



Short communication

Aromatization of hydrocarbons by oxidative dehydrogenation catalyzed by nickel porphyrin with molecular oxygen

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ABSTRACT

Some metalloporphyrins (MTPPs, M = Ni, Fe, Co, and Cu) have been introduced as catalysts for the dehydrogenative aromatization of hydrocarbons using molecular oxygen as the ultimate oxidant. The results revealed that NiTPP could efficiently catalyze the dehydroaromatization of 9,10-dihydroanthracene by O₂ to anthracene, and various substrates could be tolerated. According to the obtained results, a possible reaction pathway for the aerobic dehydrogenative aromatization of hydrocarbons under nickel porphyrin has been proposed.

1. Introduction

Selective oxydehydrogenation of hydrocarbons is an important transformation in the synthesis of some important pharmaceutical intermediates and semiconductor materials [1–3]. The research field has attracted considerable attention of chemists, and various synthetic procedures have been developed [4]. Compared with the traditional methods requiring stoichiometric oxidation reagents and/or relatively forced reaction conditions [5–7], alternative catalytic oxidation systems using molecular oxygen as the sole oxidant are of great interest. Ru(OH)_x/Al₂O₃ [8], ruthenium porphyrin complex [9,10], hexagonal SrMnO₃ perovskite [11], activated carbon [12], the mixed addenda heteropoly acid H₅PMo₁₀V₂₀ [13], high-valent iron-oxo corrolazine [14], [PV₂Mo₁₀O₄₀]⁵⁻ polyoxometalate ion [15,16], and polyoxomolybdate ([PMo₁₂O₄₀]³⁻) [17] have been reported for the efficient oxidative dehydrogenation of alkylarenes to the corresponding aromatic hydrocarbons. However, most of these catalytic systems were originated from precious metals or based on complicated preparation procedure, or required harsh reaction conditions. The development of an economical and efficient catalytic system for oxidative transformation remains highly desirable from the perspective of application.

Metalloporphyrins (MTPPs) is a typical biomimetic catalyst for oxidation, and various substrates have been investigated under the catalytic system [18–22]. However, to the best of our knowledge, MTPPs with non-noble complexed metals have not been studied in the aerobic oxidative dehydrogenation of hydrocarbons. In this context, a series of MTPPs (M = Ni, Fe, Co, and Cu) have been investigated in the dehydrogenative aromatization of hydrocarbons using molecular

oxygen as the ultimate oxidant in the present study.

2. Experimental

2.1. Materials and methods

All the chemicals were purchased from Energy. Unless otherwise specified, reagents and solvents were used as received. MTPPs (M = Ni, Fe, Co, and Cu) were prepared according to the reported method [23]. Typically, to a solution of tetraphenylporphyrin (1.63 mmol, 1.0 g) in DMF (80 mL) under stirring and refluxing, 2–3 equivalents of metal salt was added in portions. The mixture was monitored by UV–vis spectra, and the reaction was completed by the loss of free tetraphenylporphyrin adsorptions. Then, the reaction vessel was cooled in an ice-water bath for 15 min. To this, 300 mL of chilled distilled water was added, and the resulting partially crystalline precipitate was filtered. After being washed with water and dried, MTPPs (M = Ni, Fe, Co, and Cu) could be obtained. The successful insertion of metals into the porphyrins was confirmed by UV–vis spectra (Figs. S1 and S2) (ANALYTIKJENA 210 PLUS spectrophotometer).

2.2. Typical catalytic procedure for the aerobic oxidation

In a typical procedure, the oxidation was performed in a carousel reaction tube under molecular oxygen. A mixture of 9,10-dihydroanthracene (180 mg, 1 mmol), cyclohexanone (2 mL), nitrobenzene (0.5 mmol, as the internal standard), and NiTPP (0.015 mmol) was magnetically stirred at 105 °C. The qualitative analysis of the products

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was performed on a GC–MS (Shimadzu GCMS-2010), and the conversion and selectivity were calculated by a quantitative analysis using a GC (Shimadzu GC-2010AF).

2.3. UV–vis analysis of the reaction mixture

In a normal reaction, the reaction mixture was quantitatively sampled at regular time intervals and dissolved into a fixed amount of DMF to prepare a solution for the UV–vis analysis. The absorption spectra were recorded on an ANALYTIKJENA 210 PLUS spectrophotometer.

3. Results and discussion

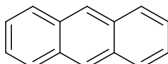
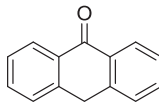
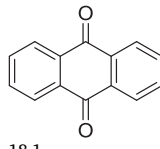
3.1. Catalytic activity of MTPPs in the dehydrogenation of 9,10-dihydroanthracene

The oxidative dehydrogenation of 9,10-dihydroanthracene with molecular oxygen as the sole oxidant was selected as the model reaction to investigate the catalytic activity of the MTPPs (M = Ni, Fe, Co, and Cu). Anthracene, anthrone, and anthraquinone were observed to be the main products under the present catalytic system. The order of the reactivity for the four catalysts was as follows: NiTPP > CuTPP > FeTPP > CoTPP. Although the highest selectivity of anthracene was obtained in the case of CoTPP, the conversion was quite low. The observed highest catalytic activity of NiTPP (Table 1, entry 3) might be due to the fact that Ni(II)TPP was first oxidized to Ni(III)TPP in the catalytic system. The species is expected to be highly reactive because of its electrodeficient character [24] and prone to accept single electron during the activation of the substrate.

Concerning the reaction solvent, it could be observed that polar solvents such as DMF and DMSO benefited to the selectivity of oxygenated products (Table 1, entries 5 and 6). Furthermore, weak-polar solvent could not give a satisfied reactivity for the transformation (Table 1, entries 7 and 8), although good selectivities of anthracene were obtained. Cyclohexanone with medium polarity provided a relatively higher conversion with an acceptable selectivity of the dehydrogenation product (Table 1, entry 10). Although a comparable conversion was also observed under polyethylene glycol (200), no preference for the three products could be obtained (Table 1, entry 11).

Table 1

Catalytic activity of MTPPs (M = Ni, Fe, Co, and Cu) in the oxidative dehydrogenation of 9,10-dihydroanthracene.^a

Entry	Catalyst	Solvent	Conv. (%)	Sel. (%)		
						
1	CoTPP	Dioxane	5.9	81.9	0	18.1
2	CuTPP	Dioxane	25.4	68.5	16.0	15.4
3	NiTPP	Dioxane	61.2	69.9	15.9	14.0
4	FeTPP	Dioxane	12.7	47.7	13.1	39.2
5	NiTPP	DMF	15.1	83.4	11.3	5.0
6	NiTPP	DMSO	39.1	67.8	22.6	9.6
7	NiTPP	<i>p</i> -xylene	31.1	75.2	16.4	8.0
8	NiTPP	Toluene	30.2	81.1	13.3	4.4
9	NiTPP	Benzonitrile	63.0	63.3	22.0	14.7
10	NiTPP	Cyclohexanone	78.4	72.9	17.5	13.6
11	NiTPP	Polyethylene glycol (200)	75.4	32.4	32.4	29.1

^a Reaction conditions: 9,10-dihydroanthracene 1 mmol, catalyst 0.015 mmol, solvent 2 mL, 95 °C, 24 h, O₂ atmosphere.

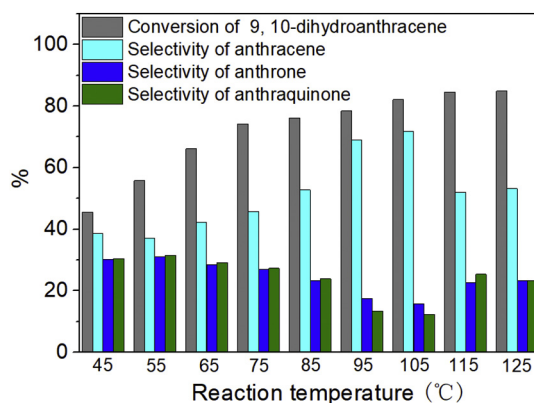


Fig. 1. Effect of reaction temperature on the oxidation of 9,10-dihydroanthracene. Reaction conditions: 9,10-dihydroanthracene 1 mmol, NiTPP 0.015 mmol, cyclohexanone 2 mL, 24 h, O₂ atmosphere.

Then, the effect of the reaction temperature was studied under the selected conditions. It can be observed from Fig. 1 that the conversion of 9,10-dihydroanthracene increased as the temperature increased, but the trend became mild when the temperature was higher than 85 °C. The selectivity of anthracene increased with the increase in temperature and reached a peak value at 105 °C. The results indicated that the relatively high temperature benefited to the dehydrogenation of 9,10-dihydroanthracene, while anthrone and anthraquinone were prone to be formed under low reaction temperature. The content of oxygenated products increased slightly when the temperature was higher than 115 °C, which might be ascribed to the appropriate activation energy for the formation of the dehydrogenative product.

To further improve the catalytic performance, some additives were introduced into the catalytic system. The results in Table S1 show that active zeolite (entry 1) suppressed the formation of anthracene. Interestingly, Al(NO₃)₃ (entry 2) could markedly accelerate the reaction, although the selectivity of the anthracene decreased to some extent. Combining the active zeolite and Al(NO₃)₃ also could not improve the catalytic performance (entry 3). Acetic acid and *p*-methylbenzenesulfonic acid as the typical proton acids did not exhibit a positive effect on the formation of the dehydrogenative product (entries 4 and 5). The introduction of Na₂CO₃ significantly reduced the catalytic activity

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