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Aerobic photocatalytic oxidation of 2-naphthol under visible light using NH_2-MIL-125(Ti)

Hoda Mollabagher[a,*], Seyed Amir Hossein Seyed Mousavi[b], Salman Taheri[a]

[a]*Chemistry and Chemical Engineering Research Centre of Iran, PO Box 14115-186, Tehran, Iran. E-mail: mollabagher.chem@yahoo.com*
[b]*Process Engineering Department, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran*

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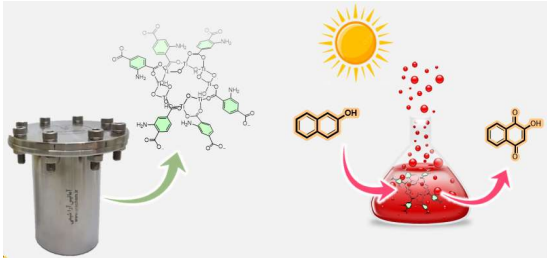
Abstract: 2-Naphthol has undergone a specific oxidation process, leading to the formation of 2-hydroxy-1,4-naphthoquinone, a compound also recognized as Lawsone. In this research, NH_2-MIL-125(Ti) was employed as a potent catalyst for photocatalytic reactions in conjunction with H_2O_2. The impact of NH_2-MIL-125(Ti) on the reaction efficiency was prominently observed, leading to noticeable enhancements in the reaction yield.



Keywords: Metal-organic frameworks (MOFs), Photocatalyst, Lawsone, Oxidation reaction

1. Introduction

Lawsone, extracted from the henna plant, stands as a prominent natural compound widely employed in the synthesis of bioactive molecules.[1] Aromatic compounds like Lawson have applications in the pharmaceutical and pigment industries.[2,3] In recent years, researchers have published numerous articles exploring the utilization of this compound in multicomponent reactions aimed at obtaining compounds with pharmaceutical properties.[4-6] Additionally, it finds application as a hair dye and serves as an ultraviolet filter in sunscreen formulations.[7] Reported articles suggest that despite the significant importance of Lawsone, there has been a scarcity of research in the field of synthesizing this compound. One of the methods for synthesizing lawsone involves the selective oxidation of 2-naphthol.[8]

Traditional oxidizing agents such as $KMnO_4$, CrO_3, Br_2, and tert-butyl hydroperoxide are commonly known for their toxicity, corrosiveness, or high cost.[9]

The utilization of a selective catalyst paired with a low-cost oxidant, which can be recovered, not only leads to savings in energy and expenses but also exhibits environmental compatibility. This approach contributes to a reduction in ecological pollutants.[10]

Recently, metal-Organic Frameworks (MOFs) have garnered attention for their unique dual composition, which intertwines metallic ions and organic ligands within a single complex. This dual composition flexibility allows for the manipulation of both organic ligands and metallic ions, leading to diverse efficiencies and yields.[10-12] Moreover, the substantial porosity of MOF structures positions them as potent nano-reactors for various chemical reactions.[13,14]

By selecting the appropriate cluster and linker pair, the tunable design of Metal-Organic Frameworks (MOFs) can reduce the solid's band gap, resulting in increased absorption of solar light and enabling photoactivation within the visible spectrum.[15,16]

This study introduces an efficient catalytic system for the selective synthesis of lawsone from 2-naphthol. The process utilizes NH_2-MIL-125(Ti) as the catalyst and hydrogen peroxide (H_2O_2) as the oxidant in an aqueous solution.

2. Results and Discussion

To further examine the morphological and facet changes of all samples over time, scanning electron microscopy (SEM) images were acquired (Figure 1).

The potential reusability of NH_2-MIL-125(Ti) as a catalyst for the synthesis of lawsone was examined. To achieve this goal, the catalyst was isolated through a straightforward filtration process after the initial reaction cycle. Subsequently, the isolated catalyst was washed with ethanol and then dried under vacuum conditions.

Subsequently, the recovered catalyst was employed for the successive reaction runs for a total of four cycles, and no significant difference in the catalyst's efficiency was observed.

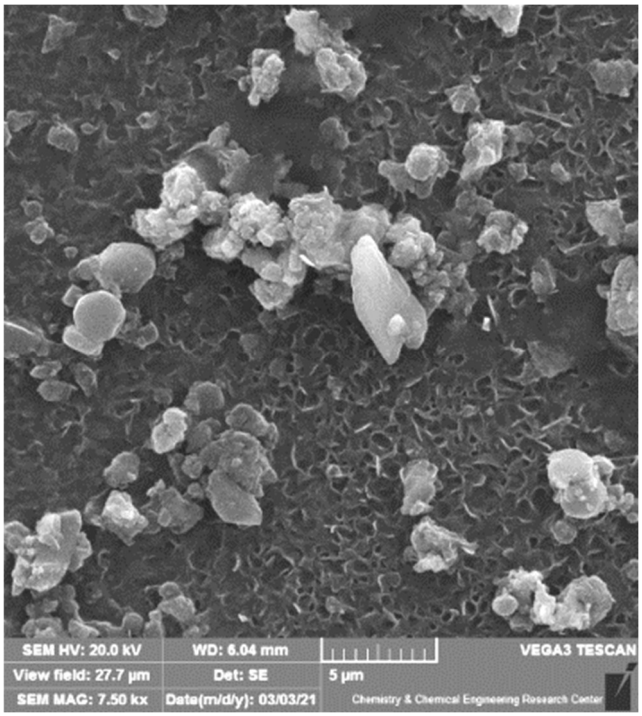


Figure 1. SEM of NH_2-MIL-125(Ti).

The FT-IR spectra before and after catalyst utilization suggest that no significant changes have occurred in the functional groups of the catalyst.

In NH_2-MIL-125(Ti), the presence of bands over 3000 cm^{-1} attributed to the symmetric and asymmetric vibrational modes associated with the $–NH_2$ groups. The distinctive peaks observed within the range of 400-700 cm^{-1} are likely attributed to the stretching vibrations of O-Ti-O bonds.[17]

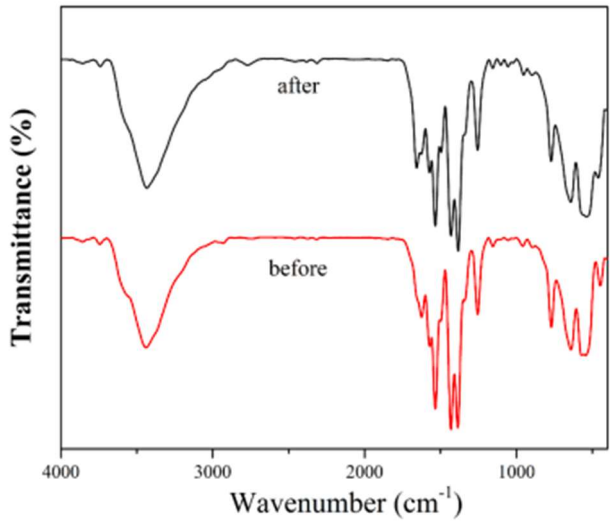


Figure 2. FT-IR of NH_2-MIL-125(Ti) before and after photocatalytic reaction.

The powder X-ray diffraction (PXRD) patterns of the synthesized samples are presented in Figure 3, confirming a significant resemblance between the samples and the previously reported NH_2-MIL-125(Ti).[18]

Crystallite size plays a crucial role as one of the primary catalyst characteristics, profoundly affecting the reaction properties of the material during surface reactions.

The crystallite size was determined using the Scherer equation, utilizing the information provided in Equation (1).

$$D = \frac{K \times \lambda}{B \times Cos\theta} \quad (1)$$

Equation (1) defines the parameters as follows: D represents the crystallite size in nanometers, K is the shape factor, typically approximated as 0.9, λ denotes the wavelength in nanometers, B stands for the half-width of the peak with the highest intensity, and θ refers to the radiation angle or Bragg angle.[19]

The full width at half maximum (FWHM) serves as a commonly utilized parameter for describing the width of a peak on a curve or function. It is determined by the distance between points on the curve where the function attains half of its maximum value. B in the equation 1 is calculated using the FWHM.

With the use of the above equation, D is obtained as 142 nanometers.

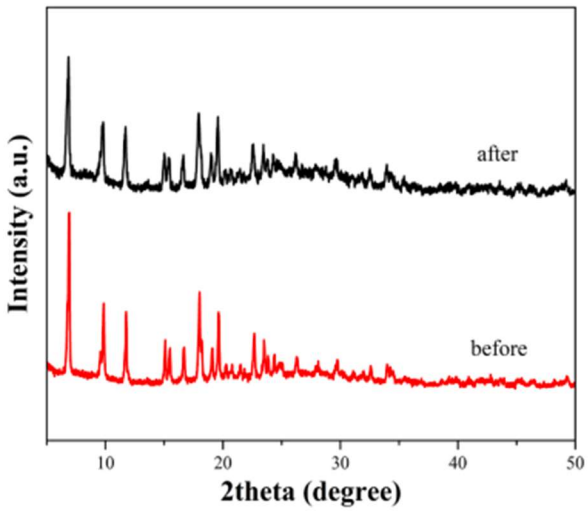


Figure 3. PXRD of NH_2-MIL-125(Ti) before and after photocatalytic reaction.

The proposed synergic effect of Ti and the ligand in NH_2-MIL-125(Ti) catalyst involves the coordinated interaction between the titanium (Ti) metal center and the organic ligand within the metal-organic framework (MOF) structure. This synergistic collaboration plays a crucial role in enhancing the catalytic activity and selectivity of the catalyst for the targeted transformation, in this case, the synthesis of Lawson from 2-naphthol.

The organic ligand within NH_2-MIL-125(Ti) incorporates amino (NH_2) groups, facilitating coordination with the titanium (Ti) metal center. This interaction establishes well-defined active sites within the catalyst, thereby influencing the reaction pathway and facilitating the desired chemical transformations. Moreover, ligand coordination with Ti contributes to stabilizing active catalytic sites, thereby preventing undesired side reactions and promoting the desired catalytic pathway.

The inclusion of Ti in the catalyst confers redox properties and Lewis acid characteristics, thereby enhancing reactant activation and overall catalytic activity. Complementarily, the ligand, featuring specific functional groups, augments these properties by offering additional binding sites and modulating the electronic environment surrounding the Ti center.

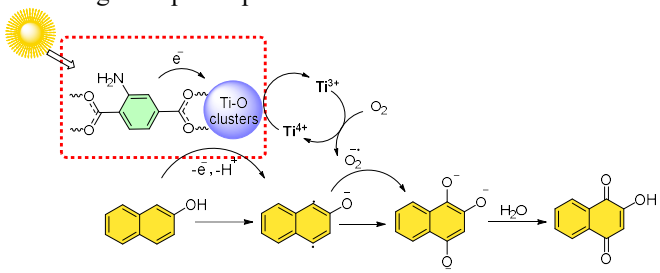
The combined impact of the ligand and Ti manifests in a synergistic enhancement of selectivity, guiding the reaction toward the desired product (Lawson) while minimizing the formation of by-products. The specific functionalities of the ligand can further influence reactant orientation at the active sites, thereby steering the reaction toward the intended outcome.

The NH_2-MIL-125(Ti) catalyst's recovery capability was assessed through four consecutive reaction cycles. Upon reuse, the catalyst displayed sustained activity without significant reduction, indicating its suitability as an initial catalyst. Figure 4 illustrates comparable efficiencies between the primary and reused catalysts, highlighting the recyclability of the catalyst for subsequent reactions.

The comparison table provided valuable insights into the performance of different catalysts for the synthesis of Lawson from 2-naphthol. Our study, utilizing NH_2-MIL-125(Ti) catalyst, demonstrated a commendable yield of 92%. Comparing this with other catalysts used in similar studies, NH_2-MIL-125(Ti) catalyst proved to be highly effective.

Entry 1 utilized a multi-step reaction involving Me_2SO_4, DMF-$POCl_3$, NBS, and anhyd. $AlCl_3$ as catalysts, resulting in yields ranging from 77% to 93%. While these yields were competitive, NH_2-MIL-125(Ti) catalyst in our study achieved a yield at the higher end of this range, showcasing its efficiency in the reaction.

Furthermore, Entry 2 employed Cobalt porphyrin as the catalyst and achieved a yield of 80%. In comparison, NH_2-MIL-125(Ti) catalyst in our study exhibited a higher yield, indicating its superior performance.



Scheme 1. Possible mechanism for the reaction over NH_2-MIL-125(Ti)

Table 1. A comparison table of similar studies on the conversion of β-naphthol to Lawson under various conditions

Entry	Catalyst	Step of reaction	Yield	Ref.
1	1) Me_2SO_4 2) DMF-$POCl_3$ 3) NBS 4) Anhyd. $AlCl_3$	4	1) 93% 2) 88% 3) 77% 4) 91%	[20]
2	cobalt porphyrin	1	80%	[21]
3	NH_2-MIL-125(Ti)	1	92%	This work

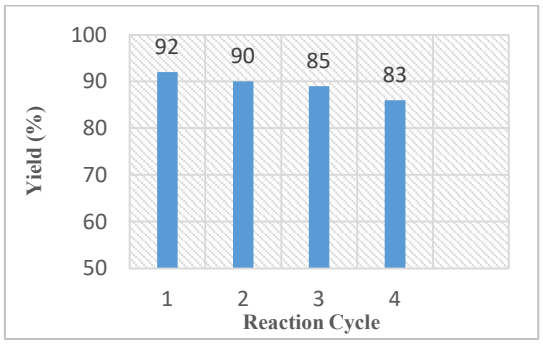


Figure 4. The recycling of NH_2-MIL-125(Ti) as catalysts for lawsone production.

Possible mechanism for the reaction

It has been established that metal catalysts, utilizing highly active sites based on half-filled d-orbitals, are capable of catalyzing reactions through a mechanism involving free radical intermediates.[22,23] In agreement with this view, MOF, due to their metallic cores, exhibit high efficacy in catalyzing chemical reactions.[19,24]

In the proposed mechanism for the conversion of 2-naphthol to Lawson in the presence of NH_2-MIL-125(Ti), exposure to light and oxygen generates oxygen radicals, initiating the reaction.[19] These radicals abstract hydrogen atoms from the hydroxyl group of 2-naphthol, forming phenoxyl radical intermediates. The titanium center in NH2-MIL-125(Ti) may assist in stabilizing these intermediates or facilitating subsequent reactions. The phenoxyl radicals undergo cyclization and rearrangement reactions, potentially catalyzed by NH_2-MIL-125(Ti), ultimately leading to the formation of Lawson. This radical-based pathway illustrates the catalytic role of NH_2-MIL-125(Ti) in the conversion process.

3. Experimental

Materials and reagents

All starting materials were purchased from Sigma-Aldrich and Merck companies and used without additional purification. All reactions were carried out in double distilled deionized water.

Spectrophotometric measurements were conducted using a Shimadzu UV-Vis Spectrometer. Infrared spectra were recorded employing a Perkin-Elmer 1420 spectrophotometer through the KBr disc technique.

Preparation of NH_2-MIL-125(Ti)

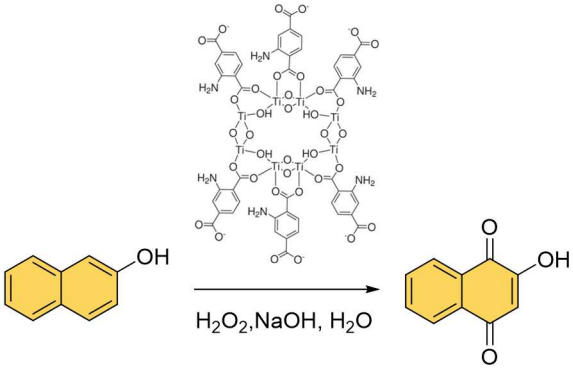
Into a solution comprising 9 mL of DMF and 1 mL of dry MeOH, 2-Aminoterephthalic acid (0.54 g, 3 mmol) and Tetra-n-butyl titanate (0.26 mL, 0.75 mmol) were introduced and stirred for 30 minutes at room temperature. Subsequently, the prepared solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave (Amatis Ara Shimi, model AR 100). The synthesis was carried out without agitation in an oven at 150°C for a duration of 3 days. Upon completion of the synthesis, the resulting suspension was filtered, washed separately with DMF and MeOH, subjected to extraction using a Soxhlet extractor with MeOH, and ultimately dried to yield a yellow solid product.

Catalytic oxidation of 2-naphthol

A solution of 2-naphthol (1.00 mmol), NaOH (1.00 mmol), and NH_2-MIL-125(Ti) (0.01 g) dissolved in 25 mL of water was stirred at 25 °C, and then hydrogen peroxide (0.80 mL) was introduced into the mixture.

Following the addition of H_2O_2, an orange color appeared in the reaction mixture. The mixture was allowed to stand at room temperature for 15 minutes. Subsequently, the resultant solution was neutralized using a 0.1 M HCl solution. The precipitate was then filtered, washed with water, vacuum-dried, and subsequently recrystallized using ethanol. The melting point of the resulting product was determined to be 192 °C.

The influence of various reaction parameters on the yield of the reaction product was evaluated using the UV-vis technique. The isolated reaction product was dissolved in 50 ml of 0.1 N NaOH and quantitatively analyzed by measuring the absorbance at 453 nm, a characteristic wavelength for the sodium salt of lawsone.

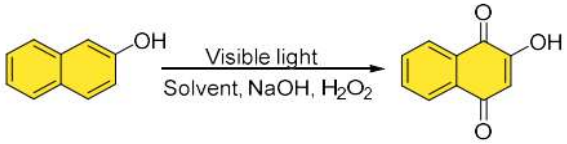


Scheme 2. Oxidation of 2-naphthol to lawsone by applying NH_2-MIL-125(Ti) as catalyst

Optimization reaction

This table presents the optimized parameters for the photocatalytic conversion of 2-naphthol to Lawson utilizing 0.01 g of NH_2-MIL-125(Ti) catalyst at and 25 mL of solvent. the substantially higher yield of 92% observed at 25 °C and with water as the solvent underscores the importance of these parameters in facilitating the catalytic process. NH_2-MIL-125(Ti), serving as the catalyst, plays a crucial role by providing active sites for the reaction to proceed. The interaction between the catalyst and the substrate molecules initiates the desired chemical transformations, leading to the formation of Lawson.

Table 2. Oxidation reaction of 2-naphthol to lawsone in presence of 1 mmol 2-naphthol, 1 mmol NaOH and 0.01 g NH_2-MIL-125(Ti) in 25 mL solvent



Entry	Solvent	T (°C)	Yield (%)
1	H_2O	50	70
2	H_2O	25	92
3[a]	H_2O	25	-
4[b]	H_2O	25	-
5	EtOH	25	50
6	DMF	25	-

[a]The reaction was carried out in the absence of light.
[b]The reaction was carried out in the absence of a NH_2-MIL-125(Ti).

4. Conclusions

The catalytic oxidation system, employing NH_2-MIL-125(Ti) in combination with hydrogen peroxide (H_2O_2) under mild reaction conditions, exhibits efficient selective conversion of 2-naphthol to 2-hydroxy-1,4 naphthoquinone with high yield. Furthermore, the catalyst was successfully recovered and reused for four consecutive cycles without any observed change in efficiency or structural integrity.

Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author(s) ID

Hoda Mollabagher: 0000-0002-4754-0405
Seyed Amir Hossein Seyed Mousavi: 0000-0001-5851-1434
Salman Taheri: 0000-0002-4230-5123

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