wt)/Al_2O_3 c) Ni(5%wt)/Al_2O_3 d) Ni(10%wt)/Al_2O_3. $T_{reduction}$ = 300°C

Characterization Results

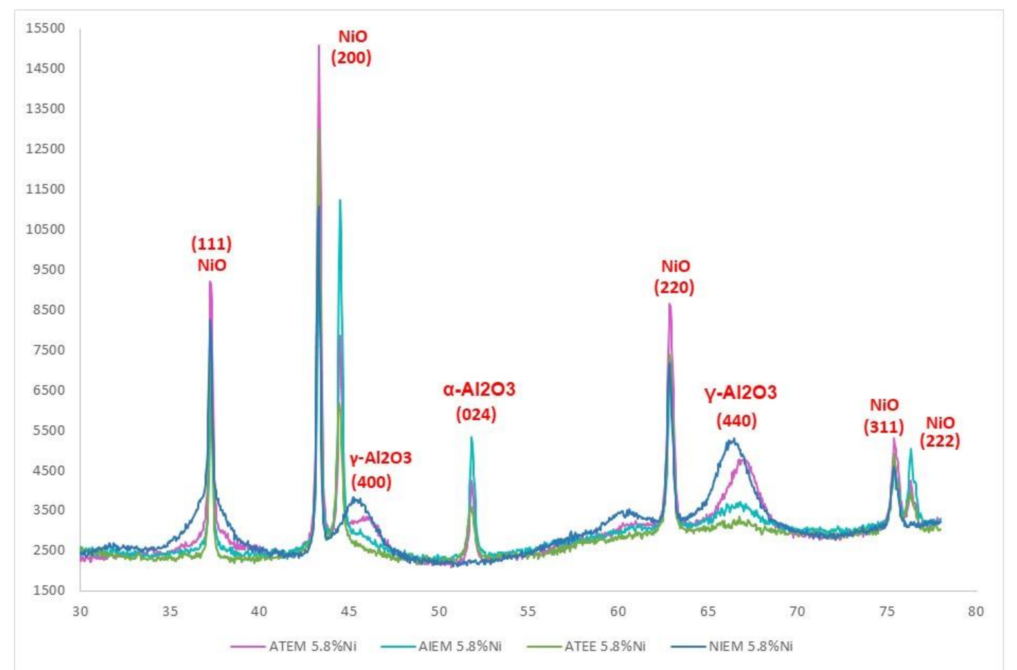

Figure 8. XRD Patterns for a) ATEM 5.8%Ni b) AIEM 5.8%Ni c) ATEE 5.8%Ni d) NIEM 5.8%Ni. Tcalcination = 900°C

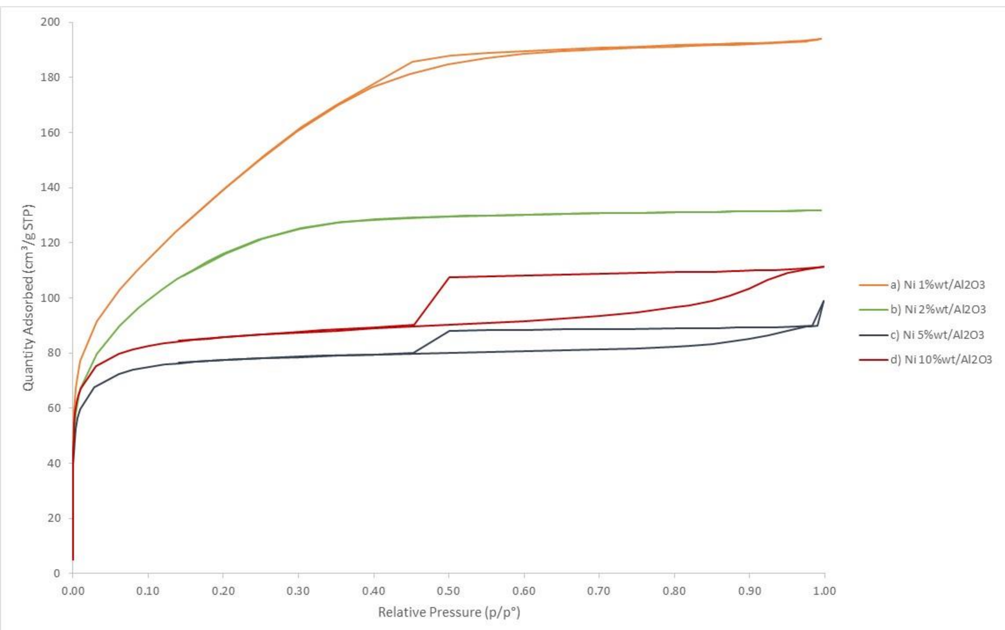

Figure 9. BET for a) Ni(1%wt)/Al_2O_3 b) Ni(2%wt)/Al_2O_3 c) Ni(5%wt)/Al_2O_3 d) Ni(10%wt)/Al_2O_3.

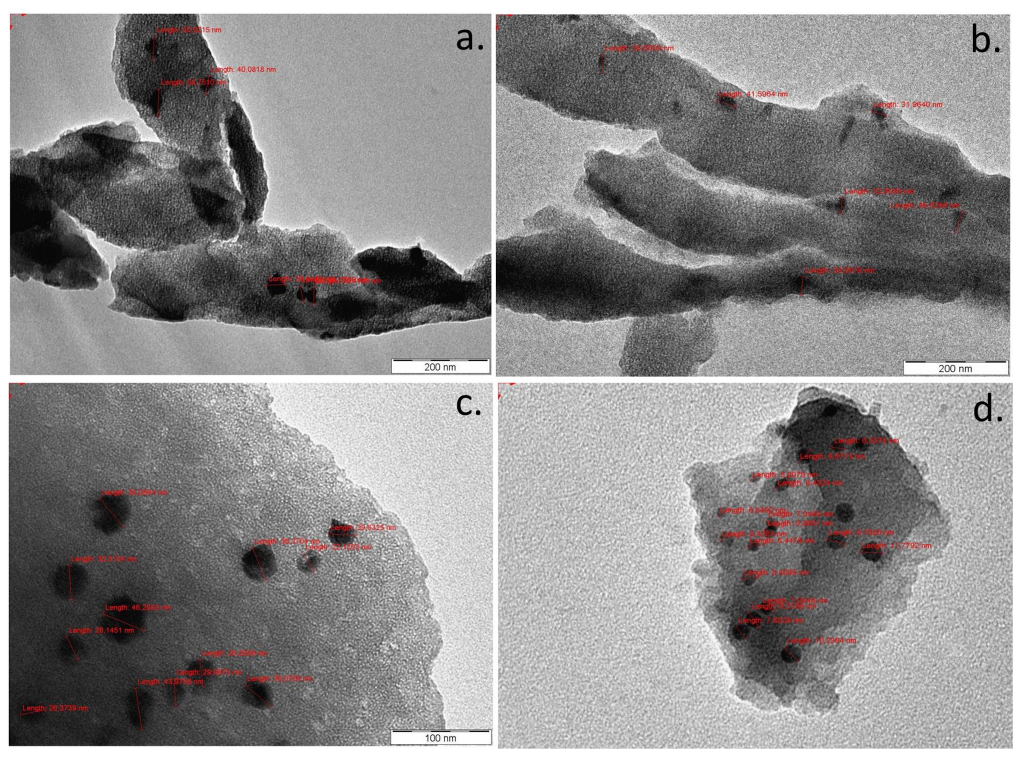

Figure 10. TEM for a) Ni(1%wt)/Al_2O_3 b) Ni(2%wt)/Al_2O_3 c) Ni(5%wt)/Al_2O_3 d) Ni(10%wt)/Al_2O_3.

SAMPLE	CONSTANTS		AVERAGE – Ni particle		
	k	ʎ	2Ɵ	B radians	D nm
Ni 1%wt/Al_2O_3	0,89	0,154	57,5	0.0089	**18**
Ni 2%wt/Al_2O_3	0,89	0,154	57,6	0.0094	**19**
Ni 5%wt/Al_2O_3	0,89	0,154	57.5	0.010	**16**
Ni 10%wt/Al_2O_3	0,89	0,154	57.5	0.0083	**22**

Table 1. Crystal size calculation for a) Ni(1%wt)/Al_2O_3 b) Ni(2%wt)/Al_2O_3 c) Ni(5%wt)/Al_2O_3 d) Ni(10%wt)/Al_2O_3.

Conclusions

- The catalysts presented a BET surface area between 250-515 m /g and an average pore size between 2 to 7 nm.
- The addition of EDAS modified the properties of γ-Al_2O_3. The formation of small and spherical γ-Al_2O_3 crystallites is directly related to the functionalized chain of EDAS.
- Ni/Al_2O_3 catalysts based on different precursors present distinct characteristics in nickel dispersion, reduction degree, and particle size.

Contacto

Hugo Fernando Solís García
CENTRAL UNIVERSITY OF ECUADOR / UNIVERSITY OF LIÈGE
Email: hfsolis@uce.edu.ec / hfsolis@student.uliege.be
Web: http://uce.edu.ec / http://www.nce.ulg.ac.be/
Teléfono: (+593) – 9 9 598 0354
(+32) – 467 71 07 85

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