

PERFORMANCE OF NICKEL SUPPORTED ON LA-HEXAALUMINATE HIBONITE TYPE SYNTHESIZED

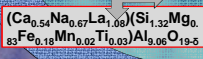
FROM ALUMINUM SALINE SLAGS IN THE DRY REFORMING OF METHANE

J.J. Torrez-Herrera, S.A. Korili, A. Gil.
INAMAT²- Science Department, Los Acebos Building, Public University of Navarra, Arrosadia Campus, 31006 Pamplona, Spain.

RESULTS

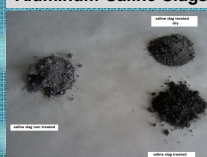
ABSTRACT

This work describes the procedures followed to obtain four hibonite-type La-hexaaluminates (La-HA) using aluminum saline slag waste as the aluminum source. Briefly, an acid-extracted aluminum solution (8.9 g_{Al}/L) was used to synthesize the hexaaluminate by mixing with a stoichiometric amount of lanthanum nitrate and 2-propanol/polyethylene glycol/methanol/1-hexanol/glucose depending on the hydrothermal conditions of the synthesis. transmission electron microscopy (HR-TEM)..



The results showed the formation of pure-phase hexaaluminate at 1473 K in all cases, with differences in the textural properties between the materials. The solids obtained were used as supports for nickel catalysts (10 wt.%) for the dry reforming of methane (DRM) at 973 K. The supports and catalysts were characterized by X-ray diffraction (XRD), N₂ adsorption at 77 K, X-ray fluorescence (XRF), temperature-programmed reduction (TPR), scanning electron microscopy (SEM) and transmission electron microscopy (HR-TEM).

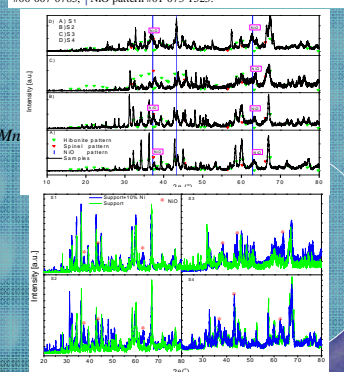
WASTE Aluminum Saline Slags



Composition	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	Cl
wt. %	0.77	8.49	53.21	4.23	0.97	0.46	0.84

Composition	TiO ₂	Cr	MnO	Fe ₂ O ₃	Ba	Cu	F	Zn
wt. %	0.05	0.07	0.26	1.25	0.07	0.51	0.41	0.17

(Top) XRD pattern of the Ni/hexaaluminate synthesized using La and Al extracted from saline slags (the hibonite, NiO and spinel patterns are included for comparison). (Bottom) Comparison between support and catalyst. Symbols: ▼ Spinel pattern #00-021-1152, ▽ Hibonite pattern #00-007-0785, | NiO pattern #01-073-1523.



- S1-AD,
- S2-MAD,
- S3-MAD+PegMn
- S4-RMAD

CONCLUSION

This study has demonstrated that it is possible to use aluminum saline slags to synthesize materials with a hexaaluminate type structure as support for Ni catalysts. The trace metals resulting from acid extraction of Al from the slag contribute positively to synthesis of the hexaaluminates since they allow an La-HA structure with an La:Al stoichiometric ratio of 1:11 to be obtained.

The hexaaluminates obtained from valorization of the aluminum saline slags and modified with Ni have been found to be active in the dry reforming of methane (DRM), with an effect of their textural properties, dispersion of the metallic phase and metal-support interaction on the performance of the catalyst in the reaction being observed. S4 was found to be the catalyst, exhibiting the best stability and catalytic performance during the 20 h of reaction, followed by S3, S2, and S1.

Another important aspect highlighted in this work is that the purity and crystallinity of the hexaaluminate affects the interaction between the support and the metal, thus resulting in low dispersion and a very large metal grain size, which influences the performance of the reaction as fewer active sites are generated in the catalyst. It is therefore advisable to maintain a compound phase that allows a greater metal-support interaction in the case of hexaaluminate-based catalysts.

Table 1: Maximum peak temperatures and area fraction of the reduction stages for the different cats.

Sample	Method	T _{max} (K); Peak Area Fraction (%)				
		α	β1	β2	γ	δ
S4	RMAD	629	628	723	1051	1001
S3	MAD+PegMn	672	643	723	1051	1001
S2	MAD	561	663	533	720	1174
S1	AD	632	599	-	-	-

Table 2: Parameters obtained from the experimental and simulated TPR curves at different heating rates for S1.

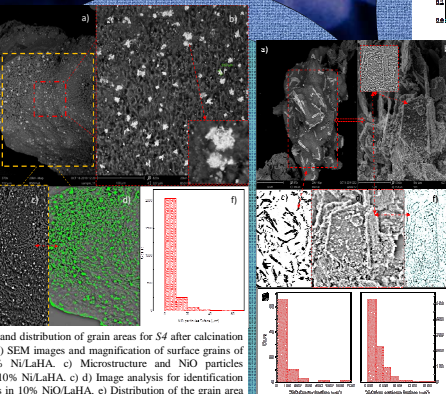
(K/min)	α ^o (%)	β ^o (%)	γ ^o (%)	δ ^o (%)	ε ^o (%)	η ^o (%)	θ ^o (%)	τ ^o (%)
10	100.7	7.95	81.5	1.99	602.85	622.35	1.627	1.624
15	100.0	6.50	61.7	1.95	648.12	647.87	1.513	1.513
20	23.3	6.16	61.7	1.93	669.54	659.81	1.429	1.427
60	82.8	7.77	60.7	2.13	707.03	707.03	1.391	1.382
80	92.3	6.95	61.9	2.62	729.24	729.24	1.289	1.232
100	98.3	6.90	61.1	2.15	749.05	730.01	1.274	1.374
479	81	61.5	2.93	-	-	-	-	-

Table 3: Parameters obtained from the experimental and simulated TPR curves at different heating rates for S4.

(K/min)	α ^o (%)	β ^o (%)	γ ^o (%)	δ ^o (%)	ε ^o (%)	η ^o (%)	θ ^o (%)	τ ^o (%)
10	100.0	1.63	1.71	1.62	606.51	610.51	1.510	1.510
15	100.0	1.63	1.71	1.62	617.26	672.66	1.467	1.467
20	100.0	1.63	1.71	1.62	697.06	697.06	1.426	1.426
60	42.8	1.62	1.69	1.69	787.00	762.36	1.380	1.376
100	98.3	1.63	1.69	1.69	866.72	866.47	1.447	1.220

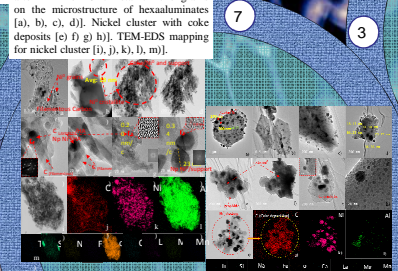
Table 4: Comparison of the kinetic parameters between the different methods.

Method	E _a (KJ/mol)	k ₀ (s ⁻¹)	R _{90%} (s ⁻¹)	m
Kininger	20.1	187.1	-	-
Ozawa	60.3	176.6	3.75 × 10 ⁵	2.50
Sestini	61.5	390.4	6.77 × 10 ⁵	2.91

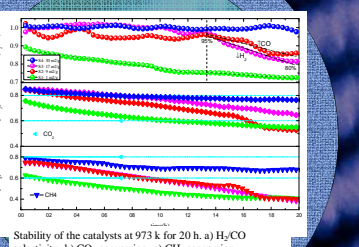
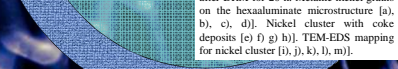


Images and distribution of grain areas for S4 after calcination a) SEM images and magnification of surface grains of 10% Ni/LaHA. b) Microstructure and NiO particles dispersed in 10% Ni/LaHA. c) Image of isolated clusters in a) using low-pass filters. d) Application and filtering of the box in b) to identify nickel particles dispersed on the hexaaluminate microstructure. e) Segmentation of the particles on the hexaaluminate microstructure to determine areas. f) Area distribution for clusters and free NiO particles.

TEM images and EDS mapping for S4 after DRM for 20 h. Metallic nickel grains on the microstructure of hexaaluminates (a), b), c), d). Nickel cluster with coke deposits (e) f) g) h). TEM-EDS mapping for nickel cluster (i), j), k), l), m).



TEM images and EDS mapping for S1 after DRM for 20 h. Metallic nickel grains on the hexaaluminate microstructure (a), b), c), d). Nickel cluster with coke deposits (e) f) g) h). TEM-EDS mapping for nickel cluster (i), j), k), l), m).



Stability of the catalysts at 973 K for 20 h. a) H₂O selectivity. b) CO₂ conversion. c) CH₄ conversion

Acknowledgments: The authors are grateful for financial support from the Spanish Ministry of Science and Innovation (AEI/MINECO) through project PID2020-112656RB-C21. JJTH thanks the Public University of Navarra for the predoctoral contract. AG also thanks Banco Santander for funding through the Research Intensification Program.