ISGC 2019
May 13rd - 17th

N°604 / OC
TOPIC(s) : Alternative technologies / Homogenous, heterogenous and biocatalysis

Enhancement of aerobic oxidation of aldehydes using ultrasonic irradiation

AUTHORS
Claire BESNARD / UNIVERSITÉ SAVOIE MONT BLANC, LCME, CHAMBÉRY
Laurent VANOYE / UNIVERSITÉ DE LYON, LGPC, VILLEURBANNE CEDEX
Gregory CHATEL / UNIVERSITÉ SAVOIE MONT BLANC, LCME, CHAMBÉRY
Alain FAVRE-RÉGUILLON / UNIVERSITÉ DE LYON, LGPC, VILLEURBANNE CEDEX
Corresponding author : Micheline DRAYE / micheline.draye@univ-smb.fr

PURPOSE OF THE ABSTRACT

Green chemistry and green engineering practices have to be integrated into the development of new reaction conditions for fine chemistry. This is particularly true for the oxidation of aldehydes where many procedures are described.[1] However, these often suffer from the application of environmentally harmful and stoichiometrically used oxidants such as permanganate, nitric acid or chromium oxides.[2]

Over the past decade, major advances have been made in the development of catalytic methods for the oxidation and extensive efforts have focused on the development of catalytic methods that use oxygen as the stoichiometric oxidant.[3] The liquid phase oxidation of aldehyde by molecular oxygen (autoxidation) is currently used for the commercial production of C4-C13 carboxylic acids from the corresponding aldehydes obtained by the hydroformylation of olefins (oxo synthesis).[4]

It has been demonstrated that this reaction is often limited by gas-liquid mass transfer. We have shown that for some aldehyde autoxidations described in the literature, the rate limiting step was still the rate of oxygen transfer into the liquid.[5] In such cases, the productivity and selectivity of the oxidation process is altered by oxygen starvation in the liquid phase. Taking advantages of the very efficient transfer properties of a continuous gas-liquid segmented flow process (Taylor flow), we have demonstrated that the productivity could be strongly improved.[6]

In this work, ultrasound irradiation is used as an alternative activation method to enhancement the aerobic oxidation of aldehydes. The results were then compared to those obtained under silent conditions. Finally, to understand how sonication influences the oxidation, the reaction mixture was stirred with a vibroacoustic mixer, also called vibromixer, which gives rise to hydrodynamic cavitation leading only to physical effects.

Identification and quantification of the reaction intermediates allow us to propose a new reaction pathway for this autoxidation reaction. Besides, ultrasonic irradiation allows decreasing the amount of instable intermediate produces during the reaction thus leading to an improvement of the safety of the process.

FIGURES

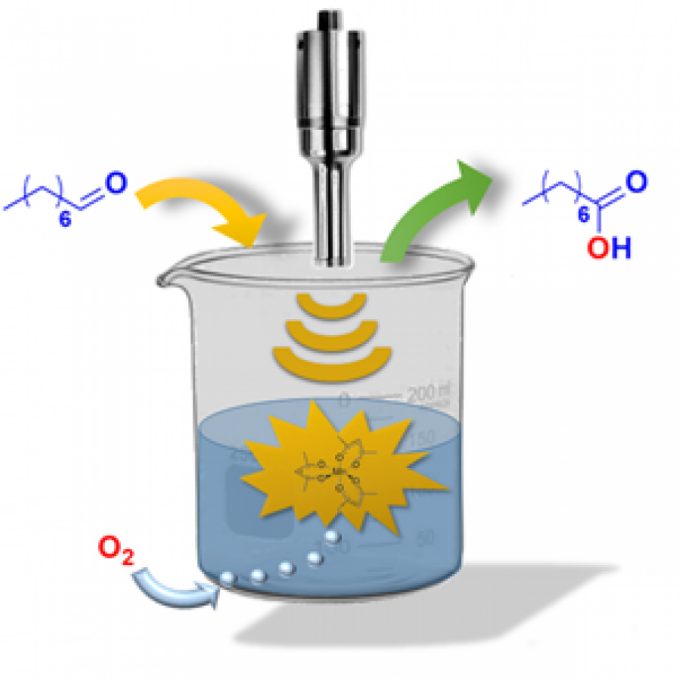

FIGURE 1

Figure

Schematic representation of aerobic oxidation of aldehyde by Mn-based catalyst under ultrasonic irradiation

FIGURE 2

KEYWORDS

Aerobic oxidation | Aliphatic aldehyde | Ultrasonic irradiations | Molecular oxygen

BIBLIOGRAPHY

[1] a) J. R. McNesby, C. A. Heller, Chem. Rev. 1954, 54, 325-346; b) T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 2005, 105, 2329-2364.

[2] J.-E. Bäckvall, Modern Oxidation Methods, 2nd Ed., Wiley-VCH, Weinheim, 2010.

[3] S. S. Stahl, P. L. Alsters, Liquid Phase Aerobic Oxidation Catalysis, Industrial Applications and Academic Perspectives, Wiley-VCH, Weinheim, 2016.

[4] W. Riemenschneider, in Ullmann's Encyclopedia of Industrial Chemistry, 6th Ed., Vol. 6, Wiley-VCH, 2003, pp. 493-508.

[5] L. Vanoye, A. Favre-Reguillon, A. Aloui, R. Philippe, C. de Bellefon, RSC Adv. 2013, 3, 18931-18937.

[6] L. Vanoye, J. Wang, M. Pablos, R. Philippe, C. d. Bellefon, A. Favre-Réguillon, Org. Process Res. Dev. 2016, 20, 90-94.