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Photocatalytic transfer hydrogenolysis of aromatic ketones using alcohols†

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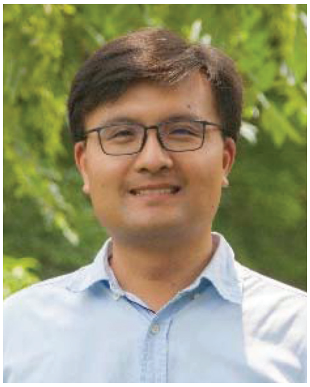
A mild method of photocatalytic deoxygenation of aromatic ketones to alkyl arenes was developed, which utilized alcohols as green hydrogen donors. No hydrogen evolution during this transformation suggested a mechanism of direct hydrogen transfer from alcohols. Control experiments with additives indicated the role of acid in transfer hydrogenolysis, and catalyst characterization confirmed a larger number of Lewis acidic sites on the optimal Pd/TiO_2 photocatalyst. Hence, a combination of hydrogen transfer sites and acidic sites may be responsible for efficient deoxygenation without additives. The photocatalyst showed reusability and achieved selective reduction in a variety of aromatic ketones.

Introduction

The development of green and atom-economical transformations is of great importance for renewable production of fine chemicals and fuels. Hydrodeoxygenation of aromatic ketones is one of the fundamental processes that has attracted considerable attention due to its general applications in chemical synthesis and biomass upgrading.[1–4] To avoid the use of stoichiometric and hazardous reductants such as Zn/Hg and hydrazine under harsh conditions in classical chemical reductions,[5,6] catalytic deoxygenation methods under mild conditions have been developed.[7,8] In the presence of hydrogen gas (H_2), a Ru complex, a bimetallic Fe–Ru catalyst, a supported Pd catalyst and a 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 the silicon industry were used to replace H_2 as hydride donors, 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 to be a type of optimal solvent with respect to green chemistry.[29–32] Utilization of alcohols as both solvents and hydrogen donors can improve the atom economy and facility of deoxygenation reactions. Initially, Zuidema and co-workers developed the transfer hydrogenolysis of aromatic ketones in 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 at 170 °C and no conversion was observed in other alcohols such as methanol, ethanol and isopropanol.[24] Despite this success,



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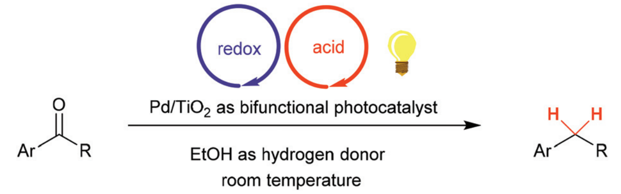


Scheme 1 Photocatalytic transfer hydrogenolysis of aromatic ketones using alcohols on bifunctional Pd/TiO_2.

these methods suffered from limited types of alcohols and harsh refluxing conditions due to difficulty in activation of alcohols under thermal conditions. Herein, we applied photocatalysis to realize mild transfer hydrogenolysis using general alcohols. We found that Pd/TiO_2 catalysed hydrogenolysis of aromatic ketones to alkyl arenes using ethanol (EtOH) as both the hydrogen donor and solvent under light irradiation (Scheme 1). Through analysis of the reaction process and characterization 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 TiO_2 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 TiO_2 (Degussa P25, 500 mg), Pd salts (Pd loading, 3 wt%) and solvent (50 mL 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 LED lamps (λ_{max} = 365 nm, 105 W) for 3 h. After completion of photo-deposition, the samples were obtained from centrifugation and washed with an excess amount of ethanol. These Pd/TiO_2 samples with palladium nitrate ($Pd(NO_3)_2$), palladium acetate ($Pd(OAc)_2$) and palladium acetylacetonate ($Pd(acac)_2$) as precursors were denoted as Pd–N/TiO_2, Pd–A/TiO_2 and Pd–AA/TiO_2, respectively.

Besides the photodeposition method, an impregnation-chemical (IC) reduction method was also used to prepare Pd/TiO_2[34] which was denoted as Pd–IC/TiO_2.

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/TiO_2 (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 LED 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 ^{13}C NMR spectra of isolated compounds were recorded using a Bruker AVIII 400 spectrometer (^1H: 400 MHz, ^{13}C: 101 MHz).

The quantification of hydrogen gas was performed with helium (He) as the internal standard. After reactions, He (500 μL) was injected into the reaction system and mixed well. Then, the mixed gas was analysed by GC equipped with a 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).

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 recorded using a Bruker 70 IR spectrometer. The spectra of the adsorbed CO or pyridine molecules have subtracted the spectra of the samples prior to the adsorption as background. Quantification of the acidity of the photocatalyst by pyridine-adsorption IR spectra was conducted as follows: the Pd/TiO_2 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 into 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 recording the spectra, the surface density of Lewis acidic sites was calculated based on the following formula:[35]

$$c = 1.42 \times \mathrm{IA} \times r^2 \div w$$

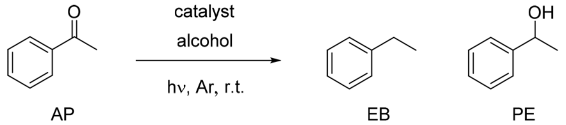
where c is the density of acidic sites [mmol g(catalyst)$^{-1}$], IA is the integrated absorbance of the assigned band (cm^{-1}), r is the radius of the sample disk (cm) and w is the mass of the sample disk (mg).

Besides, the IR spectra of pure Pd/TiO_2 samples were recorded to compare with that of TiO_2, and no obvious difference suggested hardly any adsorbates on the prepared catalysts (ESI, Fig. S1†).

Results and discussion

This investigation on transfer hydrogenolysis started with acetophenone (AP) as the substrate and EtOH as the solvent and hydrogen donor, and different Pd/TiO_2 photocatalysts were tested (Table 1). When Pd–N/TiO_2 was employed, a high selectivity (90%) of the phenethanol (PE) product was observed (entry 1). When Pd–A/TiO_2 and Pd–AA/TiO_2 were used, a stoichiometric amount of ethylbenzene (EB) was obtained (entries 2 and 3). The catalytic performance of Pd–IC/TiO_2 was similar to that of Pd–N/TiO_2, and partial hydrogenation to the alcohol

Table 1 Condition screening for transfer hydrogenolysis using alcohols by photocatalysis[a]

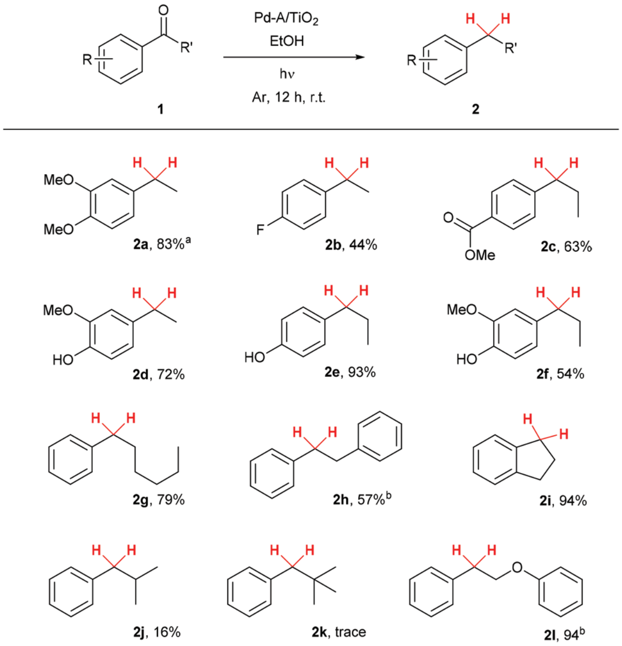


Entry	Catalyst	Solvent	Conversion of AP (%)	Yield of EB (%)	Yield of PE (%)
1	Pd–N/TiO_2	EtOH	99	9	90
2	Pd–A/TiO_2	EtOH	99	99	0
3	Pd–AA/TiO_2	EtOH	99	99	0
4	Pd–IC/TiO_2	EtOH	99	2	88
5	TiO_2	EtOH	92	0	55
6	Pd–N/TiO_2	MeOH	52	0	49
7	Pd–N/TiO_2	1-PrOH	78	1	68
8	Pd–N/TiO_2	2-PrOH	92	2	90
9	Pd–A/TiO_2	MeOH	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

[a] Conditions: 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 an internal standard. [b] Dark conditions.

product was observed (entry 4). The TiO_2 support could catalyse partial reduction of AP to PE but in a moderate yield (55%),[36,37] and no EB was obtained indicating that the loaded Pd was essential for full hydrogenolysis (entry 5). Then, the feasibility of other alcohols was tested. In the presence of Pd–N/TiO_2, the high selectivity of the PE product was maintained in methanol (MeOH), 1-propanol (1-PrOH) and 2-propanol (2-PrOH) although lower conversion was observed in MeOH and 1-PrOH (entries 6–8). However, the type of alcohol affected the selectivity of the EB product in the presence of Pd–A/TiO_2 (entries 9–11). Only 2-PrOH exhibited a similar hydrogen donating ability to that of ethanol. In view of the fact that ethanol is more available than 2-PrOH, ethanol was used for further investigation. The water-containing ethanol was also used for this transformation in view of the fact 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 the amount of water was further increased (ESI, Fig. S4†). Meanwhile, Pd–A/TiO_2 and Pd–AA/TiO_2 showed equal catalytic performance, thus one of them (Pd–A/TiO_2) was selected for further studies. Heterogeneous Pd–A/TiO_2 was successfully recycled two times, however, it deactivated in the third recycle (ESI, Fig. 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 the aryl ring were tested. The ketone with an electron-donating group (–MeO) was more readily converted to the 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 tolerated under the current hydrogenolysis conditions (**2g–i**, 57–94% yields). However, aryl ketones with the tertiary and quaternary carbon



Scheme 2 Substrate scope of aromatic ketones for Pd–A/TiO_2 catalysed transfer hydrogenolysis using ethanols under photoirradiation. Conditions: substrate, 0.2 mmol; Pd–A/TiO_2, 10 mg; EtOH, 1 mL; Ar, room temperature, 365 nm LEDs, 12 h; GC yields with mesitylene as the internal standard. [a] Isolated yield. [b] Substrate, 0.1 mmol; DCE/EtOH (1 : 1).

could not undergo efficient hydrogenolysis (**2j** and **2k**, 0–16% yields), suggesting that steric hindrance has a remarkable effect on transfer hydrogenolysis in this heterogeneous system. The lignin β-O-4′ ketone model was selectively deoxygenated at the carbonyl group with a trace amount of the ether bond cleavage (**2h**, 94% yield). This phenomenon was different from the reported methods on transfer hydrogenolysis of lignin substrates to monomers.[38,39] The possible reason for retaining the ether bond under current conditions may be the fast hydrogenation of the carbonyl group to the hydroxyl group, which could increase the bond energy of the 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 Pd/TiO_2 and hydrogenates the ketone substrates.[41] The other pathway is that hydride species is directly generated by activation of alcohol on Pd/TiO_2 and then hydrogenates the substrates.[26] To elucidate the hydrogen transfer pathway, the time curve of this reaction was performed on Pd–N/TiO_2 and Pd–A/TiO_2 (Fig. 1). It is observed that PE was gradually generated on Pd–N/TiO_2 and then hardly decomposed as reaction time was prolonged (Fig. 1a). However, PE was generated initially then rapidly converted to EB on Pd–A/TiO_2 suggesting that PE was the intermediate of the EB product (Fig. 1b). Meanwhile, as for both catalysts, hydrogen gas release did not occur until 80% conversion of AP was observed. The delay in hydrogen evolution suggested that these hydrogen transfer reactions may proceed *via* direct hydride generation from the alcohol. Moreover, acetaldehyde was continuously generated along with the conversion of AP, indicating that ethanol was the hydrogen donor responsible for the hydrogen transfer to the substrate.

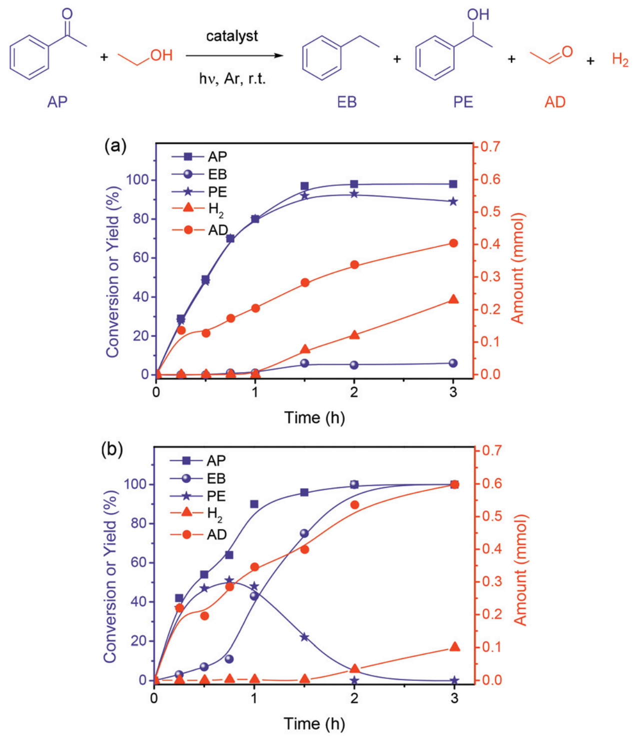


Fig. 1 Time curves of photocatalytic transfer hydrogenolysis of acetophenone using ethanol on Pd–N/TiO_2 (a) and Pd–A/TiO_2 (b). Conditions: substrate AP (0.2 mmol), catalyst (Pd 3 wt%, 10 mg), ethanol (1 mL), 365 nm LEDs, room temperature.

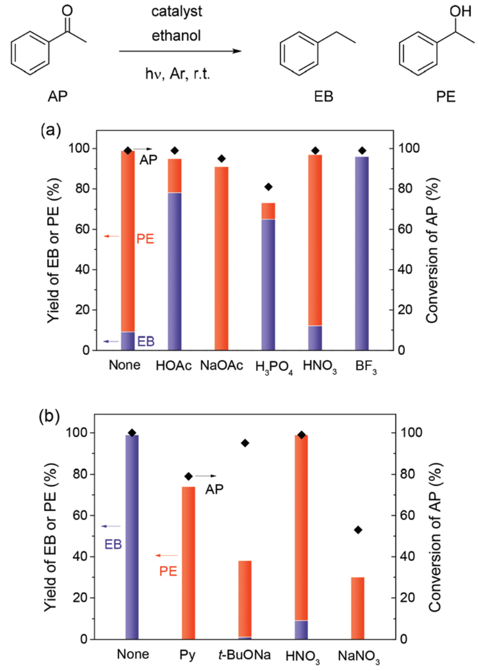


Fig. 2 The effect of additives on the transfer hydrogenolysis on Pd–N/TiO_2 (a) and Pd–A/TiO_2 (b). Conditions: substrate (0.2 mmol), catalyst (Pd 3 wt%, 10 mg), additives (0.2 mmol), ethanol (1 mL), 365 nm LEDs, 6 h, room temperature.

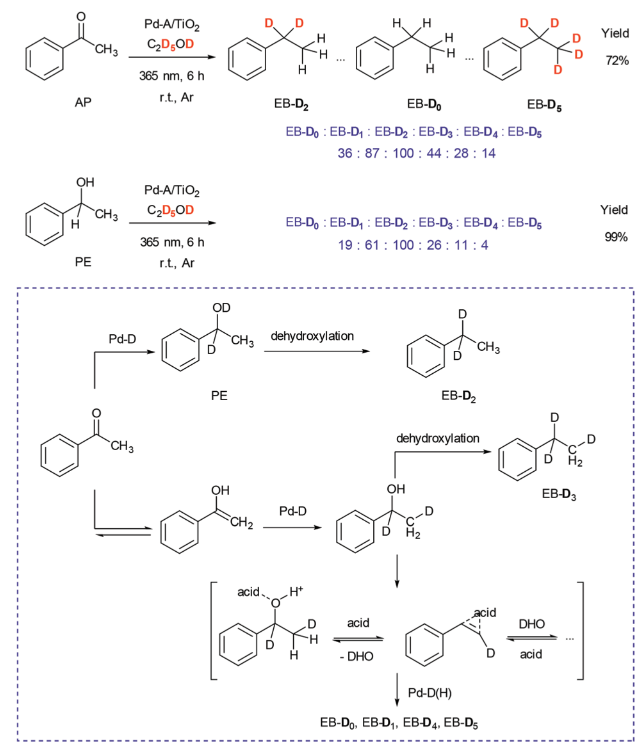
To investigate the key factor of catalysts on the selectivity of hydrogen transfer products, different additives were tested (Fig. 2). The individual Pd–N/TiO_2 delivered PE as the major product (Fig. 2a). The addition of acetic acid induced further hydrogenolysis to EB. Meanwhile, sodium acetate did not affect the product distribution. This comparison indicated that protonic acid may promote hydrogenolysis of PE. Indeed, phosphoric acid also increased the yield of EB. However, nitric acid showed no effect on the Pd–N/TiO_2 catalysed hydrogenolysis. In previous reports, nitrate ion could be hydrogenated to nitrogen gas or ammonia on Pd/TiO_2 under photoirradiation.[42] Thus, nitrate ion in nitric acid may block the hydrogenolysis of PE in the presence of protonic acid.[43,44] Besides, boron trifluoride (BF_3) also efficiently promoted the full conversion of AP to EB. These experiments indicated that the presence of a protonic or Lewis acid could assist Pd–N/TiO_2 to realize total hydrogenolysis. In the case of Pd–A/TiO_2, EB was obtained without additives (Fig. 2b). The variation of products was observed when a base or nitrate ion was added. This variation in the presence of bases (pyridine and sodium *t*-butoxide) suggested that the acidic sites on Pd–A/TiO_2 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 the nitrate ion hindered the hydrogen transfer to PE even to AP.

To verify the capability of protonic acid as a hydrogen donor, the reactions using protonic acid as additives in acetonitrile were performed (ESI, eqn (S2)–(S4)†). With addition of formic acid, a 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 that the use of protons as hydrogen donors needs suitable hole sacrificial agents, such as alcohols and formate anions.

Then, isotope labeling 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 ethanol-$\mathbf{D}_6$. Unlabeled EB (EB-$\mathbf{D}_0$) was also detected in a considerable amount. Besides, when PE was subjected to labeling experiments, the methyl group was also deuterated with a lower labeling extent compared to AP (EB-$\mathbf{D}_3$, EB-$\mathbf{D}_4$ and EB-$\mathbf{D}_5$). The formation of benzylic CH and primary C–D bonds was further proved by ^{1}H NMR analysis (ESI, Fig. S6†). One possibility is that the deoxygenation of AP may proceed with 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/TiO_2 (ESI, eqn (S1)†). As proposed in the Ru complex catalysed system,[9] a reversible keto–enol tautomerization and following hydrogenolysis process may occur, which could increase the labeling on the methyl of AP with respect to PE. Even so, if the following hydrogenolysis of PE proceeded *via* direct dehydroxylation, only EB-$\mathbf{D}_3$ 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 labeling in the product.[21]

Different precursors affected the properties of catalysts. Through comparison of TEM data from two photocatalysts (Fig. 3a and b), it was observed that the average size of Pd particles on Pd–A/TiO_2 (4.2 nm) was a bit larger than that of Pd–N/TiO_2 (3.5 nm). Then, carbon monoxide (CO) adsorption IR spectra were used to characterize the valence state of Pd particles (Fig. 3c). Only Pd^0 species (2000–1900 cm^{-1} for bridging adsorption and around 2087 cm^{-1} for linear adsorption) were observed on Pd–A/TiO_2.[45,46] However, both Pd^{2+} (2172 and 2119 cm^{-1} for linear adsorption) and Pd^0 species were observed on Pd–N/TiO_2.[47,48] These observations are consistent with previous reports, where small size particles of Pd contained Pd^0 and Pd^{2+} species while large size particles contained only Pd^0 species.[49–51] The possible reason for the residual Pd^{2+} species and smaller size of Pd particles on Pd–N/TiO_2 is that the nitrate ion could be reduced by photo-induced electrons on TiO_2 during photo-deposition (Fig. S3†), thus it competes with the reduction of the Pd^{2+} cation.[42–44]

The external acid or base additives dramatically affected the hydrogen transfer capability of Pd/TiO_2. Then, pyridine adsorption IR spectra were employed to characterize the acidity of Pd–A/TiO_2 and Pd–N/TiO_2 (Fig. 3d). Only Lewis acidic sites (1445 cm^{-1}) were observed on both catalysts.[35,52,53] Furthermore, the calculated surface density of Lewis acidic sites on Pd–A/TiO_2 (0.199 mmol g^{-1}) was double that on Pd–N/



Scheme 3 Isotope labeling experiments and the proposed pathway of photocatalytic transfer hydrogenolysis on Pd–A/TiO_2. Conditions: substrate (0.2 mmol), Pd–A/TiO_2 (Pd 3 wt%, 10 mg), ethanol-$\mathbf{D}_6$ (1 mL), 365 nm LEDs, 6 h, room temperature.

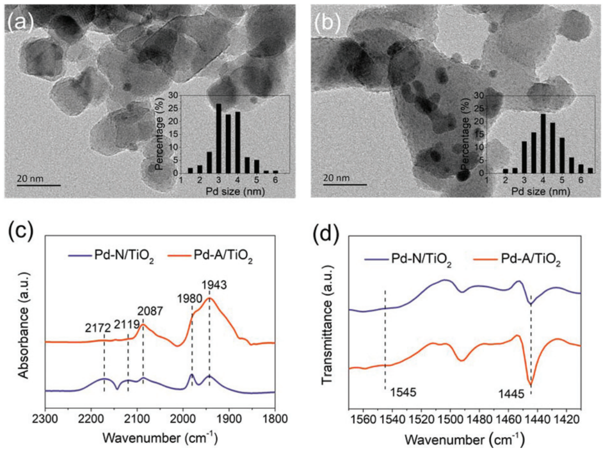
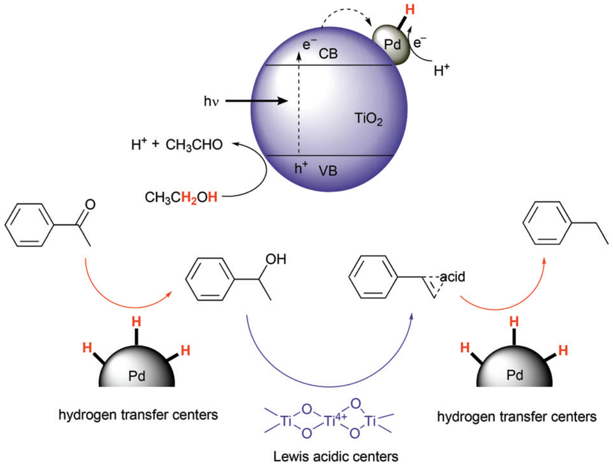


Fig. 3 Characterization of Pd/TiO_2 samples. TEM images and Pd size distribution histograms of Pd–N/TiO_2 (a) and Pd–A/TiO_2 (b). (c) IR spectra of CO adsorption on Pd/TiO_2 samples. (d) IR spectra of pyridine adsorption on Pd/TiO_2 samples.



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

TiO_2 (0.098 mmol g^{-1}) based on the band at 1445 cm^{-1}.[35] More Lewis acidic sites on Pd–A/TiO_2 may be responsible for the excellent performance on transfer hydrogenolysis from AP to EB.

Based on mechanism studies and catalyst characterization, a possible transfer hydrogenolysis mechanism on Pd–A/TiO_2 was proposed (Scheme 4).[50,54–57] Under irradiation of light, the photogenerated holes on TiO_2 oxidized the ethanol to acetaldehyde and proton. The photogenerated electrons on TiO_2 migrated to Pd^0 particles and reduced the proton to activated hydrogen species (Pd–H). Then, the ketone substrate was reduced to an alcohol intermediate by Pd–H. In the presence of abundant Lewis acidic sites on TiO_2, the alcohol intermediate was dehydrated and further hydrogenated to ethylbenzene by Pd–H. Thus, Pd–A/TiO_2 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 donors at room temperature. The Pd-hydride species could be generated from activation of alcohols under light irradiation and reduced substrates directly. The detection of a benzylic alcohol intermediate suggested a stepwise reduction pathway. The combination of Lewis acidic sites and hydrogen transfer sites on Pd/TiO_2 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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