

Ultrasound-assisted catalysis towards selective oxidation of sugars

Catalysis lies at the core of chemical synthesis, serving as the bedrock upon which diverse compounds, including essential fuels, are synthesised and refined [1-2]. Nevertheless, the prevailing reliance of our society on fossil-derived raw materials casts a looming shadow of environmental and ecological peril. If we fail to proactively seek out alternative and sustainable resources, the consequences could be catastrophic for our planet's delicate ecosystems [3-4]. Within this challenging field, a notable transformation is gradually taking shape—the integration of renewable raw materials into the chemical industry. Renewable feedstocks like carbohydrates, lignin, and polysaccharides are at the forefront of this transition, offering a plethora of possibilities for reshaping chemical syntheses and processes [5]. Yet, amidst this promising shift, a complex dilemma persists: the precise control of the selective conversion of these molecules remains an arduous puzzle within the field of chemistry. The ultimate aspiration is not merely the creation of chemical compounds with enhanced properties, but also the minimization of their environmental footprint. The convention approach of valorizing renewable feedstocks often requires harsh conditions of temperature and pressure as well as complicated downstream processing, at the expense of product yield and selectivity. Consequently, the pursuit of alternative activation technologies has become an imperative endeavor. In the context of assisted-catalysis, chemical reactions can be achieved at near-room temperatures, without compromising on product selectivity while significantly reducing complicated downstream processing [6-7]. This innovative approach offers a promising solution to the perennial challenge of selectivity in chemical transformations. In the field of sustainable chemistry, one such alternative activation technology is the application of ultrasound in chemistry, often called 'sonochemistry'. With its unconventional approach, sonochemistry has emerged as a compelling disruptive assisted-technology in the field of catalysis. By harnessing the power of ultrasonic waves, sonochemical reactions promise a unique and efficient path towards selective and sustainable synthesis. This article aims to provide an insightful exploration of the vast potential of ultrasound in activating recalcitrant chemical bonds, leading to the production of high-value-added chemicals. Whether in homogeneous or heterogeneous conditions, ultrasound emerges as a powerful ally in the quest for innovative and sustainable chemical synthesis pathways.

Sonochemistry: principles and applications

Sonochemistry involves the utilization of ultrasound (US) to facilitate chemical reactions. When ultrasonic waves propagate through a liquid, they locally modify the fluid's density. If the acoustic intensity is sufficient, these waves disrupt the cohesive forces within the liquid, leading to the formation of solvent vapor cavities or bubbles within the liquid [7-9]. Their formation and size oscillations due to the influence of the ultrasonic waves constitute a phenomenon known as acoustic cavitation, during which the bubbles subsequently undergo rapid expansion before collapsing. Depending on the applied frequency, the collapse of the bubble primarily induces physical effects like shockwaves, high-speed jets with low-frequency ultrasound (LFUS, 20-80 kHz), or chemical effects such as the release of free radicals (e.g. reactive oxygen species) within the solution with high-frequency ultrasound (HFUS, 100-800 kHz). Once these radicals disperse into the solution, they can recombine (e.g. forming H_2O_2 and H_2 during the sonolysis of water) or oxidize solutes. Indeed, a cavitation bubble can be viewed as a microreactor capable of acting on recalcitrant chemical bonds and initiating crucial reactions (figure 1).

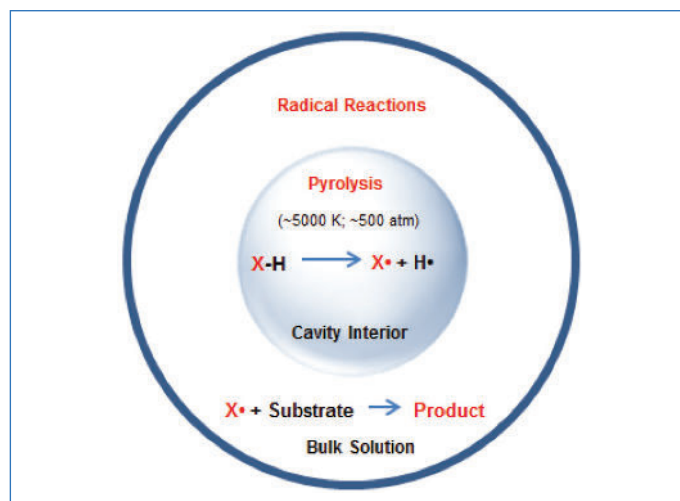


Figure 1 - Various zones involved in the production and reaction of reactive species formed by cavitation.

Sonochemistry is not only a field of scientific intrigue, but also a practical tool for researchers and industries seeking to harness the power of sound waves for innovative and sustainable chemical processes. The synergy between ultrasound and chemistry offers a promising frontier where complex reactions can be controlled and accelerated, paving the way for greener and more efficient chemical production methods.

Sonochemistry: catalyst-free application of ultrasound for chemical synthesis

The application of high-frequency ultrasound (550 kHz) has been employed as an alternative activation tool for transforming bio-sourced substrates into high-value-added products in solution (catalyst-free processes) [10-11]. This is exemplified by the oxidation of glucose into gluconic acid, a reaction that typically demands the use of expensive catalysts (Au/TiO_2 , $\text{Au-Cu}/\text{TiO}_2$, Au-PdTiO_2 , etc.) at high reaction temperatures ($> 100^\circ\text{C}$) and O_2 or air pressures ($> 5\text{ MPa}$) [12-15]. However, this transformation has been achieved with high selectivity towards gluconic acid under ultrasonic irradiation (550 kHz, 100% amplitude, 0.1 W mL^{-1}) at near-ambient temperature (30°C), without the need for any catalyst. The oxidation is facilitated by the generation of oxygen radicals such as $\text{HO}\cdot$ and $\text{HOO}\cdot$ [10]. It has been shown that the nature of the gas atmosphere significantly impacts the selectivity of products (figure 2) formed owing to the different nature of oxidizing species produced during sonolysis. The ability to perform such transformations at or near ambient conditions not only reduces energy consumption but also enhances the sustainability of chemical processes, opening up exciting possibilities for greener and more efficient industrial production. This seemingly subtle variation in the gas atmosphere exerts a profound impact on the entire reaction dynamics. Firstly, it affects the final temperature attained within the reaction medium, as well as the pressure generated during the collapse of the cavitation bubbles. These environmental factors, temperature and pressure, are pivotal determinants of reaction kinetics and product outcomes. Moreover, the nature and concentrations of the radicals generated during the sonolytic process are intricately linked to the choice of gas. In the case of argon bubbling, the predominant radical species formed are $\text{HO}\cdot$ and $\text{H}\cdot$. Conversely, when oxygen is employed as the

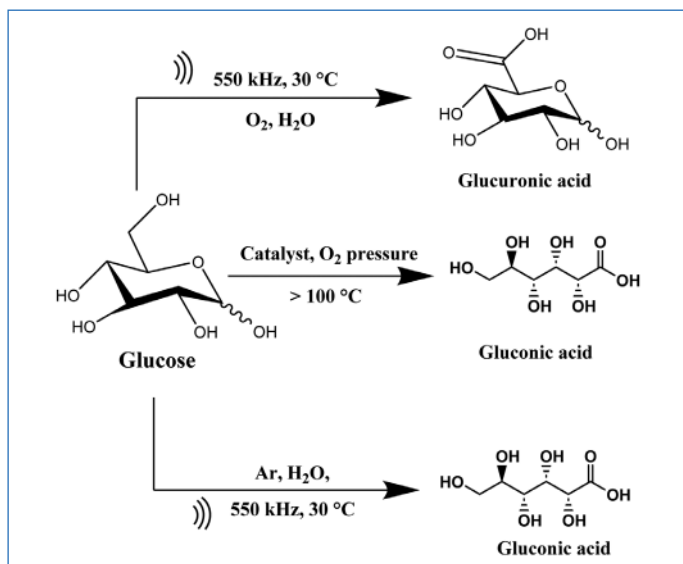


Figure 2 - Influence of the gaseous atmosphere on the oxidation of glucose under high frequency US.

gaseous environment, oxygen molecules scavenge or reacts with H^\bullet leading to the formation of highly reactive peroxy radicals (HOO^\bullet). It not only highlights the relationship between ultrasound, chemistry, and the surrounding gas environment but also offers an opportunity for tailoring reactions to yield specific products and productivity. By gaining a deeper understanding of these gas-mediated effects on sonochemical reactions, we unlock the potential to engineer processes that are not only environmentally benign but also highly controllable, offering a new frontier in the quest for sustainable chemical transformations.

Sonocatalysis: ultrasound applications in heterogeneous catalysis

Solid phases in contact with liquid solutions under ultrasonic irradiation promote heterogeneous nucleation of cavitation bubbles. Indeed, at the liquid-solid interface, the surface free energy of water is reduced compared to the rest of the solution [16]. This enables the selective nucleation of cavitation bubbles on the surfaces of solid materials thereby localising *in situ* generated radicals on catalysts or material surfaces. This phenomenon can be strategically exploited in sonocatalytic applications for selective substrate conversions. Achieving selective oxidation reactions without the use of external oxidizing agents and in the presence of an inert atmosphere represents an economically viable approach to synthesize platform molecules with oxygen-containing groups. In this context, we hypothesized that adding metal oxide-based catalysts to an ultrasonic environment under argon could enable the conversion of bio-based substrates with modified product selectivity while promoting more selective substrate oxidation. Returning to the example of glucose oxidation, it was also carried out in the presence of CuO under US irradiation (550 kHz, 100% amplitude, 0.1 W mL^{-1}) in the presence of argon. Under these conditions, glucose was selectively oxidized to glucuronic acid (figure 3). While ultrasound alone (under argon atmosphere) and Cu(II)-based catalysts (under oxygen atmosphere) can independently oxidize glucose to gluconic acid (figure 2), the presence of CuO under argon atmosphere resulted in the formation of glucuronic acid. The CuO catalyst serves as nucleation sites for the formation of cavitation bubbles. Upon bubble implosion, preferentially on the surface of the CuO catalysts, radicals (HO^\bullet and H^\bullet) released under argon are localised on the catalyst surface. HO^\bullet radicals bound to the CuO surface sites Cu3, while H^\bullet radicals adsorb

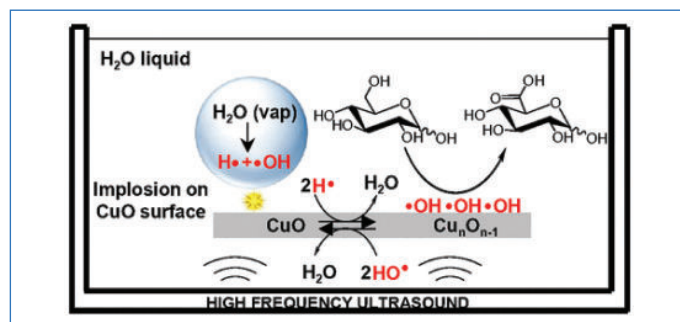


Figure 3 - Selective sonocatalytic oxidation of glucose to glucuronic acid under high-frequency ultrasound.

strongly at under-coordinated lattice oxygen sites on the surface of CuO. Adsorbed H^\bullet radicals have a diffusion barrier of 0.53 eV allowing migration and the reaction with lattice oxygen to form H_2O with a reaction energy of -0.82 eV. This process then results in generating an oxygen vacancy at the CuO surface, and a surface of CuO covered by HO^\bullet radicals. The *in situ* trapping and reaction of H^\bullet radicals inhibit the ring opening of glucose which is promoted largely by the presence of H^\bullet , and thus would shift the selectivity of the reaction towards glucuronic acid (figure 3) [17].

In conclusion, the addition of a heterogeneous catalyst in an ultrasonic irradiation environment is an intriguing strategy to harness the thermal effects associated with bubble implosion at the solid surface and develop selective catalytic reactions. It is worth noting, however, that while high-frequency ultrasound applications in chemistry may appear highly innovative (e.g. oxidation without added oxidants, using H_2O), the energy consumption they entail is a significant concern that cannot be overlooked. A comprehensive economic and energy analysis is necessary for their effective deployment and integration into sustainable chemical processes.

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