Selective photocatalytic hydrogenation of citral over pure TiO$_2$ nanoparticle

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Abstract

The $\alpha$, $\beta$-unsaturated aldehydes selective hydrogenation, especially the C=O bond, is an extremely challenging topic in the field of catalysis. In this paper, a series of pure TiO$_2$ photocatalysts obtained at various calcination temperature were tested for the hydrogenation of citral. It has been determined that inexpensive TiO$_2$ nanoparticles, calcined at 450 °C–500 °C for two hours, show hydrogenation selectivity of 100% from citral toward unsaturated alcohols (UA) with the highest conversion up to 99% under ultraviolet light. The present work reports a simple yet pragmatic approach for the efficient and selective hydrogenation of the C=O bond of citral.

1. Introduction

The $\alpha$, $\beta$-unsaturated aldehydes selective hydrogenation is one of the most fundamental processes in the chemical industry [1–3]. Among them, hydrogenation of citral, is a research focus in the field of catalysis, due to the importance of its corresponding UA for the preparation of various fine chemical products including pharmaceuticals, functional polymers, and perfumes [4–7]. From the perspectives of thermodynamics and kinetics, the conjugated C=C bond undergoes more favorable hydrogenation than the C=O bond [8], causing the C=O hydrogenation in citral (geranial and neral) (CI) toward UA to be very difficult. In recent years, many conventional catalyst materials showing highly the conjugated C=O bond hydrogenation in citral have been comprised of noble metals (Ir [9], Pt [10], Au [11], Ru [12], Rh [13], Pd [14]) thus greatly hampering reaction cost control. Meanwhile, the selective hydrogenation reaction is usually carried out under elevated temperature and pressure and a hydrogen atmosphere, leading to extremely rigorous equipment requirements with high experimental risks.

Citral and its hydrogenation products, as an important raw material of fragrance and fragrance fine chemical industry, have been studied extensively in recent decades and can achieve 99% conversion and selectivity. However, the high cost of reducing agent and the separation difficult of product, reducing agent and solvent limited the wide application of citral and its hydrogenation products [15–17]. The use of photocatalysis for citral selective hydrogenation has the advantages of low cost and green environmental protection, which is more conform to the current ‘green chemistry’ concept. However, the conversion and selectivity of the photocatalytic hydrogenation of citral are rarely reported.

Pioneered by Fujishima and Honda [18], TiO$_2$ has always been regarded as a promising photocatalyst and supporting semiconductor in both industrial and environmental research because of its high availability, nontoxicity, low cost, and chemical stability [19–24]. Various TiO$_2$-supported monometallic or bimetallic photocatalysts [25–30] have emerged in the study of hydrogenation of citral under ultraviolet light irradiation, and their photo-conversion efficiency and selectivity have received great promotion. However, the design and synthesis of these target catalysts present difficulties, as do their detailed structural characterization. To solve this problem, we prepared a series of pure TiO$_2$ nanoparticles at different calcination temperatures from 200 °C to 800 °C in a facile fashion [31–34]. The morphology and physical property of the catalysts were investigated,
followed by their photocatalytic hydrogenation of citral. It was found that TiO₂ nanoparticles prepared at 450 °C and 500 °C displayed hydrogenation selectivities of 100% from citral to UA with an ideal conversion up to 99% under ultraviolet light. Meanwhile, their excellent photocatalytic properties of stability and repeatability were confirmed under cyclic experiments. All of these results permit a simple yet pragmatic approach for the efficient and selective hydrogenation of the C=O bond of citral.

2. Experimental

2.1. General

The schematic of citral catalytic hydrogenation is shown in figure 1. All chemicals reagents used in this experiment come form commercial chemical reagents. The spectra of the TiO₂ photocatalysts were tested by the Bruker D8 X-ray diffraction (XRD) (Basel, Switzerland). The morphology of samples were characterized by the Quanta 200F FEI scanning electron microscope (SEM, Los Angeles, USA) and JEM-2100 transmission electron microscope (TEM, Okinawa, Japan). The UV–vis diffuse reflectance spectra (UV–vis DRS) of catalysts was conducted by Cary 60 UV–vis spectrophotometer (London, Europe). The specific surface area and average pore size of the sample were characterized by the Micromeritics ASAP2460 automatic surface area and porosity analyzer (BET, Atlanta, USA). The GC-2014C gas chromatography (GC, Shimadzu, Japan) was used for the analysis of the reaction products.

2.2. TiO₂ photocatalyst

The TiO₂ photocatalyst was prepared using a typical sol-gel method: Firstly, a mixed solution of the 10 ml tetra-n-butyl titanate and 40 ml anhydrous ethyl ether was prepared, and then 12 ml acetic acid was dissolved in the mixed solution to obtained the precursor solution after 30 min stirring. When 15 ml of acetic acid and deionized water with a 2:1 volume ratio was dropwise added into the precursor solution under electromagnetic stirring, the precursor solution gradually thickens and a white precipitate was observed. After standing for 24 h, the precipitates were extracted and dried at 100 °C for 24 h, thus were washed by deionized water and anhydrous ethanol to remove the residual chemicals reagents. Finally, the precipitates were calcined at 200 °C to 800 °C for 2 h. And the precipitate calcined at 500 °C for 1 h was perpaered for comparative study.
2.3. Photocatalytic hydrogenation of citral
The 40 ml anhydrous acetonitrile, 5 ml triethanolamine, 75 μl citral, and 0.2 g photocatalyst were prepared for photocatalytic reactions in a 200 ml self-made quartz reactor. Then the photoreactor was vacuumed and nitrogen was pumped in. The process of suction-ventilation was repeated three times to ensure nitrogen protection in the reactor. A 300 W Xe lamp light source with a 420 nm cut-off filter was carried out for the photocatalytic reaction, and the reaction temperature was hold on at 20 °C by the circulating water bath.

3. Results and discussion
3.1. Photocatalyst
3.1.1. XRD
Figure 2 presents the XRD spectra of the TiO2 photocatalysts obtained at various temperature. As shown, two different crystalline structures of the TiO2 photocatalysts were observed under the different calcination temperature. From 200 °C to 700 °C, broad diffraction peaks of anatase-phase TiO2 with low intensity gradually became sharper, which mainly derived from the lower average surface energy of the anatase TiO2 (101) plane than that of other crystal planes. Meanwhile, when the calcination temperature is above 600 °C, the rutile phase peaks were observed, as showed in figure 2. The intensity of the rutile phase peaks were increased with the increasing of the calcination temperature. When the temperature increased to 800 °C, the phase of the TiO2 fully changed into a rutile type as observed by the diffraction peak values. The similar results had also been reported by Chen et al [35], they claimed that anatase to rutile transition temperature of TiO2 is above 600 °C, and residual anatase phase still exists up to 700 °C. Therefore, when the calcination temperature reached to 800°C in this work, a complete transformation for rutile phase was observed, as shown in figure 2.

3.1.2. SEM and TEM
The micromorphologies of the TiO2 photocatalysts were examined by the SEM and TEM, and the results were showed in figures 3 and 4. As shown in figures 3(a)–(e), the TiO2 nanoparticles calcined at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C for two hours, respectively, all turned out to be roughly crystalline ovals, accompanied by a relatively smooth surface, which indicated that these TiO2 nanoparticles possessed satisfactory crystallinity. Meanwhile, these nanoparticles have partial stacking and large surface area, which can afford more reaction sites and promote the photocatalytic reactions. Moreover, the calcination time also affected the shape size and distribution of nanoparticles. As shown in figure 3(f), the TiO2 nanoparticles calcined at 500 °C for 1 h showed that the particles aggregated into blocks with an uneven size distribution, suggesting poor crystallinity compared with that of nanoparticles calcined at 500 °C for 2 h (figure 3(c)). The TEM diagram of TiO2 photocatalysts...
prepared at 500 °C for 2 h (in figure 4) showed that the sizes of the TiO2 nanoparticles were detected to be around 20–30 nm, which showed clear lattice spacing of 0.356 nm indicative of anatase (101) type TiO2.

3.1.3. UV–vis absorption analysis
The UV–vis DRS was used to investigate the properties of the TiO2 photocatalyst, roughly counteracting the absorbance of the catalyst in the range 200 nm–800 nm. In figure 5, the UV–vis DRS of TiO2 photocatalysts calcined at 300 °C, 400 °C, and 500 °C for 2 h turned out to be quite similar with their absorption peaks located in the region of 200–400 nm. The UV–vis DRS of TiO2 photocatalysts calcined at 600 °C for 2 h were observed to be similar to that of TiO2 photocatalysts calcined at 500 °C for 1 h, showing additional weak absorption in the region of 400 nm-800 nm. In contrast, the UV–vis DRS of TiO2 photocatalysts calcined at 700 °C for 2 h showed weak absorption in the ultraviolet region and obvious red-shift absorption in the visible region. Those spectral observations strongly indicate the suitable light source regions for photocatalytic reactions with these TiO2 photocatalysts obtained at various temperature.

3.2. Photocatalytic hydrogenation of citral
To study the properties of TiO2 photocatalyst obtained at different calcination temperatures, the photocatalytic hydrogenation of citral was performed under UV–vis light (λ: 200 nm to 400 nm), and the results were showed in table 1. Both conjugated C=C bond and C=O bond hydrogenation can be manipulated by only changing TiO2 photocatalysts, in spite of the hydrogenation conversion, as shown in table 1.
It can be seen from Table 1 that their catalytic performance increases first, and then decreases, with the increasing of the calcination temperature from 250 °C to 800 °C. Notably, the performance of catalytic TiO₂ prepared at 450 °C and 500 °C turned out to be optimal with hydrogenation conversion of the C=O bond in citral up to 99%. Moreover, the hydrogenation selectivity and conversion of the C=O bond in citral possessed an obvious law of synchronous change with high conversion corresponding to high selectivity, and both the conversion and C=O double bond selectivity increased first and then reduced with the increasing of the calcination temperature.

Table 2 shows the specific surface area and average pore size of TiO₂ at different calcination temperatures. It can be seen from Table 1 that their catalytic performance increases first, and then decreases, with the increasing of the calcination temperature from 250 °C to 800 °C. Notably, the performance of catalytic TiO₂ prepared at 450 °C and 500 °C turned out to be optimal with hydrogenation conversion of the C=O bond in citral up to 99%. Moreover, the hydrogenation selectivity and conversion of the C=O bond in citral possessed an obvious law of synchronous change with high conversion corresponding to high selectivity, and both the conversion and C=O double bond selectivity increased first and then reduced with the increasing of the calcination temperature.

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for the effective separation and transportation of reactants and products. Therefore, a higher BET surface area and lower average pore diameters for TiO$_2$ photocatalyst prepared at 500 °C in this work, is probably mainly reasons for the highest activity and selectivity of TiO$_2$ photocatalyst.

It is worth mentioning that the hydrogenation product of geraniol and nerol will also proportionally exist in the reaction, corresponding to that of the trans and cis structures in the substrate citral. That is, the ratio of geraniol and nerol was detected to be about 2:1, which is consistent with the ratio of geranial and neral in the substrate citral, although their hydrogenation conversion efficiency is greatly different. The hydrogenation conversion of citral to UA is shown in figure 6. With the increasing of irradiation time, the conversion of the C=O bond was significantly enhanced and finally reached 99% after 24 h.

Previous studies showed that most of selective hydrogenation of citral is carried out under the high temperature and high pressure with H$_2$ involved [37, 38]. The work of Steffan et al [39] showed that when T, P$_{H_2}$, and the solvent are 303 K, 0.5 MPa, and n-hexane, the conversion of citral catalyst is about 73% under the action of Pd/Al$_2$O$_3$ catalyst. The Ag-In/SiO$_2$ was prepared by equal-volume impregnation method has a conversion rate of 93% for citral and a preferential hydrogenation selectivity of 76% for C=O double bond under the reaction condition (T = 453 K, $P_{H_2}$ = 5 MPa, the solvent was n-hexane). However, the inexpensive TiO$_2$ nanoparticles, calcined at 450°C–500°C for two hours in this work, show hydrogenation selectivity of 100% from citral toward unsaturated alcohols with the highest conversion up to 99% under ultraviolet light.

The recycling and utilization of optimal TiO$_2$ photocatalysts for the photocatalytic hydrogenation of citral were then evaluated. As shown in figure 7, the conversion efficiency was maintained around 76% after three cycles of standardized experiments with only a weaken declines in selectivity from the initial 100% to 93%. The results indicate that TiO$_2$ nanoparticles calcined at 500°C for 2 h are high stability photocatalysts for the photocatalytic selective hydrogenation of citral to UA.
Figure 8 presents the schematic diagram of photocatalytic hydrogenation of citral to UA over TiO$_2$ photocatalyst. As shown in figure 8, when the energy absorbed by TiO$_2$ photocatalyst from ultraviolet light is greater than or equal to the band gap of TiO$_2$, the electrons ($e^-$) are excited to jump from the valence band to the conduction band, and the holes ($h^+$) are formed in the valence band to produce photogenerated electron hole pairs. Then, the photogenerated electrons in the conduction band and the photogenerated holes in the valence band further diffuse to the surface of the TiO$_2$ photocatalyst. The photogenerated electrons have strong electron loss ability and strong reducibility, leading to the citral adsorbed on the surface of the TiO$_2$ photocatalyst change to UA. Meanwhile, the sacrificial agent in the reaction liquid was oxidized by the photogenerated holes.

In summary, a series of pure TiO$_2$ photocatalysts obtained at various calcination temperatures were investigated for the citral hydrogenation. It was found that inexpensive TiO$_2$ nanoparticles, calcined at 450 °C and 500 °C for two hours, show a hydrogenation selectivity of 100% from citral to UA with the highest conversion rates up to 99% under ultraviolet light. Meanwhile, the nanoparticles excellent photocatalytic stability and repeatability were confirmed under cyclic experiments. All these results show a simple yet pragmatic approach for the efficient and selective hydrogenation of the C=O bond of citral.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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