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The photocatalytic $sp^{3}C-sp^{3}C$ cross-coupling between tetrahydrofuran (THF) and various alkanes was accomplished with Pt loaded titanium oxide (Pt/TiO₂) photocatalysts. The cross-coupling between THF and cyclohexane was systematically studied, which revealed that the reaction followed two routes: the main course was the photooxidation of both substrates on the Pt/TiO₂ photocatalyst to generate radical species followed by their successive coupling; while a minor one was a hybrid of photocatalysis by Pt/TiO₂ and thermal catalysis by Pt metal nanoparticles. The nature of the Pt catalysis was suggested to be the activation of an $sp^{3}C-H$ bond in THF or alkane molecule adsorbed on its surface and promote the reaction between the activated molecule and photogenerated radical species. Thus, the Pt nanoparticles on TiO₂ were believed to have a bifunctional role of an electron receiver as well as a metal catalyst.

1. Introduction

Numerous issues of the current century like sustainable energy sources,¹⁻³ carbon recycling,⁴⁻⁷ alternative carbon source,⁸⁻¹² clean air and water,¹³⁻¹⁷ green chemical synthesis,^{18–24} etc. have been successfully addressed by heterogeneous photocatalysis. Among different photocatalysts, TiO₂ remains most alluring due to its high catalytic activity, low cost, non-toxicity, and long-term stability.^{25,26} However, it is pointed out that the rapid recombination of the photogenerated electrons and holes in TiO₂, results in low quantum efficiency. Several methods have been adopted to overcome this limitation;²⁷ like introducing surface or bulk irregularities,^{28,29} constructing heterojunction with other semiconductors or carbon materials,^{30–32} adding a metal or non-metal dopant,^{33,34} deposition of noble metal $\ensuremath{\mathsf{particles}}\xspace,\ensuremath{^{35}}\xspace$ and so on. Among these, the most common strategy is the deposition of noble metal particles on TiO₂, which aligns the Fermi level of the metal with the conduction band of TiO_2 and causes the transfer of the photoexcited electrons from TiO2 to metal, thereby decreasing their

recombination with holes.^{36–38} Thus, the primary role of the metal particles deposited on TiO_2 is to act as an electron receiver.

Additionally, the metals can also participate catalytically in a photocatalytic reaction thus acting as co-catalysts.³⁹⁻⁴⁶ For example, in our previous work on the direct photocatalytic cross-coupling between various ethers and benzene with a Pd/TiO₂ photocatalyst, the Pd nanoparticles were found to have a bifunctional role.³⁹ Apart from acting as an electron receiver on TiO₂, they catalyzed a dark reaction between a photogenerated ether radical and benzene. Thus the reaction between ether and benzene can be recognized as a hybrid of TiO₂ photocatalysis and Pd metal catalysis. Intrigued by this bifunctional role of metal nanoparticles on TiO₂ in that reaction, we have explored its scope in other cross-couplings.

In the present work, we report the sp³C-sp³C cross-coupling between tetrahydrofuran (THF) and various alkanes, like cyclohexane, with Pt/TiO₂ photocatalyst (Scheme 1). The direct activation of an sp³C–H bond to make new C–C bonds is one of the most desired reactions in synthetic organic chemistry.⁴⁷⁻⁴⁹ There are several reports on the cross-coupling reactions between cyclic ethers like THF and alkanes or aromatics.⁵⁰⁻⁵⁵ However, all of them have some drawbacks e.g. use of a strong base,^{50,51} a metal complex as catalyst,^{50,52,53} a large amount of metal co-catalyst, 53,55 high reaction temperature 52,53,55 and so on. Usage of such additives makes the techniques less green, hence, a more sustainable methodology has to be developed to carry out such reactions. In the present work, we have employed a heterogeneous metal loaded titanium oxide photocatalyst and found that the photocatalyst can promote the cross-coupling reactions through C-C bond formation. We are interested in elucidating the role of the deposited metal particles which are crucial for the reaction. Different

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⁺ Electronic Supplementary Information (ESI) available: Synthesis of 2cyclohexyltetrahydrofuran (**1a**), Photochemical stability of **1a**, Photocatalytic reaction between THF and cyclohexane for 24 h, Photocatalytic reaction of THF with cyclopentane and *n*-hexane, ESR measurements, and temperature controlled reaction tests are explained in ESI. See DOI: 10.1039/X0XX00000x

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techniques like XAFS analysis, ESR measurement, isotopic experiments, and temperature controlled reactions were used to elucidate the reaction mechanism. The combined observations were used to propose a bifunctional role of Pt nanoparticles on TiO_2 for the cross-coupling reactions. These findings would be helpful to design efficient catalytic systems.



Scheme 1 Direct cross-coupling reaction between THF and cyclohexane with Pt/TiO₂ photocatalyst

2. Experimental

2.1. Preparation of catalysts

A TiO₂ sample obtained from Catalysis Society of Japan as JRC-TIO-8 (anatase, specific surface area = $338 \text{ m}^2/\text{g}$), was utilized to prepare the various metal loaded TiO₂ photocatalysts. The samples were prepared by a photodeposition method as follows. 4 g of the TiO₂ sample was dispersed in ion-exchanged water and stirred under photoirradiation for 30 min from a xenon lamp (PE300 BUV), followed by the addition of methanol and different metal precursor solutions like H₂PtCl₆ for Pt, HAuCl₄.4H₂O for Au, RhCl₃.3H₂O for Rh and PdCl₂ for Pd. Then the resultant suspension was stirred for 15 min in the dark, and 1 h in the light. Finally, the suspension was filtered, thoroughly washed with water and dried in the oven at 325 K for 12 h. The samples so obtained were labelled as M(x)/TiO₂, where x denotes the loading amount of the metal (M) in weight%.

2.2. Characterization of catalysts

A CO pulse adsorption analysis was used to determine the dispersion and the size of the Pt and Pd particles on TiO₂. Pt L_3 -edge XAFS (X-ray absorption fine structure) analysis revealed the state of Pt nanoparticles on the Pt/TiO₂ sample recovered after the reaction. The spectra were recorded at BL9C of Photon Factory at the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF, Tsukuba Japan). A Pt foil was measured in the transmission mode, whereas the fluorescence mode was used for the Pt/TiO₂ sample. The Athena software was used to analyze the obtained spectra.⁵⁶

2.3. Reaction tests

2.3.1. Materials

All of the chemicals were of analytical grade and were used without further purification (cyclohexane, cyclopentane, *n*-hexane and 1,1'-bicyclohexyl (Nacalai Tesque, 99.7%)), THF (Wako Pure Chemicals, 99%), cyclohexane- d_{12} (Aldrich, 99.6 atom%) and THF- d_8 (Euriso-Top)). An authentic sample of the

cross-coupling product from THF and cyclohexane, **1a** in Table 2, was synthesized in the manner reported in the literature^{\dagger , 57}

2.3.2. Procedure for the reaction tests

For the photocatalytic reaction tests, a Pyrex test tube and the xenon lamp served as the reactor and light source, respectively. An optical filter was used to control the wavelength of light to ≥ 350 nm. A photocatalytic reaction test consisted of the following steps; pre-treatment of the $M(x)/TiO_2$ sample in the reactor by irradiation with the xenon lamp light for 1 h, sealing of the reactor with silicon septum before 10 min purging with argon, the introduction of the reactants by syringe, and photoirradiation with stirring for the desired time. After the reaction, the analysis of the gaseous products was done by taking a small portion of the gaseous phase in an air-tight syringe and injecting into a GC-TCD (Shimadzu GC-8A). The liquid phase was diluted by ethanol, filtrated by a syringe equipped with a PTFE filter, and analyzed by a GC-MS (Shimadzu, GC-MS-QP5050A). The amount of all products, except 1a and 1e, were determined from calibration curves for reference compounds which have a similar molecular structure to the products. So there are errors to some extent in the amounts due to the difference in the sensitivity of actual compounds and the reference compounds used here. The details are shown in each Table.

2.3.3. Mechanistic studies

The reaction between THF and cyclohexane was employed to elucidate the mechanism of the $sp^{3}C-sp^{3}C$ cross-coupling reactions.

An ESR study validated the formation of radical species from cyclohexane in the presence of UV light and the $Pt(0.1)/TiO_2$ sample. The ESR measurements were performed at room temperature with an X-band spectrometer (JEOL-RE2X) by using JEOL's TE011 cavity and by the aid of a spin trapping agent. PBN (N-tert-butyl-α-phenylnitrone). For the measurements, a portion of the suspension of the $Pt(0.1)/TiO_2$ sample (0.02 g) in a cyclohexane solution (1 ml) with PBN (0.09 g) was introduced into the ESR cavity, and then, the cavity was irradiated with the light of wavelength >400 nm from another xenon lamp (Asahi Spectra MAX-150) for about 20 min with simultaneous measurement at room temperature'.

Additionally, kinetic experiments, performed with isotopically labeled compounds such as deuterated THF and deuterated cyclohexane, and temperature controlled photocatalytic reactions gave further insight into the reaction mechanism.

3. Results and Discussion

3.1. Characterization of catalysts

3.1.1. Metal dispersion and particle size

As mentioned before, CO pulse adsorption analysis was employed to determine the dispersion and the size of Pt and Pd particles on the $M(x)/TiO_2$ samples (Table 1). Well dispersed Pt nanoparticles were obtained on the Pt(0.1)/TiO₂ sample (Table 1, entry 1). On the other hand, for the same loading Catalysis Science & Technology Accepted Manuscript

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amount, poorer dispersion and a larger particle size were obtained for Pd particles on the $Pd(0.1)/TiO_2$ (Table 1, entry 2).

 Table 1 Dispersion and average particle size of Pt and Pd particles on TiO₂ estimated by the CO adsorption method

Entry	Sample	Metal dispersion (%)	Particle size (nm)
1	Pt(0.1)/TiO ₂	42.6	2.7
2	Pd(0.1)/TiO ₂	19.8	5.6

3.1.2. State of Pt nanoparticles on TiO₂

Pt L_{III}-edge XAFS analysis was used to determine the state of Pt nanoparticles on the Pt/TiO₂ sample recovered after the reaction. Figure 1 shows the normalized Pt L_{III}-edge XANES of the Pt(0.1)/TiO₂ sample along with the reference samples of Pt foil and PtO₂. The results indicate that the state of Pt in the Pt/TiO₂ sample (Fig. 1b) was closer to that in Pt foil (Fig. 1a) and very different from PtO₂ (Fig. 1c). The photoexcitation of the Pt/TiO₂ sample generates electrons in the conduction band of TiO₂, which can be transferred to the deposited Pt nanoparticles, making them electron rich. Thus, the state of Pt nanoparticles in the Pt/TiO₂ sample should be metallic. This result also confirms that the Pt nanoparticles in Pt/TiO₂ sample can efficiently work as an electron receiver and reduce the recombination of photoelectron and holes.



Fig.1 Normalized Pt-L_{III} edge XANES spectra of (a) Pt foil (b) $Pt(0.1)/TiO_2$ sample after the reaction test and (c) PtO_2

3.2. Reaction between THF and Cyclohexane

3.2.1. Reaction with Pt(0.1)/TiO₂ sample

Before the examination of the photocatalytic cross-coupling between THF and cyclohexane with the $M(x)/TiO_2$ samples, the homo-coupling of the two reactants was tested. Under the UV light irradiation and with the Pt(0.1)/TiO_2 sample, the homo-coupling of THF proceeded to give two isomers in the liquid

phase: octahydro-2,2'-bifuran (1b, 2.4 µmol) and octahydro-2,3'-bifuran (1c, 1.9 µmol) (Table 2, entry 1). Hydrogen was the sole product observed in the gaseous phase. The other byproduct observed in the liquid phase was 2butyltetrahydrofuran (1d, 0.7 $\mu mol),$ which would be formed by the deoxygenation of 1b by the produced hydrogen. A similar reaction with cyclohexane gave 1,1'-bicyclohexyl (1e) and hydrogen (Table 2, entry 2). The absence of light or the Pt(0.1)/TiO₂ sample did not result in any product formation, proving that the homo-coupling reactions are photocatalytic. Thus, it is suggested that the photogenerated holes on TiO₂ can oxidize both THF and cyclohexane to generate the radical species and proton (eq. 1 and 2) and the radical species can combine to give the homo-coupling products.

$$\stackrel{O}{\longrightarrow} \stackrel{h\nu, h^+}{\operatorname{Pt}(0.1)/\operatorname{TiO}_2} \stackrel{O}{\longrightarrow} + H^+$$
 (1)

$$\frac{h\nu, h^{+}}{Pt(0.1)/TiO_{2}} + H^{+} (2)$$

Then, with the same procedure as before, the reaction was performed with a mixture of THF and cyclohexane, where the volumes of them were even at first. This reaction gave 2-cyclohexyltetrahydrofuran (1a) as the only cross-coupling product along with 1b, 1c, and 1d, which decreased the selectivity for 1a (Table 2, entry 3). It should be noted that 1e was not detected in these conditions.

The amount of the two reactants were varied to improve the selectivity for **1a**. Reaction with a small amount of cyclohexane did not give any **1a** (Table 2, entry 4). On the other hand, the reaction with a small amount of THF in cyclohexane gave **1a** with high selectivity (Table 2, entries 5 and 6). As entry 6 gave the highest selectivity for **1a** based on THF (S_{THF}), this condition was employed for further experiments.

The products were not observed in the reactions performed without the light or the Pt/TiO_2 sample (Table 2, entries 7 and 8), confirming that it is a photocatalytic reaction. The photostability of the cross-coupling product **1a** was also studied and it was found that **1a** exhibited a high photochemical stability (Table S1)[†]. On the other hand, a 24 h reaction between THF and cyclohexane with the $Pt(0.1)/TiO_2$ sample revealed that the photocatalytic stability of **1a** was not high (Table S2)[†]. These results are discussed in detail in the ESI[†].

3.2.2. Reaction with M(x)/TiO₂ samples

Table 3 shows the results of the reaction tests between THF and cyclohexane with various $M(x)/TiO_2$ samples under the optimized conditions. Although all the samples gave **1e**, the formation of **1a** proceeded only on the Pt and Au loaded TiO₂ samples (Table 3, entries 1–4). The Pt(0.1)/TiO₂ sample gave the maximum amount of **1a** with high selectivity S_{THF} (Table 3,

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Table 2 Photocatalytic reaction tests between THF and cyclohexane with the Pt(0.1)/TiO₂ sample ^a



Entry Reactants (ml)		Products (μmol) ^b			Selectivity ^c			
	THF	Cyclohexane	1a	1b+1c	1d	1e	S_{THF}	S _{CyH}
1	2.00	0.00	-	2.7	1.3	-	-	-
2	0.00	2.00	-	-	-	5.2	-	-
3	2.00	2.00	0.4	19.2	0.7	0.0	2	> 99
4	3.00	0.01	0.0	6.7	0.0	0.0	-	-
5	0.10	3.00	1.9	1.5	0.5	0.3	51	80
6	0.01	3.00	1.4	0.0	0.0	3.9	> 99	26
7 ^d	0.01	3.00	0.0	0.0	0.0	0.0	-	-
8 ^e	0.01	3.00	0.0	0.0	0.0	0.0	-	-

^{*a*} Reaction conditions: various amount of the reactants with 50 mg of the Pt(0.1)/TiO₂ sample was used, reaction time was 1 h, wavelength of incident light was \geq 350 nm and the light intensity was 21 mW cm⁻², reactor's temperature was ca. 298 K. ^{*b*} Amount of **1a**, **1b**, **1c** and **1d** was determined from the calibration curve of **1a** that was synthesized as per a literature⁺. Amount of **1e** was determined from the calibration curve of **1a** that was synthesized as per a literature⁺. Amount of **1e** was determined from the calibration curve of authentic sample of **1e** purchased from the company. ^{*c*} Selectivity for **1a**. S_{THF}: Selectivity for **1a** based on the converted THF was calculated as: $[100 \times \text{amount of$ **1a**(µmol)]/ [(**1a+1b+1c+1d**) (µmol)]; S_{CyH}: Selectivity for**1a** $based on the converted cyclohexane was calculated as: <math>[100 \times \text{amount of$ **1a**(µmol)]/ [(**1a+1e**) (µmol)]. ^{*d*} Reaction was performed in the dark. ^{*e*} Reaction was performed under irradiation but without the Pt/TiO₂ sample.

entry 1). Pt loading was necessary for the cross-coupling reaction, as the reactions performed with the bare TiO_2 sample **Table 3** Photocatalytic reaction tests between THF and

cyclohexane with the $M(x)/TiO_2$ samples ^a

Entry	Sample	Products (µmol)			Selectivity	
		1a	1b+1c	1e	S_{THF}	S _{CyH}
1	Pt(0.1)/TiO ₂	1.41	0.00	3.91	> 99	26
2	Pd(0.1)/TiO ₂	0.00	0.00	0.09	-	-
3	Au(0.1)/TiO ₂	0.09	0.00	0.16	> 99	36
4	Rh(0.1)/TiO ₂	0.00	0.00	0.27	-	-
5 ^b	TiO ₂	0.02	0.00	0.03	> 99	40
$^{\it a}$ Reaction conditions: 0.01 ml (123 $\mu mol)$ THF, 3 ml (27.7 mmol)						
cyclohexane and 50 mg of the $M(x)/TiO_2$ sample were used, for other						
details see Table 2. ^b Reaction was done with the pristine TiO ₂ .						

3.2.3. Effect of water

Effect of the addition of water to the reaction mixture was also studied (Table 4). The introduction of a small amount of water significantly improved the amount of **1a**, but a further increase was unproductive (Table 4, entries 1–5). On the other hand, the formation of **1e** gradually decreased with water which enhanced the selectivity of **1a**, S_{CYH} based on cyclohexane (Table 4, entries 2–5). For a fixed amount of water, the amount of **1a** increased with time and 4% yield based on THF was achieved, albeit with low overall selectivity (Table 4, entry 6). A further increase in the reaction time decreased the amount of **1a** (Table 4, entry 7).

gave only a small amount of **1a** (Table 3, entry 5).

Table 4 Effect of water on the reaction between THF and cyclohexane with the $Pt(0.1)/TiO_2$ photocatalyst ^{*a*}

		- 11 - 2				
Entry	Water (µl)	Products (µmol)		Selectivity		
		1a	1e	S_{THF}	S _{CyH}	
1	0	1.41	3.91	> 99	27	
2	2	2.06	2.92	> 99	41	
3	10	1.12	1.08	> 99	51	
4	20	0.35	0.12	> 99	74	
5	50	0	0	-	-	
6 ^b	2	5.72	7.37	> 99	44	
7 ^c	2	4.74	7.45	> 99	39	

^{*a*} Reaction conditions: Various amount of water was added, 50 mg of Pt/TiO_2 photocatalyst was used, reaction temperature was ca. 308 K, for other details see Table 3. No by-product from THF was obtained in these conditions. ^{*b*} Reaction time was 2 h. ^{*c*} Reaction time was 4 h.

3.3. Scope of the reaction

The reaction of THF proceeded well with other cyclic and acyclic alkanes (Scheme 2)^{\dagger}. The reaction between THF and cyclopentane gave 2-cyclpentyltetrahydrofuran (**2a**) as the only cross-coupling product (Table S3). On the other hand, in the reaction between THF and *n*-hexane, only 2-hexyltetrahydrofuran (**3a**) was detected (Table S4). Based on the amount of the cross-coupling product formed in the three reactions it can be proposed that the cyclic alkanes were more reactive than acyclic one for these cross-coupling reactions.

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Scheme 2 Reaction of THF with different alkanes with \mbox{Pt}/\mbox{TiO}_2 photocatalyst

3.4. Mechanistic Studies

The mechanism of the cross-coupling reactions was elucidated by examining the reaction between THF and cyclohexane with various experimental techniques as follows.

3.4.1. ESR measurements

ESR measurements were carried out to evidence the generation of the radical species in the cross-coupling reaction[†]. Figure 2 shows the ESR spectrum of the cyclohexane solution with PBN under the UV light in the presence of the Pt(0.1)/TiO₂ photocatalyst. The spectrum consists of three broad signals between the two signals of Mn marker (Mn²⁺). Computer simulations unveiled that each line consisted of a doublet. Thus, together, they represent a triple-doublet generated by nitrogen and the α -hydrogen of PBN in its spin adduct with the cyclohexyl radical (species **a** in eq. S1)[†]. Although the wavelength limitation did not allow the observation of a hyperfine structure, the g-value and the coupling constants of nitrogen and the α -hydrogen could be calculated to be 2.0011 and A_N= 1.43 mT, A_H= 0.206 mT, respectively.

The measurements performed without the light or the Pt/TiO_2 sample did not give any signals in the ESR spectrum. Thus, the formation of the cyclohexyl radical (eq. 2) with the Pt/TiO_2 sample under photoirradiation was evidenced.

On the other hand, efforts to trap the THF radicals by PBN were in vain, because PBN rapidly undergoes photodissociation in THF.⁵⁸ However, in our previous study, we found that the photogenerated holes on the Pd/TiO₂ photocatalyst could oxidize diethyl ether (DEE, $(C_2H_5)_2O$) to the radical species.³⁹ The radicals were successfully trapped and identified by the ESR measurement. The reported result was available to propose the photooxidation of THF to the radical species (eq. 1).

Thus, it was revealed that the cross-coupling reaction between THF and cyclohexane with the Pt/TiO_2 photocatalyst involves the photooxidation of both substrates to corresponding radicals by the photogenerated holes (eqn. 1 and 2).



Fig. 2 ESR spectrum of cyclohexyl radical with PBN as a spin trap in the presence of the Pt/TiO_2 photocatalyst under photoirradiation

3.3.2. Kinetic Experiments

The next point to be clarified was which radical formation process determines the rate of reaction. Table 5 shows the results of the kinetic experiments between THF and cyclohexane with the Pt(0.1)/TiO₂ photocatalyst by using deuterated compounds. When compared to the amount of **1a** obtained without any isotopically labeled molecule, it decreased in the case with deuterated cyclohexane (Table 5, entries 1 and 2). The value of k_H/k_D , a measure of the isotopic effect, was more than unity, which indicates a primary kinetic isotopic effect (KIE), originating from the higher dissociation energy of a C–D bond than that of a C–H bond.

On the other hand, a larger amount of **1a** was obtained in the reaction performed with deuterated THF (Table 5, entry 3). The value of $k_{\rm H}/k_{\rm D}$ obtained for this reaction was less than unity which symbolizes an inverse KIE.

Table 5 Kinetic experiments for the reaction between THF and cyclohexane with the Pt/TiO_2 photocatalyst ^{*a*}

1	÷ 21		
Entry	Deuterated reactant	Amount of 1a	k _H /k _D ^b
		(µmol)	
1	None	1.2	-
2	Cyclohexane-d ₁₂	0.6	2.0
3	THF-d ₈	2.4	0.5
a Decention		4 E	

^{*a*} Reaction conditions: 0.5 ml of THF, 1.5 ml of cyclohexane and 50 mg of the $Pt(0.1)/TiO_2$ photocatalyst were used for the reaction. Remaining conditions were same as those in Table 3. ^{*b*} k_H/k_D was determined from the amount of **1a** produced in entries 1 and 2 for entry 2, and those in entries 1 and 3 for entry 3, respectively.

The difference of the dissociation energy can be used to explain the observations in the kinetic experiments. The C–H bond in cyclohexane is stronger than that in THF, making its oxidation difficult than THF (C–H bond dissociation enthalpy in cyclohexane is 416.3 kJ/mol and that in THF is 385.3 kJ/mol).⁵⁹ So, if the reaction rate depends on the step involving the cleavage of C–H bond, then the reaction of THF and deuterated cyclohexane will give a normal KIE, $k_H/k_D > 1$ (Table 5, entry 2).

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Here, it is proposed that the oxidation of THF and cyclohexane would be a competitive process. The weak C-H bond in THF would make its photooxidation faster than that of cyclohexane. However, on replacement with the deuterated THF, this process would slow down, due to the increased bond strength of the C-D bond. At the same time, due to slightly increased availability of holes, the competitive reaction, i.e., the oxidation of cyclohexane to the radical species, should be accelerated in this condition. It is important that the reaction rate of this rate-determining step would increase when the rate of the competitive reaction decreases. The amount of 1a thus increased would give an inverse KIE (Table 5, entry 3). Therefore, it is suggested that the cross-coupling proceeds in the radical coupling mechanism, and the photooxidation of cyclohexane to generate cyclohexyl radical is the rate determining step in the present reaction condition.

3.3.3. Temperature controlled experiments

It is generally acceptable that the high activity of the Pt/TiO₂ photocatalyst would be due to the efficient function of the Pt nanoparticles as an electron receiver. In the present study, we propose that the high activity would be contributed also by the function of the Pt nanoparticles as metal catalyst. To elucidate the possibility of the metal catalysis by the Pt nanoparticles, we studied the effect of temperature on the photocatalytic reaction between THF and cyclohexane⁺.

As shown in Table S5, the photocatalytic reaction with the $Pt(0.1)/TiO_2$ sample in the present condition gave 1a, 1b, and 1c as the main products. The produced amount of 1a increased with the reaction temperature. Figure S1 shows the pseudo-Arrhenius plot of these data, from which the apparent activation energies for the products formation were calculated. The apparent activation energy for the formation of 1a ($E_{a,cross}$) was 65.5 kJ mol⁻¹ (Table 6). This high value suggests that acceleration of a thermal catalysis at high temperatures increases the amount of **1a**. The amount of the homo-coupling product of THF also increased with temperature, for which the value of $E_{a,homo}$ was 37.0 kJ mol⁻¹. Similar experiments were performed with the pristine TiO₂. The value for **1a** ($E_{a,cross}$) was found to be 21.3 kJ mol⁻¹ while that for homo-coupling products of THF ($E_{a,homo}$) was 33.8 kJ mol^{-1} . The similar values of $E_{a,homo}$ for the homo-coupling of THF on both the Pt/TiO_2 and TiO_2 samples indicate that this process will be a purely photocatalytic process. The thermal energy would be used for a certain dark process such as migration of electrons and holes, surface reactions, and desorption of products. On the other hand, the different values of $E_{a,cross}$ obtained for **1a** suggest that formation of **1a** will involve the metal catalysis by the Pt nanoparticles. Further, the reaction did not give any product at high temperatures and without light, which clarifies that the thermal catalysis by the Pt nanoparticles cannot proceed without the Pt/TiO₂ photocatalysis.

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Table 6 Summary of E_a for reaction between THF and cyclohexane with different photocatalysts

Entry	Photocatalyst	E _{a,cross} (kJ mol ⁻¹)	E _{a,homo} (kJ mol ⁻¹)
1	Pt/TiO ₂	65.5	37.0
2	TiO ₂	21.3	33.8

There have been several reports about the activation of various molecules on the surface of Pt metal nanoparticles.⁶⁰⁻⁶² Based on those reports, it can be proposed that the nature of Pt catalysis is the thermal activation of the C-H bond in THF or cyclohexane molecules adsorbed on its surface. Such activated molecules would more readily react with the photogenerated radicals to give 1a, hence making the reaction a hybrid of Pt/TiO₂ photocatalysis and Pt metal catalysis.

When the pristine TiO₂ was used, the photocatalytic activity was low and the rate determining step using the thermal energy should be a certain step during the dark processes after the photoexcitation, as mentioned above. However, when the Pt nanoparticles, deposited on the TiO₂ surface, function as an electron receiver in the photocatalytic reaction, the observable rate determining step using the thermal energy would not be any dark process mentioned above but the other step, i.e., the catalytic process on the metal surface.

3.3.5. Proposed mechanism

Scheme 3 shows the reaction mechanism proposed for the reaction between THF and cyclohexane with the Pt/TiO₂ photocatalyst, which is described as follows.

The excitation of TiO₂ generates photoexcited electrons and holes (1). The electrons would move to Pt nanoparticles and the holes would reach to the TiO₂ surface. The holes on the surface can oxidize the adsorbed THF, C₄H₈O, and cyclohexane, C_6H_{12} , molecules to generate the corresponding radicals $({}^{\bullet}C_{4}H_{7}O \text{ and } {}^{\bullet}C_{6}H_{11})$ and protons (2 and 3). The two radicals can combine to give 1a (4), and the two protons can be reduced by the photoexcited electron to form hydrogen on the surface of the Pt nanoparticles (5). This is a radical coupling process driven by two photons.

Simultaneously, the photogenerated radicals of THF and cyclohexane can move to the Pt nanoparticles and react with the adsorbed molecule of cyclohexane or THF, respectively. Although the reaction between the radical species and molecule may not take place naturally, the Pt metal catalyst would assist the reaction between them by the activation of C-H bond of the molecules. This provides additional pathway for the formation of 1a (6 and 7), which is the hybrid route consisting of the photocatalytic and catalytic steps. This is a one photon process.

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Pt/TiO2 photocatalytic process

$$Pt/TiO_2 \xrightarrow{hv} TiO_2(h^+) + Pt(e^-)$$
(1)

$$C_{4}H_{8}O \xrightarrow{C_{4}H_{7}O + H^{\dagger}} (2)$$

TiO₂ (h⁺) TiO₂

$$\begin{array}{c} C_6H_{12} \longrightarrow C_6H_{11} + H^{\dagger} \\ TiO_2 (h^{\dagger}) & TiO_2 \end{array}$$
(3)

$$\dot{C}_4 H_7 O + \dot{C}_6 H_{11} \longrightarrow 1a$$
 (4)

$$2 H^{\dagger} \xrightarrow{2 Pt(e^{-})} 2 Pt \qquad (5)$$

Hybrid process: Pt/TiO₂ photocatalysis + Pt thermal catalysis

$$\dot{C}_4H_7O + C_6H_{12} \xrightarrow{\Delta} 1a + H$$
 (6)

$$C_4H_8O + C_6H_{11} \xrightarrow{\Delta} 1a + H$$
 (7)

Scheme 3 Proposed hybrid reaction mechanism for the cross-coupling reaction between THF (C_4H_8O) and cyclohexane (C_6H_{12}) to give **1a** with Pt/TiO₂ photocatalyst.

4. Conclusions

In conclusion, we found that the Pt/TiO_2 photocatalyst can successfully catalyze the cross-coupling reaction between THF and various alkanes. The reaction proceeds predominantly through the radical-radical coupling mechanism, while it also takes place through a hybrid process of Pt/TiO_2 photocatalysis and Pt metal catalysis, partly.

This study clarified that the metal nanoparticles on the TiO_2 photocatalyst have a bifunctional role. While acting as an electron receiver to reduce the recombination of electron and hole, they can contribute to the photocatalytic reactions by behaving as a metal catalyst. In the present system, the catalytic role of the Pt nanoparticles was proposed to be activation of adsorbed cyclohexane or THF molecules on their surface. These adsorbed molecules can readily react with the photogenerated radicals and improve the formation of cross-coupling product.

Although the product yields reported in this study are still very low, this study has provided some mechanistic insights on the catalytic role of the metal nanoparticles loaded on the photocatalyst's surface.

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Journal Name

Graphical abstract

Pt loaded titanium oxide photocatalysts were utilized for the direct cross-coupling between tetrahydrofuran and various alkanes with hydrogen evolution. A detailed investigation revealed that the reaction was a hybrid of Pt/TiO_2 photocatalysis and Pt metal catalysis. Thus, the Pt nanoparticles were found to have a bifunctional role as an electron receiver and a metal catalyst.

