



Application of Photocatalysis in Cleaning Organic Synthesis

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For studying the application of photocatalysis in cleaning organic synthesis, the use of hole selective oxidation of organic compounds is explored, and photogenerated electrons are applied to reduce hydrogen for producing new hydrogen. The reaction is carried out at normal temperature and pressure, the reaction material is simple, and the by-product is clean energy hydrogen. By replacing the Mn^{2+} that is commonly used in this type of experiment as Ce^{3+} , from the experimental results, it is found that the replacement results have a better effect on the stability and adaptability of the system. The experimental water system was changed into organic solvent system, and it was found that the utilization range of photocatalysis in organic synthesis could be greatly expanded, and some reactions that the traditional chemistry can hardly have may occur. In this part, toluene is used as a reactant and also a solvent, and a coupling reaction between the self-dehydrogenation and the molecular reaction is used to generate the benzyl chloride. The experimental results show that, on the one hand, the reaction does not need to consume energy; on the other hand, it can produce hydrogen. Based on the above research, the conclusion is drawn that it saves the complex steps and environmental pollution of the traditional chemical synthesis.

1. Introduction

In the related research, it is shown that the Mn^{2+} can be used as the medium to realize the photoelectric cooperation indirect oxidation of toluene to benzaldehyde and the selectivity of benzaldehyde reaches 86.5%, which better makes use of light to produce electrons and holes. But there are some problems in the experiment. First of all, a small number of Mn^{3+} has disproportionation reactions and generates solid MnO_2 . In addition, the generated small part of Mn^{3+} continue to react with holes to generate MnO_2 or even manganese with higher valence state. The bad results are mainly reflected in three aspects; firstly, the precipitation of solid manganese led to a reduction of Mn circulating medium in the system, and it will directly lead to a weakening of the hole capture ability, which will further lead to the decrease of the activity of the whole reaction system, shown as the reduction of quantum efficiency. Secondly, the precipitation of a large part of solid manganese oxide occurred in the surface of TiO_2 . On the one hand, it hinders the light capture, and on the other hand, it hinders the contact between the Mn^{2+} ion and photocatalyst so that the catalytic activity decreased (Mozia, 2015; Mahadeven and Sendilvelan, 2017; Rossetti et al., 2017; Vaiano et al., 2017; Silv et al., 2017; Almeida et al., 2017). Thirdly, manganese with higher valence state always has higher oxidation capacity. If it contacts with toluene or benzene formaldehyde, it can cause further oxidation as other by-products, which leads to the selectivity and yield of benzaldehyde decreased. To solve this problem, we choose Ce^{3+}/Ce^{4+} as the circulating medium. Because cerium in the general conditions does not exist other higher valence state, Ce^{4+} salt solubility is good and it is not easy to precipitate. It is not easy to produce oxide under acidic conditions, so it can solve the problems of Mn^{3+} .

2. Experiment

2.1 Reagents and raw materials

The reagents and raw materials used in the experiments are as follows in Table 1:

Table 1: Reagents and raw materials used in the experiments

Reagent name	Reagent specification	Manufacturer
Concentrated hydrochloric acid	AR	Shanghai Zhenxing Chemical Factory
Concentrated sulfuric acid	AR	Shanghai Zhenxing Chemical Factory
Concentrated nitric acid	AR	China Pharmaceutical Group Shanghai Chemical Reagent Company
Manganese sulfate	AR	China Pharmaceutical Group Shanghai Chemical Reagent Company
Copper sulphate	AR	China Pharmaceutical Group Shanghai Chemical Reagent Company
Isopropyl titanate	AR	Aladdin
Anise aldehyde	GC	Aladdin
Benzaldehyde	GC	Aladdin
Para tert butyl toluene	GC	Aladdin
Tolylchloride	GC	Aladdin
P-chlorotoluene	GC	Aladdin
Bibenzyl	GC	Aladdin
Methoxy toluene	GC	Aladdin
benzene	GC	Aladdin
Acetophenone	GC	Aladdin
Para tert butyl benzaldehyde	GC	Aladdin

2.2 Preparation of photocatalytic materials

TiO₂/FTO electrode is synthesized according to the literature method. The specific method is 30mL ultra pure water mixed with 30mL concentrated hydrochloric acid, and then drop with 2mL isopropyl titanate and transfer to the hydrothermal reactor, and then place into the washing FTO. On the condition of 155 DEG C, heat for 4h. After cooling, the FTO was removed and the TiO₂/FTO thin film electrode was obtained by the treatment under 200 DEG C for 2h.

The synthesis method of M/TiO₂-x% material is to weigh 500mg P25, which is dispersed in 50mL ultra-pure water, and take a certain amount of 1g/100mL water chlorine platinum acid. After mixing, make low pressure rotary evaporator at 75 DEG C (Palmisano et al., 2016). And then transfer to the quartz grinding bowl for grinding ten minutes. The milled samples were placed in quartz boat, and in a tube furnace, under 275 DEG C, with 10% H₂ - 90% Ar mixed gas atmosphere, reduce for 2h. After cooling, take it out for standby and name it as Pt/P25-x%, where x is the percentage of Pt elements in the catalyst. Similarly, take Sanshui palladium chloride, six aqueous chloroauric acid and cupric chloride as Pd source, Au source and a copper source, to produce Pd/P25-x%, Au/P25-x%, and Cu/P25-x%. Pt/anatase-x%, Pt/ rutile-x%, and Pt/C3N4-x% were prepared by replacing P25 by rutile, anatase and C3N4.

2.3 Photoelectric catalytic performance test with Ce³⁺/Ce⁴⁺ as the medium

At 25 DEG C, prepare 0.12mol/L Ce₂(SO₄)₃ nitric acid solution (nitric acid concentration of 1mol/L) as the anode solution and 1mol/L nitric acid solution as cathode liquid. Cathode nitrogen exhaust 10min. Reaction conditions: reaction bias 0.7V, light source 300W xenon lamp simulated sunlight, reaction time of 2h, and reaction temperature of 25 DEG C. Add 5uL methyl anisole to the anode before the reaction. TiO₂/FTO is a photo anode, Pt is a cathode, and mercury mercury sulfate is reference electrode (Sprick, et al., 2015). After the reaction, 2mL toluene was used to extract the anode solution, and chromatographic analysis is made after the extraction. 0.5mL gas was extracted directly from cathode and the content of hydrogen was measured by chromatography.

3. Indirect catalytic oxidation of alkyl aromatics by photoelectric co catalysis with Ce³⁺/Ce⁴⁺ as the medium

3.1 Choice of reaction medium

When the system does not contain Ce³⁺ ions, hydrogen generation and 4- methyl anisole conversion rate are particularly low, indicating that when the system does not contain Ce³⁺, the reaction is difficult to be carried out. Because 4- methyl ether is insoluble in water, it is difficult to directly contact with photocatalyst, resulting in

that the formation of photogenerated hole cannot react quickly, almost all recombining with electron. Only a small number of electrons are transferred to the cathode to generate hydrogen. A small amount of hole oxidized 4- methyl anisole. When the cerium sulfate was used as cerium source and sulfuric acid was used as the medium, the hydrogen production was increased obviously (see table 2). The reason was that the Ce^{3+} dissolved in water consumed some of the holes, which promoted the transfer of electrons and production of hydrogen. But at this time, the conversion rate of 4- methyl anisole was not obviously improved, which is only 7.2% high than the conversion rate without Ce^{3+} (Reddy, et al., 2015). This is because at room temperature, the oxidation resistance of Ce^{4+} ions in sulfuric acid is not strong enough, and it is difficult to oxidize 4- methyl anisole to anise aldehyde. If we change to nitric acid cerium nitrate system, we can see that the hydrogen production rate is lower than that of sulfuric acid cerium sulfate system, but the conversion rate of 4- methyl anisole is greatly improved. At this time, however, the yield of anise aldehyde is very low. Because in the nitric acid solution, Ce^{4+} oxidation is strong, and it is easy to oxidize 4- methyl anisole to methoxy benzoic acid. The same reason, the oxidativity of Ce^{4+} is stronger in the nitric acid solution.

Table 2: Selection of cerium source and acid. Reaction conditions: sunlight for 2h, mercury/mercury sulfate reference electrode, and 0.7V bias

75.1	Hydrogen production (μmol)	Anise aldehyde (μmol)	Conversion (%)	Selectivity (%)
1M nitrate +5uL 4- methyl anisole	1.63	0.3	16.3	4
$Ce_2(SO_4)_3$ 0.10M and 1M nitric acid	28.1	-	-	-
$Ce_2(SO_4)_3$ 0.1M, 1M	33.6	5.8	23.5	62.1
$Ce(NO_3)_3$ 0.20M and 1M nitric acid +5uL	24.2	0.8	83.4	2.3
$Ce_2(SO_4)_3$ 0.10M and 1M nitric acid +5uL 4- methyl anisole	57.8	26.5	88.7	75.1

3.2 Effect of reaction bias

As can be seen from Table 3, with the increase of the bias voltage, both the yield of hydrogen and the yield of anise aldehyde are increased. The increase of bias voltage is beneficial for the photoinduced electron transferring to the photocathode, so the hydrogen production activity increases with the increase of bias voltage (Šuligoj, et al., 2016). The corresponding hole products - Ce^{4+} ions also increased, while the yield of anise aldehyde obtained by Ce^{4+} aldehyde oxidation organic compounds was also increased.

Table 3: Selection of cerium source and acid. Reaction conditions: 2h, mercury/mercury sulfate reference electrode, 0.7V bias

Bias voltage (V)	Hydrogen production (μmol)	Anise aldehyde (μmol)	Conversion rate (%)	Yield (%)	Selectivity (%)
0.7	57.8	26.5	88.7	66.6	75.1
0.5	48.7	18.3	76.1	46.0	60.4
0.3	32.0	15.1	64.8	37.9	58.5
0.1	18.1	13.3	58.5	33.4	57.1

3.3 Effect of nitric acid concentration

As can be seen from Table 4, the concentration of nitric acid can affect the oxidation and redox properties of Ce^{3+}/Ce^{4+} . When the concentration of nitric acid is low, Ce^{3+} is easier to be oxidized, and the corresponding hydrogen production activity is higher. But at this time, the corresponding Ce^{4+} oxidation capacity is weak, then the oxidation rate of 4- methyl ether is slow, so the yield and selectivity of anise aldehyde are relatively low. With the increase of the concentration of nitric acid, the reaction achieves the optimal.

Table 4: Effect of nitric acid concentration

$Ce_2(SO_4)_3$ (mol/L)	Hydrogen production (μmol)	Anise aldehyde (μmol)	Conversion rate (%)	Yield (%)	Selectivity (%)
0.12	58.7	26.8	90.8	67.4	74.2
0.10	57.8	26.5	88.7	66.6	75.1
0.08	51.8	22.7	87.7	57.0	65.0
0.06	42.3	16.6	81.9	41.7	50.9

3.4 Influence of Ce^{3+} concentration

As can be seen from Table 5, Ce^{3+} ion concentration will affect the capture of photogenerated holes. When the Ce^{3+} concentration is high, the ability to capture the hole will be stronger, the corresponding Ce^{4+} ion generation rate and the hydrogen generation rate will increase, and the production of anisaldehyde ratio will also be increased. When the concentration of Ce^{3+} ions in the system is low, some of the holes have not been able to react with Ce^{3+} ions, which results in the decrease of the reaction activity (Alfieri, et al., 2017). However, due to limitation of the solubility of the sulfite, it is unable to continue to increase the concentration of Ce^{3+} ions. Therefore, the concentration of Ce^{3+} ions has a great influence on the reaction, which not only affects the rate of hydrogen production, but also affects the yield of anise aldehyde and the conversion rate of toluene.

Table 5: Influence of Ce^{3+} concentration

Photoanode (mol/L)	Hydrogen production (μ mol)	Anise aldehyde (μ mol)	Conversion rate (%)	Yield (%)	Selectivity (%)
1.20	51.1	26.0	93.5	65.3	69.9
1.00	57.8	26.5	88.7	66.6	75.1
0.80	59.8	17.9	82.3	51.0	62.0
0.60	61.9	15.7	72.9	39.5	54.2

3.5 Modulation of reaction time

As can be seen from Figure 1, with the extension of time, regardless of the yield of hydrogen or the formation of the formaldehyde content of Anise aldehyde, they increase linearly with time. The yield of Anise aldehyde and the conversion rate of 4- methyl anisole also increased with time. However, the selectivity of Anise aldehyde was only slightly fluctuated with time. The results show that the time has little effect on the hydrogen production activity and the selectivity of the Anise aldehyde, and the reaction system has little effect on the catalyst that there was little change in the reactivity of the catalyst after several hours.

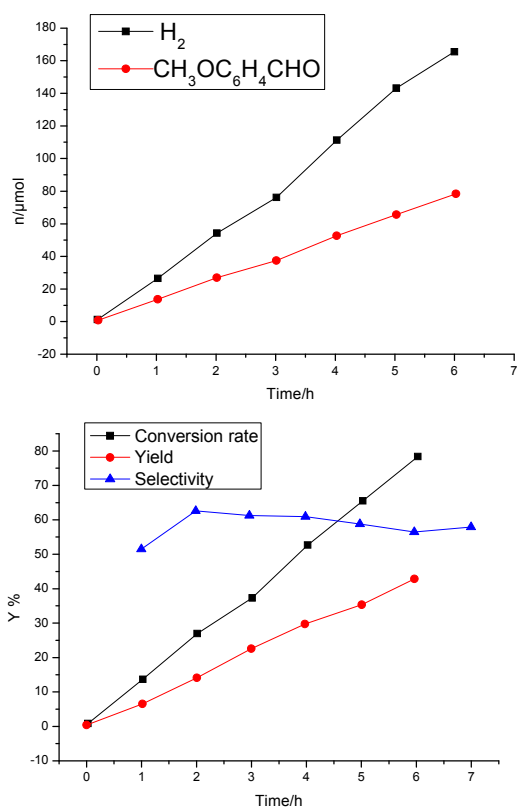


Figure 1: Oxidation of methyl anisole over time

4. Photocatalytic removal of hydrogen from toluene

In the previous part, we used metal ions as the circulating medium to realize the photocatalytic oxidation of alkyl aromatics to the corresponding aldehydes/ketones. The by-products of the reaction are all hydrogen. We all know that hydrogen is a clean energy, which further reduces the energy consumption of our reactions. Although we have achieved good results in the first two chapters, we know that most of the organic reactions are carried out in non-aqueous media (Molinari, et al., 2017). In order to further broaden the application of photocatalytic technology in clean organic synthesis, we studied the photocatalytic organic reaction in non-aqueous solvent system.

Table 6: Catalytic activity of different samples

No.	Catalyzer	H ₂ (μmol)	Benzyl (μmol)	Selectivity (%)	Quantum yield (%)
1	Pt/P25-0.5%	98.8	96.2	97.4	0.22
2	Pt/P25-1.0%	108.3	99.7	92.1	0.24
3	Pt/P25-1.5%	116.4	107.8	92.6	0.26
4	Pt/P25-2.0%	129.7	121.1	93.4	0.29
5	Pt/P25-2.5%	92.6	89.6	96.8	0.20
6	Pt/P25-3.0%	76.2	61.7	81	0.16
7	Au/P25-2.0%	114.8	108.4	94.4	0.25
8	Pd/P25-2.0%	58.7	38.5	65.6	0.13
9	Cu/P25-2.0%	0	0	-	0.00
10	Pt/anatase-2.0%	36.4	10.2	28	0.08
11	Pt/ rutile-2.0%	13.2	0	-	0.03
12	Pt/C3N4-2.0%	0	0	-	0.00

Reaction conditions: 50mg catalysts, 20mL toluenes, nitrogen gas for 6min, and sunlight reaction for 1h. A: no nitrogen, other conditions are the same as shown above. b: add 200uL water, other conditions are the same as shown above.

The Catalytic activity of different samples is listed in table 6, from which, we can see that as the loading amount of Pt increased, the production of hydrogen and bibenzyl and quantum yield are improved. The activity is the highest when the Pt loading is 2%, the hydrogen production capacity is 129.7umol, the bibenzyl generation is 121.1, and the quantum efficiency is 0.29%. When the Pt load is higher than 2%, the activity decreases with the increase of Pt load. The reason is that Pt plays two roles, one is hydrogen additive and the other is that Pt is a good hydrogen production assistant. From the number of 4, 7, 8, 9, we can see that the load Pt/P25 activity was significantly higher than that of Au/P25, Pd/P25 and Cu/P25 and so on. There are many factors that cause this gap. The first one is the capacity of hydrogen evolution. We know that in the above several hydrogen evolution metal materials, Pt hydrogen over potential is the minimum. That is to say, on the surface of Pt, the energy required for electron reduction of hydrogen ion is the minimal. Because the reaction involves hydrogen reduction, from this aspect, the activity of Pt/P25 is higher than that of other catalysts (Tahir, et al., 2016). Secondly, the dispersion degree of Pt is obviously higher than that of other metals, which is more conducive for the electron transport. Based on the above two factors, the activity of Pt was higher than that of other samples.

5. Conclusions

1. In this experiment, Ce³⁺/Ce⁴⁺ was used as the medium, and the photoelectric synergistic catalytic oxidation of toluene was applied to the production of hydrogen peroxide, to produce hydrogen by-products that can be used as energy at the same time. It makes the most efficient use of the value of the electron hole and better reflects the advantages of photocatalysis.

2. The influence of acidity, Ce³⁺ concentration, bias voltage and reaction time on the reaction was investigated. The results showed that Ce₂(SO₄)₃ was 0.12M, and the reaction was the best when the concentration of nitric acid was 1M. Furthermore, the reaction rate increases with the increase of bias voltage. The reaction time had great effect on the conversion of reactants, but had little effect on the selectivity and yield.

3. We use this system to expand to other alkyl aromatics, and get better results. For example, making oxidation of chloro toluene, we generate the reaction of chlorobenzene formaldehyde. After 2h, the yield was 100%, and the selectivity reached 77.9%. And the oxidation product of ethylbenzene is acetophenone.
4. We take Ce^{3+}/Ce^{4+} as a medium to overcome the shortcomings of Mn^{3+} instability, which can prolong the life cycle of the circulating medium and the catalyst.

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