

# Solvent controlled selective photocatalytic oxidation of benzyl alcohol over Ni@C/TiO<sub>2</sub>

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## Abstract

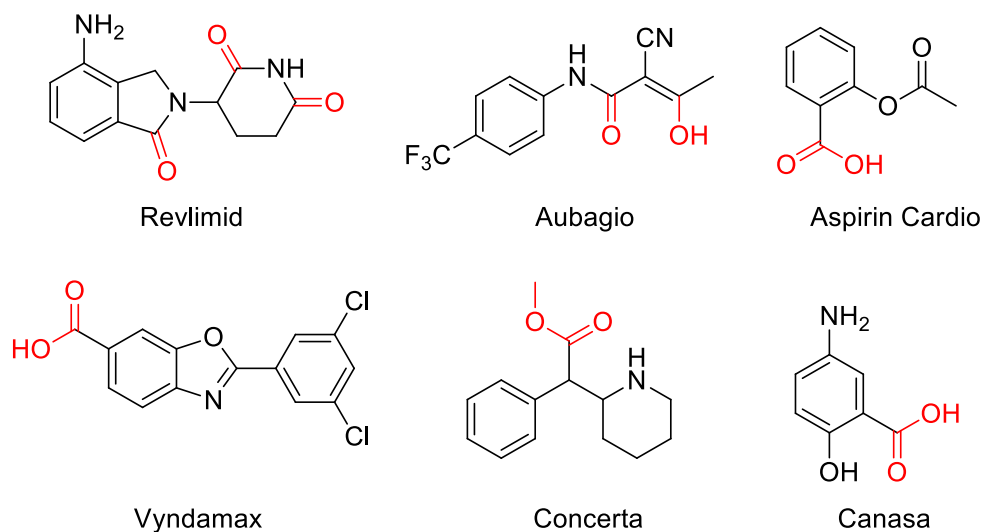
The oxidation of aromatic alcohols to produce carbonyl compounds is of great significance in fine chemical production. The traditional oxidation produces waste gas and pollutes the environment during the reaction. As a new field, photocatalysis has attracted people's attention because of its environmental friendliness. At present, there have been much research on TiO<sub>2</sub>, or noble metal modified TiO<sub>2</sub> to catalyze alcohol oxidation, but the high cost is not conducive to large-scale production. Herein, a Ni@C/TiO<sub>2</sub> catalyst was prepared by in-situ hydrothermal synthesis. This catalyst has a better oxidation effect on benzyl alcohol than Ni@C supported on TiO<sub>2</sub> on the market and has a good catalytic effect on aromatic alcohols with different substituents. It is more interesting that the selectivity of the product can be adjusted by choosing different reaction solvents. The highly active catalyst with low cost and wide applicability has certain significance for the large-scale use of photocatalytic alcohol oxidation.

**Keywords:** photocatalysis, alcohol oxidation, solvent controlled, titanium oxide.

## 1. Introduction

As important chemical products, benzaldehyde or benzoic acid is widely used in perfumes, dyes, and pharmaceutical intermediates<sup>[1]</sup>. At present, the preparation methods of benzaldehyde mainly include the oxidation of benzyl alcohol, the oxidation of toluene, and the hydrolysis of benzyl chloride<sup>[2]</sup>. Among them, benzyl alcohol oxidation is widely used because of its low cost. Commonly used oxidants or catalysts for the oxidation of benzyl alcohol include chromic acid, dichromate, permanganate, and precious metal catalysts<sup>[3-6]</sup>. However, these oxidation methods

have some disadvantages. For example, the waste generated from the used oxidant would pollute the environment and is prone to excessive oxidation. So, it is very important and necessary to find a green oxidant.



**Figure 1** Carbonyl-containing pharmaceutical intermediates

As a green and cheap oxidant,  $O_2$  can be used to replace traditional  $KMnO_4$  or tert-butyl hydroperoxide, which helps reduce reaction costs and reduce pollutant emissions<sup>[7]</sup>. To promote the oxidation of benzyl alcohol, a series of nanoparticle catalysts have been prepared, such as Au, Ru, Pd, and other nanoparticles<sup>[8]</sup>. Among them, Pd-based catalysts have a strong ability to activate oxygen and can generate aldehydes with high selectivity, so they are widely used<sup>[9-11]</sup>. The catalytic activity of precious metal nanoparticle catalysts is greatly affected by size and valence<sup>[12]</sup>. Therefore, to control the reaction selectivity and improve the catalytic ability of the catalyst, people try to dope the catalyst with other metals<sup>[13]</sup>. Au/Pd- $TiO_2$  catalysts can efficiently oxidize primary alcohols to produce aldehydes under solvent-free conditions, in which Au doping influences the structure and electrons of Pd nanoparticles<sup>[14]</sup>. While the precious metal catalyst is difficult to use on a large scale due to its high cost. Therefore, the development of an environmentally friendly and cheap benzyl alcohol oxidation method is of great significance for the industrial preparation of benzaldehyde and benzoic acid.

Since Fujishima et al.<sup>[15]</sup> discovered that  $TiO_2$  can photolyze water to hydrogen under UV irradiation, the field of photocatalysis has attracted much attention. Photocatalysis is a process of converting light energy into chemical energy. Under the excitation of photons, electrons transition from the valence band to the conduction

band and generate holes, thereby generating active free radicals-hydroxyl radicals to promote the oxidation of the substrate<sup>[16, 17]</sup>. At present, photocatalytic technology has been widely used in the fields of photolysis of water to produce hydrogen, alcohol oxidation, and oxidative degradation of organic waste<sup>[18-20]</sup>. Common photocatalysts include ZnO<sup>[21, 22]</sup>, SnO<sup>[23, 24]</sup>, CdS<sup>[25-27]</sup>, TiO<sub>2</sub><sup>[28-32]</sup>, etc. Among them, TiO<sub>2</sub> is favored because of its low price, stable properties, and non-toxicity. The bandgap energy of TiO<sub>2</sub> is 3.2 eV, which inhibits its absorption of visible light. In addition, the electrons, and holes of TiO<sub>2</sub> recombine quickly, which also leads to a lower quantum yield<sup>[33]</sup>. The Carbon dot/TiO<sub>2</sub> catalyst<sup>[34]</sup> overcomes the problem of the short excited state lifetime of carbon quantum dots and has a good catalytic effect under the irradiation of blue or green light. Lu Xu<sup>[35]</sup> modified carbon quantum dots on N-doped TiO<sub>2</sub> and prepared C-N-TiO<sub>2</sub>-x composite material, and found that this material has stronger visible light absorption capacity and higher charge separation efficiency than TiO<sub>2</sub> without N or carbon quantum dots. In addition, adding an appropriate amount of citric acid to remove holes can significantly increase the reduction rate of Cr (VI). More research on metal-modified TiO<sub>2</sub>, such as Pd/TiO<sub>2</sub><sup>[36, 37]</sup>, Au/TiO<sub>2</sub><sup>[38]</sup>, Pt/TiO<sub>2</sub><sup>[39, 40]</sup> showed their great significance photocatalytic oxidation of aromatic alcohols.

In this study, Ni@C was loaded on self-made TiO<sub>2</sub> by in-situ hydrothermal synthesis, which has a better photocatalytic effect on the oxidation of benzyl alcohol than the by commercial TiO<sub>2</sub> supported by Ni@C. In addition, aromatic alcohols with different substituents are used as reaction substrates, and good conversion rate and selectivity are also obtained, which shows that the catalyst has a wide range of applicability. What is interesting is that the catalytic effect of the catalyst is significantly different in different solvents. By controlling the reaction solvent, the production of aldehydes or acids can be regulated. This is conducive to the application of the catalyst in actual production.

## **2. Experimental section**

### *2.1 Catalyst preparation*

Ni@C was prepared according to the method of Liu<sup>[41]</sup>. Weigh 0.03 mol of Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and citric acid and dissolve them in 20 ml of absolute ethanol. The mixture was stirred at 70 °C for 8 h and dried at 100 °C for 48 h after stirring. The dried green solid was ground into a powder and calcined in an N<sub>2</sub> atmosphere for 3 h, the calcining temperature was 700 °C. The black solid obtained after calcination was

washed with 1M H<sub>2</sub>SO<sub>4</sub> until it was colorless, and then washed with deionized water until the pH of the waste liquid was 7, and then the solid was freeze-dried at -48 °C for 12 h to obtain Ni@C.

Place 10ml of tetrabutyl titanate and 10ml of ethanol in the lining of a 100ml polytetrafluoro reactor, stir for 5 minutes, add 150 mg of Ni@C and 3 ml of deionized water, and magnetically stir at room temperature for 3 hours. After that, the autoclave reactor (Anhui Kemi Machinery Technology Co., Ltd, Anhui, China) was heated at 150°C for 12 hours. When it was cooled to room temperature washed and filtered. Then put the filtered solid into an oven at 100°C, and evaporate and dry to obtain the Ni@C/TiO<sub>2</sub>-Z.

Weigh 120 mg of commercially available TiO<sub>2</sub> and 120 mg of Ni@C into 80 ml of ultrapure water, stir at room temperature for 24 h under shading. After centrifugation and washing with ultrapure water, the obtained solid is freeze-dried to obtain Ni@C-TiO<sub>2</sub>. The commercially available TiO<sub>2</sub> used is all anatase TiO<sub>2</sub> from Macklin, and the prepared catalyst is named according to the particle size of the TiO<sub>2</sub>. They are Ni@C/TiO<sub>2</sub>-5 nm, Ni@C/TiO<sub>2</sub>-5~10 nm, Ni@C/TiO<sub>2</sub>-10~25 nm, Ni@C/TiO<sub>2</sub>-40 nm, Ni@C/TiO<sub>2</sub>-100 nm, Ni@C/TiO<sub>2</sub>-150 nm.

## 2.2 Product quantification

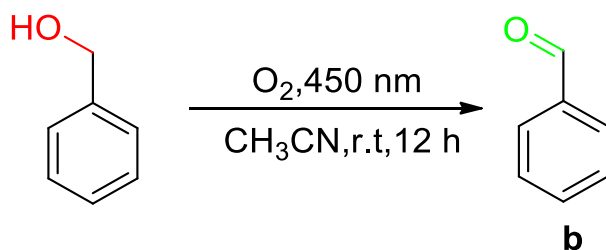
The composition of reaction filtrate was performed on the GC-2014C (Shimadzu, Japan) with the SH-Stabilwax-DA capillary column (30 m × 0.25 mm × 0.25 μm) and FID detector.

# 3. Results and discussion

## 3.1 Screening catalyst

To test the photocatalytic oxidation of benzyl alcohol, various Ni@C/TiO<sub>2</sub> have been used in the oxidation of benzyl alcohol, and results are shown in **Table 1**. It can be seen that the Ni@C/TiO<sub>2</sub> shows the good performance in producing benzaldehyde with a selectivity up to 100%. The conversion over the commercially available TiO<sub>2</sub> supported Ni@C gradually decreases with the increase of the TiO<sub>2</sub> particle size. Because the smaller the catalyst particle size, the larger the specific surface area, which promotes the contact between the substrate and oxygen and the catalyst. The radiation under 450 nm and 520 nm wavelengths were used in the reaction. The shorter the wavelength taken, the greater the energy input. Therefore, the conversion rate of the same catalyst under the radiation of 450 nm wavelength is higher than that

of 520 nm (**Table 1**, entry 2-13). It is interesting that under the same conditions, self-made TiO<sub>2</sub> supported Ni@C catalyst is better than Ni@C/TiO<sub>2</sub>-5 nm, which is the commercially available TiO<sub>2</sub> supported Ni@C. **Table 1** Different catalysts catalyzed the oxidation of benzyl alcohol to benzaldehyde

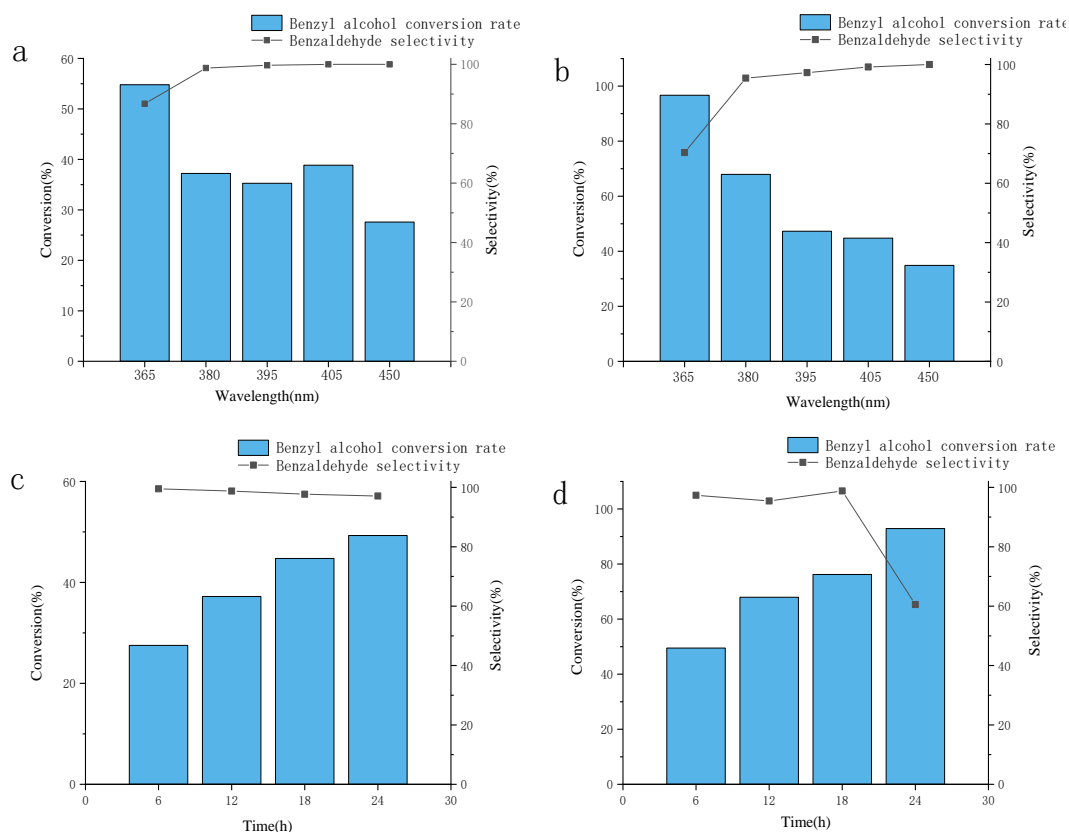


Entry	Catalyst	$\lambda$	Solvent	Con. (%)	Sel. <sup>b</sup> (%)
1	Ni@C/TiO <sub>2</sub> -Z	450	CH <sub>3</sub> CN	34.86	100.00
2	Ni@C/TiO <sub>2</sub> -5 nm	450	CH <sub>3</sub> CN	27.59	100.00
3	Ni@C/TiO <sub>2</sub> -5 nm	520	CH <sub>3</sub> CN	1.94	100.00
4	Ni@C/TiO <sub>2</sub> -5~10 nm	450	CH <sub>3</sub> CN	18.60	100.00
5	Ni@C/TiO <sub>2</sub> -5~10 nm	520	CH <sub>3</sub> CN	5.48	100.00
6	Ni@C/TiO <sub>2</sub> -10~25 nm	450	CH <sub>3</sub> CN	8.39	100.00
7	Ni@C/TiO <sub>2</sub> -10~25 nm	520	CH <sub>3</sub> CN	1.90	100.00
8	Ni@C/TiO <sub>2</sub> -40 nm	450	CH <sub>3</sub> CN	7.50	100.00
9	Ni@C/TiO <sub>2</sub> -40 nm	520	CH <sub>3</sub> CN	0.65	100.00
10	Ni@C/TiO <sub>2</sub> -100 nm	450	CH <sub>3</sub> CN	14.90	100.00
11	Ni@C/TiO <sub>2</sub> -100 nm	520	CH <sub>3</sub> CN	1.56	100.00
12	Ni@C/TiO <sub>2</sub> -150 nm	450	CH <sub>3</sub> CN	0.48	100.00
13	Ni@C/TiO <sub>2</sub> -150 nm	520	CH <sub>3</sub> CN	0.26	100.00

<sup>a</sup> Reaction conditions: 0.2 mmol benzyl alcohol, 20 mg catalyst, r.t. <sup>b</sup>the conversion and selectivity are determined by GC analysis.

### 3.2 Optimization of reaction conditions

Based on the above results, Ni@C/TiO<sub>2</sub>-5 nm and Ni@C/TiO<sub>2</sub>-Z were taken to catalyze benzyl alcohol oxidization at different wavelengths and in different reaction time. The results are shown in **Figure 1**. As the wavelength decreasing, the conversion of benzyl alcohol gradually increases, but when the wavelength is reduced to 365 nm, the selectivity of benzaldehyde is significantly reduced. The greater the energy from the radiation of the shorter wavelength leads to further oxidation of benzaldehyde to benzoic acid.



**Figure 2** Optimization of conditions for oxidation of benzyl alcohol (a: Ni@C/TiO<sub>2</sub>-5 nm at different wavelengths; b: Ni@C/TiO<sub>2</sub>-Z at different wavelengths; c: Ni@C/TiO<sub>2</sub>-5 nm at different reaction times; d: Ni@C/ TiO<sub>2</sub>-Z at different reaction times)

Considering that benzaldehyde oxidized to benzoic acid at 365 nm wavelength, the subsequent choice of 380 nm wavelength is to investigate the effect of reaction time on product yield and selectivity. The conversion of benzyl alcohol increased with the increase of the reaction time. When the Ni@C/TiO<sub>2</sub>-Z was used, the conversion rate of benzyl alcohol was 49.48% after 6 h, and the conversion rate of benzyl alcohol increased to 92.88% after 24 h of reaction (**Figure 2 c and d**). In general, the activity of Ni@C/TiO<sub>2</sub>-Z is better than that of Ni@C/TiO<sub>2</sub>-5 nm under the same reaction

conditions. To obtain a high conversion of benzyl alcohol while preventing excessive oxidation of benzaldehyde, Ni@C/TiO<sub>2</sub>-Z is selected as the catalyst, and a reaction at a wavelength of 380 nm for 18 h is a suitable condition.

### 3.3 Solvent screening and catalyst recycling performance

**Table 2** Photocatalytic oxidation of benzyl alcohol in different solvents

Entry	Catalyst	Solvent	Polarity	Con. (%)	Sel. <sup>b</sup> (%)	Sel. <sup>c</sup> (%)
1	Ni@C/TiO <sub>2</sub> -Z	EtOH	4.30	4.40	83.63	16.37
2	Ni@C/TiO <sub>2</sub> -Z	Dioxane	4.80	21.67	79.01	20.99
3	Ni@C/TiO <sub>2</sub> -Z	H <sub>2</sub> O	10.20	30.13	75.64	24.36
4	Ni@C/TiO <sub>2</sub> -Z	CH <sub>3</sub> CN	6.20	76.22	98.79	1.21
5	Ni@C/TiO <sub>2</sub> -Z	CH <sub>2</sub> Cl <sub>2</sub>	3.40	87.88	0.82	99.18
6	Ni@C/TiO <sub>2</sub> -Z	Acetone	5.40	94.67	5.42	94.58
7	Ni@C/TiO <sub>2</sub> -Z	Ethyl Acetate	4.30	98.84	2.24	97.76
8	Ni@C/TiO <sub>2</sub> -Z	DCE	3.50	100.00	1.59	98.41

<sup>a</sup> Reaction conditions: 0.2 mmol benzyl alcohol, 20 mg catalyst, r.t. <sup>b,c</sup> The conversion and selectivity are determined by GC analysis.

Different solvents were then tested in photocatalytic oxidation of benzyl alcohol. When ethanol, 1,4-dioxane and water are used as the reaction solvent, the conversion rate of benzyl alcohol is low. When acetonitrile is selected as the reaction solvent, the conversion of benzyl alcohol is higher, and the selectivity of benzaldehyde reaches 98.79%. When dichloromethane, acetone, ethyl acetate and 1,2-dichloroethane are selected as the reaction solvent, a higher conversion rate of benzyl alcohol is also obtained, but the product is mainly benzoic acid. Ethanol and ethyl acetate have the

same polarity, but the conversion rate of benzyl alcohol and product selectivity are quite different. It seems that the polarity of the solvent has little effect on the reaction, and the solvent's ability to dissolve oxygen is the main factor affecting the reaction effect. From the perspective of environmental protection, acetonitrile and ethyl acetate are selected as the reaction solvent from the above solvents to generate benzaldehyde and benzoic acid, respectively.

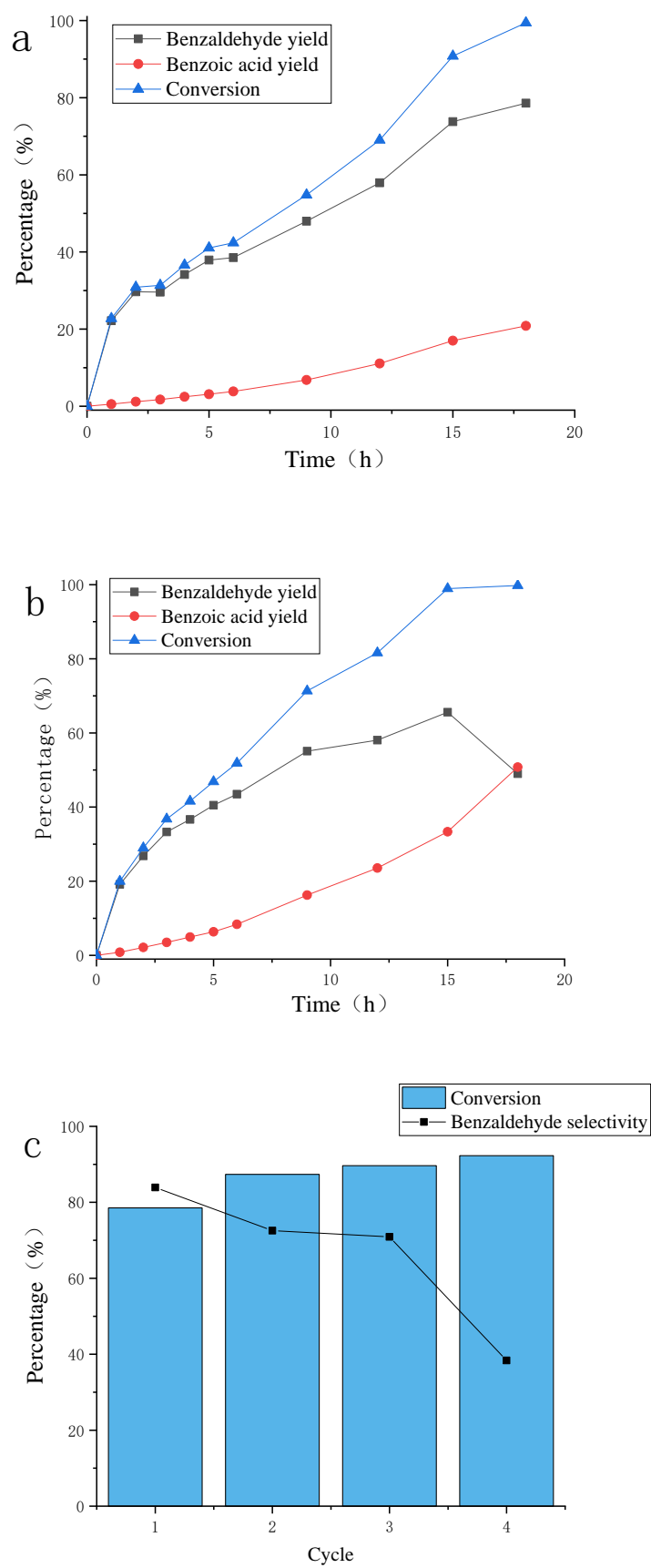
**Table 3** The effect of different volume ratios of acetonitrile and ethyl acetate on product selectivity<sup>a</sup>

Entry	CH <sub>3</sub> CN: Ethyl Acetate	Con. (%)	Sel. <sup>b</sup> (%)	Sel. <sup>c</sup> (%)
1	1:0	76.22	98.79	1.21
2	10:1	75.39	83.18	16.82
3	1:1	75.86	75.10	24.90
4	1:10	80.98	56.22	43.78
5	0:1	98.84	2.24	97.76

<sup>a</sup> Reaction conditions: 0.2 mmol benzyl alcohol, 20 mg catalyst, r.t. <sup>b,c</sup> The conversion and selectivity are determined by GC analysis.

To further study the influence of the solvent on the product selectivity, acetonitrile and ethyl acetate with different volume ratios were selected as the reaction solvents under the premise of keeping the volume of the reaction solvent unchanged (**Table 3**). The results showed that as the volume of ethyl acetate increased, the conversion of the continued to increase, the selectivity of benzaldehyde decreased and the selectivity of benzoic acid increased, which indicated that the presence of ethyl acetate could make the reaction system more oxidative.





**Figure 3.** Product yield at different stages of the reaction and reusability of

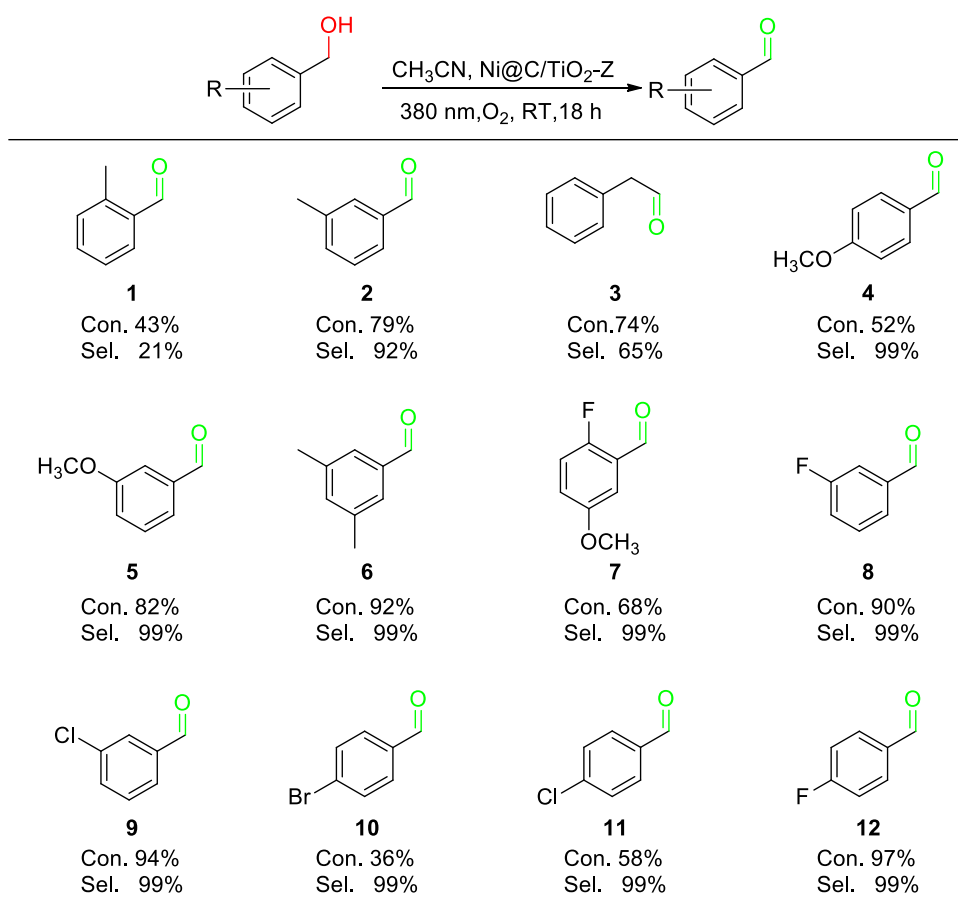
Ni@C/TiO<sub>2</sub>-Z. a: Product yield at different stages of the reaction in CH<sub>3</sub>CN -D<sub>3</sub>; b: Product yield at different stages of the reaction in Acetone-D<sub>8</sub>; c: Reusability of Ni@C/TiO<sub>2</sub>-Z

Monitoring the changes of products and substrates at each stage of the reaction process is of great significance to the study of the reaction mechanism. Therefore, deuterated reagents are used to replace conventional reagents, samples are continuously taken out, and tested by NMR to study the changes of various substances. Choose CH<sub>3</sub>CN -D<sub>3</sub> and acetone-D<sub>8</sub> as reaction solvents (Due to the high price of ethyl acetate-D<sub>8</sub>, Acetone-D<sub>8</sub> which has the same effect as it is chosen). Studies have shown that benzoic acid is formed at the beginning of the reaction. In the two solvents, benzaldehyde is mainly generated in the early stage of the reaction. When the benzyl alcohol is exhausted, the benzaldehyde in acetone-D<sub>8</sub> continues to be oxidized to generate benzoic acid (**Figure 3** a and b) .

The stability and recycling capacity of the catalyst is a key index to evaluate the performance of the catalyst. So, Ni@C/TiO<sub>2</sub>-Z recycling experiment was carried out. After reacting in acetonitrile solvent at 380 nm wavelength for 18 h, the conversion of benzyl alcohol did not decrease after 4 cycles (**Figure 3** c).

#### 3.4 Substrate expansion

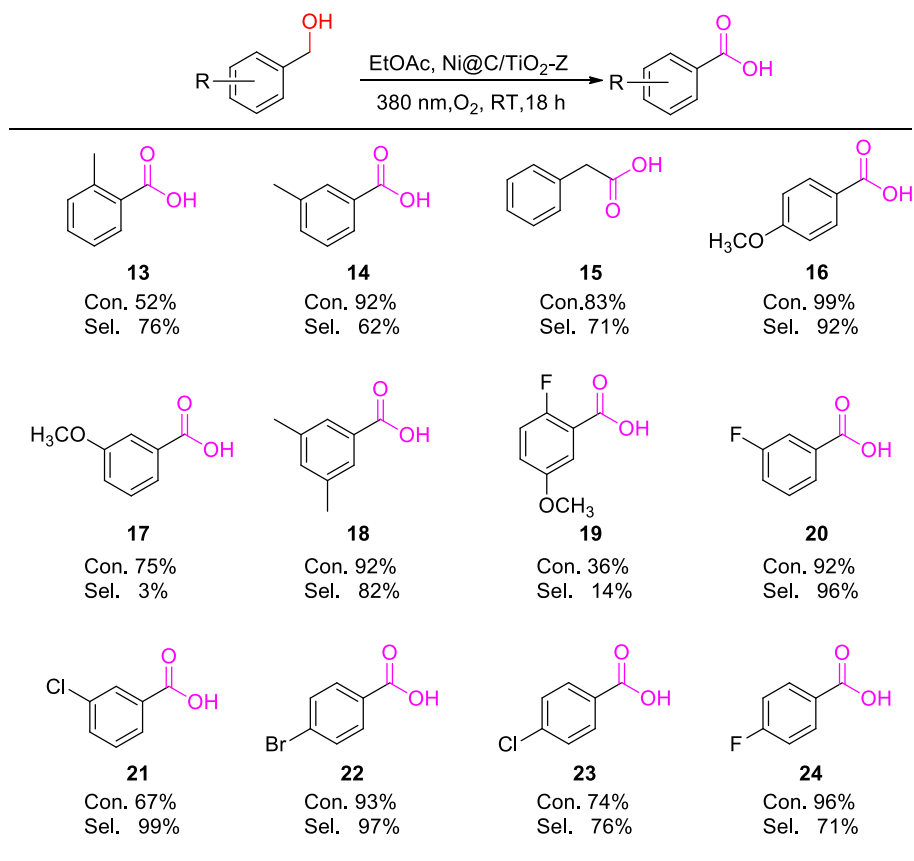
**Table 4** The substrate scope of alcohols in CH<sub>3</sub>CN



Reaction conditions: 0.2 mmol benzyl alcohol, 20 mg catalyst, r.t. The conversion and selectivity are determined by GC analysis.

Acetonitrile and ethyl acetate were selected as the reaction solvents, and Ni@C/TiO<sub>2</sub>-Z was used to catalyze aromatic alcohols with different substituents (**Table 4** and **5**). The results show that Ni@C/TiO<sub>2</sub>-Z also has a general catalytic effect on other substrates, and acetonitrile solvent still tends to generate aldehydes, while ethyl acetate solvent tends to generate acids.

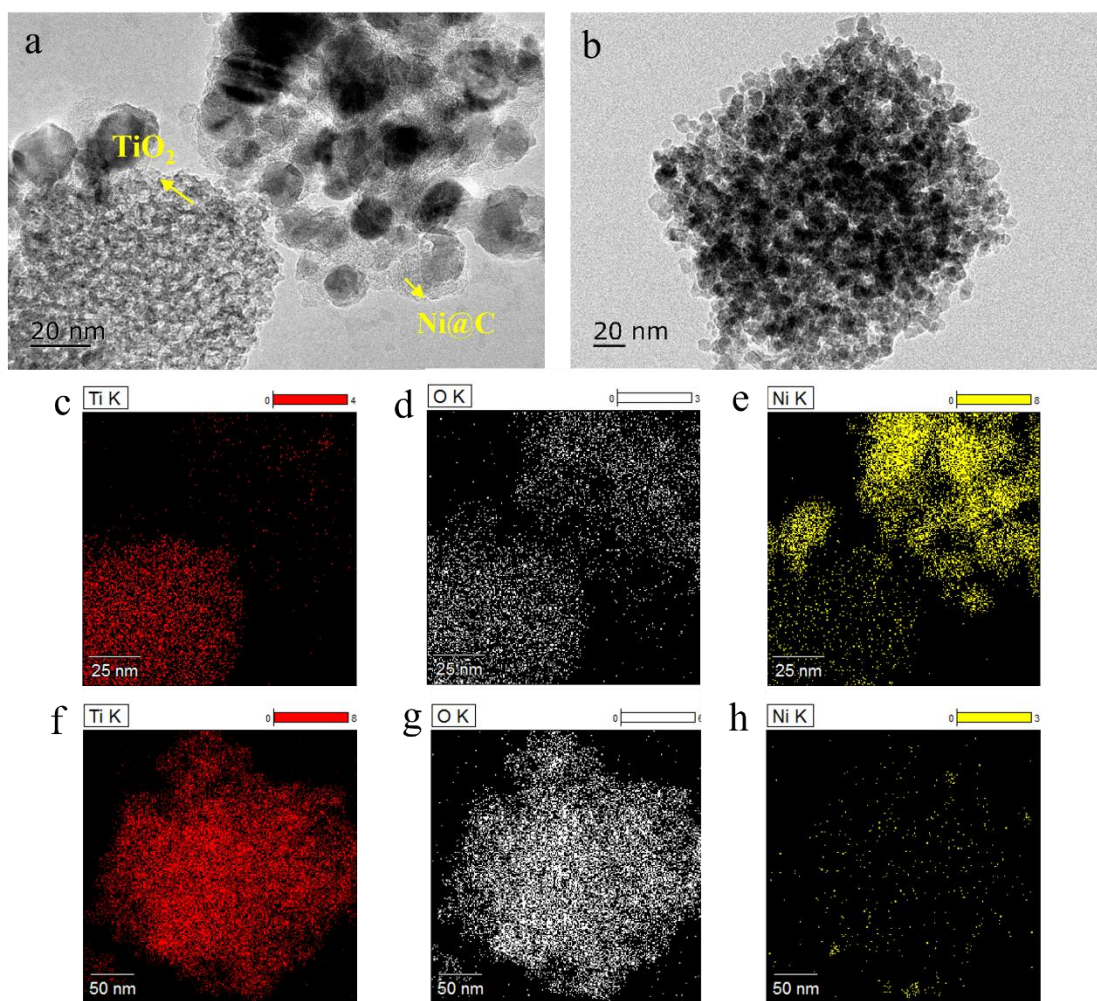
**Table 5** The substrate scope of alcohols in ethyl acetate



Reaction conditions: 0.2 mmol benzyl alcohol, 20 mg catalyst, r.t. The conversion and selectivity are determined by GC analysis.

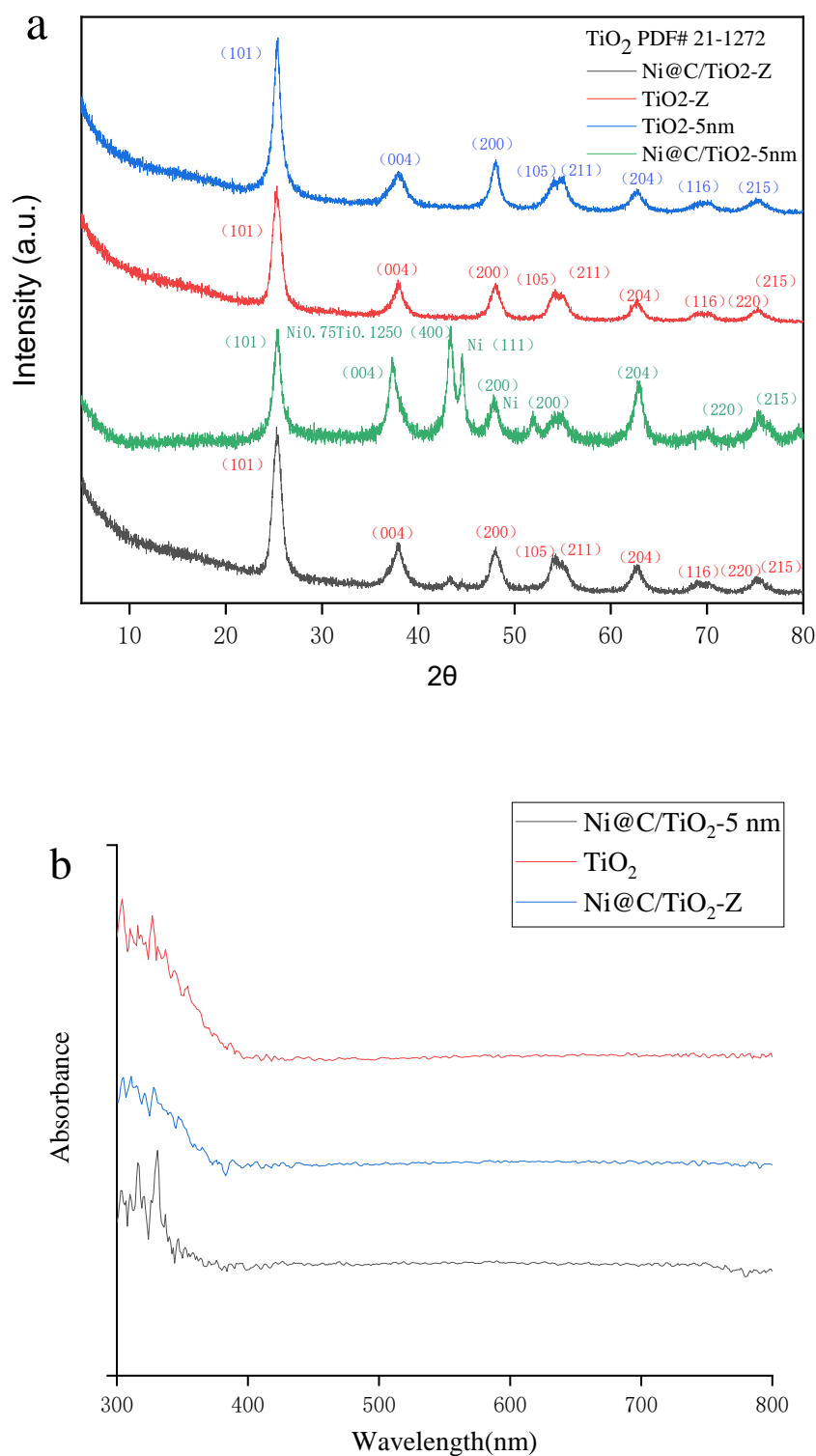
The presence of electron withdrawing groups is beneficial to the oxidation of the substrate, and this promoting ability is consistent with the electron withdrawing ability (F->Cl->Br->MeO-). And the electron withdrawing effect in the para position is stronger than that in the meta position. While the existence of the electron-donating group at the ortho position inhibits the oxidation reaction of the substrate, which has almost no effect at the meta position. When there is a methyl group at the meta position, the oxidation reaction of the substrate is not inhibited. This shows that the steric hindrance effect is stronger than Me- (**Table 4**, 2 and 6) .

### 3.5 Catalyst's physicochemical properties



**Figure 4.** TEM image and MAP energy spectrum. a: TEM image of Ni@C/TiO<sub>2</sub>-5 nm; b: TEM image of Ni@C/TiO<sub>2</sub>-Z; c: MAP image of Ni@C/TiO<sub>2</sub>-5 nm Ti; d: MAP image of Ni@C/TiO<sub>2</sub>-5 nm O; e: MAP image of Ni@C/TiO<sub>2</sub>-5 nm Ni; f: MAP image of Ni@C/TiO<sub>2</sub>-Z Ti; g: MAP image of Ni@C/TiO<sub>2</sub>-Z O; h: MAP image of Ni@C/TiO<sub>2</sub>-Z Ni.

To differentiate the catalytic activities, microstructures of the Ni@C/TiO<sub>2</sub>-5 nm and Ni@C/TiO<sub>2</sub>-Z were studied by TEM. It can be seen from **Figure 4** that TiO<sub>2</sub> and Ni@C in Ni@C/TiO<sub>2</sub>-5 nm is not uniformly mixed, while TiO<sub>2</sub> and Ni@C in Ni@C/TiO<sub>2</sub>-Z prepared in situ are uniformly mixed. The distribution of Ti and Ni elements in MAP also provides evidence for the above conclusions.



**Figure 5.** XRD and UV-Vis absorption spectra of the catalyst. a: XRD of catalyst; b: UV-Vis absorption spectra of the catalyst.

**Figure 5** (a) is the XRD diffraction patterns of  $\text{TiO}_2\text{-5 nm}$ ,  $\text{TiO}_2\text{-Z}$ ,  $\text{Ni@C/TiO}_2\text{-5 nm}$ , and  $\text{Ni@C/TiO}_2\text{-Z}$ . The lattice types of  $\text{TiO}_2$  in these catalysts are the same. The

difference is that there are two larger Ni (1 1 1) peaks at 43.3 ° and 44.5 ° in Ni@C/TiO<sub>2</sub>-5 nm, while Ni@C/TiO<sub>2</sub>-Z has only two small peaks here. It may be due to uneven dispersion of Ni@C in Ni@C/TiO<sub>2</sub>-5 nm. In addition, the UV-Vis spectra of TiO<sub>2</sub>-Z, Ni@C/TiO<sub>2</sub>-5 nm and Ni@C/TiO<sub>2</sub>-Z were measured. From **Figure 5(b)** their absorption peak of the UV-Vis absorption spectrum were around 380 nm. Therefore, according to the Kubelka-Munk formula, there is no significant difference in the forbidden band width among them.

## 4. Conclusion

Herein, Ni@C/TiO<sub>2</sub>-Z catalyst was prepared by in-situ hydrothermal synthesis, which has better catalytic effect than the commercially available TiO<sub>2</sub> supported by Ni@C. And Ni@C more evenly dispersed. Ni@C/TiO<sub>2</sub>-Z can catalyze the oxidation of a variety of aromatic alcohols to produce aldehydes or acids, and the catalytic activity did not decrease after 4 cycles of experiments. Choosing different solvents could adjust the products, such as aromatic aldehydes or aromatic acids. This provides a theoretical basis for the industrial utilization of photocatalytic alcohol oxidation to produce aldehydes or acids in the future.

### Declaration of Competing Interest

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 work.

### Author Contributions

J.G. L. and Q. Z. conceived and designed the experiments. Z.L.S. performed the experiments, analyzed the data and prepared the Supplementary Information. Z.L.S. wrote the original manuscript. J.G.L and Q. Z. corrected the paper. All authors discussed the results and commented on the manuscript.

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