Ni/Al_2O_3 xerogel catalysts for biogas cleaning

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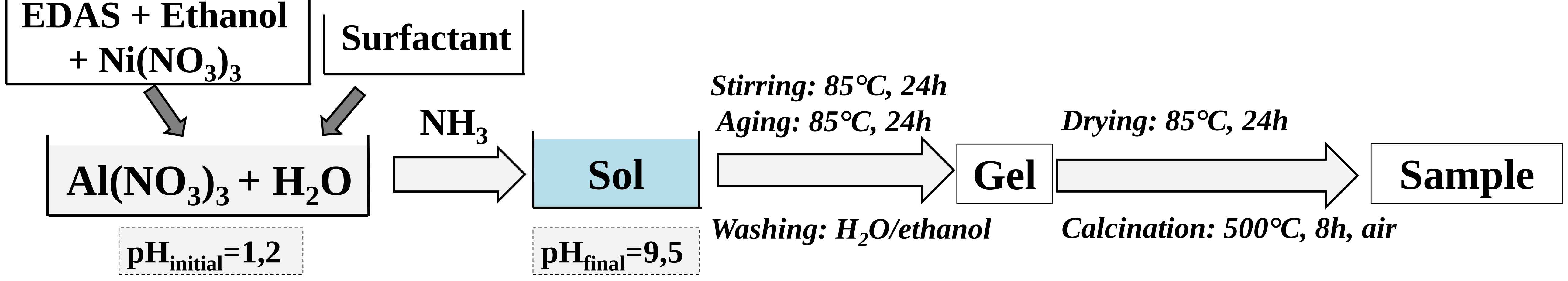
Introduction

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, and s tearic acid in water and ethanol used as solvents.

Synthesis of Ni/Al_2O_3 xerogel catalysts



EDAS + Ethanol + $Ni(NO_3)_3$

Surfactant

$Al(NO_3)_3 + H_2O$

$pH_{initial}$=1,2

NH_3

Sol

pH_{final}=9,5

Stirring: 85°C, 24h

Aging: 85°C, 24h

Washing: H_2O/ethanol

Gel

Drying: 85°C, 24h

Calcination: 500°C, 8h, air

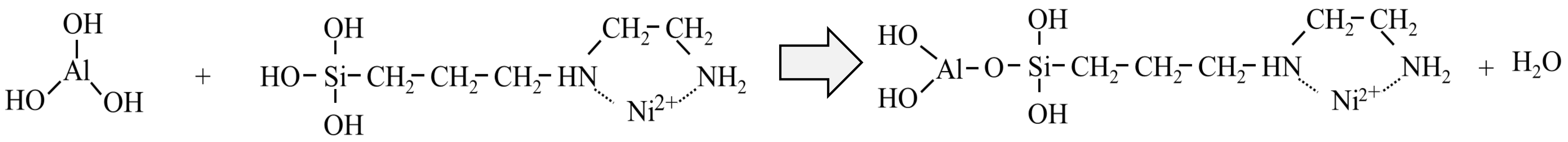
Sample

Composition

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

Note: *Ni loading = 2%wt.*

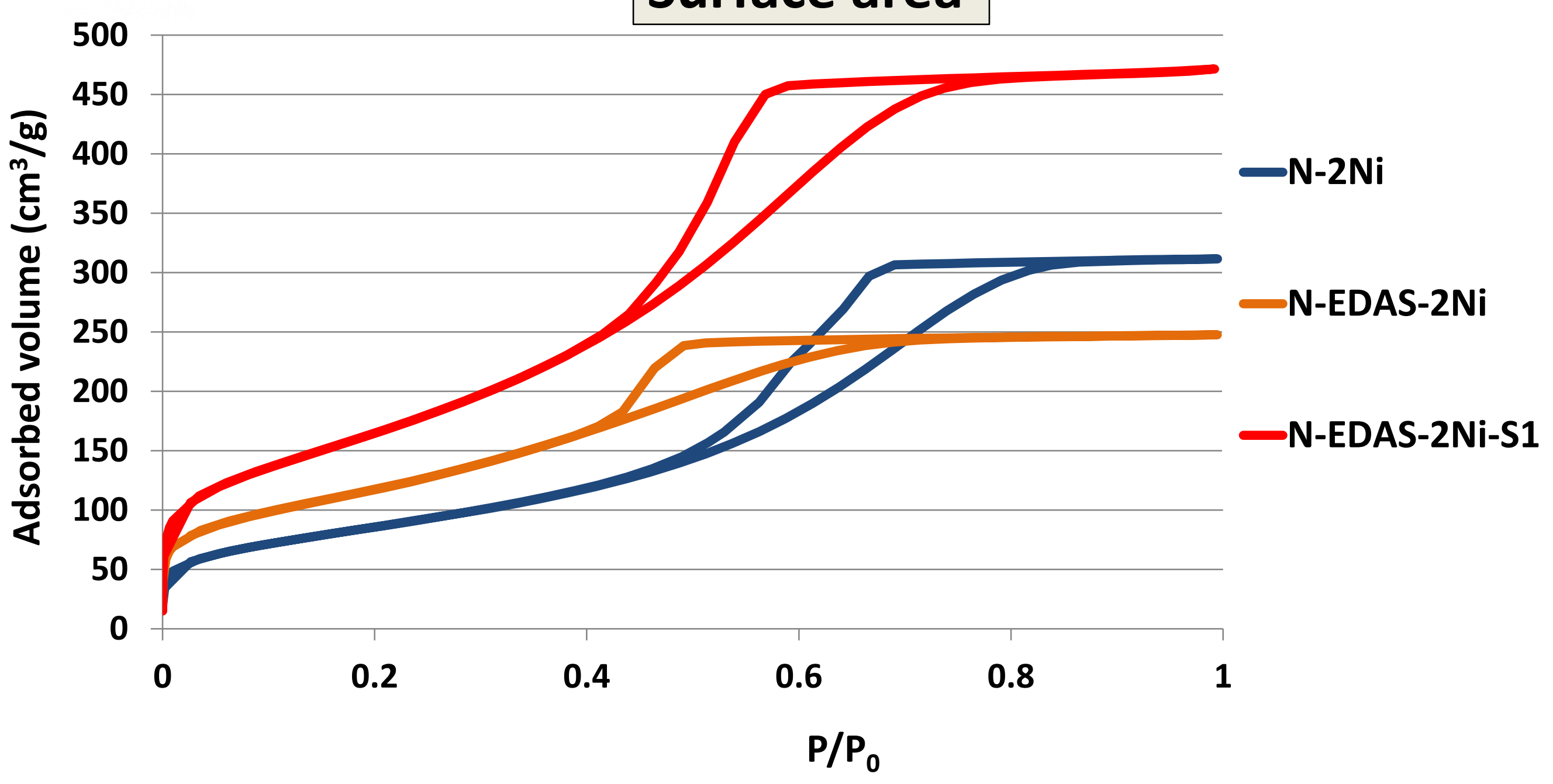
Suggested mechanism:



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

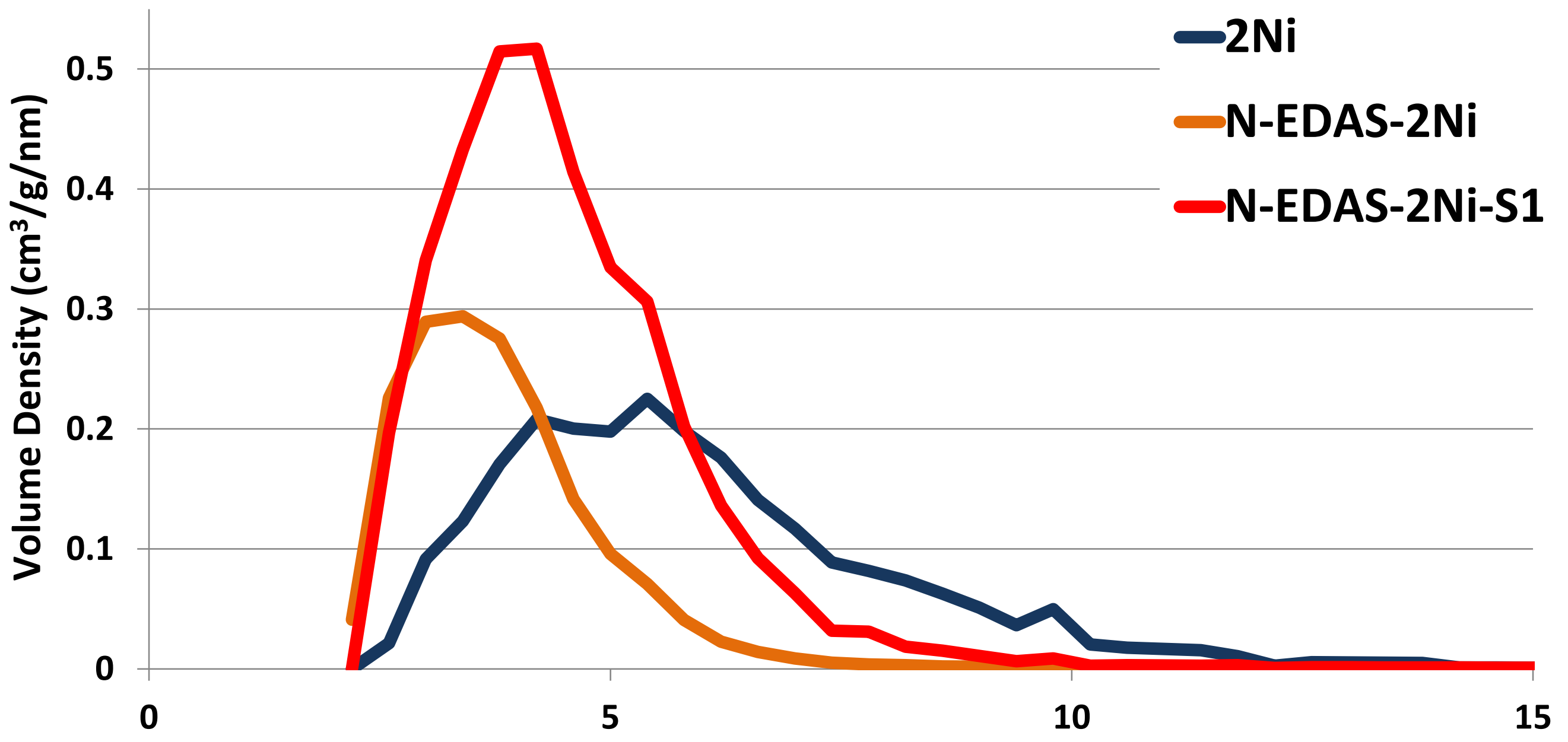
Porous texture

Surface area



	Standard	EDAS	EDAS + S1
S_{BET} (m^2/g)	315	436	604
V_p (cm^3/g)	0,5	0,35	0,74

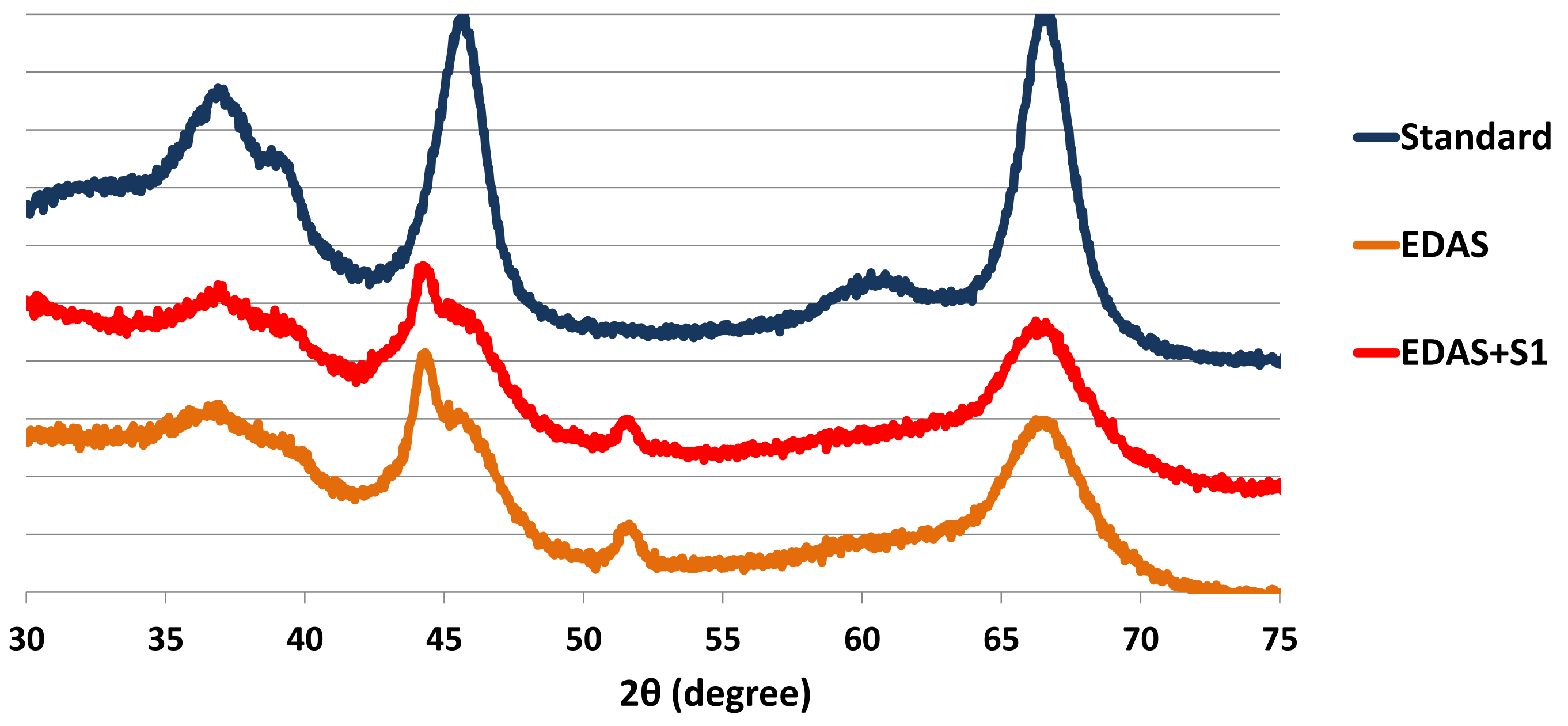
Pore distribution



- All samples are micro-mesoporous.
- EDAS highly improves S_{BET} and the presence of small mesopores (3-10 nm).
- Stearic acid enhance mesopores content

Crystallinity

XRD measurements were realized on samples after H_2 reduction (750°C, 1h, 5°C/min)

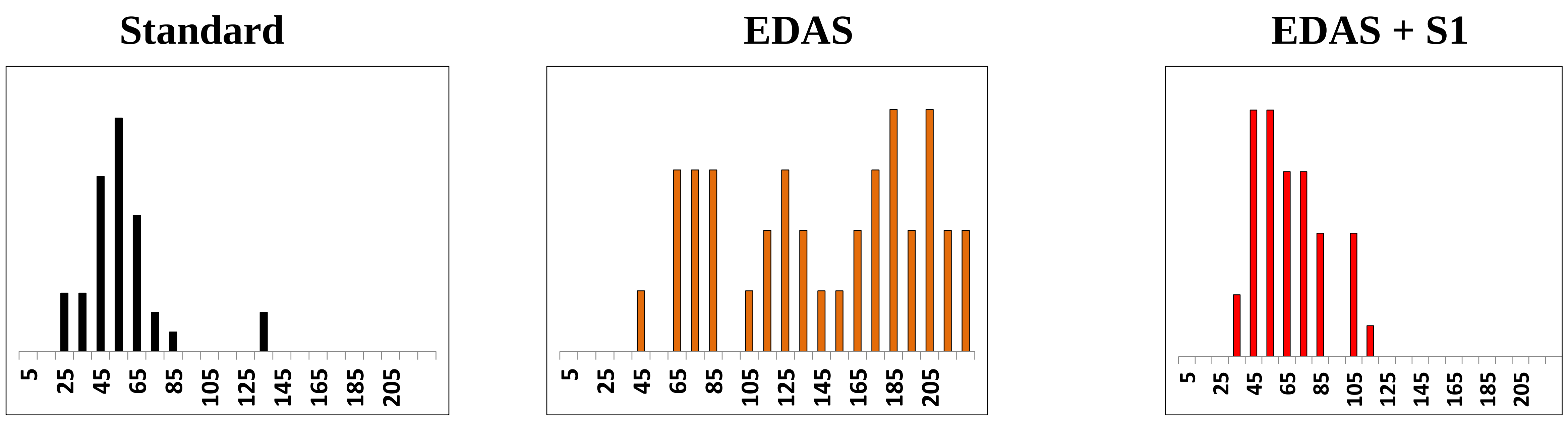


- γ-Al_2O_3 in all samples
- $Ni_{(0)}$ presence with EDAS
- $NiAl_2O_4$ presence without EDAS
- Higher alumina cristallites size without EDAS

Ni particle size (XRD)	Standard	EDAS	EDAS + S1
Ni particle size	N.A.	12	12,2
Al_2O_3 cristallite size	5,4	3,2	3,3

Sintering resistance

TEM observations after Temperature Programmed Reduction (25-1000°C, 2°C/min, H_2)



Standard

EDAS

EDAS + S1

- Stearic acid affords a very effective influence against nanoparticles sintering

Conclusions and perpectives

- EDAS and surfactants increase the specific surface area of Ni/Al_2O_3 xerogel catalysts and the dispersion of Ni particles.
- Further experiments using others surfactants (P123®, TMAH) will be investigated.
- Catalytical tars reforming will be done with the two best catalyst synthesized