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Short communication

Hydrogenolysis and hydrogenation of β-O-4 ketones by a simple photocatalytic hydrogen transfer reaction

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ABSTRACT

Efficient cleavage of C—O bonds in lignin and its models is of great importance for the production of value-added aromatic compounds. A simple TiO_2 photochemical approach was applied for β-O-4 ketone hydrogenolysis by an electron transfer photocatalytic reaction. The conversion of the substrate 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone was 89.8% in 30 min, with the yield of products 4-methoxy acetophenone of 75.2% and *o*-methoxyphenol of 98.9%. Compared to the selective hydrogenolysis role of TiO_2, Pd/TiO_2 catalyst prefers to simultaneously catalyzing the hydrogenative cleavage of C—O ether bond and the hydrogenation of C═O to CH—OH.

1. Introduction

Lignin, the most abundant, renewable aromatic biopolymers on earth, is comprised of non-identical phenolic units interconnected by a network of C—C and C—O bonds. It is regarded as a potential substitute for aromatic chemicals and platform compounds. Though acidolysis, enzymatic hydrolysis, hydrogenolysis, and hydrodeoxygenation technologies, C-O-C linkages in lignin can be selectively cleaved into phenolic monomers or cyclic compounds [1–8]. Among these technologies, hydrogenolysis allows direct access to valuable platform chemicals by the cleavage of C—C and C—O bonds in lignin. However, some hydrogenolysis processes require high pressure and temperature and excess amount of H_2 gas. Alternatively, the using of hydrogen-donor molecules such as formic acid and alcohols has been reported to generate *in-situ* hydrogen in the reductive depolymerization or hydrogenation of lignin and models [9–11].

Photocatalysis was recently emerged as a potential alternative to degrade organic compounds. It is commonly accepted that the generated electrons and holes are responsible when the photocatalyst is exposed to light enough for energy. In photocatalytic reduction process, alcohols are usually used as hole scavengers that undergo fast and irreversible oxidation, thus making photo-generated electrons more readily available for the reaction. Recent years, considerable attention has been paid to photocatalytic acceptorless alcohol dehydrogenation reactions, in which alcohols are dehydrogenated to form aldehydes/ketones or successive reaction products, with simultaneous liberation of H_2 molecule [12–15]. Based on the integration of acceptorless dehydrogenation of alcohol and *in situ* consumption of generated hydrogen equivalents [16,17], several groups have developed photocatalytic transfer hydrogenation systems for hydrogenative cyclization and reduction of NO without using molecular H_2 at moderate temperatures [18–20]. In the research of photocatalytic depolymerization of lignins, most studies are focused on oxidation of lignin and its models [21–25]. Very few works were devoted to the photo-induced reduction of lignin and models. In this study, attention is paid to the C—O cleavage in β-O-4 ketone of lignin model by a simple TiO_2 photocatalytic reaction. An attempt will be also made to demonstrate the hydrogen transfer system mediated by ethanol oxidation into ketone hydrogenolysis and hydrogenation.

2. Experimental

2.1. Chemicals and materials

Commercial Degussa TiO_2 titanium dioxide (P25), with 80% anatase and 20% of rutile, was used in the present work without any treatment. β-O-4 models were synthesized according to the previous procedures [26]. In a typical synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanone (named as **1**), 4-*O*-methyl- bromoacetophenone (10 mmol, 2.299 g) was added to a stirred solution of K_2CO_3 (15 mmol, 2.072 g) and guaiacol (12.5 mmol, 1.552 g) in acetone (100 mL). The mixture was stirred at 100 °C for 5 h, after which it was filtered off and

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concentrated under vacuum. The residue was purified by column chromatography with hexane: ethyl acetate (3:1).

2.2. Catalyst preparation

Metal doped TiO_2 (M/TiO_2, M = Pd, Ni, Co, Ag, Cu) was prepared by a wet-impregnation and photochemical-reduction method similar to the procedures described by Li et al. [27]. The metal loading in these catalysts was set as 10 wt%. In the typical preparation of Pd/TiO_2, 81 mg of TiO_2 was first dispersed into 20 mL water. A solution of $PdCl_2$ in 2 M HCl was added into the TiO_2 dispersion and stirred overnight. A certain amount of NaOH solution was added until the pH value was 13. Then, 10 mL of $NaBH_4$ (0.1 mol/L) was added dropwisely at a temperature below 15 °C. After 6 h, the obtained mixture was separated, washed with distilled water and dried at 60 °C for 12 h. The fresh catalyst was further reduced by a photochemical method under the irradiation of a commercial UV lamp (15W) for one week at room temperature.

2.3. Reaction procedures and analysis

0.02 mmol substrate **1** and 10 mg catalyst were added to 5 mL ethanol in a 10 mL quartz tube, and then purged with N_2 for 5 min before reaction. To initiate the reaction, the quartz tube was irradiated with a 250 W high pressure Hg lamp under N_2 atmosphere. Main wavelength of the lamp was around 365 nm, and the light intensity was 6 mW/cm^2, with the distance between lamp and quartz tube of 10 cm. The products were quantified using gas chromatography–mass spectrometry (GC–MS) on an Agilent 6890/5973N instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in diameter). The temperature was initially kept at 60 °C for 2 min, then was heated at a rate of 15 °C/min to 260 °C, and maintained for another 2 min. Conversion and yield were determined using decane as the internal standard.

3. Results and discussion

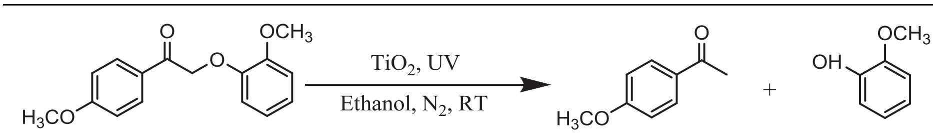
3.1. Hydrogenolysis of β-O-4 ketone

To evaluate the photocatalytic effect of TiO_2 for C—O cleavage of lignin, β-O-4 ketone **1** was selected as a model compound, and the results are shown in Table 1. Usually, the cleavage of lignin needs to be performed under a high temperature even in the presence of homogeneous or heterogeneous catalysts [28]. As expected, the transformation of **1** was fairly low by heating at 160 °C for 240 min without any catalysts (entry 1). UV photolysis dramatically accelerated the decomposition of the model, with a conversion sharply increased to 73.6% in a short time of 30 min, and a low yield of 4-methoxy acetophenone (**a**) and *o*-methoxyphenol (**b**) (entry 2), suggesting the efficient cleavage of C—O bond in β-O-4 ketone under UV light irradiation under N_2 atmosphere. When the same photo reaction was performed in the presence of TiO_2, a further increase of the conversion to 89.8% was observed. Moreover, the yield of **a** and **b** was significantly improved to 75.2% and 98.9% respectively (entry 3). This may be caused by the participation of the produced photo-generated electron and hydrogen from the solvent as the reductive species. In addition, when N_2 atmosphere was replaced by air atmosphere, the transformation of substrate **1** to corresponding products (**a** and **b**) declined substantially, with or without TiO_2 (entry 4 and 5), suggesting the importance of oxygen-free condition for the reaction. Thus, these results represented a simple and efficient method focused on photo-induced hydrogenolysis of C—O in β-O-4 ketone into aromatic fragments.

3.2. Mechanism investigation

Presumably the β-O-4 ketone hydrogenolysis occurs by photocatalytic hydrogen transfer mechanism, active hydrogen should be generated from an oxidative reaction. Then the simple photochemistry only contains solvent of ethanol, TiO_2 and UV radiation, so the active hydrogen may come from the radiated ethanol. Recently, many researchers were devoted to H_2 generation from neat or aqueous aliphatic alcohol by photocatalytic technology, during which the primary and secondary alcohols can be effectively dehydrogenated to aldehydes or ketones through radicals with the evolution of H_2 gas [18,29]. Based on this, it is guessed that alcohol dehydrogenation reaction may occur in our study. Electron paramagnetic resonance (EPR) technology was then used for *in situ* analysis of intermediate species during the reaction, using DMPO as a radical trapping agent. As shown from Fig. 1, 1-hydroxylethyl radical was formed as the main active species in the irradiated TiO_2-ethanol suspension. It is reported as a key radical intermediate in the oxidation of ethanol [30–32]. After adding substrate **1** in the suspension, there was a significant shift in some resonance signals. The change was consistent with another photocatalytic intermolecular hydrogen transfer reaction, suggesting the formation of new intermediates [20]. In addition, 1,1-diethoxyethane was found in the GC–MS spectrum during the photocatalytic hydrogenolysis of β-O-4 ketone (Fig. 2), further indicating the existence of alcohol dehydrogenation reaction in our system. Thus, it can be deduced that the active hydrogen liberated from ethanol dehydrogenation will participate in the photocatalytic reduction of substrate **1** by a photocatalytic hydrogen transfer process, with ethanol used as solvent and hydrogen donor at the same time. Usually, photocatalytic reaction does not efficiently proceed on

Table 1
Hydrogenolysis of β-O-4 ketone under different reaction conditions.[a]



1 a b

Entry	Method	Atmosphere	TiO_2	Conversion (%)	Yield of products (%)	
					a	b
1[b]	Heating	N_2	–	3	16.5	12.7
2	UV	N_2	–	73.6	40.4	35.7
3	UV	N_2	+	89.8	75.2	98.9
4	UV	Air	–	69.2	29.4	45.4
5	UV	Air	+	86.5	28.1	43.3

[a] Reaction conditions: Substrate 1 0.02 mmol, ethanol 5 mL, TiO_2 10 mg, UV 250 W, 30 min.
[b] 160 °C, 240 min.