纳米 TiO₂ 光催化萘转化为 α -萘酚史慧贤¹, 张天永^{1,2}, 王红亮³, 王 晓¹, 何 萌¹¹ 天津大学化工学院, 天津 300072² 福州大学福建省光催化重点实验室, 福建福州 350002³ 天津大学药物科学与技术学院, 天津 300072

摘要: 研究了共溶剂、电子受体和表面改性等因素对 TiO₂ 光催化萘直接合成 α -萘酚反应的影响。纳米 TiO₂ 催化剂在紫外光照射下产生 $\cdot\text{OH}$, 使得萘羟基化得到 α -萘酚。在 TiO₂ 体系中加入 Fe³⁺, Fe²⁺, Fe³⁺ + H₂O₂ 和 Fe²⁺ + H₂O₂ 时, 均可有效提高萘转化率和 α -萘酚收率, 其中以体系中加入 Fe³⁺ + H₂O₂ 时, α -萘酚收率最大, 为 22.2%。TiO₂ 经表面改性后所得样品 La-Eu/TiO₂, La-Y/TiO₂, H₃PW₁₂O₄₀/TiO₂, H₃PMo₁₂O₄₀/TiO₂, Fe/TiO₂, Ag/TiO₂, Cu/TiO₂ 和 N/TiO₂, 萘转化率和 α -萘酚收率均有所提高, 其中以 Fe/TiO₂ 光催化效率最高。

关键词: 二氧化钛; 改性; 光催化; 萘; α -萘酚

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Photocatalytic Conversion of Naphthalene to α -Naphthol Using Nanometer-Sized TiO₂SHI Huixian¹, ZHANG Tianyong^{1,2,*}, WANG Hongliang³, WANG Xiao¹, HE Meng¹¹ School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China² State Key Laboratory Breeding Base of Photocatalysis, Fuzhou University, Fuzhou 350002, Fujian, China³ School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China

Abstract: The effects of various parameters (co-solvents, electron acceptors, and surface modification) on the direct synthesis of α -naphthol from naphthalene using photocatalytic processes were investigated. The $\cdot\text{OH}$ radicals generated on UV-illuminated TiO₂ photocatalysts led to the direct hydroxylation of naphthalene to α -naphthol. The addition of Fe³⁺, Fe²⁺, Fe³⁺ + H₂O₂, and Fe²⁺ + H₂O₂ greatly increases the conversion of naphthalene and the yield of α -naphthol in TiO₂ suspensions. The addition of Fe³⁺ + H₂O₂ to a TiO₂ suspension increased the yield to 22.2%. Surface modified-TiO₂ had a significant influence on the hydroxylation reaction. La-Eu/TiO₂, La-Y/TiO₂, H₃PW₁₂O₄₀/TiO₂, H₃PMo₁₂O₄₀/TiO₂, Fe/TiO₂, Ag/TiO₂, Cu/TiO₂, and N/TiO₂ enhanced the conversion and yield more than TiO₂. Fe/TiO₂ has the highest photocatalytic efficiency among these species.

Key words: titanium dioxide; modification; photocatalysis; naphthalene; α -naphthol

α -Naphthol is considered to be an important organic chemical and pharmaceutical intermediate because of its wide use as a disinfectant, a rubber auxiliary, and a dye auxiliary. The traditional production of α -naphthol requires a multistage process and a large amount of energy, and undesirable by-products are generated. It is necessary to develop a new synthetic process for α -naphthol that is more efficient and environmentally friendly. Thus, the direct hydroxylation of naphthalene to α -naphthol is a most challenging task.

Some methods are available for the direct hydroxylation of aromatic organics such as oxidation with H₂O₂, the Fenton process, and semiconductor photocatalysis [1–11]. Among them, TiO₂ photocatalytic reactions for organic synthesis have recently been the subject of many reports [6–11]. It is widely accepted that $\cdot\text{OH}$ radicals can be generated on illuminated nanometer TiO₂ surfaces. Hydroxyl radicals are considered to be efficient electrophilic substitution agents. Therefore, TiO₂ photocatalysis has been used

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for the hydroxylation of aromatic compounds. Surface modifications of TiO₂ should change reaction yields and selectivity. The kinetics and mechanisms of the photocatalytic reactions of surface modified TiO₂ are often different from those of pure TiO₂ [12–16].

Most studies focus on the hydroxylation of benzene and its derivatives by photocatalytic reactions [1–3,6,8]. The reported yield and selectivity for phenol production from benzene were 0.5% and 80% after TiO₂ photocatalysis [17], respectively. Tanarungsun et al. [8] studied the liquid phase hydroxylation of benzene to phenol on Fe/TiO₂ catalysts loaded with different types of secondary metals and they found that doping with 1 wt% Pt or Pd on Fe/TiO₂ improved the phenol yield noticeably. Although their conversion efficiency was still low, the organic synthesis process that they used was energy-efficient and environmentally benign. However, only a few reports exist about the direct hydroxylation of naphthalene to α -naphthol by surface modified TiO₂ nanoparticles using photocatalysis. We thus investigated the hydroxylation reactions of naphthalene using several photocatalytic systems with TiO₂ and surface-modified TiO₂ as heterogeneous photocatalysts. The effect of various solvents (acetonitrile, acetone, acetic acid) and electron acceptors such as Fe²⁺, Fe³⁺, H₂O₂, (NH₄)₂S₂O₈, and KBrO₃ was investigated to determine the optimal conditions for α -naphthol synthesis. Surface modified TiO₂ such as La-Eu/TiO₂, La-Y/TiO₂, H₃PW₁₂O₄₀/TiO₂, H₃PMo₁₂O₄₀/TiO₂, Fe/TiO₂, Ag/TiO₂, Cu/TiO₂, and N/TiO₂ were also used to investigate how the surface properties affect the hydroxylation reaction. This study mainly focused on the feasibility of the hydroxylation of naphthalene and should aid in the choice of a photocatalyst. The effect of catalyst characteristics will be studied in further work.

1 Experimental

1.1 Preparation of the modified catalysts

Catalysts were prepared by the sol-gel process according to the following procedure. Solution A, 34 ml Ti(Obu)₄ (AR, Kewei Chemical Reagents Company, Tianjin, China) was dissolved in 44 ml absolute ethanol with stirring for several minutes and then 3 ml acetic acid was added as a hydrolysis suppressant. Solution B containing 44 ml absolute ethanol, 7.2 ml H₂O, and nitrates or polyoxometalate (AR, Kewei Chemical Reagents Company, Tianjin, China) in the required stoichiometry were slowly added to solution A. The mixture was hydrolyzed at 25 °C for 30 min under agitation and a transparent sol was obtained. Gelation was complete after aging the sol for 24 h at room temperature. The gel was dried at 60 °C, ground to a powder and calcined for 3 h at 500 °C. La-Eu/TiO₂, La-Y/TiO₂, H₃PW₁₂O₄₀/TiO₂,

H₃PMo₁₂O₄₀/TiO₂, Fe-TiO₂, Cu-TiO₂, Ag-TiO₂, and N/TiO₂ were prepared according to this process. SEM (scanning electron microscopy, TESCAN VEGA TS-5130SB Czech) images of the catalysts showed that the samples have a relative uniform particle diameter distribution in a range of 80–90 nm.

1.2 Photocatalytic synthesis and product analysis

The photocatalytic conversion reactions of naphthalene were carried out in an aqueous catalyst suspension and in a solvent. TiO₂ (P-25 from Degussa Co., BET surface area 50 m²/g, mean diameter 30 nm, 87% anatase and 13% rutile) or surface modified TiO₂ powder (20 mg) was suspended in 30 ml of distilled water and then 20 ml of cosolvent containing 0.5 g naphthalene was added to the suspension and mixed well. Depending on the experiment we then added electron donors, acceptors, or other reagents to the suspension. The photocatalytic reactor consists of a 160 ml Pyrex glass bottle with an outer jacket and a 125 W high pressure Hg lamp as a light resource that was placed parallel to the reactor. In all the experiments, the reaction temperature was kept at (25±1) °C by the continuous circulation of water through the jacket around the reactor. The samples were collected at regular intervals during illumination. Naphthalene, α -naphthol, and other intermediates were analyzed with GC (gas chromatography, Agilent 6890N).

The reaction performance was defined as follows: conversion of naphthalene = moles of naphthalene reacted/initial moles of naphthalene; yield of α -naphthol = moles of α -naphthol produced/moles of naphthalene reacted.

2 Results and discussion

2.1 The effect of cosolvents

Acetonitrile, acetic acid, and acetone were used as the co-solvents for these reactions and the results are shown in Table 1. When acetic acid and acetone were used as co-solvents only a trace amount of α -naphthol was detected. The reaction media for the hydroxylation could be rated according to the order acetonitrile > acetic acid > acetone.

Figure 1 shows the effect of acetonitrile as a cosolvent on the production of α -naphthol. The addition of acetonitrile at

Table 1 Hydroxylation of naphthalene using illuminated TiO₂ and various solvents

Solvent	Conversion (%)	Yield (%)
Acetic acid	5.3	5.1
Acetone	4.8	7.1
Acetonitrile	19.5	22.2

Fig. 1. Effect of the acetonitrile co-solvent amount on the conversion of naphthalene and the yield of α -naphthol.

up to 20 ml slightly increased the conversion and yield but any further addition gradually reduced the conversion and yield. Therefore, 20 ml of solvent per experiment was used throughout the remainder of this work.

Naphthalene can be directly converted into α -naphthol by reaction with $\cdot\text{OH}$ (Eq. (1)):

$\cdot\text{OH}$ attacks naphthalene to produce a hydroxycyclohexadienyl (HCHD) radical [6], which subsequently undergoes H-atom abstraction by oxidants and gives α -naphthol. Although the presence of CH_3CN as a co-solvent can prevent the naphthalene in water from volatilizing during the reaction it is also a $\cdot\text{OH}$ scavenger. Therefore, the high concentration of CH_3CN can decrease the amount of $\cdot\text{OH}$ and thus reduce the conversion and yield [6]. In addition, water is an essential precursor of $\cdot\text{OH}$ because its production cannot be sustained in a non-aqueous environment. Therefore, the conversion and yield in high concentrations of acetonitrile were low.

2.2 Effect of electron acceptors

The type of electron acceptor available in the TiO_2 suspension is important in determining yield because a reductive electron transfer and reactions of $\cdot\text{OH}$ radicals are involved in the overall reaction mechanism. Conduction band (CB) electron transfer to electron acceptors should improve the reaction process because of a retarded charge pair recombination. Therefore, the presence of suitable electron acceptors is essential for photocatalytic oxidative reactions. In the TiO_2 suspension dissolved O_2 serves as an electron acceptor. The presence of additional electron acceptors may

enhance the conversion of naphthalene. Results from the hydroxylation of naphthalene in a TiO_2 suspension in the presence of additional electron acceptors are shown in Table 2.

Table 2 Hydroxylation of naphthalene in illuminated TiO_2 with various electron acceptors

System	Conversion (%)	Yield (%)
TiO_2	2.3	not detected
$\text{TiO}_2 + \text{H}_2\text{O}_2$	20.5	10.2
$\text{TiO}_2 + \text{Fe}^{2+} + \text{H}_2\text{O}_2$	43.1	5.3
$\text{TiO}_2 + \text{Fe}^{3+} + \text{H}_2\text{O}_2$	89.5	22.2
$\text{TiO}_2 + (\text{NH}_4)_2\text{S}_2\text{O}_8$	7.3	not detected
$\text{TiO}_2 + \text{KBrO}_3$	5.6	not detected
$\text{TiO}_2 + \text{Fe}^{3+}$	17.0	7.6
$\text{TiO}_2 + \text{Fe}^{2+}$	25.3	9.1

The addition of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and KBrO_3 can increase the naphthalene conversion slightly but α -naphthol was not detected in the reaction products. However, the addition of H_2O_2 significantly increased the conversion and yield compared with TiO_2 because H_2O_2 generates additional $\cdot\text{OH}$ radicals as it reacts with a conduction band electron (Eq. (2)) [18]. Fe^{3+} has also been reported to be a conduction band electron acceptor (Eq. (3)) and a good oxidant of HCHD radicals (Eq. (4)) [19,20]. The addition of both Fe^{3+} and H_2O_2 to a TiO_2 suspension increased the conversion and yield even more compared with systems where only Fe^{3+} was added or only H_2O_2 was added. The addition of $\text{Fe}^{3+} + \text{H}_2\text{O}_2$ to a TiO_2 suspension increased the yield to 22.2%, which was the highest yield obtained in this study mainly because of the photo-Fenton reaction.

2.3 Effect of TiO_2 surface modification

Table 3 summarizes the effects of TiO_2 surface modification on the hydroxylation of naphthalene. Simultaneously doping TiO_2 with two kinds of rare earth ions can enhance the photocatalytic reactivity significantly compared with undoped TiO_2 . The data listed in Table 3 shows that the conversion of naphthalene increased rapidly although the yield of α -naphthol was not very high. The ionic radii of La^{3+} (10.61 nm), Y^{3+} (9.0 nm), and Eu^{3+} (9.47 nm) are larger than that of Ti^{4+} (6.05 nm). Therefore, it is difficult for La^{3+} , Y^{3+} , and Eu^{3+} to enter the TiO_2 lattice. This might be due to the substitution of La^{3+} , Y^{3+} , and Eu^{3+} atoms in the lattices

Table 3 Hydroxylation of naphthalene in a surface-modified TiO₂ suspension

Catalyst	Conversion (%)	Yield (%)
TiO ₂	2.3	not detected
La-Y/TiO ₂	41	2.9
La-Eu/TiO ₂	46	4.1
H ₃ PW ₁₂ O ₄₀ /TiO ₂	35	2.3
H ₃ PMo ₁₂ O ₄₀ /TiO ₂	47	2.8
Fe/TiO ₂	50	5.6
Ag/TiO ₂	6.5	5.5
Cu/TiO ₂	11.4	6.6
N/TiO ₂	4.9	4.9

of La₂O₃, Y₂O₃, and Eu₂O₃ by Ti⁴⁺. Ti-O-La, Ti-O-Y, and Ti-O-Eu bands can be formed at the Ti⁴⁺ interface. If Ti⁴⁺ replaces La³⁺, Y³⁺, and Eu³⁺ a charge imbalance would result. Therefore, the formation of Ti-O-La and Ti-O-Eu bonds and the charge balance might affect the photocatalytic activity of La-Eu/TiO₂ and La-Y/TiO₂ catalysts. With a charge imbalance more OH⁻ would adsorb onto the surface to balance the charge. These surface OH⁻ ions can accept the holes generated by light irradiation to form hydroxyl radicals, which leads to the oxidation of adsorbed substrates [20]. Therefore, the surface state modification of the catalyst might result in an effective separation of electron-hole pairs.

As a homogenous photocatalyst, polyoxometalate has been widely investigated for its high oxidizing power, which is strong enough to oxidize a variety of organic compounds. Polyoxometalate is similar to the heterogeneous TiO₂ photocatalyst in terms of light absorption and electrochemical band edge positions [7,19,21,22]. As shown in Table 3, TiO₂ modified with polyoxometalate greatly enhances the reaction process and the conversion of naphthalene increased about 20 times compared to that for pure TiO₂. Additionally, the yield of α -naphthol increased and this can be attributed to the dual roles of polyoxometalate as both a photocatalyst and an electron shuttle [6].

Metal ions that deposit onto the TiO₂ surface often enhance photocatalytic activity because they trap conduction band electrons by reducing the charge pair recombination and promoting interfacial electron transfer [13,16]. Fe/TiO₂ is the most effective among those photocatalysts for this conversion and it can reach 50% but the yield was only 5.6% mainly because the •OH radicals are so reactive and non-selective that oxidative degradation and mineralization are prevalent. Therefore, minimizing unwanted pathways such as oxidative degradation is important to achieve selective hydroxylation. Ag/TiO₂ and Cu/TiO₂ lead to a higher yield for α -naphthol although the conversion of naphthalene is low because the conduction band electrons are trapped and the charge pair recombination is reduced while interfa-

cial electron transfer is promoted, which can prevent the peroxide and mineralizing reactions. These factors benefit the hydroxylation of naphthalene.

N/TiO₂ was also used for the hydroxylation of naphthalene because it has been reported that N/TiO₂ produces more free •OH radicals than pure TiO₂. The conversion of naphthalene was twice as high as that of pure TiO₂ (Table 3). The yield of α -naphthol was also significantly enhanced. The conversion of naphthalene was lower when Ag/TiO₂ and N/TiO₂ were used as the photocatalyst. However the selectivity was higher than for the other modified TiO₂ catalysts, which benefits the recycling of naphthalene and the separation of α -naphthol. Therefore, lower operation and workup costs should result.

3 Conclusions

The photocatalytic synthesis of α -naphthol from naphthalene under various conditions was studied. The role of conduction band electron acceptors was critical in determining conversions and yields. The addition of Fe³⁺ + H₂O₂ in a TiO₂ suspension increased the yield to 22.2%, which was the highest yield obtained in this study. TiO₂ surface modification plays an important role in the hydroxylation of naphthalene. La-Eu/TiO₂, La-Y/TiO₂, H₃PW₁₂O₄₀/TiO₂, H₃PMo₁₂O₄₀/TiO₂, Fe/TiO₂, Ag/TiO₂, Cu/TiO₂, and N/TiO₂ can enhance the conversion and yield rapidly compared with TiO₂. The photocatalytic synthesis was carried out at ambient temperature and at atmospheric pressure and no complex equipment was used, which make this process energy-efficient and environmentally benign.

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2009 年国内化学类期刊影响因子和总被引频次排序表

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期刊名称	影响因子		总被引频次		他引率
	数值	排名	数值	排名	
色谱	1.750	1	1918	6	0.87
分析化学	1.290	2	4042	2	0.86
分析测试学报	1.155	3	1814	8	0.71
分子催化	1.151	4	679	21	0.62
催化学报	0.940	5	1916	7	0.82
化学学报	0.905	6	3052	3	0.79
燃料化学学报	0.867	7	1128	15	0.78
高等学校化学学报	0.855	8	4265	1	0.82
物理化学学报	0.848	9	2035	5	0.79
分析试验室	0.770	10	1527	11	0.79
无机化学学报	0.751	11	2042	4	0.74
化学进展	0.740	12	1249	14	0.88
环境化学	0.704	13	1548	10	0.93
高分子学报	0.700	14	1500	12	0.82
分子科学学报	0.631	15	244	32	0.47
分析科学学报	0.626	16	879	19	0.85
有机化学	0.614	17	1383	13	0.69
煤炭转化	0.558	18	491	26	0.68
应用化学	0.529	19	1579	9	0.86
中国科学 B 辑	0.443	20	1026	17	0.96
影像科学与光化学	0.413	21	223	34	0.78
化学通报	0.407	22	1061	16	0.94
高分子通报	0.400	23	620	23	0.92
化学研究与应用	0.396	24	964	18	0.84
Chemical Research in Chinese Universities	0.366	25	266	31	0.68
电化学	0.345	26	292	30	0.93
结构化学	0.333	27	567	24	0.42
Chinese Chemical Letters	0.326	28	686	20	0.85
化学试剂	0.313	29	666	22	0.86
Chinese Journal of Polymer Science	0.309	30	179	35	0.74
化学与生物工程	0.309	30	515	25	0.94
化学与黏合	0.291	32	297	29	0.89
化学研究	0.270	33	244	32	0.87
合成化学	0.244	34	441	27	0.89
化学分析计量	0.235	35	301	28	0.89