Ni/Al_2O_3 xerogel catalysts for biogas cleaning

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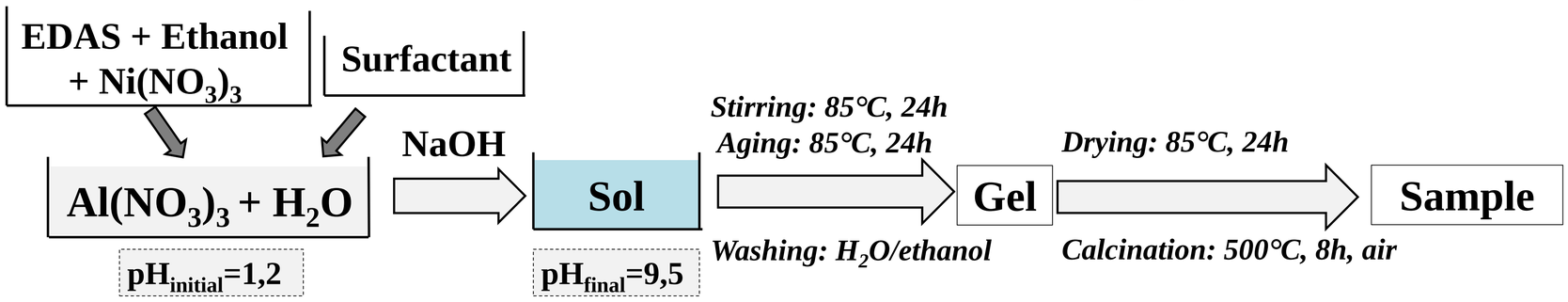
Introduction

The thermo-chemical conversion method that is biomass gasification is generating emphatic interest for the production of biogas (CO + H_2). However, this process presents two major drawbacks: (i) the tar formation and (ii) the presence of sulphur compounds in gaseous effluents. In order to counter these effects, two solutions are commonly used: physical cleaning (washing, cyclone, filter…) and chemical destruction. The chemical way, which consists in catalytic removal of tars by a catalyst composed of a metallic element dispersed on a refractory oxide matrix, appears to be a very interesting solution. In this way, Ni/Al_2O_3 xerogel catalysts were synthesized by the sol-gel process by using aluminium precursors, 3-(2-aminoethylamino)propyltrimethoxysilane (**EDAS**) to complex Ni^{2+} ions, stearic acid and Pluronic P123® in water and ethanol used as solvents.

Synthesis of Ni/Al_2O_3 xerogel catalysts

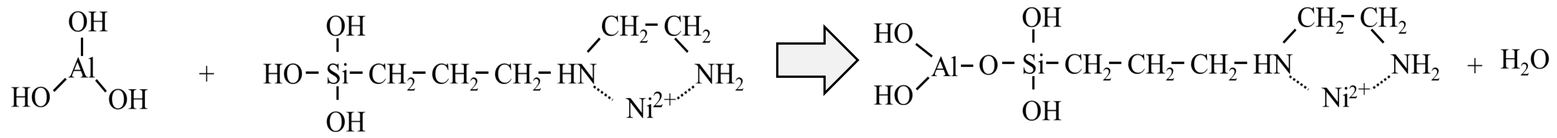


Composition

	Standard	EDAS	EDAS+ S1	EDAS +S2
$Al(NO_3)_3$	✓	✓	✓	✓
H_2O	✓	✓	✓	✓
Ethanol	✓	✓	✓	✓
$Ni(NO_3)_2$	✓	✓	✓	✓
EDAS		✓	✓	✓
Stearic acid			✓	
P123®				✓

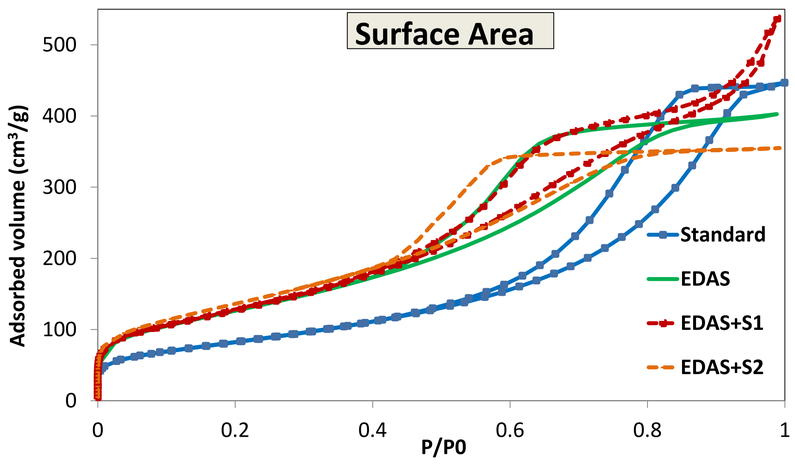
Note: *Ni loading = 2%wt.*

Suggested mechanism:

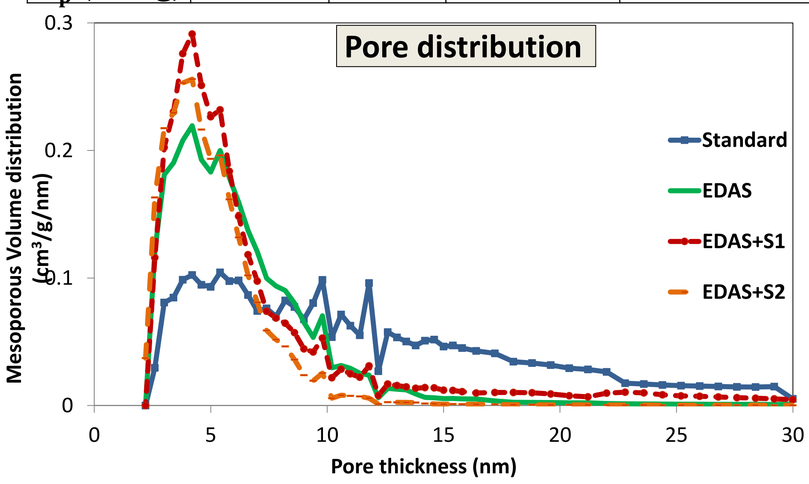


The complexation of Ni^{2+} ions by EDAS allows to disperse homogeneously, after calcination and reduction steps, Ni nanoparticles into the alumina network

Porous texture



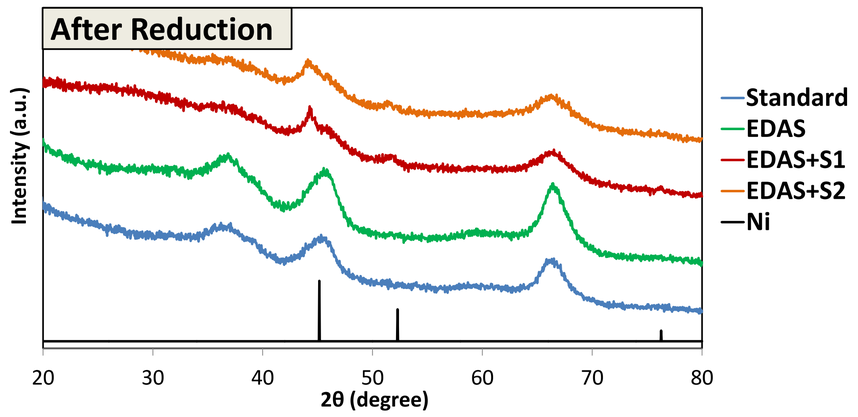
	Standard	EDAS	EDAS + S1	EDAS + S2
S_{BET} (m^2/g)	270	425	430	435
V_p (cm^3/g)	0,65	0,60	0,75	0,55



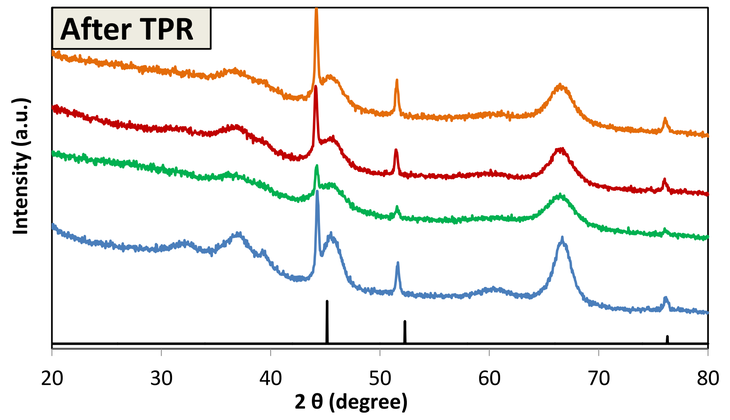
- All samples are micro-mesoporous.
- EDAS highly improves S_{BET} and the presence of small mesopores (3-10 nm).
- Surfactants slightly increase the amount of small mesopores.

Crystallinity

XRD measurements were realized on samples after H_2 reduction (600°C, 5h, 5°C/min) and after TPR (1000°C, 2°C/min, H_2).



- Presence of γ-Al_2O_3
- Ni peaks absent of *Standard* and *EDAS*

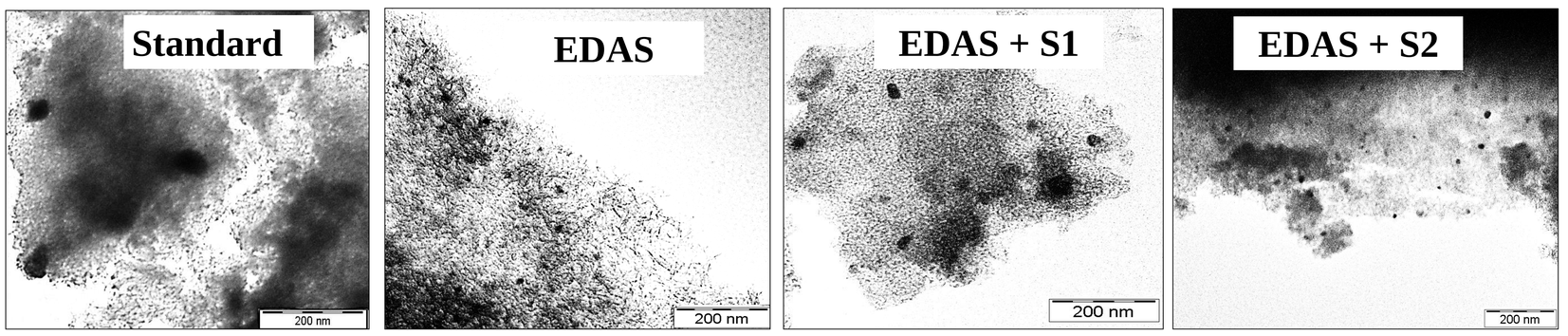


- Presence of γ-Al_2O_3
- Ni peaks for all samples

Ni particle size (XRD)	Standard	EDAS	EDAS + S1	EDAS + S2
After Reduction	?	?	17	8
After TPR	34	37	33	33

TEM observations

Samples after reduction (600°C, 5h, 5°C/min, H_2)



- Ni particles: 5 to 100 nm
- Ni particles: 5 to 20 nm
- Ni particles: 5 to 30 nm
- Ni particles :5 to 20 nm
- Higher Ni dispersion

Conclusions and perpectives

- EDAS and surfactants (Stearic acid & Pluronic P123®) increase the specific surface area of Ni/Al_2O_3 xerogel catalysts and the dispersion of Ni particles.
- In order to study the stability and the sintering resistance of Ni/Al_2O_3 xerogel catalysts , reductions at higher temperature (750°C) followed by XRD measurements will be realized.
- H_2 chimisorption measurements are currently done in order to determine the Ni dispersion in Ni/Al_2O_3 xerogel catalysts .