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Photocatalytic transfer hydrogenolysis of aromatic ketones using alcohols

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A mild method of photocatalytic deoxygenation of aromatic ketones to alkyl arenes was developed, which utilized alcohols as the green hydrogen donor. No hydrogen evolution during this transformation suggested a mechanism of direct hydrogen transfer from alcohols. Control experiments with additives indicated the role of acid on the transfer hydrogenolysis, and catalyst characterization confirmed a higher content of Lewis acidic sites on the optimal Pd/TiO₂ photocatalyst. Hence a combination of hydrogen transfer sites and acidic sites may be responsible for the efficient deoxygenation without additives. The photocatalyst showed reusability and achieved selective reduction in a variety of aromatic ketones.

Introduction

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Developing green and atom-economic transformations is of great importance for renewable production of fine chemicals and fuels. Hydrodeoxygenation of aromatic ketones is one of fundamental processes that has attracted considerable attention due to its general applications in chemical synthesis and biomass upgrading.¹⁻⁴ To avoid using stoichiometric and hazardous reductants such as Zn/Hg and hydrazine under harsh conditions in the classical chemical reductions,^{5, 6} catalytic deoxygenation methods under mild conditions have been developed.^{7,8} In the presence of hydrogen gas (H₂), Ru complex, bimetallic Fe-Ru catalyst, supported Pd catalyst and Co-Ce/C catalyst have been exploited to achieve general and selective deoxygenation.9-12 Considering operational safety and facility, liquid silanes which are by-products from silicon industry were used to replace H₂ as the hydride donor, allowing reduction to occur under relative mild conditions.¹³⁻¹⁷ Even so, organic silicon waste was generated during the silane-involved reduction. Therefore more environmentally benign hydrogen donors are urgently needed for sustainable deoxygenation reactions.

Recently emerging hydrogen donors such as formic acid and alcohols have been employed to realize green reduction transformations via transfer hydrogenolysis.¹⁸⁻²⁸ Alcohols are readily available from diverse sources and they are considered as a type of the optimal solvents with respect to green chemistry.²⁹⁻³² Utilization of alcohols as both solvent and hydrogen donor can improve the atom economy and facility of deoxygenation reactions. Initially, Zuidema and co-workers developed the transfer hydrogenolysis of aromatic ketones in

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refluxing isopropanol using excess Raney nickel.²⁰ Fernandes and co-workers developed the deoxygenation of ketones catalysed by oxo-rhenium complexes in 3-pentanol. Selective partial hydrogenation to alkenes was realized under 170 °C and no conversion was observed in other alcohols such as methanol, ethanol and isopropanol.²⁴ Despite this success, these methods suffered from the limited types of alcohols and harsh refluxing conditions due to difficulty in activation of alcohols under thermal conditions. Herein we seek help from photocatalysis to realize mild transfer hydrogenolysis using general alcohols. We found that Pd/TiO₂ catalysed hydrogenolysis of aromatic ketones to alkyl arenes using ethanol (EtOH) as both hydrogen donor and solvent under light irradiation (Scheme 1). Through analysis of reaction process and characterizations of catalyst, a photocatalytic hydrogen transfer mechanism was proposed. This method provided a green route for deoxygenation of aromatic ketones using alcohols.

Experimental

Catalyst preparation

Three samples of TiO₂ loaded with Pd were prepared by a photodeposition method using different Pd salts as precursors.³³ In a typical procedure, a 150 mL quartz reactor equipped with a stir bar was loaded with the TiO₂ (Degussa P25, 500 mg), Pd salts(Pd loading, 3 wt%) and solvent (50 mL



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dichloroethane and 3.2 mL methanol). Then the atmosphere was changed to argon (Ar) before sealing the reactor. This mixture was irradiated at room temperature with homemade LEDs lamps ($\lambda_{max} = 365$ nm, 105 W) for 3 h. After completion of photo-deposition, the samples were obtained from centrifugation and washed with excess ethanol. These Pd/TiO₂ samples with palladium nitrate (Pd(NO₃)₂), palladium acetate (Pd(OAc)₂) and palladium acetylacetonate (Pd(acac)₂) as precursors were denoted as Pd-N/TiO₂, Pd-A/TiO₂ and Pd-AA/TiO₂, respectively.

Besides the photodeposition method, an impregnationchemical reduction method was also used to prepare the Pd/TiO₂, 34 which was denoted as Pd-IC/TiO₂.

Catalytic activity measurement

In a typical run, a 5 mL quartz reactor equipped with a stir bar was loaded with aromatic ketone (0.2 mmol), Pd/TiO₂ (3 wt%, 10 mg) and alcohol (1 mL). Then the atmosphere was changed to argon before sealing the reactor. This mixture was irradiated at room temperature (fan cooling) with LEDs lamps (λ_{max} = 365 nm, 6 W) for 6 h. After completion of the reaction, the standard solution (mesitylene) was added. After filtration using a Nylon syringe filter, the solution was analysed by gas chromatography (GC, Agilent 7890B, DB-FFAP column). ¹H and ¹³C NMR spectra of isolated compounds were measured on a Bruker AVIII 400 spectrometer (¹H: 400 MHz, ¹³C: 101 MHz).

The quantification of hydrogen gas was performed with helium (He) as the internal standard. After reactions, He (500 μ L) was injected into the reaction system and well mixed. Then the mixed gas was analysed by GC equipped with thermal conductivity detector (GC-TCD, Techcomp 7900) with Ar as the carrier gas. The quantification of acetaldehyde was performed via a 2,4-dinitrophenylhydrazine (DNPH) derivatization method with *p*-chloroanisole as the internal standard. The derivatization mixture was analysed by high performance liquid chromatography (HPLC, waters XSelect HSS-PFP column).



Feng Wang received his B.Sc. at Zhengzhou University (1999) and Ph.D. at Dalian Institute of Chemical Physics, the Chinese Academy of Sciences (2005). He spent 2005-2006 as а postdoctoral fellow at the University of California-Berkeley in USA and 2006–2009 at the Hokkaido University-Catalysis Research Center in Japan. He serves as a full professor and an

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Catalyst characterization

Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope with an accelerating voltage of 200 kV to observe the size and morphology of nanoparticles. The carbon monoxide (CO) and pyridine adsorption IR spectra were acquired on a Bruker 70 IR spectrometer. The spectra of adsorbed CO or pyridine molecules have subtracted the spectra of the samples prior the adsorption as background. Quantification of acidity of photocatalyst by the pyridine-adsorption IR was conducted as follows: the Pd/TiO₂ samples (21.1-21.8 mg) were placed in a homemade IR cell and evacuated ($P < 10^{-3}$ Pa) at 423 K for 0.5 h. Then pyridine vapor was introduced to the cell at 303 K and left for 1 h. The cell was then evacuated at 393 K for 0.5 h ($P < 10^{-2}$ Pa) to remove the physically adsorbed pyridine and then cooled to 303 K. After collecting the spectra, the calculation of surface density of Lewis acidic sites was based on the following formula³⁵: $c = 1.42 \times IA \times r^2 \div w$

Where *c* is the density of acidic sites [mmol/g(catalyst)], *IA* is the integrated absorbance of assigned band (cm⁻¹), *r* is the radius of the sample disk (cm) and *w* is the mass of sample disk (mg).

Besides, the IR spectra of pure Pd/TiO_2 samples were collected to compare with that of TiO_2 , no obvious difference suggested hardly any adsorbates on the prepared catalysts (SI, Figure S1).

Results and discussion

This investigation on transfer hydrogenolysis started with

Table 1 Condition screening for transfer hydrogenolysis using alcohols by photocatalysis.^a



			Convers	Yield	Yield
Entry	Catalyst	Solvent	ion of	of EB	of PE
			AP (%)	(%)	(%)
1	Pd-N/TiO ₂	EtOH	99	9	90
2	Pd-A/TiO ₂	EtOH	99	99	0
3	$Pd-AA/TiO_2$	EtOH	99	99	0
4	Pd-IC/TiO ₂	EtOH	99	2	88
5	TiO ₂	EtOH	92	0	55
6	$Pd-N/TiO_2$	MeOH	52	0	49
7	Pd-N/TiO₂	1-PrOH	78	1	68
8	$Pd-N/TiO_2$	2-PrOH	92	2	90
9	Pd-A/TiO ₂	MeOH	99	42	51
10	Pd-A/TiO ₂	1-PrOH	92	27	61
11	Pd-A/TiO ₂	2-PrOH	99	99	0
12 ^b	Pd-A/TiO ₂	EtOH	0	0	0

^aConditions: AP (0.2 mmol), catalyst (Pd 3 wt%, 10 mg), solvent (1 mL), 365 nm LEDs, 6 h, room temperature; The conversion and yields were quantified by GC using mesitylene as internal standard. ^bDark conditions.

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acetophenone (AP) as the substrate and EtOH as the solvent and hydrogen donor, and different Pd/TiO₂ photocatalysts were tested (Table 1). When Pd-N/TiO₂ was employed, a high selectivity (90%) of phenethanol (PE) product was observed (entry 1). When Pd-A/TiO₂ and Pd-AA/TiO₂ were used, a stoichiometric amount of ethylbenzene (EB) was obtained (entries 2, 3). The catalytic performance of Pd-IC/TiO₂ was similar with Pd-N/TiO₂, and partial hydrogenation to alcohol product was observed (entry 4). The support TiO₂ could catalyse partial reduction of AP to PE but in a moderate yield (55%),^{36, 37} and no EB was obtained indicating loaded Pd was essential for full hydrogenolysis (entry 5). Then the feasibility of other alcohols was tested. In the presence of Pd-N/TiO₂, the high selectivity of PE product was kept in methanol (MeOH), 1-propanol (1-PrOH) and 2-propanol (2-PrOH) though lower conversion was observed in MeOH and 1-PrOH (entries 6-8). However, the type of alcohols affected the selectivity of EB product in the presence of Pd-A/TiO₂ (entries 9-11). Only 2-PrOH exhibited similar hydrogen donating ability with ethanol. In view of that ethanol is more available than 2-PrOH, thus ethanol was used for further investigation. The water-contained ethanol was also used for this transformation in view of that abundant bio-ethanol from biomass refinery contains water. A small amount of water (5 equiv) did not affect the EB generation, however, the selectivity of EB decreased as further increasing the amount of water (SI, Figure S4). Meanwhile, Pd-A/TiO₂ and Pd-AA/TiO₂ showed the equally catalytic performance, thus one of them (Pd-A/TiO₂) was selected for further studies. The heterogeneous Pd-A/TiO₂ was successfully recycled for two times,



Conditions: substrate, 0.2 mmol; Pd-A/TiO₂, 10 mg; EtOH, 1 mL; Ar, room temperature, 365 nm LEDs, 12 h; GC yields with mesitylene as the internal standard. ^aIsolated yield. ^bSubstrate, 0.1 mmol; DCE/EtOH (1:1).

Scheme 2 Substrate scope of aromatic ketones for post of a comparison of a com

however, it deactivated in the third recycle (SI, Figure S5). No conversion under dark conditions indicated that this transfer hydrogenolysis was photo-induced (Table 1, entry 12).

With the optimized conditions in hand, the substrate scope of aromatic ketones was explored (Scheme 2). Firstly, aryl methyl ketones with different substituent groups on aryl ring were tested. The ketone with electron-donating group (-MeO) was more readily converted to corresponding alkyl arene (2a, 83% yield) than those with electron-withdrawing groups (2b and 2c, 44-63% yields). The existence of phenolic hydroxyl did not affect the transfer hydrogenolysis (2d-f, 54-93% yields) which showed a promising application on hydrogenation of lignin-derived monomers. Then aryl ketones with substituent groups on aliphatic carbon were tested. Aryl ketones with secondary carbon were still tolerable under current hydrogenolysis conditions (2g-i, 57-94% yields). However, aryl ketones with the tertiary and quaternary carbon could not undergo efficient hydrogenolysis (2j and 2k, 0-16% yields), suggesting that the steric hindrance has a remarkable effect on transfer hydrogenolysis in this heterogeneous system. The lignin β-O-4' ketone model was selectively deoxygenated at carbonyl group with trace amount of ether bond cleavage (2h, 94% yield). This phenomenon was different from reported methods on transfer hydrogenolysis of lignin substrates to monomers.^{38, 39} The possible reason for retaining ether bond under current conditions maybe the fast hydrogenation of carbonyl group to hydroxyl group, which could increase the bond energy of ether bond.⁴⁰ Hence, this transfer hydrogenolysis method can be applied in the selective deoxygenation of side-chains in lignin without depolymerization.

There are two possible pathways for hydrogen transfer from alcohol to substrates. One is that alcohol dehydrogenates to release hydrogen gas, then hydrogen gas is activated on the Pd/TiO₂ and hydrogenates the ketone substrates.⁴¹ The other pathway is that hydride species is directly generated by activation of alcohol on the Pd/TiO₂ and then hydrogenates the substrates.²⁶ To elucidate the hydrogen transfer pathway, the time curve of this reaction was performed on Pd-N/TiO₂ and Pd-A/TiO₂ (Figure 1). It is observed that PE was gradually generated on Pd-N/TiO₂ and then hardly decomposed as reaction time was prolonged (Figure 1a). While PE was generated initially then rapidly converted to EB on Pd-A/TiO₂ suggesting that PE was the intermediate of EB product (Figure 1b). Meanwhile, as for both catalysts, the hydrogen release did not occur until 80% conversion of AP was observed. The delay of hydrogen evolution suggested that these hydrogen transfer reactions may undergo via a direct hydride generation from the alcohol. Moreover, acetaldehyde was continuously generated along with the conversion of AP that indicated ethanol was the hydrogen donor responsible for the hydrogen transfer to substrate.

To investigate the key factor of catalysts on the selectivity of hydrogen transfer products, different additives were tested (Figure 2). The individual $Pd-N/TiO_2$ delivered PE as a major product (Figure 2a). The addition of acetic acid induced the further hydrogenolysis to EB. Meanwhile, the sodium acetate

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Figure 1 Time curves of photocatalytic transfer hydrogenolysis of acetophenone using ethanol on $Pd-N/TiO_2$ (a) and $Pd-A/TiO_2$ (b). Conditions: substrate AP (0.2 mmol), catalyst (Pd 3 wt%, 10 mg), ethanol (1 mL), 365 nm LEDs, room temperature.



Figure 2 The effect of additives on the transfer hydrogenolysis on Pd-N/TiO₂ (a) and Pd-A/TiO₂ (b). Conditions: substrate (0.2 mmol), catalyst (Pd 3 wt%, 10 mg), additives (0.2 mmol), ethanol (1 mL), 365 nm LEDs, 6 h, room temperature.

did not affect the products distribution. This comparison indicated that protonic acid may promote the hydrogenolysis of PE. Indeed, phosphoric acid also increased the yield of EB. However, nitric acid showed no effect on the Pd-N/TiO₂ catalysed hydrogenolysis. In previous reports, nitrate ion could be hydrogenated to nitrogen gas or ammonia on Pd/TiO₂ under photo-irradiation.⁴² Thus nitrate ion in nitric acid may block the hydrogenolysis of PE.^{43, 44} Besides, boron trifluoride (BF₃) also efficiently promoted the full conversion of AP to EB. These experiments indicated the presence of a protonic or Lewis acid could assist the Pd-N/TiO₂ to realize the total hydrogenolysis. In the case of Pd-A/TiO2, EB was obtained without additives (Figure 2b). The variation of products was observed when a base or the nitrate ion was added. This variation in the presence of bases (pyridine and sodium *t*-butoxide) suggested the acidic sites on Pd-A/TiO₂ may be responsible for the hydrogenolysis of PE thus blocking of acidic sites hinders the dehydroxylation. The variation of products in the presence of nitrate ion further proved that nitrate ion hindered the hydrogen transfer to PE even to AP.

To verify the ability of protonic acid as a hydrogen donor, the reactions using protonic acid as additives in acetonitrile were performed (SI, eq S2-4). With addition of formic acid, trace amount of EB and 10% yield of PE were obtained. However, no hydrogenated products were obtained with addition of phosphoric acid. These experiments suggested the usage of proton as hydrogen donor needs a proper hole sacrificial agent, such as alcohols and formate anion.

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Scheme 3 Isotopic labelling experiments and a proposed pathway for photocatalytic transfer hydrogenolysis on Pd-A/TiO₂. Conditions: substrate (0.2 mmol), Pd-A/TiO₂ (Pd 3 wt%, 10 mg), ethanol-**D**₆ (1 mL), 365 nm LEDs, 6 h, room temperature.



Figure 3 Characterization of Pd/TiO_2 samples. TEM images and Pd size distribution histograms of Pd-N/TiO₂ (a) and Pd-A/TiO₂ (b). (c) IR spectra of CO adsorption on Pd/TiO₂ samples. (d) IR spectra of pyridine adsorption on Pd/TiO₂ samples.

Then isotopic labelling experiments were performed to investigate the trend of hydrogen transfer (Scheme 3). It was observed that not only carbonyl carbon but also the adjacent methyl carbon of AP were deuterated in the ethanol- D_6 . Unlabelled EB (EB- D_0) was also detected with a considerable amount. Besides, when PE was subjected into the labelling

experiments, the methyl group was also deuterated with a lower labelling extent than AP (EB-D₃, EB-D₄, and EB-D₅)?786 formation of benzylic C-H and primary C-D bonds were further proved by the ¹H NMR analysis (SI, Figure S6). A possibility is that the deoxygenation of AP may undergo via the styrene intermediate, where the aliphatic C-H bond would be activated and deuterated. However, no styrene was detected in the dark reaction of PE catalysed by Pd-A/TiO₂ (SI, eq S1). As proposed in Ru complex catalysed system,9 a reversible keto-enol tautomerization and following hydrogenolysis processes may occur, which could increase the labelling on methyl of AP with respect to PE. Even so, if following hydrogenolysis of PE underwent via direct dehydroxylation, only EB-D₃ would be obtained and this is not the case. Hence, an acid-participated H/D exchange without free styrene generation during reduction of PE may occur to induce further labelling in the product.²¹

Different precursors affected the properties of catalysts. Through comparison of TEM data from two photocatalysts (Figure 3, a-b), it was observed that the average size of Pd particles on Pd-A/TiO₂ (4.2 nm) was a bit larger than that of Pd-N/TiO₂ (3.5 nm). Then carbon monoxide (CO) adsorption IR spectra were used to characterize the valence state of Pd particles (Figure 3c). Only Pd⁰ species (2000~1900 cm⁻¹ for bridging adsorption and around 2087 cm⁻¹ for linear adsorption) was observed on Pd-A/TiO₂.^{45, 46} However, both Pd²⁺ (2172 and 2119 cm⁻¹ for linear adsorption) and Pd⁰ species were observed on Pd-N/TiO₂.^{47, 48} These observations are in consistent with previous reports where small size particle of Pd contained Pd⁰ and Pd²⁺ species while the large size particle only contained Pd⁰ species.⁴⁹⁻⁵¹ The possible reason for residual Pd²⁺ species and



Scheme 4 Proposed mechanism of $Pd-A/TiO_2$ photocatalysed transfer hydrogenolysis of aromatic ketone using ethanol as hydrogen donor.

smaller size of Pd-N/TiO₂ is that the nitrate ion could be reduced by photo-induced electrons on TiO_2 during photo-deposition (Figure S3) thus it competes with reduction of Pd²⁺ cation.⁴²⁻⁴⁴

The external acid or base additives dramatically affected the hydrogen transfer ability of Pd/TiO_2 . Then pyridine adsorption IR spectra were employed to characterize the acidity of Pd-

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A/TiO₂ and Pd-N/TiO₂ (Figure 3d). Only Lewis acidic sites (1445 cm⁻¹) were observed on both catalysts.^{35, 52, 53} And the calculated surface density of Lewis acidic sites on Pd-A/TiO₂ (0.199 mmol g⁻¹) was double of that on Pd-N/TiO₂ (0.098 mmol g⁻¹) based on the band at 1440 cm⁻¹.³⁵ More Lewis acidic sites on Pd-A/TiO₂ may be responsible for the excellent performance on transfer hydrogenolysis from AP to EB.

Based on mechanism studies and catalyst characterizations, a possible transfer hydrogenolysis mechanism on Pd-A/TiO₂ was proposed (Scheme 4).^{50, 54-57} Under irradiation of light, the photogenerated holes on TiO₂ oxidized the ethanol to acetaldehyde and proton. The photogenerated electrons on TiO₂ migrated to Pd⁰ particles and reduced the proton to activated hydrogen species (Pd-H). Then the ketone substrate was reduced to alcohol intermediate by Pd-H. In the presence of abundant Lewis acidic sites on TiO₂, the alcohol intermediate was dehydrated and further hydrogenated to ethylbenzene by Pd-H. Thus Pd-A/TiO₂ acted as the bifunctional photocatalyst containing hydrogen transfer sites and Lewis acidic sites, which realized the transfer hydrogenolysis using alcohols without addition of other additives.

Conclusions

Herein we developed a photocatalytic transfer hydrogenolysis of aromatic ketones using alcohols as hydrogen donor at room temperature. The Pd-hydride species could be generated from activation of alcohols under light irradiation and reduced substrates directly. The detection of benzylic alcohol intermediate suggested a stepwise reduction pathway. The combination of Lewis acidic sites and hydrogen transfer sites on Pd/TiO₂ may be the key to achieve efficient deoxygenation without external additives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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