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Reduction of alkenes by hydrazine produced from ammonia under high frequency ultrasound

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PURPOSE OF THE ABSTRACT
When a liquid is subjected to an ultrasonic irradiation at a high frequency, cavitation bubbles are formed. Inside the cavitation bubbles, extreme conditions of temperature and pressure are reached. As a result, gaseous molecules diffusing inside cavitation bubbles are instantaneously pyrolysed, leading to the formation of radicals. At the bubble collapse time, these radicals are propelled into the solution where they can be recombined or react with other compounds in the solution to initiate chemical reactions.

In a previous work, we demonstrated the possibility to use high frequency ultrasound for the activation of ammonia and its subsequent conversion to hydrazine.[1] Here, we extended this concept for the reduction of alkenes, which is usually performed by hydrogenation with gaseous hydrogen in the presence of a catalytic amount of transition metal catalyst. We demonstrated that under high frequency ultrasound, it is possible to use ammonia as a source of hydrogen for the reduction of olefins in water, through the formation of diimide N2H2.

A typical experiment was performed using a 5 wt% aqueous solution of ammonia containing a non-activated alkene (1-octene for model reactions) supported on activated charcoal. The solution was subjected to an ultrasonic irradiation at 525 kHz in a high frequency ultrasound reactor. The solution was maintained at 30 °C. The reduction of 1-octene to n-octane was monitored by GC-FID. Under these conditions, the hydrogenation reaction occurred, and n-octane was formed in 52% yield after 6 hours of sonication. The n-octane yield was increased up to 87% after 28 hours of reaction. (Figure 1) In the same system but with gaseous H2 bubbled in water instead of an ammonia solution, less than 5% of 1-octene was reduced. This is partly due to the low solubility of hydrogen in water, which makes it less available for the hydrogenation reaction. This demonstrates that ammonia can be used as a hydrogen source for an efficient hydrogenation of alkenes in these conditions.

To maximize the yield of the hydrogenation reaction in this system, the influence of different parameters was studied: the amount of ammonia, the charge of the alkene on the activated charcoal and the amount of activated charcoal.

Then, the mechanism of the reaction was investigated. Two pathways are possible for the reduction of alkenes from ammonia under high frequency ultrasound:
1) according to our previous work, hydrazine N2H4 is formed when aqueous ammonia is submitted to high frequency ultrasound, then hydrazine can be oxidized to diimide N2H2 with molecular oxygen from air, and the formed diimide reduces the double bond and releases nitrogen;
2) the pyrolysis of ammonia inside the cavitation bubbles generates the formation of NH radicals, whose presence was confirmed by sonoluminescence analysis[2]. Then, NH radicals recombine directly to diimide which reduces the alkene. The second pathway was determined as the main mechanism. Indeed, when the reaction is performed under argon atmosphere, the hydrogenation of 1-octene occurs at the same rate, which indicates that no oxygen is needed to perform the reaction, and the oxidation of hydrazine to diimide is less likely to occur.

In this system, in the presence of activated charcoal as a support for olefins, the phenomenon of heterogeneous cavitation takes place: the cavitation bubbles produced under high frequency ultrasound are formed at the surface of the charcoal particles, grow and implode on the particles, propelling the radicals on the surface. NH radicals formed from the pyrolysis of ammonia in the cavitation bubbles recombine to form diimide N2H2 which reduces the alkene on the surface of the activated charcoal particles. (Figure 2)

This reduction of olefin using ammonia under high frequency ultrasound was extended to other unsaturated compounds to study the scope of the reaction. Interestingly, other primary or secondary alkenes and alkyne were

FIGURES

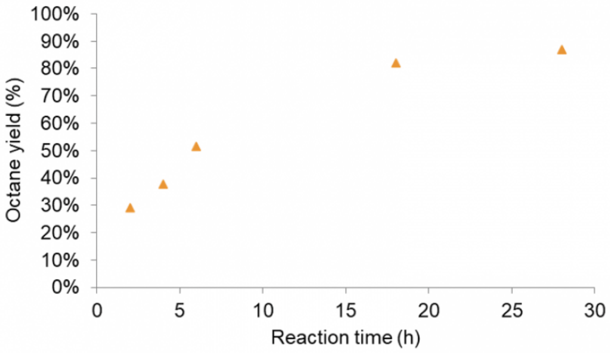

Figure 1. Kinetics of 1-octene reduction with ammonia

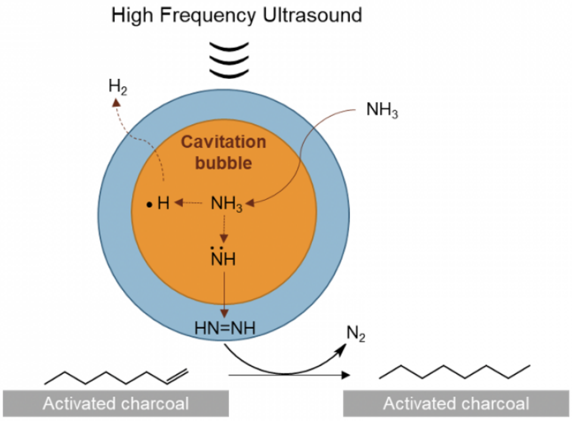

FIGURE 1

Figure 1.

Kinetics of 1-octene reduction with ammonia

FIGURE 2

Figure 2

Figure 2. Proposed mechanism for 1-octene reduction with ammonia under high frequency ultrasound

KEYWORDS

hydrazine | hydrogenation | ultrasound | ammonia

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Acknowledgements

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