Olefin Photocatalytic Epoxidation by Highly Crystalline Carbon Nitrides: A Sustainable Epoxide Production

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Abstract

*ABSTRACT -* Epoxides are important platform molecules applied in various industrial sectors. However, conventional methods for synthesizing these compounds use harmful routes that generate acidic waste and highly toxic chlorinated by-products. Therefore, efforts have been made to develop innovative, sustainable and low-cost synthesis methods for the production of epoxides, for example by catalysis. Carbon nitrides, a recent semiconductor, have gained notable attention due to their suitable visible light band structure, high versatility, robustness, low cost and non-toxic nature, offering great potential for various technological applications, including photocatalysis. Within the extensive family of carbon nitrides, crystalline carbon nitride stands out as a promising photocatalyst for chemical conversion through redox reactions. In this work, the synthesis, characterization and application of crystalline carbon nitrides on poly(triazine imide) for the photocatalytic epoxidation of olefins, such as styrene, to their respective epoxides proved to be favourable. In view of the challenge of sustainable epoxide production, the yields of over 24 and 30% using CH3CN and 1,4-dioxane/water as solvents ensure the initial achievements.

Keywords: photocatalysis, carbon nitrides, epoxides, organic synthesis, green chemistry.

*RESUMO -* Os epóxidos são moléculas plataforma importantes aplicadas em vários setores industriais. No entanto, os métodos convencionais de síntese destes compostos recorrem a vias nocivas que geram resíduos ácidos e subprodutos clorados altamente tóxicos. Com isso, tem sido realizados esforços para desenvolver métodos de síntese inovadores, sustantáveis e de baixo custo, para a produção de epóxidos, por exemplo, por catálise. Os nitretos de carbono, um semicondutor recente, ganharam uma atenção notória devido à sua estrutura de banda de luz visível adequada, elevada versatilidade, robustez, baixo custo e natureza atóxica, oferecendo um grande potencial para várias aplicações tecnológicas, incluindo a fotocatálise. Dentro da extensa família dos nitretos de carbono, destaca-se o nitreto de carbono cristalino como um fotocatalisador promissor para a conversão química através de reações redox. Neste trabalho, a síntese, caracterização e aplicação de nitretos de carbono cristalinos em poli(triazina imida) para a epoxidação fotocatalítica de olefinas, como estireno, aos respectivos epóxidos se mostrou favorável. Tendo em vista o desafio da produção sustentável de epóxidos, os rendimentos acima de 24 e 30% utilizando CH3CN e 1,4-dioxano/água como solventes asseguram as conquistas iniciais.

Palavras-chave: fotocatálise, nitretos de carbono cristalinos, epóxidos, síntese orgânica, química verde.

## Introduction

 Epoxides are considered platform molecules due to their extensive applicability in various approaches, e.g. organic synthesis, polymer industry and large-scale chemical processes (1, 2). Despite the high efficiency of industrial synthesis of epoxides, reagents such as peroxyacid and peroxyacetic acid are adopted, which generate chlorinated by-products, making the process unsustainable and costly. Therefore, new more sustainable paths, such as catalytic routes, should be adopted.

As a catalytic route, photocatalysis, considered a green technology (3), which uses light to drive desired reactions. Carbon nitrides, a recent organic polymer consisting essentially of carbon and nitrogen arranged in a graphene-like structure, are recognized for their semiconducting properties in promising synthetic methods in the field of photocatalysis. Within this class, Lithium Poly(triazine imide) (Li-PTI) deserves to be highlighted, due to its formation from triazine units linked by negative nitrogens, compensated by lithium ions. The generation of a well-ordered structure confers a dual advantage to Li-PTI: superior structural control and increased robustness as a photocatalyst, facilitating effective charge transport and promoting efficient transfer of the charge generated from light. Thus, knowing these advantages make this a potential material for catalytic reactions driven by light, Li-PTI is synthesized, characterized and employed in this project for styrene photocatalytic epoxidation, which represents a favorable and sustainable epoxide production.

## Experimental

*Li-PTI synthesis*

 Lithium-Poly(triazine imide) was synthesized by the ionothermal method. In this step, a mixture of melamine and LiCl (1:10) was grinded in a ball mill and heated at 600 °C in a muffle furnace under inert nitrogen atmosphere. Then, the final product was intensively washed to remove the remaining excess of salt, resulting in a grayish powder.

*Photocatalytic tests*

 The obtained catalyst was employed in the styrene epoxidation reaction, configured in a photoreactor equipped with a water bath to control the operating temperature. The reactor contains a purple LED lamp (410 nm, 10 W) used as the light source of the system. The reaction medium was arranged in 5 mL flasks containing the substrate dissolved in an appropriate organic solvent (i.e., CH3CN or 1,4-dioxane) and under oxidizing O2 atmosphere.

##  Results and Discussion



**Figure 1.** XDR patterns and FT-IR spectrum of Li-PTI material.

With the narrow peak pattern of the XRD (**Figure 1**), it can be concluded that the synthesized catalyst is crystalline. Peaks around 12°, 21°, 24° and 25° are related to the (100), (110), (200) and (111) planes, respectively. The most intense peak near 27° is associated with the d-spacing, which indicates the interplanar spacing (002). Consecutively, peaks around 29°, 32°, 34°, 35°, 37°, 43°, 45° and 46° are related to the (102), (210), (112), (211), (300), (220), (310) and (302) planes, respectively (4). As for infrared spectroscopy, C-N and C=N bond stretching can be both identified in 1050-1600 cm-1. The FT-IR bands at 800 describe the presence of characteristic stretching of triazine units, confirming their formation. Finally, bands around 3200 and 3350 cm-1 are related to amine groups.

*Photocatalytic Tests*

**Table 1** The primary challenge in this reaction lies in controlling the formation of the epoxide rather than the generation of benzaldehyde, which is a commonly produced byproduct. Among the catalysts, Li-PTI exhibits the most favorable outcomes, especially at elevated temperatures. Additionally, employing a solvent mixture consisting of water and 1,4-dioxane enhances the epoxide yield. However, the use of alcohols as solvents is not conducive to epoxide formation due to their susceptibility to oxidation by photogenerated holes, instead of the substrate. The highest yield achieved was30.4% (10 mg Li-PTI, 1 mL dioxane, 1 mL water, 10 µL styrene, 60 °C, O2 flush), signifying a notable advancement towards sustainable epoxide synthesis.

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| **Entry** | **Solvent** | **Temperature (°C)** | **Yield (%)** |
| 1 | CH3CN | ~ 25 | 10.9 |
| 2 | CH3CN | 60 | 24.1 |
| 3\* | 1,4-dioxane + water | 60 | 30.4 |
| 4 | ethanol | 60 | 0.5 |
| 5 |  isopropanol | 60 | 1.8 |
| 6 | 1,4-dioxane | 60 | 9.4 |
| 7 | water | 60 | - |

## **Table 1**. Photocatalytic results of styrene epoxidation.

Reaction conditions: 10 mg of Li-PTI, 2 ml of solvent, 10 µL of styrene, O2 flush and 24 h of reaction time. \*1 mL of 1,4-dioxane and 1 mL of water.

Conclusions

 With the obtained data, it is concluded that the proposed investigation for styrene epoxidation is promising using Li-PTI as a catalyst and adopting mainly 1,4-dioxane and water (1:1) as solvent, under moderate higher temperatures (60°C).

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