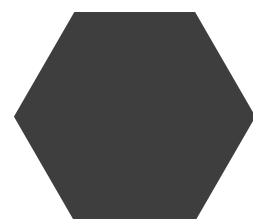


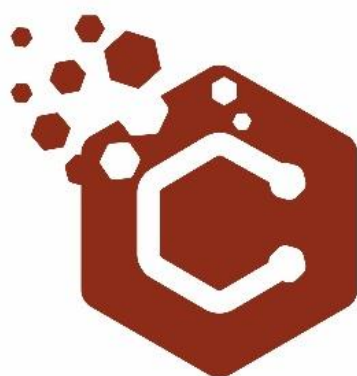
CARBOCATVIII

8TH INTERNATIONAL
SYMPOSIUM
ON CARBON
FOR CATALYSIS

PORTO, PORTUGAL
JUNE 26 - 29, 2018



Book of Abstracts



CARBOCAT VIII

26-29 JUNE 2018

VIII International Symposium on
Carbon for Catalysis

Porto - Portugal

VIII INTERNATIONAL SYMPOSIUM ON CARBON FOR CATALYSIS
ALMEIDA GARRETT MUNICIPAL LIBRARY, PORTO (PORTUGAL)

ISBN

978-989-8124-22-7 (Digital edition)

Editors

José L. Figueiredo
Joaquim L. Faria
Bruno F. Machado
Adrián M.T. Silva
Cláudia G. Silva
Manuel F. Pereira
Raquel Rocha
Salomé Soares

Edition

Sociedade Portuguesa de Química

Design

Local Organizing Committee of CarboCat-VIII

This book of abstracts was produced from the works submitted directly by the authors. Only minor editing changes were introduced, which in no way altered the scientific content. The final online version was established for the VIII International Symposium on Carbon for Catalysis according to the published template. The authors are responsible for the scientific content of their abstracts.

© Sociedade Portuguesa de Química

All rights reserved. No part of this document may be reproduced in any form or by any means without the written agreement of the editors.

INTERNATIONAL SCIENTIFIC COMMITTEE

Antonio Guerrero Ruiz (CCIA, UNED, Spain)

Bastian J. M. Etzold (TU Darmstadt Germany)

Bert F. Sels (KU Leuven, Belgium)

Cuong Pham-Huu (University of Strasbourg, France)

Dangsheng Su (IMR, CAS, Shengyang, China)

Daniel E. Resasco (University of Oklahoma, U.S.A.)

De Chen (NTNU, Norway)

Dmitry Y. Murzin (Åbo Akademi University, Finland)

Enrique Garcia-Bordeje (ICB, CSIC, Spain)

Fei Wei (Tsinghua University, China)

Gabriele Centi (Messina University, Italy)

Giuliano Giambastiani (ICCOM-CNR, Italy)

Harry J. Bitter (Wageningen UR, The Netherlands)

Jean-Philippe Tessonier (Iowa State University, U.S.A.)

M. Fernando Pereira (FEUP, Portugal)

Martin Muhler (Bochum University, Germany)

Petra de Jongh (Utrecht University, The Netherlands)

Philippe Serp (Toulouse University, France)

Zinfer F. Ismagilov (ICCMS, Novosibirsk, Russia)

LOCAL ORGANIZING COMMITTEE

José Luís Figueiredo (Chair, Faculdade de Engenharia, Universidade do Porto)

Adrián M. T. Silva (Faculdade de Engenharia, Universidade do Porto)

Bruno Fernandes Machado (Faculdade de Engenharia, Universidade do Porto)

Cláudia Gomes Silva (Faculdade de Engenharia, Universidade do Porto)

Joaquim Luís Faria (Faculdade de Engenharia, Universidade do Porto)

Manuel Fernando Pereira (Faculdade de Engenharia, Universidade do Porto)

Raquel Rocha (Faculdade de Engenharia, Universidade do Porto)

Salomé Soares (Faculdade de Engenharia, Universidade do Porto)

Cristina Campos (Sociedade Portuguesa de Química)

Leonardo Mendes (Sociedade Portuguesa de Química)

MODIFIED CARBIDE-DERIVED CARBONS USED IN THE CATALYTIC WET PEROXIDE OXIDATION OF OILY WASTEWATERS

Jose L. Diaz de Tuesta^{1,2*}, Macarena Munoz³, Carmen M. Dominguez⁴, Jose A. Casas³, Jan Gläsel⁵, Bastian J.M. Etzold⁵, Adrián M.T. Silva², Joaquim L. Faria², Helder T. Gomes^{1,2}

¹ Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal

² Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, 4200-465 Porto, Portugal

³ Sección Departamental de Ingeniería Química, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, Ctra. De Colmenar Km 15, 28049 Madrid, Spain

⁴ Dpto. de Ingeniería Química, Facultad C.C. Químicas, Universidad Complutense de Madrid, 28040- Madrid, Spain

⁵ Technische Universität Darmstadt, Ernst-Berl-Institut für Technische und Makromolekulare Chemie,

Alarich-Weiss-Straße, 64287 Darmstadt, Germany

*j.l.diazdetuesta@ipb.pt

Modified carbide-derived carbon (CDC) materials, prepared from TiC, were tested as catalysts in the decomposition of H₂O₂ and in the catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP), either in aqueous phase or in biphasic medium. The reactive extraction of Ti from the metal carbide (2 μm) was carried out to prepare the CDC materials, as described elsewhere [1]. Briefly, 0.03 m s⁻¹ Cl₂ gas was used (1.5 mol m⁻³ in He) as extraction agent during 5 h at 800, 1000 and 1200 °C. Afterwards, H₂ was used for 0.5 h at the extraction temperature to remove residual chlorine, resulting in CDC-800, CDC-1000 and CDC-1200 materials, respectively. Additionally, CDC-800 was treated with a mixture of 98% H₂SO₄ and 30% w/v H₂O₂ (3:1) at room temperature for 3 h by two methods: (1) wetting the material in the oxidative solution and (2) oxidizing the material partially encapsulated with WAX paraffin, resulting in CDC-800-Ox and CDC-800-Wax, respectively. Firstly, the materials were tested in the decomposition of H₂O₂ and, then, in the adsorption and CWPO of 4-NP, adapting the experimental procedure described in previous works [2-3] at the following operating conditions: 25-50 °C, pH₀ = 3.0, and concentrations of solid material, 4-NP and H₂O₂ of 2.5 g/L, 5.0 g/L and 17.8 g/L, respectively. Cyclohexane, *c*-C₆ (O/W volume ratio = 1:5) was used to simulate oily wastewater and study the influence of the oil phase presence in the medium.

The materials were characterized by temperature-programmed desorption and water contact angle measurements in order to determine the content of oxygen surface groups (OSGs) and the hydrophobic character. CDC-800, CDC-1000 and CDC-1200 materials showed a negligible oxygen content and a remarkable hydrophobic character (contact angle ca. 145°) when compared with other materials [3]. Functionalization of CDC-800 allows the incorporation of OSGs and the decrement of its hydrophobicity.

The results obtained for the decomposition of H₂O₂ in 4 h, adsorption and CWPO of 4-NP are depicted in Figure 1. Non-functionalized CDC materials showed a high catalytic activity in the decomposition of H₂O₂ when compared with other carbonaceous solids [2], and a significant increase of the H₂O₂ conversion was found when temperature was increased (Fig. 1-A). However, the presence of *c*-C₆ strongly affected the catalytic activity of the materials, decreasing substantially the conversion of H₂O₂ and restricting their use when an oil phase is present in effluents (oily wastewaters). That was ascribed to the hydrophobic character of the catalysts that lead to migration of the carbon materials to the oil phase (Fig. 1-B). The oxidized samples, CDC-800-Ox and CDC-800-Wax, showed lower catalytic activity in H₂O₂ decomposition and 4-NP adsorption (Fig. 1-C) when compared to non-functionalized samples. The negligible adsorption can be ascribed to the functionalization of the surface that can block the access to the pores of the material.

However, the removal of 4-NP by CWPO was higher when using oxidized samples (subtracting adsorption contribution) and the efficiency of H₂O₂ consumption (measured as converted 4-NP moles per consumed H₂O₂ moles) obtained was increased by using those materials. In addition, the asymmetric functionalized sample prepared by selective superficial oxidation (CDC-800-Wax) is capable of stabilizing a Pickering emulsion of *c*-C₆-water that is essential to maximize the interfacial area in the treatment of oily wastewaters.

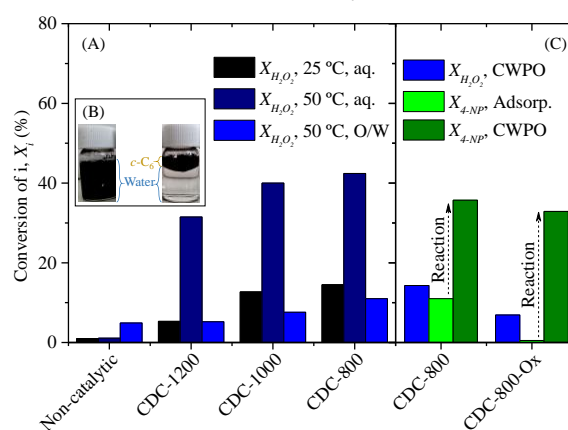


Figure 1. (A) Decomposition of H₂O₂ at 4 h, (B) photographs of CDC-800 dispersion in aqueous phase and in the water-*c*-C₆ mixture and (C) adsorption and CWPO of 4-NP at 50 °C after 4 h.

Acknowledgements. This work is a result of project “AIPProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through FEDER and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - POCI – and by national funds through FCT. M. Munoz thanks the Spanish MINECO for the Ramón y Cajal postdoctoral contract (RYC-2016-20648).

- [1] A.V. Kirilin, B.Hasse, A.V. Tokarev, L.M. Kustov, G.N. Baeva, G.O. Bragina, A.Yu. Stakheev, A. Rautio, T. Salmi, B.J.M. Etzold, J. Mikkola, D.Yu. Murzin. *Catal. Sci. Technol* 4 (2014) 387-401.
- [2] R.S. Ribeiro, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes. *Carbon* 62 (2013) 97-108.
- [3] M. Martin-Martinez, R.S. Ribeiro, B.F. Machado, P. Serp, S. Morales-Torres, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, H.T. Gomes. *ChemCatChem* 8 (2016) 1-12.