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- S. Canchari Chacon
  - Co-Authors: G. Picasso Escobar , C. Santolalla , R. Sun Kuo .

- Preparation of catalysts based on supported and unsupported mixed oxides of Ni-Ga for application in the Oxidative Dehydrogenation of Ethane

"Preparation of catalysts based on supported and unsupported mixed oxides of Ni-Ga for application in the Oxidative Dehydrogenation of Ethane"

Silvia Canchari [a], C. Santolalla [b], G. Picasso [a], R. Sun [c]

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Abstract

In the present work, catalysts based on Ni-Ga-α (α = 0.04-0.10) oxides, both unsupported and supported on γ-Al_2O_3, were synthesized by the methods of co-precipitation and impregnation by volume in excess. The addition of small charges of Ga to the NiO matrix had notable effects on the physicochemical properties of the oxide, with a notable increase in the BET surface area. The TPR analyzes of the mixed unsupported catalysts compared to the simple oxides revealed wide bands displaced at higher temperature, indicating that the Ga tends to inhibit the Ni^{2+} reduction process. Additionally, the Ni-Ga system (0.04-0.08) shows two reduction peaks, which suggests the existence of two reducible Ni species. The TGA analysis shows almost flat curves from 400°C for both supported and unsupported catalysts, which indicates that the calcination temperature was adequate for the synthesis of the catalysts (450 ° C). The XRD analysis allowed to observe peaks attributed to the NiO phase with bunsenite structure, which is the predominant phase in supported and unsupported Ni-Ga catalysts. Also, the DRS evidences the charge transfer between the metal atoms and the oxygen of the crystal arrangement, and a change of coordination after the addition of Ga. The ethylene selectivity obtained in the supported ones was increased up to 84%, a higher value than that obtained in the unsupported catalysts (45%), which can be attributed to the greater presence of nucleophilic oxygens with respect to the electrophilic ones in the surface of those supported, as confirmed by the XPS analysis.

Introduction

The production of ethylene from ethane can be carried out by various processes such as steam cracking of hydrocarbons, dehydration of alkanes, dehydration of ethanol; reported by A. Gartner. [1] Thus, among the proposed processes, the oxidative dehydrogenation of ethane (ODH) appears as one of the most promising, because it is exothermic and operates belows 500 °C.

In that sense, the key to a large-scale implementation of the ODH reaction of ethane is the development of a selective to ethylene catalytic system, capable of activating ethane for the selective production to ethylene, minimizing the route of total oxidation. [2]

Goal

- Synthesize the catalysts based on mixed Ni-Ga mixed and supported oxides on γ-Al_2O_3, modifying the Ni / Ga mass ratios and the metallic charge on the support by the Co-precipitation and impregnation methods respectively.
- Characterize the catalysts by the techniques: sorption of N_2 (BET method), TGA, XRD, DRS and XPS to relate the preparation with the activity and ethylene selectivity of the catalysts.
- Evaluate the activity (for a W/F ratio) and ethylene selectivity (for different W/F) of the Ni-Ga samples to relate it for the structural and chemical properties of the catalysts.

Preparation of the catalyst

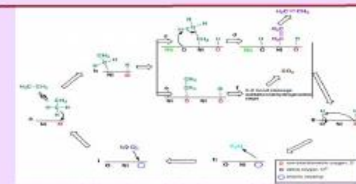
$Ni(NO_3)_2.6H_2O(s) + Ga(NO_3)_3.XH_2O(s)$

- NH_4OH -0.5M
- Stirr x 2h

Precursor mix Ni-Ga

- Rotavapor (60ºC x 30min)
- Filter/wash
- Dry at 110ºC x 12h
- Calcine at 450ºC x 5h

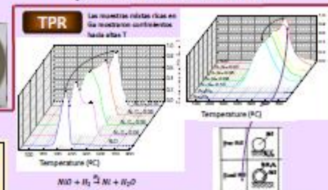
$Ni_{1-\alpha}Ga_{\alpha}O(s)$



Probable mechanism for the formation of ethylene-selective species in the ODH reaction of ethane [3].

Characterizations

TPR



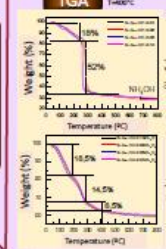
$NiO + H_2 \rightarrow Ni + H_2O$

	Catalyst	S_{BET} (m^2/g)	Pore size BJH (nm)
Unsupported	NiO	48	9
	Ni-Ga-0.06	103	9
	Ni-Ga-0.08	113	10
	Ni-Ga-0.10	115	9
Supported	NiO/Al_2O_3	111	11
	Ni-Ga-0.06/Al_2O_3	111	12
	Ni-Ga-0.08/Al_2O_3	104	11
	Ni-Ga-0.10/Al_2O_3	109	11
	Ga_2O_3/Al_2O_3	112	10
	γ-Al_2O_3	153	18

Bunsenita

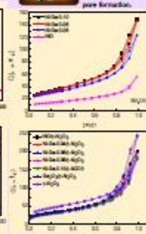
TGA

Oxide formation at T=400°C



BET

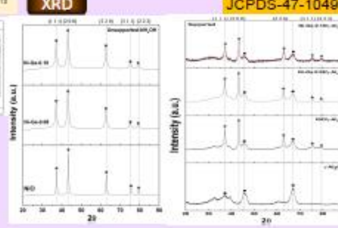
Type IV isotherms with cylindrical pore formation.



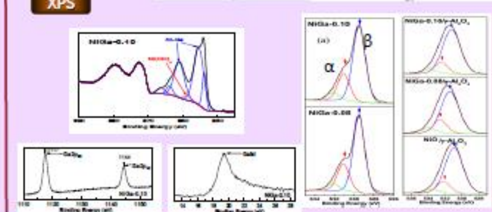
SEM

XRD

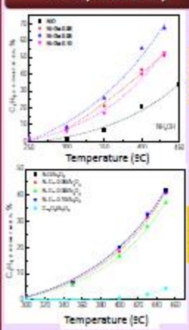
JCPDS-47-1049



XPS



Catalytic activity



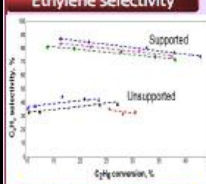
Unsupported

Ethane conversion for Ni-Ga unsupported samples 6, 8 and 10% (reaction condition W/F=0.48 gscm^{-3}, W=300mg, C_2H_6/O_2=1/1), the mixed were more active than the NiO.

Supported

Ethane conversion for supported catalysts (reaction condition W/F=0.48 gscm^{-3}, W=300mg, C_2H_6/O_2=1/1) supported catalysts had an activity similar to pure NiO oxide.

Ethylene selectivity



The supported catalysts were more selective to ethylene than the unsupported catalysts (reaction condition range W/F=0.18-1.44 gscm^{-3}, W=300mg, T=430ºC, C_2H_6/O_2=1/1).

Conclusions

- The addition of Ga has the effect of increasing the surface area of the unsupported catalysts, while the impregnation on γ -alumina decreases the total area of the system. Therefore, the deposition of the catalyst on the pores of the support has a greater influence on the final area that the system will exhibit, when compared with the effect that the addition of Ga has.
- As expected, the addition of Ga to the NiO network produces a decrease in the reducibility in the unsupported catalysts.
- The widening of the diffraction peaks of the mass systems suggests a smaller crystallite size for those obtained from precursors deposited with NH_4OH.
- The favorable effect of Ni-Ga was greater in catalysts supported on γ-alumina, probably due to the increase in nucleophilic oxygens compared to unsupported catalysts, which was verified by XPS measurements.

Acknowledgements

CIENCIACTIVA

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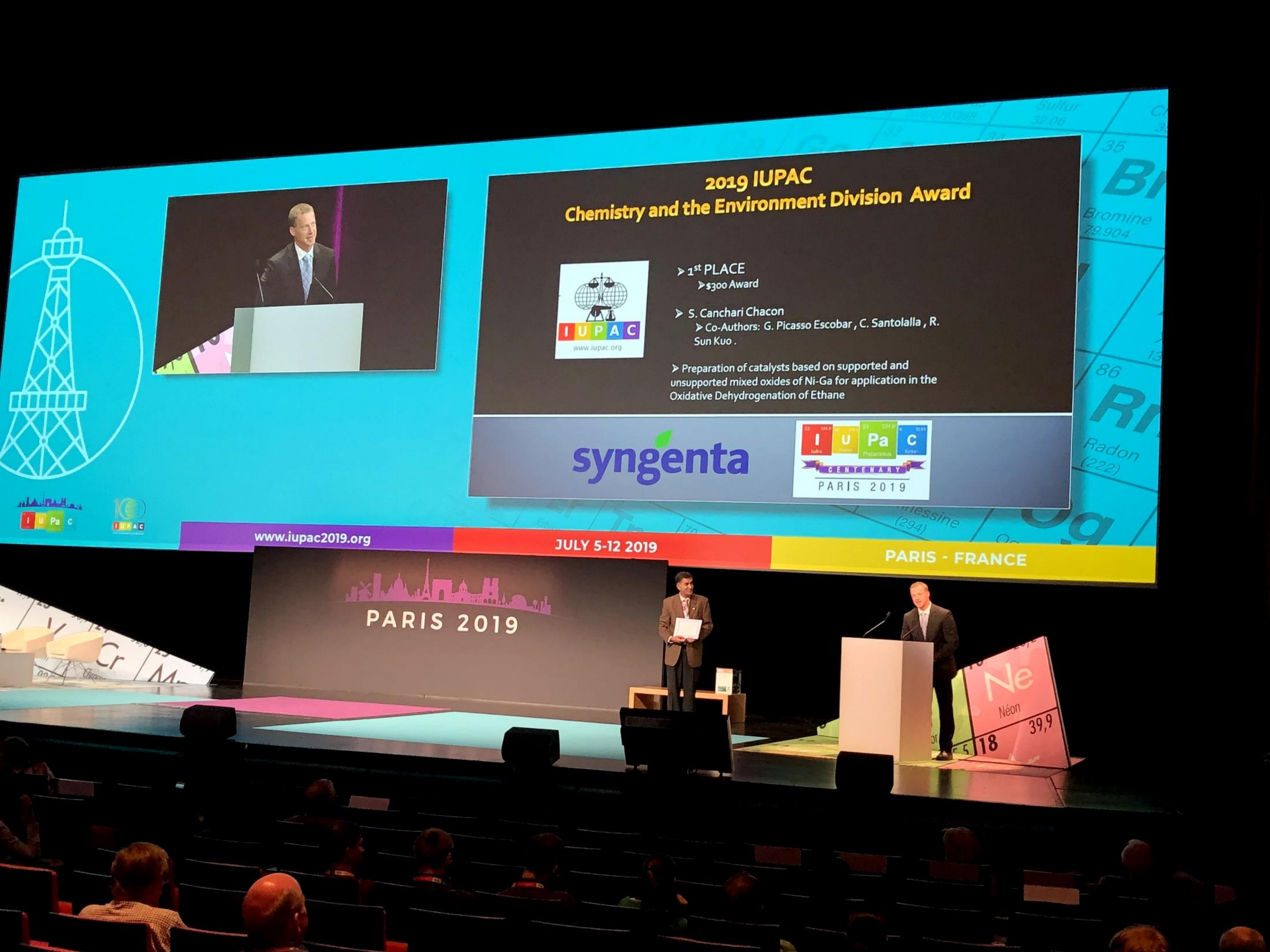
References

1. Gärtner, C. A., van Veen, A. C., & Lercher, J. A. (2013). *ChemCatChem*, 5(11), 3196-3217.
2. Heracleous, E., & Lemonidou, A. A. (2010). *Journal of Catalysis*, 270(1), 67-75.
3. Skoufa, Z., Heracleous, E., & Lemonidou, A. A. (2015). *Journal of Catalysis*, 322, 118-129.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- P.A. Diaw
  - Co-Author: M. Mbaye , N. Oturan , M.D. Gaye-Seye , A. Coly , A. Tine , J.J. Aaron , M. Oturan .

- Advanced electro-Fenton process for removal of monolinuron in aqueous medium.

Université Alioune Diop - Bambey
Université Paris-Est Marne-La-Vallée
Université Cheikh Anta Diop - Dakar

ADVANCED ELECTRO-FENTON PROCESS FOR REMOVAL OF HERBICIDE MONOLINURON IN AQUEOUS MEDIUM

P. A. DIAW [1,2,3], N. OTURAN [2] M. D. GAYE-SEYE [2,3], J. J. AARON [2], M. A. OTURAN [2]

[1] Laboratoire des Matériaux, Electrochimie et Photochimie Analytiques, Université Alioune Diop, Bambey, Sénégal
[2] Université Paris-Est, Laboratoire Géomatériaux et Environnement (EA4508), UPEM, 77454 Marne-la-Vallée Cedex 2, France
[3] Laboratoire de Photochimie et d'Analyse, Faculté des Sciences et techniques, Université Cheikh Anta Diop, Dakar, Sénégal

INTRODUCTION

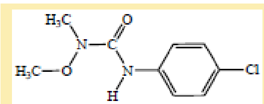
Monolinuron is an phenyhurea herbicide largely used in agriculture for the control of weeds in potato plantations [1]. Its relatively high solubility induced a great mobility and then makes it a potential contaminant of water [2, 3]. Previous studies have revealed their presence in waters but also in food. Although its toxicity is lower, its degradation products like aniline, parachloroaniline are considered highly toxic and therefore harmful to human health [4]. It become interesting to develop some methods for water decontamination to ensure environmental safety [5, 6]. In this work, advanced oxidation electro-Fenton process is used to treat aqueous solution of MLN by using Pt and BDD anodes. It depends to electricity to support Fenton's reaction between added Fe^{2+} and H_2O_2 electrogenerated at the O_2-diffusion cathode for the continuous production *in situ* of large amounts of oxidant hydroxyl radical (•OH). Efficiency of BDD anode is cited in many studies [7-9]. Advanced oxidation electro-Fenton process was recently succesfully used for the removal phenyhurea pesticides such as diuron and fluometuron [10-13].

TOOLS AND METHODOLOGY

GOAL OF THE WORK

- Degradation and mineralization of MLN in aqueous solution by the electro-Fenton process.
- Optimization of the experimental conditions (current intensity, catalyst concentration, type of anode).
- Identification of the intermediates, inorganic ions and carboxylic acids during the MLN treatment.
- Evaluation of TOC removal, energy and mineralization current efficiency during electrolysis of MLN.

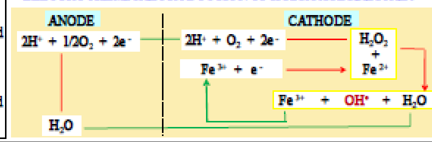
MONOLINURON MOLECULAR STRUCTURE



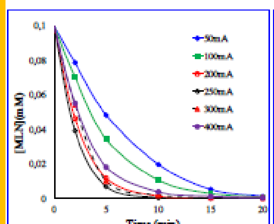
INSTRUMENTS AND EXPERIMENTAL CONDITIONS

- Cylindrical glass cell equipped with an carbon felt cathode, Pt or BDD anode.
- Electrolysis of 230-mL MLN (0.1 mM) in a cylindrical glass cell were performed with a potentiostat-galvanostat EG&G.
- Electrolyte: $FeSO_4$, Na_2SO_4 (50 mM) at pH 3.
- Identification by HPLC, GC-MS and IC of the intermediate products and inorganic ions formed during the electro-Fenton treatment.

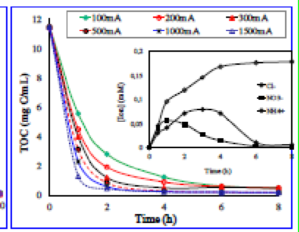
ELECTROCHEMICAL PRODUCTION OF HYDROXYL RADICALS



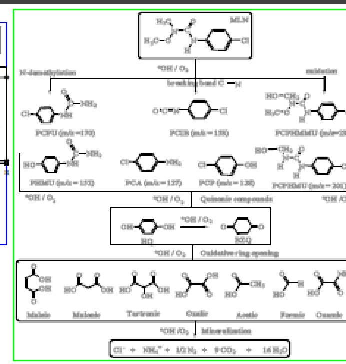
RESULTS



Effect of current intensity (I) on the degradation rate of of MLN with BDD anode, $[Fe^{2+}] = 0.2$ mM.



Effect of current on the TOC removal with BDD anode, $[Fe^{2+}] = 0.1$ mM. Insert: Evolution of inorganic ions formed during electrolysis at I= 500 mA.



Mechanism for MLN mineralization in aqueous solution on BDD anode.

EVOLUTION OF TOC REMOVAL, ENERGY CONSUMED AND MINERALIZATION CURRENT EFFICIENCY DURING ELECTROLYSIS

Process	TOC abattement (%)	E_c (kWh (g TOC)$^{-1}$)	MCE (%)
AO-BDD	97.0	10.2 ± 0.3	22.2
EF-Pt	69.7	12.4 ± 0.4	16.0
EF-BDD	98.2	10.0 ± 0.3	22.5

- Mineralization percentage depends on the process and the type of anode.
- Lower TOC values (about 70%) and mineralization efficiency with Pt anode.
- Highest mineralization rates obtained with BDD anode (up to 98%, I = 500 mA).
- Lower energy consumed for high mineralization current efficiency (22.5%).

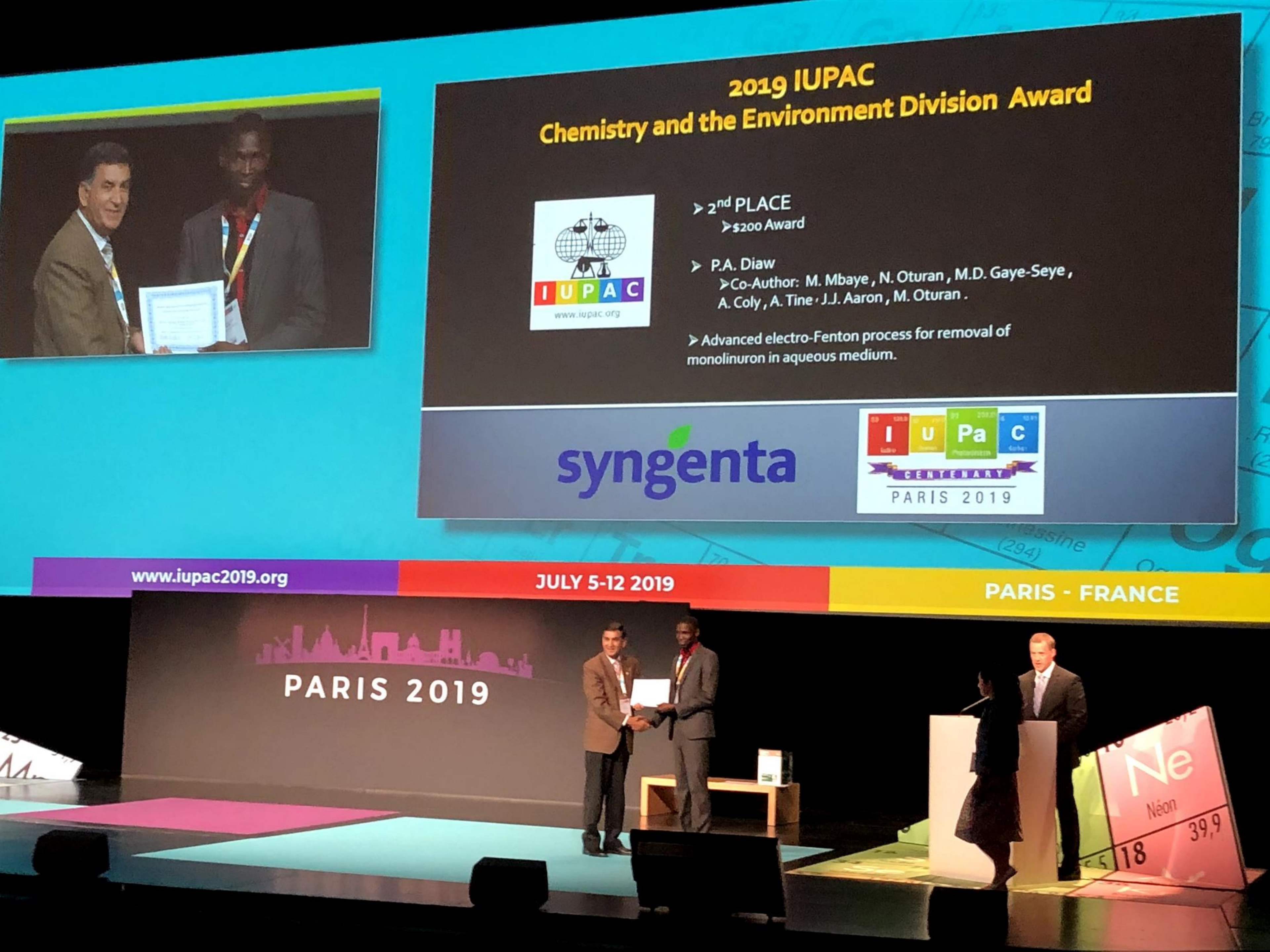
CONCLUSION

- The electro-Fenton process efficiency is proved for the degradation and the mineralization of MLN in aqueous solution.
- Quasi-complete TOC removal (> 98%) on BDD anode with lower energy consumed (10.0 ± 0.3 kWh (g TOC)$^{-1}$) was obtained.
- MLN degradation rate obeys to pseudo-first order reaction kinetics with absolute rate constant value of $3.1 \pm 0.2 \times 10^{9}$ M^{-1} s^{-1}.
- Electro-Fenton process can be easily used for the treatment of surface and ground water containing residual pesticides and also for domestic and industrial wastewater recycling.

REFERENCES

[1] Freitag D. and Scheunert I. Ecotoxicol. and environ. Saf., 20 (1990) 256-268
[2] INERIS. Monolinuron, validation groupe d'experts: Version 2, Octobre 2009.
[3] Guzzella L., Pozzoni F. & Giuliano G. Inter. J. Environ. Anal. Chem., 78:1 (2000) 87-106.
[4] Osano O., Klamero H. J. C., Pastore D., Bleeker E. A. J. Environ. Poll., 119 (2002) 195–202.
[5] Rodrigo M. A., Oturan N., Oturan M. A. A Review. Chem. Rev., 114 (2014) 8720–8745.
[6] Zouaghi R., Zertal A., David B. and Guittonneau S. J. Wat. Sci., 20:2 (2007) 163-172.
[7] Panizza M., Brillas E. and Comninellis C. J. Environ. Engin. Manag., 18:3 (2008) 139-153.
[8] Urtiaga A., Fernandez-Castro P., Gómez P., Ortiz I. Chem. Engin. J., 239 (2014) 341–350.
[9] Bringas E., Saiz J., Ortiz I. Chem. Engin. J.,172 (2011) 1016– 1022.
[10] Oturan M. A., Edelahi M. C., Oturan N., El kacemi K., Aaron J. J. Appl. Catal. B: Environ., 97 (2010) 82–89.
[11] Oturan M. A., Oturan N., Edelahi M. C., Podvorica F. I., El Kacemi K. Chem. Engin. J., 171 (2011) 127–135.
[12] Bringas E., Saiz J., Ortiz I. Chem. Engin. J., 172 (2011) 1016 – 1022.
[13] Diaw P. A., et al., Sep. Pur. Technol. 186 (2017) 197–206.

Pape A. Diaw thanks the RIF (Research Impulse Fund) of Bambey University -Senegal



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- S.D.S. Carvalho
  - Co-Authors: N.M.F. Carvalho
- Synthesis and Characterization of Iron (III) Complexes as catalysts for the degradation of methyl orange and methylene blue dyes.

SYNTHESIS AND CHARACTERIZATION OF IRON(III) COMPLEXES AS CATALYSTS FOR THE DEGRADATION OF METHYL ORANGE AND METHYLENE BLUE DYES

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INTRODUCTION

This work describes the application of mononuclear iron(III) complexes using the ligands: *N,N*-bis-(2-pyridylmethyl)amine (BMPA), *N*-methylpropanoate-*N,N*-bis-(2-pyridylmethyl)amine (MPBMPA), *N*-propanoate-*N,N*-bis-(2-pyridylmethyl)amine (PBMPA), *N*-propanamide-*N,N*-bis-(2-pyridylmethyl)amine (PABMPA), as homogeneous catalysts in the degradation of the dyes methyl orange and methylene blue (Figure 1). The complexes adopted octahedral geometry, with *NNN* coordination environment, as shown in Figure 2.

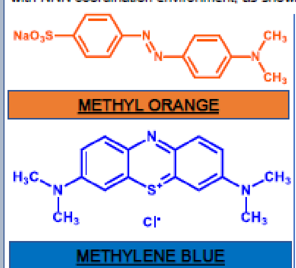


Figure 1: Dyes methyl orange and methylene blue.

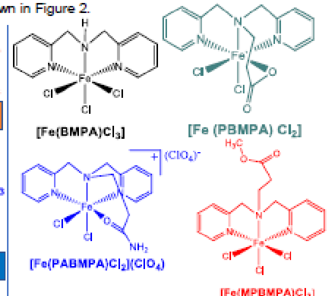
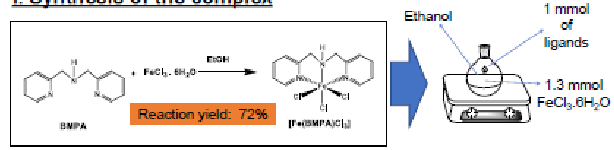


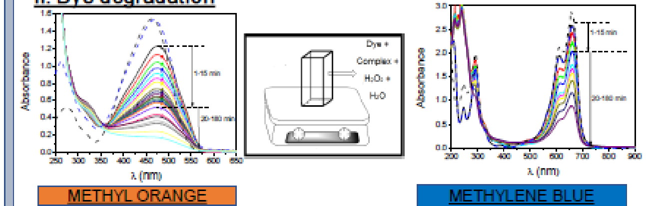
Figure 2: Mononuclear iron (III) complexes.

EXPERIMENTAL PROCEDURE

I. Synthesis of the complex



II. Dye degradation



RESULTS AND DISCUSSION

I. Characterization of the complexes

FT-IR

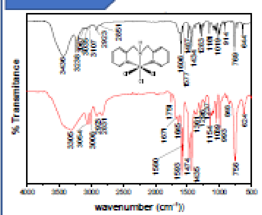


Figure 3: Infrared spectra of BMPA and [Fe(BMPA)Cl₃].

UV-VIS

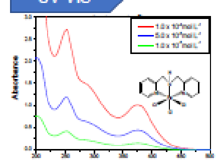


Figure 4: Electronic spectra of the [Fe(BMPA)Cl₃].

λ (nm)	ε (dm³ cm⁻¹ mol⁻¹)	Assignment
252	2.56 x 10⁴	TCIL (π→π*)
296	1.30 x 10⁴	TCML (d→π*py)
375	9.58 x 10³	TCLM (pCl→d)

ESI-MS-Q-TOF

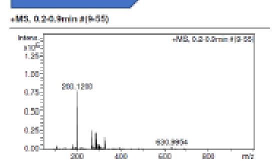


Figure 5: (+) ESI-MS-Q-TOF mass spectra of the [Fe(BMPA)Cl$_3$] complex in 1:1 (MeOH: H_2O) at 1.0x10-^{4} mol L^{-1}.

m/z: 324,9861: [Fe^{III}(BMPA)Cl$_2$]$^+$;
m/z: 630,9954: [Fe$^{III}_2$(BMPA)$_2$Cl$_3$O].

CONDUCTIVITY

Table 2: Conductivity data of the complexes.

Complex	Conductivity (µS. cm⁻¹)	electrolyte type	Solvent
[Fe(BMPA)Cl$_3$]	22.5	neutro	CH_3CN
[Fe(MPBMPA)Cl$_3$]	32.1	neutro	CH_3CN
[Fe(PBMPA)Cl$_2$]	25.5	neutro	CH_3CN
[Fe(PABMPA)Cl$_2$](ClO$_4$)	180.7	1:1	CH_3CN

II. kinetics of dye degradation

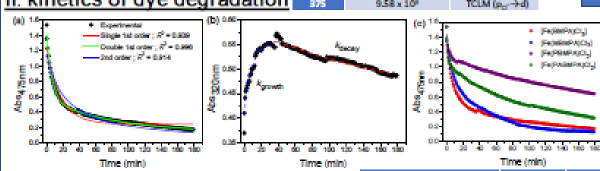


Figure 6: Degradation of methyl orange dye.

$$Abs_t = Abs_0 e^{-k_1 t} + Abs_0 e^{-k_2 t}$$

Table 3: kinetic parameters for methyl orange degradation.

Complex	k_1(min⁻¹)	k_2(min⁻¹)	R²	Discoloration (%)
[Fe(BMPA)Cl$_3$]	0.154	0.012	0.996	88.9
[Fe(MPBMPA)Cl$_3$]	0.192	0.020	0.998	91.6
[Fe(PBMPA)Cl$_2$]	0.406	0.005	0.995	58.4
[Fe(PABMPA)Cl$_2$](ClO$_4$)	0.676	0.012	0.997	79.3

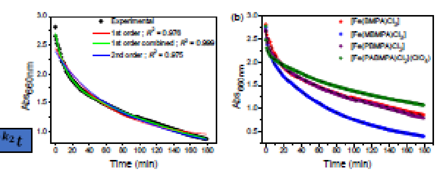


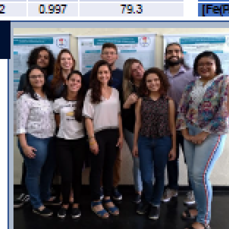
Figure 7: Degradation of methylene blue dye.

Table 4: kinetic parameters for methylene blue degradation.

Complex	k_1(min⁻¹)	k_2(min⁻¹)	R²	Discoloration (%)
[Fe(BMPA)Cl$_3$]	0.0868	0.00506	0.999	69.3
[Fe(MPBMPA)Cl$_3$]	0.280	0.0126	0.999	85.5
[Fe(PBMPA)Cl$_2$]	0.196	0.00813	0.998	70.6
[Fe(PABMPA)Cl$_3$](ClO$_4$)	0.806	0.00879	0.997	61.5

CONCLUSIONS

The reactions were followed by UV-VIS spectroscopy, where the dye chromophore band decayed with time, following pseudo-first order kinetics. After 180 minutes of reaction, 100% of degradation was achieved for methyl orange in presence of the complex [Fe(PBMPA)Cl$_2$]. For methylene blue, 97% of degradation after 180 minutes was achieved for [Fe(MPBMPA)Cl$_3$]. In overall, more than 85% of degradation was achieved for all catalysts. It was also possible to observe the increase of a new band at 320 nm and an isosbestic point 360 nm, indicating the formation of an Fe(III)-OOH intermediate as the active species. This intermediate band increased in the first minutes of the reaction and then decayed, following pseudo-first order kinetics. In conclusion, the studied complex presented promising results in the remediation of pollutant organic dyes, being able to achieve complete degradation after three hours of reaction, at mild reaction conditions.



REFERENCES

1-FORGACS, E., CSERH_ATI, T., OROS, G., 2004. Environ. Int. 30, 953-971.
2-CARVALHO, N. M. F.; HORN JR, A. ; ANTUNES, O. A. C. Applied Catalysis. A, General , Amsterdam, v. 305, p. 140-145, 2006.

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