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Research Paper

Use of pectin as a suitable substrate for catalyst synthesis Fe_3O_4@Pectin@Ni (II) and its application in oxidation reaction

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Abstract

In this paper, the properties of a catalyst that composed of magnetic nanoparticles and Pectin biopolymer that is widely found in nature (Fe_3O_4@Pectin) to support nickel (II) acetate are discussed, and this catalyst was then used in response to the synthesis of aaldehyde derivatives. The heterogeneous catalyst was characterized by techniques such as FT-IR spectroscopy, FE-SEM, TEM, XRD spectroscopy, EDX spectroscopy and ICP spectroscopy. Then the catalyst was explored in the oxidation reaction of alcohols that has high efficiency and selectivity and the synthesized aldehydes. The most important advantages of this method are easy to work up procedure, perform the reaction in solvent-free conditions, and the catalyst can be separated by an external magnet and used several times without reducing the activity, which prevents environmental pollution.

Keywords: Pectin; Nano Catalyst; Oxidation; Solvent-free

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Introduction

Oxidation reactions are ubiquitous in the pharmaceutical and fine-chemical industries, and are fundamentally important for introducing oxygen-rich functional groups to organic molecules. For example, aldehyde and ester-containing molecules are heavily employed as flavouring and fragrance agents owing to their volatility and distinctly aromatic nature they are often pleasing to smell and taste [1]. Benzaldehyde is a key component for most almond-based flavourings, although it finds other uses as a precursor for plastic additives and as an intermediate in the synthesis of antibiotic drugs such as chloramphenicol and ampicillin, as well as stimulants like ephedrine [2]. On the other hand, in recent years, extensive studies have been done on the design and development of green catalysts, thereby taking useful steps to protect the environment [3, 4]. The important advantages of heterogeneous catalysts that have recently attracted the attention of scientists include easy separation, low waste generation, reduced cost, and the ability to recover catalysts from reaction environments [5-7]. The magnetic nanoparticles are a class of advanced nanomaterials with specific applications, properties, and sizes. Applications of these nanoparticles can be described as magnetic drug carriers, magnetic cell separators, and biological sensors, these nanoparticles are used in the treatment of some cancers [8-11]. Magnetic nanoparticles are highly efficient in the synthesis of heterogeneous catalysts due to their biological, biomedical, environmental, low toxicity, and cost-effective properties [12]. On the other hand, the choice of supporting materials for catalytic reactions is very important, because they

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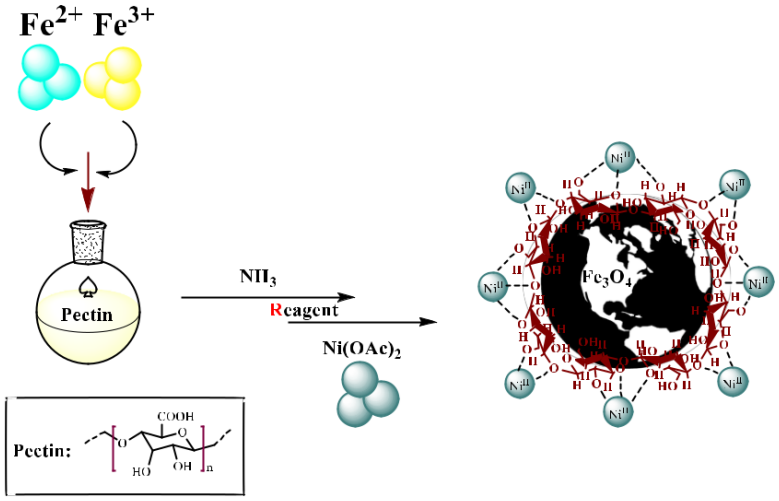
determine the amount of activity, thermal durability, and reproducibility of the catalyst [13]. Hence, the synthesis of biopolymer and magneto-based nanocomposites such as Fe_3O_4 as a substrate for the catalyst is of particular importance due to its large surface area, ease of preparation, and green nature [14]. Pectin is a sugar-acid polymer that is extracted from fruits and vegetables and its main chemical constituent is galacturonic acid. Pectin has a complex structure that depends on the source and the extraction process; it also has properties such as biodegradable, biocompatible, and bioactive. Pectin is used in foods, cosmetics, medicine, and biology. Due to the presence of carboxylate groups in the structure of pectin, these compounds can be coordinated with metals [15]. Khazaei and other [16] used pectin for supporting Pd-nanoparticles for the catalysis of Heck coupling. Research results Douskhah and other [17] that used magnetic pectin to support Cu (II) in the click reaction showed that catalyst herein is a recyclable and sustainable catalyst in the click synthesis.
Talat Baran [13] used pectin-supported palladium as the catalyst for Suzuki-Miyaura coupling reactions. Herein, the goal of our research team is to provide a novel multi-core catalyst that has high power, short reaction time, recyclable in multi-stage and non-toxic reactions. This protocol from both the economic and synthetic point of view with several advantages like reduced pollution, lower cost, and simplicity in processing, which are beneficial to the industry as well as to the environment. In this work, due to the importance of Fe_3O_4 and pectin and the novelty of this polymer, we are encouraged to synthesize a core/shell catalyst with Fe_3O_4 and pectin and also use nickel metal, which has not been studied on pectin in the past. This natural and green substrate. Pectin, due to its features such as eco-friendly, safe, nontoxic, nonflammable, clean, green, inexpensive as well as readily available. Therefore, the metal is well placed on the metal cavities covered with pectin to have high performance and resistance to the synthesis of aldehydes, which these compounds have good medicinal properties. Herein, we have developed a reaction to prepare aldehyde's analogs using alcohol and Ni (II) supported Fe_3O_4@Pectin is effective as a novel catalyst and inexpensive based on green chemistry. This catalyst Fe_3O_4@Pectin@Ni (II) greatly reduced the cost of this transformation, and the resulted operation and work-up procedures were greatly simplified.



Scheme1: The synthesis route for Fe_3O_4@Pectin@Ni (II)

Experimental section and procedures:
Material and instruments
Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, >99%) and ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$) were used as an iron source. Pectin with the degree of esterification of 76% and other of the materials used in this article were from Merck (Germany) and Sigma Aldrich and were used without further purification. The reaction progress and purity of the products were determined using TLC on silica-gel Polygram SILG/UV254 plates. FT-IR spectra were recorded with a Nicolet system 800 beam splitter KBr SCAL = 800 in the range 400− 4000 cm^{-1}. Transmission electron microscope (TEM) investigations were performed using a Philips EM 208S Transmission Electron Microscope. The powder X-ray diffraction (XRD) was performed within Philips PW1730 with a Cu Kα (λ = 1.54060 Å) radiation. SEM-EDX were recorded by Fe-SEM TESCAN MIRA3.

Synthesis of Fe_3O_4@Pectin
Synthesis of Fe_3O_4@Pectin was performed with a little modification [18]. According to this, 0.5 g of

pectin dissolve in 50 ml of distilled water under stirring until a homogeneous dispersion of pectin is obtained .$FeCl_3.6H_2O$ (3 g) and $FeCl_2.4H_2O$ (1.6 g) dissolve in 25 ml of distilled water separately and then add them. Then slowly added them to the mixture containing pectin which resulted in a brown gel. The reaction mixture was stirred under a gentle flow of N_2 at 85°C for 2 h. After which an excess of ammonium hydroxide (25 wt%) to the reaction mixture was added until the pH reaches 11-12 and the mixture becomes black indicating the formation of magnetite and again the mixture was under a gentle flow of N_2 at 85° C for 30 min. Finally, the precipitate was separated by an external magnet and washed with distilled water several times until the pH dropped to approximately 7 then dried under vacuum.

Synthesis of Fe_3O_4@Pectin @Ni (II)

The synthesis of Fe_3O_4@Pectin @ Ni is performed by the saturation method [17]. Based on this method, an excess amount of nickel (II) acetate dissolve in 5 ml of ethanol, then add 1 g of Fe_3O_4@Pectin to the solution and allow to react for 12 h under vigorous stirring. Finally, it separated the solid product from the solution and washed it with ethanol several times and dried under vacuum at 60°C.

The method of synthesizing aldehyde derivatives

The method of synthesizing aldehyde derivatives: Benzyl alcohol (1.0 mmol), TBHP (2.0 mmol), catalyst (1.25 mol %) were placed in a test tube on a stirrer at 65 ° C for 90 minutes under solvent-free condition.

Result and discussion:

Catalyst synthesis/characterization

The catalyst synthesis was very efficient and simple for the reaction of the synthesis of aldehyde derivatives from alcohol. We used pectin to synthesize the catalyst because pectin is a biopolymer that is widely found in nature. Pectin has carboxylic acid groups that can act as a covalently chelating agent to Fe_3O_4 nanoparticles and direct the nanostructure. A general schematic for the synthesis of Fe_3O_4@Pectin@Ni (II) is shown (Scheme 1). The structure of the synthesized catalyst was characterized by various analyses like FT-IR, ICP, FE-SEM, XRD, and TEM.

FT-IR spectra of Fe_3O_4, Pectin, Fe_3O_4@Pectin, Fe_3O_4@Pectin@Ni (II) catalyst are given in (Figure. 1). FT-IR spectrum of Pectin (Fig. 1a) shows characteristic peaks at 3400-3600 cm^{-1} (O-H stretching alcoholic and acidic), 2923 cm^{-1} (C-H stretching), 1725 cm^{-1} (C=O of ester), 1618 cm^{-1} (COO^- asymmetric stretching), 1412 cm^{-1} (COO^- symmetric stretching), The FT-IR spectrum of Fe_3O_4 (Figure. 1b) the stretching vibrations Fe-O and O-H at 574 cm^{-1} and 3420 cm^{-1} that allow the establishment of Fe_3O_4 nanoparticles. After core-shell the Pectin with Fe_3O_4, shows the peaks at 3422 cm^{-1} (O-H stretching), 2923 cm^{-1} (C-H stretching), 1626 cm^{-1} (COO^- asymmetric stretching) and 577 cm^{-1} can be assigned to Fe_3O_4 (Figure.1c), in addition to the above-mentioned bands, complexation of Nickel ions to Fe_3O_4@Pectin causes absorption to lower wave O-H stretching 3418 cm^{-1} and COO^- asymmetric stretching 1622 cm^{-1} Indicates the involvement of the OH group along with the COO^- in bonding with the nickel metal and confirming the coordination through the oxygen group drawn to the metal (Figure.1d).

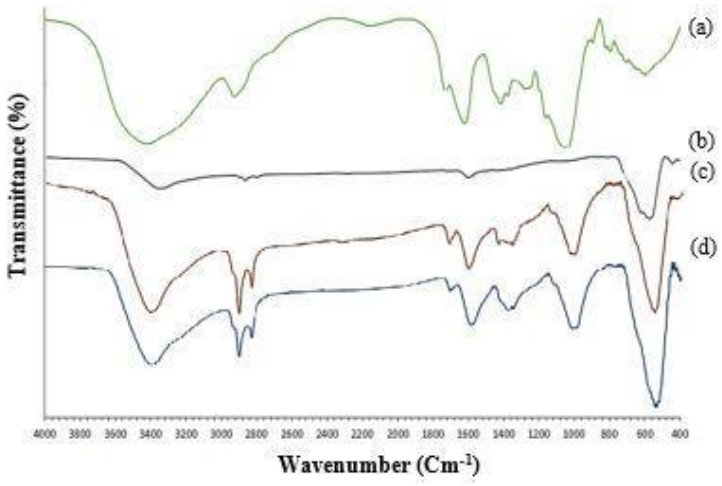


Figure 1: FT-IR spectra of a) Pectin, b) Fe_3O_4, c) Fe_3O_4@Pectin, d) Fe_3O_4@Pectin@Ni (II)

Due to the importance of heterogeneous catalysts, we used Fe (III) and Fe (II) to magnetize the catalyst, that structure is core-shell according to SEM results. EDX analysis (Figure. 2) shows the logical type of percentages of Fe, C, O, Ni atoms in Fe_3O_4@Pectin@ Ni (II) catalyst. The SEM image and elemental analysis of Fe_3O_4@Pectin@Ni (II) complex were characterized by SEM, EDX. The SEM image of the Fe_3O_4@Pectin@Ni (II) complex indicated the formation of the desired complex.

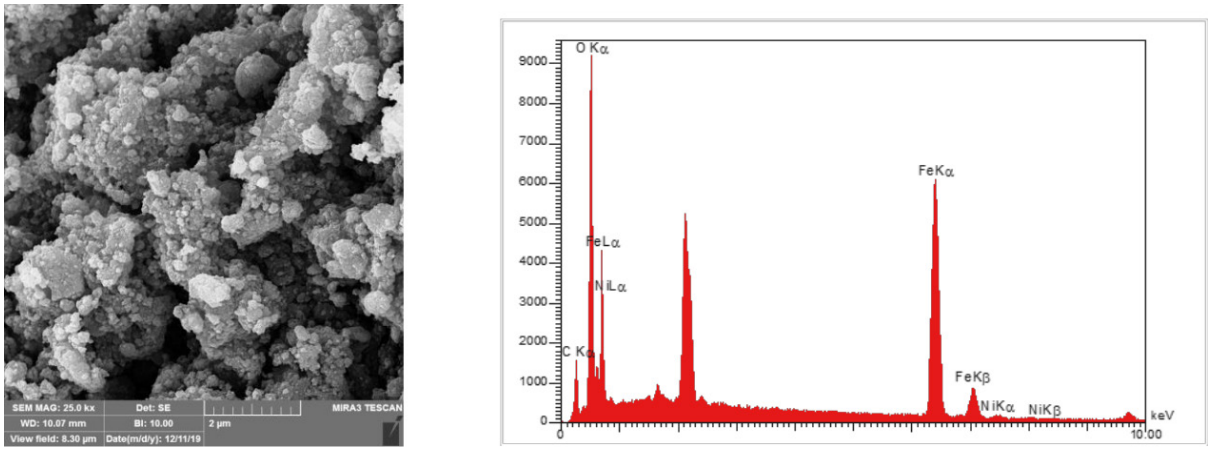


Figure 2: SEM image and EDS spectra of Fe_3O_4@Pectin@Ni (II)

Figure 3 shows the XRD spectrum for the Fe_3O_4, Ni (II), Fe_3O_4@Pectin@Ni (II) catalyst. The spectrum of Fe_3O_4@Pectin@Ni (II) catalyst shows peaks at 30.51°, 35.81°, 43.21°, 54.06°, 56.91°, 62.46° degrees, respectively, which correspond to the peaks of Fe_3O_4 and Ni (II). Also, the peak at 18°, which is related to magnetized pectin, indicates that it is also present in the structure of the pectin catalyst. Therefore, it can be concluded that the catalyst is well synthesized.

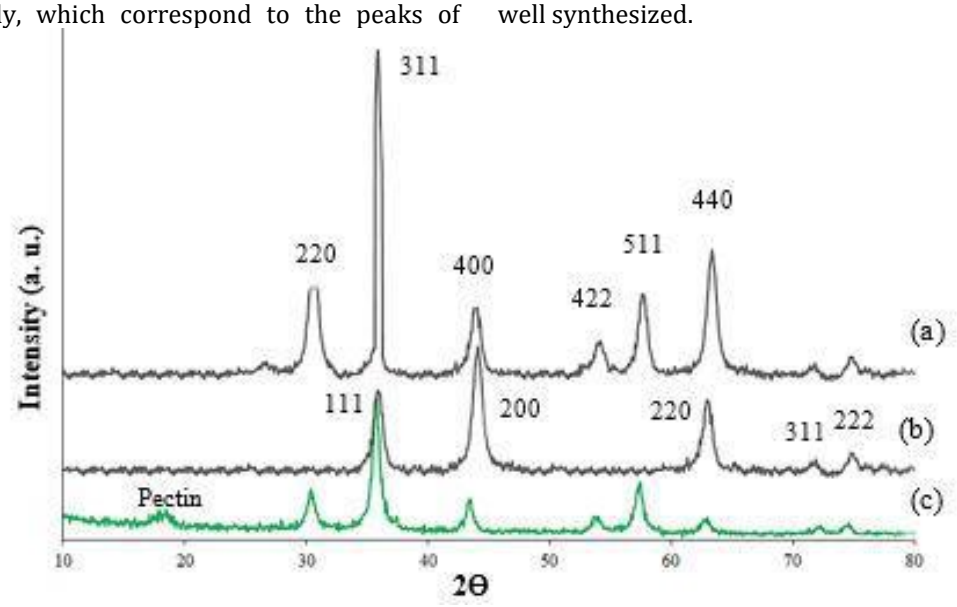


Figure 3: XRD of a) Fe_3O_4 b) Ni (II) c) Fe_3O_4@Pectin @ Ni (II)

TEM images show a biopolymer network of pectin as well as encapsulated Fe_3O_4 nanoparticles, that supporting Nickel (II) acetate on Fe_3O_4@Pectin had no significant effect on its structure. The size of the nanoparticles is about 6 to 25 nm and averages about 11 nm (Figure 4).

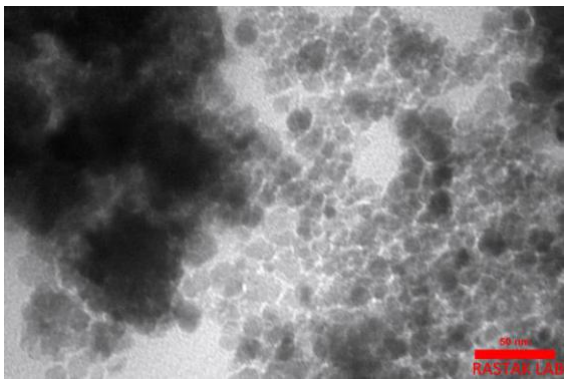


Figure 4: TEM images of the Fe_3O_4@Pectin @ Ni (II)

2.1. Catalytic activity studies

After investigating the properties of the Fe_3O_4@Pectin @ Ni (II) catalyst it was investigated its function in the synthesis reaction of aldehyde derivatives of alcohols. In this reaction, first, oxidation of the alcohols occurred in the presence of TBHP and catalysts to the aldehyde derivatives. Various conditions in this reaction were investigated for the oxidation of benzyl alcohol to find an optimized condition for its reaction. The several solvents, the solvent-free state was more favorable than the other solvents in terms of product yields and green chemistry, water and ethanol are also green and suitable solvents for producing efficient benzaldehyde (Figure 5).

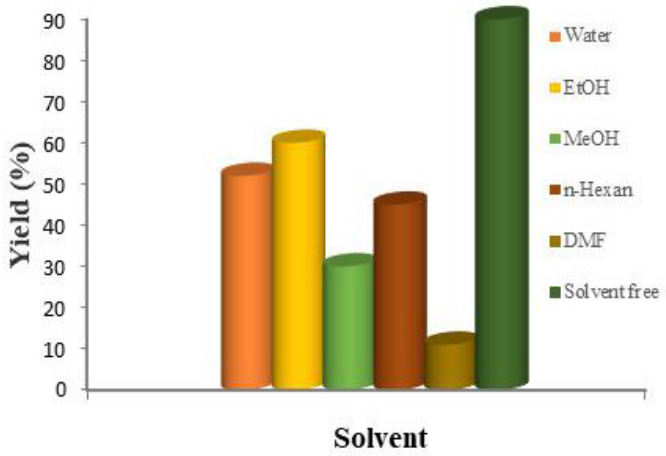
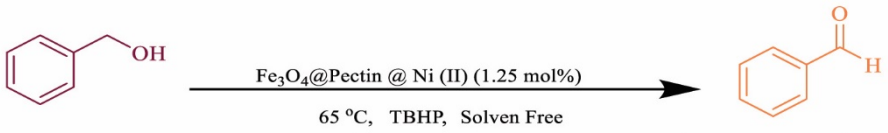


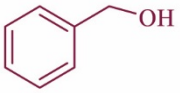
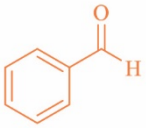
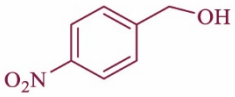
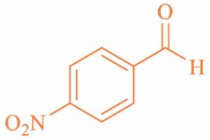
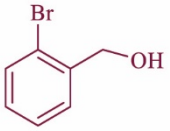
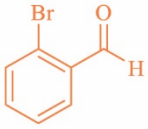
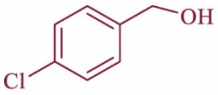
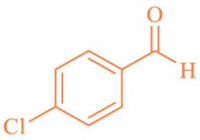
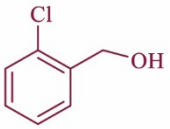
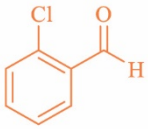
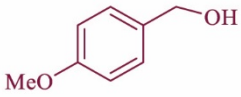
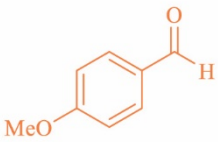
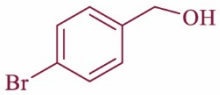
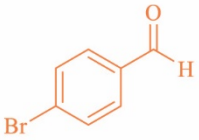
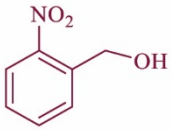
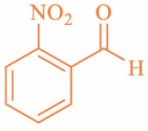
Figure 5: Screening of solvent for oxidation reaction with a molar ratio of benzyl alcohol, TBHP and Fe_3O_4@Pectin @ Ni (II), 65 °C

Various temperatures were investigated (from RT to 90 ℃) and the best temperature for producing a high-efficiency product was 65℃ and a quantity of catalyst (1.25 mole %) has good efficiency for the preparation of benzaldehyd.

After optimizing the reaction, the conditions for the oxidation of alcohol derivatives to benzaldehyde derivatives were investigated.

Table 1: Fe_3O_4@Pectin@ Ni (II) catalysed oxidation reaction of various alcohols [a]



Entry	Substrates	Products	Time (m)	Yield [b] (%)
1			90	96
2			130	83
3			80	90
4			60	95
5			60	91
6			150	92
7			60	85
8			120	80

[a] Reaction conditions: alcohol (1 mmol), TBHP (2 mmol), Fe_3O_4@Pectin@ Ni (II) catalysed (1.25 mol%) at 65 °C and solvent-free.
[b] Isolated yield.

The study showed that the electron donor groups on the ring slow the reaction and reduce the yield, but the electron-withdrawing accelerates and increases the reaction yield. It also has good selectivity for the synthesis of benzaldehyde (Table 1).

Compared to other methods (Table 2), the method we chose is a milder, greener, and rapid pathway with higher conversion and selectivity towards the production of benzaldehyde from benzyl alcohol and this clearly shows that the proposed catalyst performs, the catalytic role well.

Table 2: Comparison of catalytic activity of Fe_3O_4@Pectin@Ni (II) results for the synthesis of oxidation benzylic alcohol to benzaldehyde using other catalysts

Entry	Catalyst	Oxidant	Solvent	T (°C)	t (min)	Yield[a] (%)	Ref.
1	Fe^{3+}-Proline/Zeolite	TBHP	-	98	60	~99	19
2	Fe^{3+}/montmorillonite-K10	H_2O_2	CH_3CN	65	240	>31	20
3	Fe_3O_4/HMM	H_2O_2	CH_3CN	M.W[b]	3	~30	21
4	Pd/GO/P123	O_2	H_2O	80	210	>98	22
5	Fe_3O_4-CSDTC/Fe^{3+}	H_2O_2	H_2O	rt	120	98	23
6	$Mg_{2.5}$ $Ni_{0.5}$ Al HT	O_2	toluene	60	360	50.6	24
7	Ni $(OH)_2$	O_2	toluene	90	60	98	25
8	**Fe_3O_4-Pectin@ Ni (II)**	**TBHP**	**-**	**65**	**90**	**96**	**This work**

[a] Yields of isolated product

[b] Microwave irradiation

Conclusion

In summary, a novel nanocomposite of a magnetic-based pectin biopolymer that widely found in nature successfully modified to form a catalyst support material for the support of Ni (II) using the carboxylate groups of the pectin. In other words, the Carboxylate groups in the pectin biopolymer were the main function in the support of Ni (II). Then the Fe_3O_4@Pectin @ Ni (II) catalyst, which is a heterogeneous catalyst, reacted to synthesize the aldehyde derivatives from alcohols under the terms of solvent-free and observation that the reaction has good efficiency. Also, the recycling test showed that the catalyst has a recyclable and stable property for the xanthine synthesis reaction.

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