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Catalysis under ultrasonic irradiation: a sound synergy

Prince Nana Amaniampong and François. Jérôme*

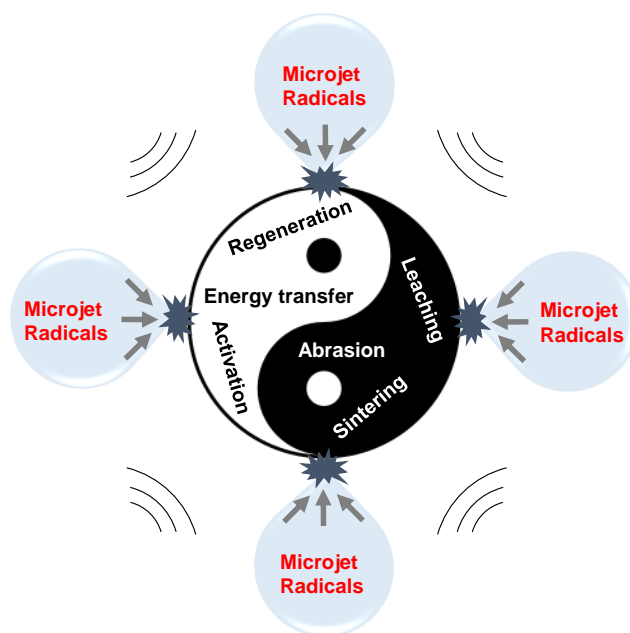
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Abstract : Through selected examples, we report here that ultrasound is capable of assisting a solid catalyst in various reactions. Beside improvement of heat and mass transfer induced by the implosion of cavitation bubbles, we show that a synergistic effect can occur between catalysis and ultrasound. In particular, the physical and chemical effects locally exerted on a catalytic surface upon implosion of cavitation bubbles can oxidize metal ions, provide energy to the catalyst/reaction, *in situ* activate or create catalytic sites and even prevent the catalyst from deactivation. The impact of ultrasound on solid catalyst structures, which may positively or negatively impact the performances of catalysts, is also discussed.

Keywords : Ultrasound ; Catalysis ; Synergistic effect ; Cavitation bubbles ; Radical reactions ; Shear forces

Graphical abstract



1. Introduction

Ultrasonic irradiation of liquids locally leads to rapid changes of pressure. When the liquid is locally subjected to depression, the pressure becomes lower than the vapor pressure of the sonicated liquid, thus generating a cavitation bubble composed of gas and vapors of liquid (Fig. 1). Once formed, these cavitation bubbles absorb energy from the sound waves, grow and then collapse, locally resulting in the formation of shock waves, high speed jets or radicals.[1] The effect of the cavitation bubble collapse on a liquid is depending on the applied frequency. For instance, the popular Low Frequency Ultrasound (LFUS) (20-80 kHz) generate large cavitation bubbles (~170 μm at 20 kHz)[2] and their implosions induce mostly physical effects such as shock waves, high speed jets, etc. As a consequence, LFUS are typically used, for example, for the erosion of particles, emulsification, crystallization, extraction, etc.[3, 4] In contrast, High Frequency Ultrasound (HFUS, 300-800 kHz) generate a large amount of small size cavitation bubbles (4.6 μm at 550kHz) which leads to a higher production of radicals that can further initiate chemical reactions (Fig. 1).[2, 5] More information on ultrasound can be found in a recent excellent review from Ashokkumar and Qiao.[6] With the growing demand of our society for alternative activation technologies, ultrasound is now witnessing a sort of renaissance, in particular in the field of organic chemistry and catalysis. In this context, the terms sonochemistry and sonocatalysis have been coined.

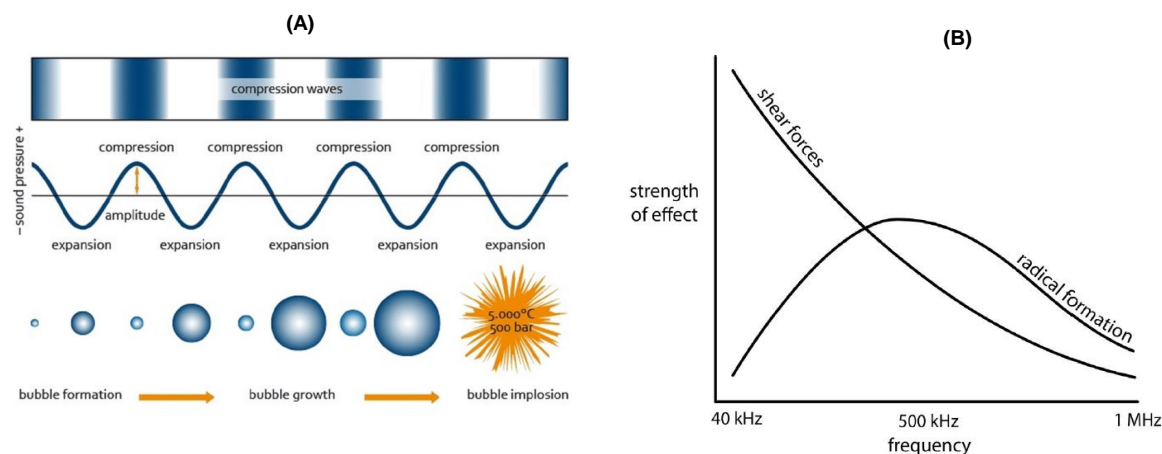


Figure 1. (A) formation, growth and implosion of cavitation bubbles; (B) Effect of the ultrasound frequency on shear forces and radical formation. Adapted from Ashokkumar *et al.*,[6] and Johansson *et al.*[7]

2. Chemical reactions induced by ultrasound

From a chemical point of view, a cavitation bubble can be viewed as a micro-reactor.[8] Due to the extreme conditions of pressure (up to 1,000 bar) and temperature (up to 5,000 K) at the interior of the cavitation bubbles, pyrolysis takes place inside the cavitation bubble. For instance, when water is subjected to an ultrasonic irradiation at a high frequency (100-800 kHz), small size cavitation bubbles are formed inside which water is dissociated to $\cdot\text{H}$ and $\cdot\text{OH}$ radicals. Upon implosion of the cavitation bubble, these radicals are propelled into the bulk solution where they react with organic solutes.

Conducting organic reactions under ultrasonic irradiation requires a careful selection of reactants. Reactants exhibiting a high vapor pressure tend to diffuse inside the cavitation bubbles where they are pyrolyzed.[9] In contrast, chemicals with a low vapor pressure remain into the bulk solution where they are subjected to shock waves or react with radicals released by the implosion of the cavitation bubbles. Hence, according to the reaction conditions, two reaction pathways take place under ultrasonic irradiation (i) pyrolysis-like reactions or (ii) radical-like reactions. Recently, P. Amaniampong investigated the reactivity of aqueous and alcoholic solutions of glucose under HFUS (550 kHz) (Fig. 2). Using a high concentration of glucose (> 40 wt. %), the probability of contact between glucose and the cavitation bubbles is high leading to a pyrolysis-like mechanism, with the *in situ* formation of levoglucosane.[10] Conversely, at low concentration (< 10 wt. %), glucose reacts with $\text{H}\cdot$ and $\cdot\text{OH}$ radicals propelled into the solution, leading to its major oxidation either to gluconic or glucuronic acid, depending on the atmosphere used.[11]

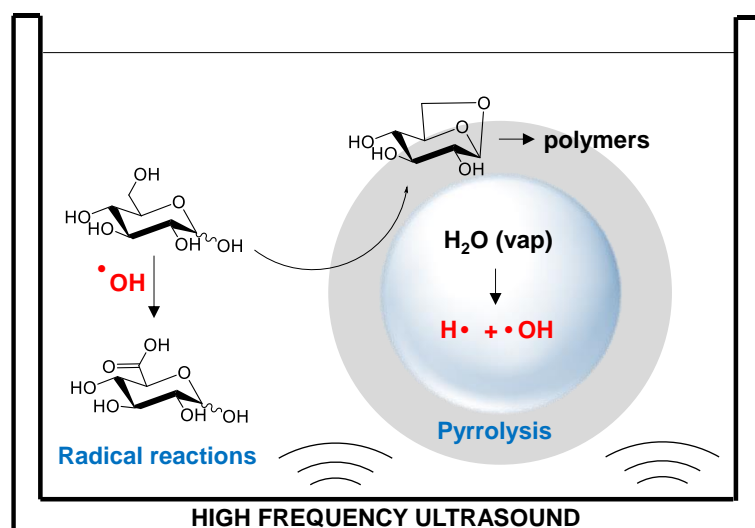


Figure 2. Difference of reaction selectivity according to the reaction zone

These examples showed that the ultrasound technology could be considered as a tunable technology for the conversion of strategic biobased building blocks to industrially relevant specialty chemicals. However, being able to control the rate and, even more importantly, to optimize the reaction selectivity under ultrasonic irradiation is much more difficult to achieve and, to date, it remains a challenging task. To tackle this issue, few groups have investigated the addition of a catalyst into the ultrasonic reactor.

3. Sonocatalysis

The concept of sonocatalysis has been investigated for decades but mostly with the popular low frequency ultrasound (<80 kHz), *i.e.* the *in situ* formation of radicals was very low and mainly physical effects occur in this case. Here, the turbulent flow and shock waves produced by the implosion of cavitation bubbles improve the dispersion of catalyst/reactant and mass transfer and increase the temperature at the catalyst surface, thus resulting in an improvement of the reaction rate. More importantly, cavitation on catalyst particle surfaces generates unpassivated and highly reactive surfaces. A chemical reaction that will normally not occur as a result of its low kinetic energy can be feasible under ultrasonication. The rate enhancement induced by ultrasound was observed in various reactions, for instance in Fenton-like reactions such as oxidation of carbohydrates,[12] vanillin,[13] oxidative depolymerization of lignin,[14] among many other examples.

In more interesting cases, a synergistic effect between the catalyst and ultrasound occurs, paving the way to reactions which are usually not feasible under silent conditions. This synergistic effect between ultrasound and catalysis was mainly observed in the presence of solid catalysts. Indeed, the formation of cavitation bubbles preferentially occurs on a particle surface *via* heterogeneous nucleation. In contrast to homogeneous solution, close to a surface, the implosion of cavitation bubbles is very asymmetric and thus the physical and chemical effects arising from the implosion of cavitation bubbles are concentrated on the catalyst surface, inducing the activation or generation of catalytic sites.[15]

For example, with a combined use of low frequency ultrasound (24 kHz) and Fe₃O₄ as catalyst, Taghizadeh and co-workers reported the sonocatalytic depolymerization of 2-hydroxyethyl cellulose (HEC).[16] At low frequency ultrasound, the amount of *in situ* produced radicals is very low and, under catalyst-free conditions, the depolymerization of HEC is a very slow reaction. Interestingly, in the presence of Fe₃O₄ as catalyst, the implosion of cavitation bubbles on the Fe₃O₄ surface provides locally enough energy to induce an

electron transfer between Fe_3O_4 and water, generating *in situ* $\cdot\text{OH}$ radicals and H^+ , both species being involved in the depolymerization of 2-hydroxyethyl cellulose (Fig. 3). As a result, the catalytic depolymerization rate of HEC was greatly enhanced under ultrasonic irradiation. The solid catalyst acting as a nuclei for the formation of cavitation bubbles, this reaction is of course sensitive to the type and the amount of catalyst used (particle size, surface area, etc.).

As above mentioned, under ultrasonic irradiation of water at a high frequency (300-800 kHz), $\cdot\text{OH}$ radicals stemming from the sonolysis of water are formed in a much larger amount than at low frequency. Parizot et al.[17] reported a very elegant work where *in situ* produced radicals activate the catalyst. In this concept, authors investigated the sonocatalytic degradation of ethylenediaminetetraacetic acid (EDTA) in water under ultrasonic irradiation at a high frequency (345 kHz), and in the presence of a $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst. Under optimized conditions, a conversion as high as 90% was obtained at 40 °C under an Ar/O_2 atmosphere. From a mechanistic point of view, radicals stemming from the sonolysis of water are propelled onto the surface of the $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst where they induce the oxidation of Co^{2+} site to Co^{3+} . Adsorbed EDTA is then oxidized by Co^{3+} , this later being consequently reduced to Co^{2+} (Fig. 3). In the absence of the $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst, no reaction occurred, confirming the synergistic effect between ultrasound and the $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst.

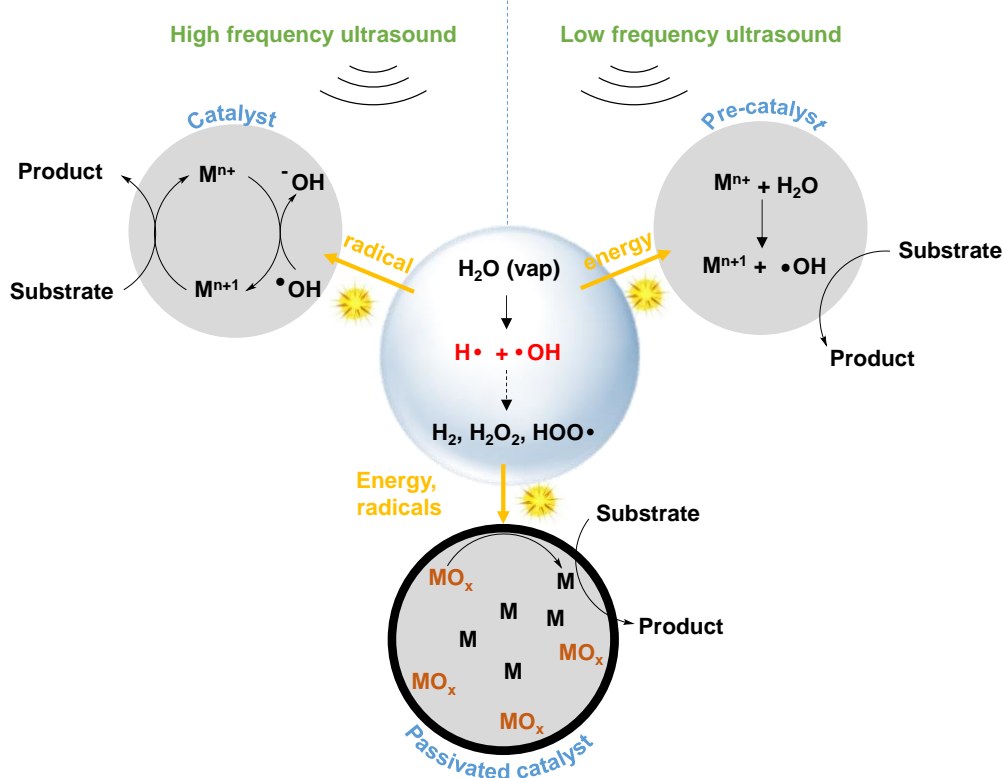


Figure 3. Different scenario of synergistic effects between solid catalysts and ultrasound

In another case in point, ultrasound can be beneficial for catalysis, thanks to the *in situ* “cleaning” of the catalyst surface (*e.g.* removal of oxide layer or passivating coatings from the catalyst surface) during the reaction, an important aspect as regards catalyst deactivation. This was reported for instance by Disselkamp *et al.* who investigated the effects of sonication on the hydrogenation *vs* isomerization of 3-buten-1-ol in the presence of palladium black in water.[18] They showed that applying ultrasound during the hydrogenation/isomerization of 3-buten-1-ol allowed a fast *in situ* reduction of Pd black, caused by the implosion of cavitation bubbles on the Pd surfaces, leading to a 5 fold increase of the reaction rate. Very interestingly, under conventional heating, the isomerization/hydrogenation rate ratio decreased as a function of the reaction time, suggesting a deactivation of catalytic sites responsible for the isomerization of 3-buten-1-ol during the course of the reaction. Under ultrasound, no change of the isomerization/hydrogenation rate ratio was observed over time indicating that applying ultrasound protect Pd black against deactivation (Fig. 3). A similar effect was observed by Carcenac *et al.* who reported an *in situ* surface cleaning of PtO₂ in the catalytic hydrogenation of fluorinated alkenes.[19]

4. Stability of catalysts

Solid catalysts (particles) act as nuclei for the formation of cavitation bubbles. The collapse of cavitation bubbles on the catalyst surface induce high-speed jets of liquid towards the surface which generate strong shear forces on the catalyst surface that may fragment it into smaller particles or modifies the chemical composition of the catalyst surface.[15, 20] On one hand, this could be viewed as a positive effect for catalysis since it results in (i) an erosion of the catalyst particles to smaller particle sizes, thus increasing the catalytic surface area and/or (ii) the *in situ* “cleaning” of the catalyst surface, both aspects dramatically enhancing the catalytic reaction rate. However, implosion of cavitation bubbles on the catalyst surface may also lead to severe damages on the catalytic surface.[21] The effect of ultrasound on catalyst stability is closely depending on the catalyst particle sizes and applied frequencies. Solid catalysts with particle sizes much larger than the cavitation bubbles tend to be severely subjected to abrasion, which is often accompanied by the ejection of matter from the catalyst surface to the solution (*i.e.* leaching). Conversely, due to turbulent flow, small size catalyst particles tends to collide each other, which may also induce a leaching of active species or agglomeration of particles through mechanical friction (Fig; 4).

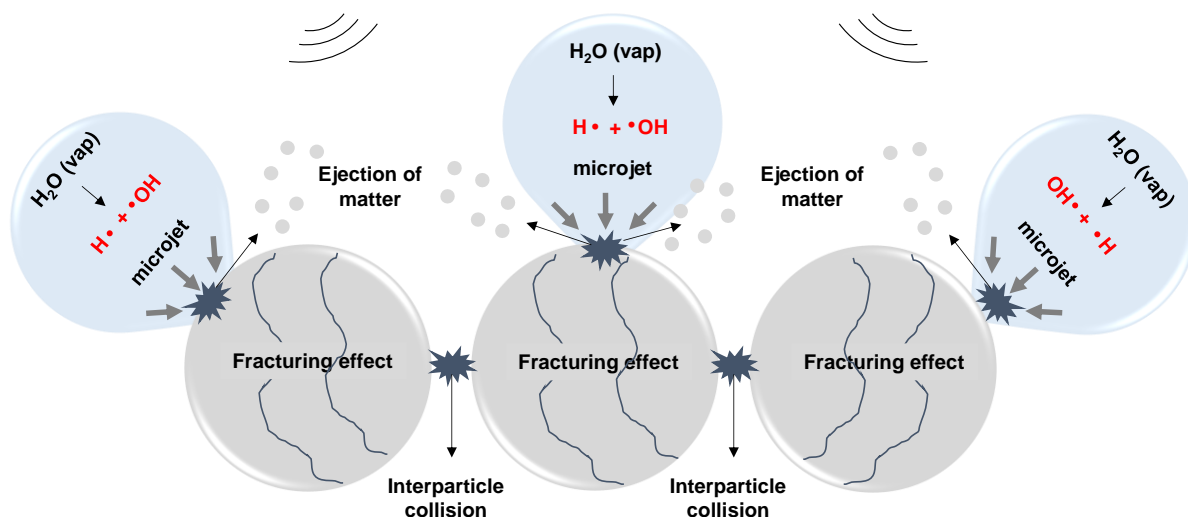


Figure 4. Effect of cavitation bubbles on the catalyst particles

Tripathi and co-workers reported the effect of ultrasound frequencies on the stability of a Lindlar catalyst during the hydrogenation of 2-methyl-3-butyn-2-ol.[22] They noticed a significant leaching of Pd and Pb (40%) for all catalysts treated by ultrasound. In addition, the particle sizes were also drastically reduced from 20 μm to 5 μm , further illustrating the fracturing of the catalyst induced by ultrasound. Interestingly, the fracturing effect of ultrasound was dependent on the applied ultrasound frequency, with the major effect being observed at low frequency. At high frequency (380, 850 kHz), cavitation bubbles are much smaller ($< 10 \mu\text{m}$) than at low frequency ($> 150 \mu\text{m}$), leading to lower cavitation energy, thus lowering the physical effects (shear forces, inter particle collisions, etc.) on the catalyst surface. As a taken home message, prior to coupling solid catalysts with ultrasound, a particular attention should be given to the applied frequency to keep a positive effect of ultrasound on the catalytic reaction rates, while preventing the solid catalyst from damage.

5. Challenges and Future Perspectives

The combination of catalysis and ultrasound, in most instances, leads to interesting effects on chemical reactions. Beside improvement of heat and mass transfer resulting in reaction rate enhancement, we have shown through selected examples that a synergistic effect can occur between catalysis and ultrasound. For instance, the physical and chemical effects locally exerted on a catalytic surface can oxidize metal ions, provide energy to the catalyst and even *in situ* reactivate the catalytic sites. The most interesting effects are observed under

heterogeneous conditions, mostly because solid particles act as nuclei for the growth of cavitation bubbles, thus locally concentrating the effect of ultrasound on the catalyst surface.

Although the term sonocatalysis has been coined few years ago, this is a fast moving field which is currently knowing a sort of renaissance, boosted by the demand of our society for alternative activation technology. However, few scientific questions still need to be addressed in the future. For instance, most of catalytic reactions under ultrasound have been done in water. Clearly, much efforts should be paid in the future to understand all phenomenon of sonocatalysis in organic solvents. In addition, most of previous works focused on the combination of LFUS with catalysis. The synergistic effect of catalysis with HFUS is however more scarcely investigated. The selectivity of radical reactions induced by HFUS is quite difficult to control and, for this reason, the combination of HFUS with catalysis was mainly used for the total free oxidation of aqueous pollutants. The ability to control or tune the selectivity of these radical oxidative reactions with the help of a catalyst is highly desirable to the implementation of this technology to the synthesis of specialty chemicals but, to date, it remains an elusive task. Finally, the design of microfluidic reactors is also an important perspective to this work, in particular to reduce the overall energy consumption of this technology.

Comments

Authors have no competing interests to declare

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