Green Chemistry

Accepted Manuscript

Cite this: DOI: 10.1039/c0xx00000x

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Hydrogenative cyclization of levulinic acid into γ-valerolactone by photocatalytic intermolecular hydrogen transfer

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

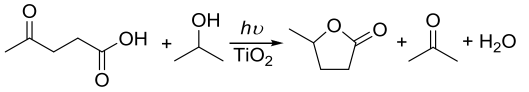
DOI: 10.1039/b000000x

The hydrogenative cyclization of levulinic acid (LA) into γ-valerolactone (GVL) is an attractive route toward the use of renewable bio-sources but normally suffers from the consumption of H_2. In this study, we report that an intermolecular hydrogen transfer from isopropanol to LA can be realized efficiently under a photocatalytic condition over gold-loaded TiO_2 catalysts. In this manner, isopropanol is dehydrogenated as acetone and pinacol with total selectivity of > 99%, whereas LA is hydrogenated and cyclized as GVL with selectivity of up to 85%. In this reaction process, the production of GVL is mediated with a hydrogenated dehydration of LA into acetyl propionyl radical, which is further hydrogenated and cyclized as GVL. This hydrogenation–dehydrogenation coupling process provides an atom-economical green way for the conversion of LA into GVL.

Levulinic acid (LA) is one of the most important biomass platform molecules because it can be readily obtained from lignocellulosic biomass by simple hydrolysis processes.[1-3] The variety of functional groups in LA endows this molecule with versatile chemical properties. Thus, the rational conversion of LA to downstream chemical chains has drawn significant attention for future sustainable energy and chemical industries.[1, 2, 4] For example, the selective hydrogenation of LA can generate a variety of value-added chemicals, such as γ-valerolactone (GVL), diphenolic acid, 2-methyl-tetrahydrofuran, 1,4-pentanediol.[1, 5, 6] As a stable and liquid chemical, GVL exhibits a remarkable potential to act as a green solvent, food additive and organic intermediate in the synthesis of fine chemicals.[7-9] GVL can also be used as a promising fuel additive to replace ethanol in gasoline–ethanol blends or as a precursor for diesel production.[10-12]

The conversion of LA into GVL has been extensively studied in recent years.[1-3, 13, 14] This process is normally realized by direct hydrogenative cyclization under noble-metal-based thermo-catalysis conditions with a H_2 molecule as hydrogen source.[1, 13-21] Although H_2-fed catalytic conversion is highly efficient and able to obtain high GVL yield and selectivity, it requires significant H_2 consumption. Given that H_2 generation relies on fossil fuels, particularly coal, H_2 consumption will make the thermo-catalytic process unsustainable.[22] Therefore, alternative routes should be explored for the green conversion of LA into GVL.[23, 24]

Photocatalysis has been extensively used in diverse applications, such as water splitting, organic synthesis and polluted effluent recovery[25-27] and some important progress has been achieved on chemical synthesis.[28-31] Numerous studies have proven that various organic reactions can selectively operate under light irradiation with help from semiconductor or molecular photocatalysts; this finding displays the great potential of using renewable solar energy to drive chemical synthesis.[28-33] We recently found that under a $NaTaO_3$-supported photocatalysis condition, intermolecular hydrogen transfer from isopropanol to acetone can be achieved efficiently, thus leading to a selective production of pinacol.[34] In this process, both the hole-induced oxidation half-reaction and electron-induced reduction half-reaction are effectively utilized, thus increasing the efficiency and atomic-economy of the total reaction. Inspired by this strategy, we attempt to convert LA to GVL by a light-driven dehydrogenation–hydrogenation coupling process without external hydrogen consumption. In this process, the hydrogen required for LA hydrogenation is directly fed from isopropanol dehydrogenation, which simultaneously produces usable acetone and pinacol selectively (Equation 1 and Scheme 1).



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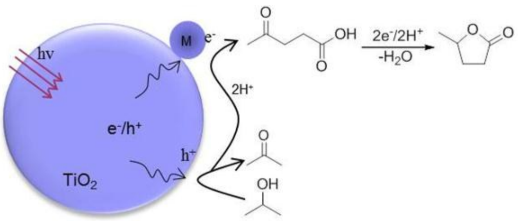

Scheme. 1 Schematic illustration of the TiO_2-photocatalytic hydrogenation–dehydrogenation coupling reaction for LA/isopropanol.

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Table 1 Experimental data of the TiO_2-photocatalytic hydrogenated cyclization for LA into GVL.[a]

Entry	Catalyst	LA Conv. (%)	Sel.(%) of LA				Sel.(%) of isopropanol		H_2 Amount(mmol)
			GVL	HMHD[b]	IL[c]	PA+HOAc	Pinacol	Acetone	
1	Non	3.6	0.5	ND[d]	1.8	97.0	ND	ND	ND
2	Pt/P25-TiO_2	54	55.2	33.7	2.3	6.8	10.8	88.2	10.3
3	Pt/P25-TiO_2[e]	0.0	ND	ND	ND	ND	ND	ND	ND
4	Pt/NT-TiO_2	47	48.1	40.8	2.1	7.1	11.6	87.3	2.6
5	Pt/R-TiO_2	56	59.2	31.4	2.3	6.4	13.2	86.8	2.9
6	Pt/RA-TiO_2	69	69.5	21.9	2.0	4.5	11.4	88.6	10.9
7	Pd/RA-TiO_2	71	76.4	17.4	1.9	4.5	12.9	87.1	9.8
8	Au/RA-TiO_2	79	85.3	8.2	2.0	3.1	10.3	89.7	4.6
9	RA-TiO_2	5.6	2.5	ND	2.0	89.2	9.8	90.2	0.1

[a] Reaction conditions: LA, 0.02 mol; isopropanol, 20 ml; TiO_2, 0.05 g; noble metal co-catalyst, 0.5 wt%; atmosphere, argon; temperature, 20 °C; Light source, 300 W high-pressure Hg-lamp; irradiation time, 9 h. [b] HMHD is 6-hydroxy-6-methylheptane-2,5-dione. [c] IL is isopropyl levulinate. [d] ND, not detected. [e] without light irradiation.

The experiments for the coupling of LA hydrogenative cyclization and isopropanol dehydrogenation were performed in a tubular quartz reactor (20 ml) and an argon atmosphere, irradiated by a high-pressure Hg-lamp (300 W) at room temperature. First, we irradiated a mixture of LA and isopropanol (1.0 mol/L for LA), without any catalyst. After 9 h irradiation, only a small amount (3.6%) of LA was converted (Table 1, Entry 1). Product analysis showed a production of GVL but in trace quantity (approximately 0.5% selectivity). LA dominantly behaves in a photolysis process and generates propionic acid (PA) and acetic acid (HOAc).[35] Furthermore, isopropyl levulinate (IL) was also detected in small amounts. In the presence of a Platinum-loaded TiO_2 photocatalyst (Pt/P25-TiO_2) prepared from commercial TiO_2 (Degussa P25) and an in-situ Platinum deposition,[26] LA conversion sharply increases to 54% and GVL is readily produced at a selectivity of 55% (Table 1, Entry 2) with low formation of photolysis products. Considering of the failed reaction under dark condition (Table 1, Entry 3), this result suggests that Pt/P25-TiO_2 has significant photocatalytic function on the hydrogenative cyclization of LA. In this case, one new product is formed from LA. As analyzed by gas chromatography-mass spectrometry (GC-MS) and related ion fragments (Fig. 1a), this new product can be well assigned to 6-hydroxy-6-methylheptane-2,5-dione (HMHD) (assignment details see Supporting Information). HMHD can be viewed as the geometric isomer of IL and is formed from a unique LA-isopropanol intermolecular dehydration process, wherein the α-H in isopropanol participates in the dehydration and leads to a C-C construction (unlike in esterization reaction). This dehydration process seems more favorable than the esterization reaction because HMHD forms at a considerably high selectivity (Table 1, Entry 2, Fig. 1b), as estimated from the peak-area analysis of gas chromatography (GC).

During the hydrogenative cyclization of LA, isopropanol is majorly dehydrogenated as acetone with a selectivity of approximately 88% (Table 1, Entry 2, Fig. 1b). Isopropanol also behaves as a dehydrogenation C-C coupling process[34] and produces pinacol with a selectivity of approximately 10%, following a mechanism mediated with the formation of hydroxyl isopropyl ($(CH_3)_2COH$) radical (see Supporting Information). These data indicate that intermolecular hydrogen transfer is successfully realized under the photocatalytic function of Pt/P25-TiO_2. In this process, part of the hydrogen atoms derived from isopropanol dehydrogenation is converted into molecular H_2 and competes with the hydrogenative cyclization of LA.

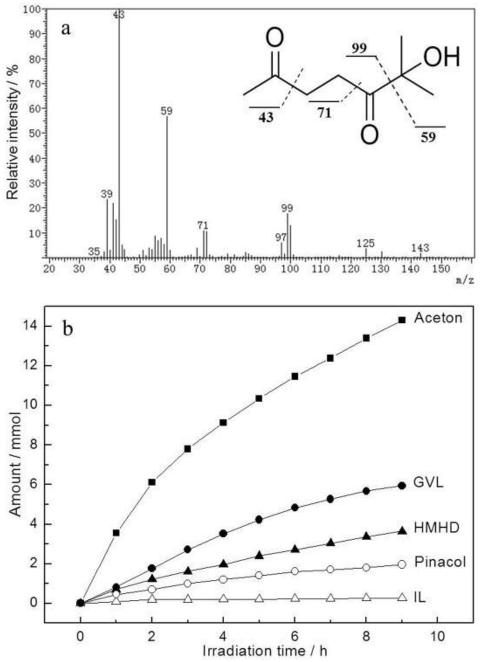


Figure 1. a) Mass spectrum of HMHD; b) Products generation during the photocatalytic process in the LA/isopropanol. Reaction conditions: solution, 20 ml 1 M LA in isopropanol; catalyst, 0.05 g P25-TiO_2 loaded 0.5 wt% platinum; atmosphere, argon; temperature, 20 ℃; Light source, 300 W high-pressure Hg-lamp.

To investigate the effect of photocatalyst structure on the hydrogenation–dehydrogenation coupling process, we modulated the TiO_2 structure and inspected the effect of the TiO_2 structure on catalyst performance. A commercial TiO_2 powder (Degussa P25) was calcinated at 600 ℃ to obtain mixed rutile and anatase structure TiO_2 (RA-TiO_2), and at 800 ℃ to obtain rutile phase structure TiO_2 (R-TiO_2) (Fig. 2a). TiO_2 nanotube (NT-TiO_2) with the anatase phase was prepared by a hydrothermal process by using P25-TiO_2 as starting material.[36] The TEM observations (Fig. S4) showed that the particle size is approximately 20–30 nm for RA-TiO_2 and approximately 100 nm for R-TiO_2. The diameter of NT-TiO_2 is approximately 8 nm and the length is approximately 150 nm. Catalysis tests showed that different phase structure catalysts exhibited different activities (Fig. 2b and Table 1, Entry 4–6). Pure phase NT-TiO_2 and R-TiO_2 catalysts give lower conversion and selectivity than P25-TiO_2, whereas the mixed structure Pt/RA-TiO_2 exhibits better LA conversion (69%) and GVL selectivity (66%) than P25-TiO_2 because of the facilitation of the mixed phase-resulted heterojunctions for electron and hole separation.[26]

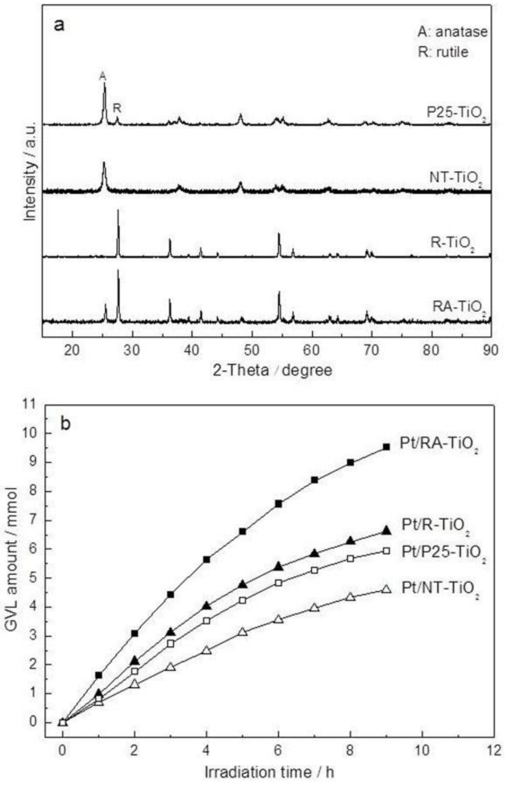


Figure 2. a) XRD pattern of catalysts; b) Catalysts effect on hydrogenated product GVL during the photocatalytic process in the LA/isopropanol. Conditions: solution, 20 ml 1 M LA in isopropanol; 0.05 g catalyst loaded 0.5 wt% platinum; atmosphere, argon; temperature, 20 ℃; Light source, 300 W high-pressure Hg-lamp.

A co-catalyst is necessary to promote LA hydrogenative cyclization, as witnessed by the performance of bare RA-TiO_2, which exhibits low activity (Table 1, Entry 9). Although platinum displays a significant catalytic activity for LA hydrogenative cyclization, it has a high work function and can greatly facilitate H_2 generation from H^+,[26, 37] which is theoretically competitive to LA hydrogenation. To suppress H_2 generation, we inspected the performance of palladium and gold co-catalysts that exhibit low work functions.[26, 37] The results showed that such catalysts can significantly reduce H_2 generation while improving LA hydrogenative cyclization (Table 1, Entry 6–8, Fig. 3a). Au exhibited the highest LA conversion as 79% and GVL selectivity as 85%. The calculated rate of GVL production is 29.8 mmol GVL per gram catalyst per hour, which is comparable to the rates obtained from previous H_2-fed thermocatalysis with Cu/ZrO_2[15] and Ru/C catalysts[18, 19] (see details in Table S1). If only active metal (Au) is considered, the specific rate of GVL production is 5968.9 $mmol \cdot g^{-1} \cdot h^{-1}$, about 5 and 120 times higher than Ru and Cu, respectively. In addition, compared to the previous thermocatalytic process that was operated at high temperature (>100°C) and high pressure, the present photocatalytic process runs at normal pressure and temperature, which is beneficial to a system operation.

On the basis of molar quantity of H_2 and GVL obtained from RA-TiO_2-based catalysts, we inspected the effect of metal co-catalyst on the efficiency (η) of hydrogen transfer from isopropanol to LA by using the following equation: $\eta = \{M_{GVL}/(M_{H2} + M_{GVL})\} \times 100\%$. η is 46%, 52%, and 74% for Pt, Pd, and Au, respectively. The results show that gold is a more suitable co-catalyst for LA hydrogenative cyclization, benefiting from its low work function and catalytic activity for the undesired H^+-to-H_2 reduction. This characteristic of gold allows a suppression of the H^+-to-H_2 reaction and consequently encourages the interaction between H^+ and LA and thus the photoexcited electron-induced hydrogenative cyclization of LA.

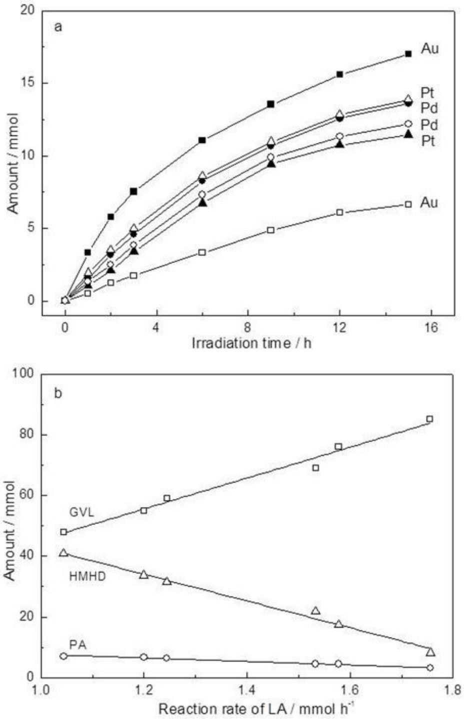
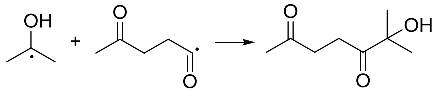


Figure 3. a) H_2 (hollow) and GVL (solid) generation with different co-catalyst. b) The changes of GVL, HMHD and LA generation with the reaction rate of LA during the photocatalytic process in LA/isopropanol. Conditions: solution, 20 ml 1 M LA/ethyl levulinate in isopropanol; 0.05 g RA-TiO_2 loaded 0.5 wt% co-catalyst; atmosphere, argon; temperature, 20 ℃; light source, 300 W high-pressure Hg-lamp.

As described above, LA also exhibits a photolysis behavior and produces PA and HOAc, likely following a water-facilitated mechanim (see supporting information) because the hydrogenative cyclization of LA can by-produce water stoichiometrically. This reaction is theoretically competitive to the hydrogenative cyclization of LA. On the basis of all data obtained, we observed that with increasing LA conversion rate, GVL production steadily increases and photolysis products nearly remain a constant quantity (Fig. 3b). This result suggests that although photolysis is difficult to avoid, it can be suppressed to a relative low level by improving the hydrogen transfer efficiency. Furthermore, the intermolecular dehydration between LA and isopropanol to produce IL and HMHD seems also competitive with target hydrogenative cyclization. For HMHD, its formation linearly decreases with increasing LA conversion rate (Fig. 3b). HMHD selectivity can be greatly reduced from 40.8% for Pt/NT-TiO_2 and 21.9% for Pt/RA-TiO_2 to 8 % for Au/RA-TiO_2 (Table 1), thus suggesting that an efficient hydrogen transfer can effectively suppress HMHD formation. For IL formation, it should theoretically be favorable in the present photocatalysis environment because H^+ ions that are intrinsically formed from a hole-induced dehydrogenation of isopropanol[32] will act as acid catalyst for esterization reaction. However, IL was actually detected in small quantities (approximately 2% selectivity). This situation is likely due to the subsequent hydrogenation conversion of IL. This result was verified by employing ethyl levulinate as starting reactant to perform the photocatalytic hydrogen transfer reaction (Fig. S5). Ethyl levulinate can be readily hydrogenated and cyclized into GVL with a selectivity of approximately 75%.

To understand the photocatalytic reaction mechanism, we monitored the radicals formed during photocatalytic processes via a radical capture technique and in situ analysis by electron paramagnetic resonance spectrum (EPR). Fig. 4a shows the EPR spectrum obtained from the Pt/RA-TiO_2-catalytic dehydrogenation of isopropanol in the absence of LA by employing 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 0.05 M) as a radical capture molecule. A simulated analysis of the spectrum by using Easyspin software[38] reveals that both isopropoxy $(CH_3)_2CHO$ and hydroxyl isopropyl $(CH_3)_2COH$ radicals are produced as intermediates with relative contents of approximately 70% and 30%; this analysis agrees with previous EPR observations for photocatalytic alcohol reaction over TiO_2-based catalysts.[39–41] Acetone formation is believed to originate from the further dehydrogenation of radicals whereas pinacol formation is caused by the C-C coupling reaction of $(CH_3)_2COH$ radicals.[34]

Fig. 4b shows the EPR spectrum obtained from the LA-isopropanol hydrogen transfer reaction. This EPR spectrum is different from the spectrum for sole isopropanol system, with a significant shift in some resonance signals, thus suggesting a change in electron spin coupling constant and the formation of new carbon-related radical intermediates. Although the identification of the new radicals is difficult, they are assumed to originate from LA reaction. According to the formation of HMHD in considerable quantity, HMHD is formed via a C-C coupling reaction between $(CH_3)_2COH$ radical and an acetyl propionyl radical (following Equation 2):



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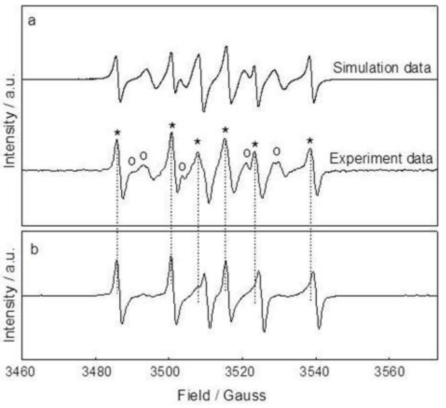
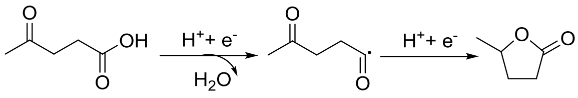


Figure 4. a) Measured EPR spectrum in neat isopropanol and its simulated EPR data with 30% $[DMPO\text{-}(CH_3)_2C(OH)]^{\cdot}$($a_N$ = 15.03, a_H = 22.67, g = 2.0057) marked as * and 70% $[DMPO\text{-}(CH_3)_2CHO]^{\cdot}$ (a_N = 13.2, a_H = 8.4, a_H = 0.8, g = 2.0057) marked as ^{O}; b) EPR spectrum in LA + isopropanol (0.1 M LA). EPR are obtained upon irradiation of Pt/RA-TiO_2 suspensions in the presence of spin trapping agent DMPO (DMPO = 0.05 M).

Acetyl propionyl radical can be formed by the hydrogenation dehydration of LA. On the basis of these observation and deduction, we propose that the photocatalytic hydrogenative cyclization of LA is mediated with the formation of acetyl propionyl radicals, which is further hydrogenated and cyclized as GVL, as expressed in Equation 3:



(3)

This proposal can well explain the other data observed, such as the profiles of GVL and HMHD production (Fig. 3b). The GVL and HMHD formations are intrinsically competitive because both of them are derived from the same intermediate; thus, HMHD formation must be suppressed when GVL formation is promoted by a facilitated hydrogen transfer.

Conclusions

This study is the first to report that an intermolecular hydrogen transfer from isopropanol to LA can be realized efficiently under a photocatalytic condition over gold-loaded TiO_2 catalysts. In this manner, isopropanol is dehydrogenated as acetone and pinacol with total selectivity of > 99%, whereas LA is hydrogenated and cyclized as GVL with selectivity of up to 85% and the hydrogen transfer efficiency (η) up to 74%. This hydrogenation–dehydrogenation coupling process provides an atom-economical green way for the conversion of LA into GVL. The further improvement of reaction efficiency and GVL selectivity is possible via the modification of photocatalyst composition and structure or the development of new catalysts.

Experimental Section

All chemicals were analytical-grade reagents and used without further purification. RA-TiO_2 and R-TiO_2 were prepared using a calcination method with commercial TiO_2 powder (P25, Degussa) as a starting material. A typical calcination was carried out in a muffle furnace in air at 600 ^{o}C for 60 h (RA-TiO_2) and 800 ^{o}C for 8 h (R-TiO_2). TiO_2 nanotube (NT-TiO_2) photocatalysts were prepared by a hydrothermal process.[36] Titania powder (1 g) and an aqueous solution of NaOH (10 M, 100 ml) were mixed under magnetic stirring. After stirring for 30 min, the resulting milk-like suspension was transferred to a Teflon-lined autoclave, kept at 150 ℃ for 48 h, and then allowed to cool down to room temperature. The resulting precipitate was washed with deionized water, and ion exchanged with 0.1 mol/L hydrochloric acid until a pH value near 8 was reached, and then treated at 300 ℃ for 5 h to obtain TiO_2 nanotube (NT-TiO_2). Noble metal co-catalysts were loaded onto the catalyst by in situ photodeposition.[26] $H_2PtCl_6{\cdot}6H_2O$, $PdCl_2$ and $HAuCl_4{\cdot}3H_2O$ were used as precursors.

Phase structure was characterized by X-ray diffraction on a D8 Advance power X-ray diffractometer with Cu Kα (λ = 0.15406 nm) radiation. The morphology and microstructure of samples were examined using a transmission electron microscope (JEM-2010).

The EPR studies were carried out in a flat quartz cell, and the spectra recorded on a Bruker EMXPlus-10/12 EPR spectrometer. Two samples were prepared: isopropanol solution containing 0.05 M 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2.5 mg/ml TiO_2 with 0.5 wt% platinum; isopropanol solution containing 1 M LA, 0.05 M DMPO and 2.5 mg/ml TiO_2 with 0.5 wt% platinum. The samples were firstly sonicated for 5 min in an ultrasonic bath, and then were carefully deoxygenated by a stream of argon, subsequently filled in the quartz flat cell. During the EPR photochemical experiments the samples were irradiated at 298 K directly in the EPR resonator, and the EPR spectra were recorded in situ during a continuous photoexcitation. The operating condition was as follows: microwave frequency ν = 9.86 GHz, power of microwave W = 10.02 mW, scanning range 3416–3616 G. The irradiation of the sample in EPR cavity was carried out using a 100W UV lamp. The g-values (±0.0001) were determined using a built-in magnetometer. The EPR spectra so obtained were analyzed and simulated using the Easyspin software.[38]

In a general photocatalytic synthetic procedure, LA (20 mmol) was dissolved in 20 ml isopropanol and added 0.05 g TiO_2 catalyst (loading 0.5 wt% noble metal). All reactions were performed in a tubular quartz photoreactor with pure Ar continuously bubbling. A 300 W high-pressure Hg lamp was used as light source and was cooled by 20^{o}C water circulation. Liquid products were analyzed by a gas-chromatograph (GC-950 equipped with a flame ionization detector (FID) and Rtx-Wax column from Restek) and gas chromatograph-mass spectrometer (Shimadzu GCMS-QP2010 with a mass spectrometer and DB-5 ms column from Alltech). The sample analysis was confirmed by comparison mass spectrum and retention time of pure products. A GC-9790 (equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID)) was used to detect CH_4, CO, CO_2 and H_2.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21173250 and 21573137), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Natural Science Foundation of Shanxi (2014011014-3), and the Foundation of State Key Laboratory of Coal Conversion (J13-14-913).

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