PAPER

Preparation of a platinum nanoparticle catalyst located near photocatalyst titanium oxide and its catalytic activity to convert benzyl alcohols to the corresponding ethers†

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A novel platinum nanoparticle catalyst closely located near the surface of titanium oxide, PtNP/TiO$_2$, has been prepared. This catalyst has both the properties of a photocatalyst and a metal nanoparticle catalyst, and acquired environmentally friendly catalytic activity, which cannot be achieved by just one of these catalysts, to afford ethers from benzyl alcohols under the wavelength of 420 nm.

The electrolysis of water by a heterogeneous metal oxide semiconductor (MOS) photocatalyst, called the Honda–Fujishima effect,[1] received considerable attention because it enables the conversion of solar energy. As a result, photoreactions by heterogeneous photocatalysts based on MOS have been reported until now, including numerous practical applications such as carbon dioxide reduction[2] and pollutant removal.[3]

Research on photocatalytic reactions using visible light is progressing steadily. Among them, TiO$_2$ has been extensively studied due to its high catalytic activity, low cost, non-toxicity, and long-term stability.[4,5]

Titanium oxide has a very strong oxidizing power, but it does not have a strong reducing power.[6] By using a transition metal such as platinum on titanium oxide as a support, its reducing power can be increased, and the amount of hydrogen generated in the electrolysis of water can be improved eight times compared to the case of titanium oxide alone.[7]

Furthermore, when MOS contacts the metal, a potential barrier called Schottky barrier is formed at the interface. The basic characteristic of this Schottky barrier lies in the Schottky barrier height (Φ), which represents the difference between the CB of the MOS distorted by the contact with a metal and the Fermi level (E_F) of the metal. Although it has been studied for

almost half a century, how to determine the barrier is still not well understood. Due to the formation of the Schottky barrier height, the energy required to move the electrons from the valence band of MOS to the conductor changes from E_g to Φ, and the energy becomes smaller and it changes to a longer wavelength. As a result, a photoreaction with titanium oxide using light with a wavelength longer than 387 nm has also been reported (Scheme 1)[8]

On the other hand, we have recently developed a sulfur-modified Au-supported Pd NP catalyst (SAPd) that is applicable in Suzuki–Miyaura coupling[9a,9b] and C–H functionalization[9c] (Scheme 2a). It was constructed by approximately 10 layers of self-assembled Pd(0) NPs (mean size: <5 nm) supported on a sulfur-modified Au surface. We speculated that the self-assembled Pd NPs, which were encapsulated in a sulfated *p*-xylene polymer matrix,[9d] were formed using *in situ* metal NP and nanospace simultaneous organization (PSSO), as illustrated in Scheme 2b: (i) the reduction of a high-valence metal source, (ii) growth of transition metal NPs, (iii) growth of a matrix with appropriately sized nanopores, and (iv) encapsulation of the metal NPs in these nanopores. To prepare SARu,[10] SANi,[11] SAFe(ɪɪ),[12] and SAFe(0)[13] (Scheme 2a), the PSSO method involves the *in situ* reduction of a noble metal precursor to produce *in situ* metal NPs.

In this research project, we decided to create a novel metal NP catalyst having metal NPs near the surface of TiO$_2$ by

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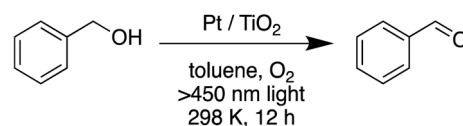
Scheme 1 Effect of sunlight exposure on aerobic oxidation of alcohols with the Pt/TiO$_2$ catalysts.

(a) previous work

Au mesh

H_2SO_4 aq.
$Na_2S_2O_8$

S - Au

Pd(OAc)$_2$
p-xylene
100 °C
→ SAPd[9]
use:
  Suzuki-Miyaura coupling
  C-H functionalization

Ru(acac)$_3$
4-MBA
p-xylene
135 °C
→ SARu[10]
use:
  Suzuki-Miyaura coupling

Ni(acac)$_2$
4-MBA
durene
190 °C
→ SANi[11]
use:
  Kumada coupling
  Negishi coupling

Fe(acac)$_3$
ethylene glycol
190 °C
→ SAFe(II)[12]
use:
  Kumada coupling

FeCl$_3$
Si-DHP
p-xylene
150 °C
→ SAFe(0)[13]
use:
  Suzuki-Miyaura coupling
  C-H amination

4-MBA =

Si-DHP =

(b) *in situ* PSSO method

metal source
+
solvent

i)
ii)
iii)

metal NPs

matrix

iv)

S-Au

i) reduction of metal source
ii) growth of transition metal NPs
iii) matrix growth
iv) encapsulation of metal NPs
  by matrix nanospaces

= Pd(0) NP
  (< 5 nm)

= sulfated
  p-xylene polymer

Au

(c) **This work**

TiO$_2$

step 1
H_2SO_4 aq.
$Na_2S_2O_8$
30 min

step 2
Pt(acac)$_3$
4-MBA
p-xylene
130 °C, 12 h

PtNP / TiO$_2$

TiO$_2$

= Pt(0) NP
  (< 5 nm)

= sulfated
  p-xylene polymer

Scheme 2 (a) Preparation of SAPd, SARu, SANi, SAFe(II) and SAFe(0) by combining *in situ* PSSO with an organic reductant, (b) *in situ* metal nanoparticle and nanospace simultaneous organization (PSSO) method and the image of the SAPd structure and (c) the preparation of PtNP/TiO$_2$.
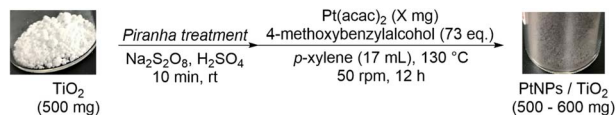
Scheme 3 Preparation of PtNPs/TiO$_2$.

substituting the gold-supported SAPd for gold with a titanium oxide (TiO$_2$) photocatalyst. Alternatively, by substituting the solid gold support for a photocatalyst, we thought that we could create a novel metal NPs catalyst with an unprecedented reactivity by combining the properties of both photocatalyst and metal nanoparticle catalyst (Scheme 2c).

Preparation and properties of catalysts

The preparation of PtNPs/TiO$_2$ using TiO$_2$ as the supported solid was carried out. As the result of examining numerous preparation conditions, since TiO$_2$ is a powder, *p*-xylene, which is a liquid at room temperature, was found to be more suitable than 1,2,4,5-tetramethylbenzene (melting point: 179.2 °C). A solution containing TiO$_2$ (500 mg), Pt(acac)$_2$ (60 mg) and 4-methoxybenzyl alcohol (1.0 mL) in *p*-xylene (17 mL) was slowly stirred at 50 rpm to obtain a gray solid (Scheme 3). At this time, the amount of platinum supported on TiO$_2$, based on inductively coupled plasma-mass spectrometry (ICP-MS), was 0.00044 wt%.

Next, to investigate the state of Pt supported on the surface of PtNPs/TiO$_2$, the Pt-L$_3$ orbital of PtNP/TiO$_2$ and Pt standard samples were measured *via* the X-ray absorption near edge structure (XANES) analysis. That is, as a result of comparing the spectra of PtNP/TiO$_2$ with those of the standard samples, Pt foil, H$_2$PtCl$_6 \cdot$ 6H$_2$O, PtCl$_2$, Pt(acac)$_2$, and PtO$_2$, Pt on PtNP/TiO$_2$ was closest to the Pt foil, and it was found that the Pt supported on was Pt(0) such as an organometallic catalyst, or Pt(0) formed into a bulk state by a metal bond (Fig. 1, left). It was also found
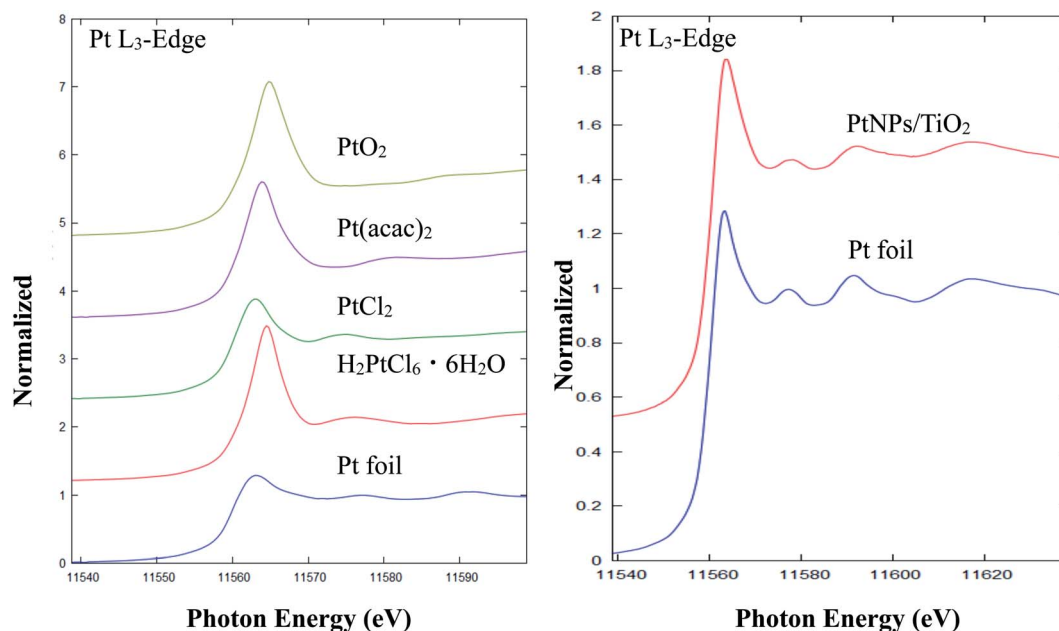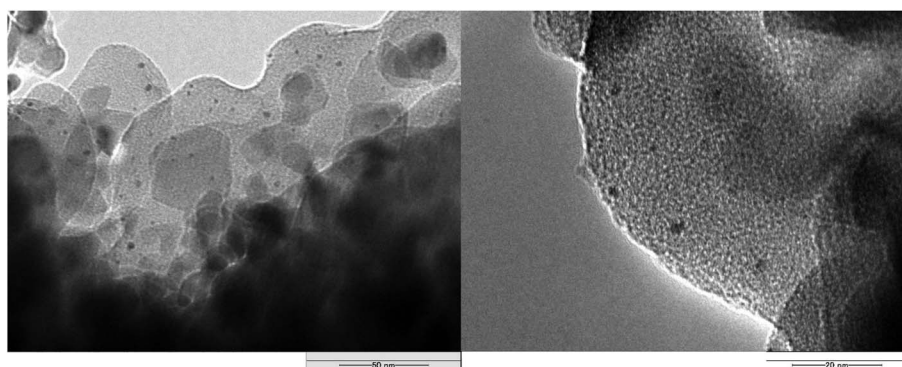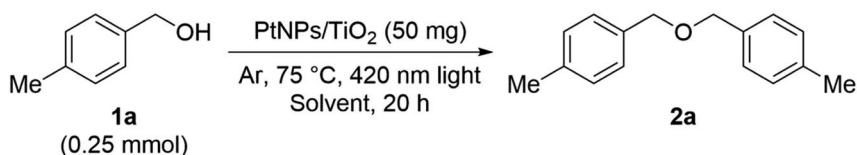

Fig. 1 XANES spectra; Pt-L$_3$ orbital.

Fig. 2 TEM image of PtNP/TiO$_2$.

Table 1 Etherification of **1a** using PtNP/TiO$_2$: effects of solvent

Entry	Solvent	Yield (%)
1	Toluene	53
2	Ethylene glycol	NR
3	DMF	NR
4	MeNO$_2$	82
5	Diethyl carbonate	89

that platinum supported on all PtNPs/TiO$_2$ is Pt(0) regardless of the amount of platinum supported (Fig. 1, right).

Furthermore, we observed PtNPs/TiO$_2$ via transmission electron microscopy (TEM) (Fig. 2). As a result, it was clarified that a polymer layer was present on the surface of titanium oxide similar to SAPd. Similar to SAPd, this polymer layer is considered to form a matrix of p-xylene and SO$_4^{2-}$ derived as (p-xylene)$_m$·(SO$_4$)$_n$ polymer and Pt(0)NPs. This polymer stabilizes Pt(0)NPs at around 3–4 nm and prevents aggregation.

Catalytic activity

As the result of investigating the catalytic activity of the as-prepared PtNPs/TiO$_2$, it was found that this catalyst can be used as a catalyst for the etherification reaction (Table 1). Therefore, the reaction solvent aiming to improve the yield of this reaction was investigated. When using the hydrocarbon solvent toluene, **2a** was obtained in moderate yield (entry 1). On the other hand, when ethylene glycol or DMF, which are highly polar solvents, were used, the reaction did not proceed at all (entries 2 and 3). Probably, ethylene glycol is oxidized and

decomposed into an aldehyde, and DMF is decomposed due to the generation of radicals, so that the desired reaction could not proceed. When nitromethane and diethyl carbonate, which are frequently used in electrolytic synthesis, were used, the yields were improved to 82% and 89%, respectively.[14] The use of a stable aprotic high-dielectric solvent under these conditions resulted in an improved yield.

Next, we confirmed the essential elements required for this etherification reaction (Table 2). When TiO$_2$ was examined without the PtNP catalyst, the reaction did not proceed at all (entries 1 and 2). When sulfur-modified titanium oxide was used, the yield was 7% and a slight progress of the reaction could be confirmed, but the result was far below 89% (entry 3). The reaction did not proceed even in entry 4, where the PtNP catalyst and SAPt with Au as the supported solid were used, and the reaction did not substantially proceed even when PdNPs/TiO$_2$ in which PtNPs were replaced with PdNPs were used (entry 5). In addition, the reaction hardly proceeded without the light irradiation (entry 6). In addition, when this reaction was examined in air, more benzaldehyde as a by-product was obtained than in the argon atmosphere, so the reaction was
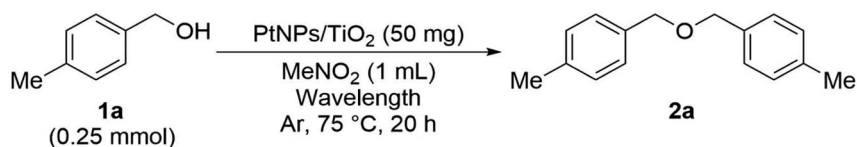
Table 2 Control experiments of the PtNP/TiO$_2$-catalyzed etherification of 4-methoxybenzylalchol
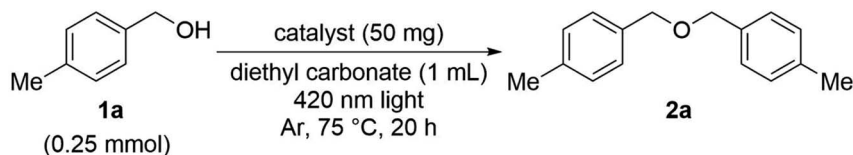
Entry	Catalyst	Yield (%)
1	Nothing	NR
2	TiO$_2$	NR
3	S–TiO$_2$	7
4	SAPt	NR
5	PdNPs/TiO$_2$	Trace
6[a]	PtNPs/TiO$_2$	Trace

[a] No light.

Table 3 Control experiments using several wavelengths of light

Entry	Wavelength (nm, W)	Yield (%)
1	365 (12)	22
2	400 (14)	35
3	420 (12)	82
4	470 (14)	14

Table 4 Substituent effects on the benzene ring
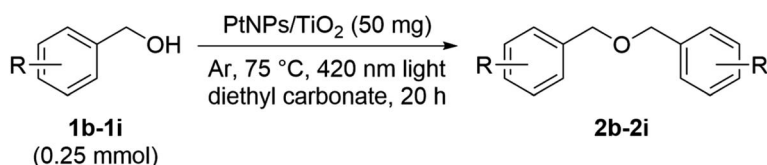
Entry	R		Yield (%)
1	H	**1b**	17
2	4-tBu	**1c**	76
3	4-Cl	**1d**	Trace
4	4-Br	**1e**	Trace
5	4-NO$_2$	**1f**	NR
6	2-Me	**1g**	44
7	3-Me	**1h**	17
8	2,4,6-Trimethyl	**1i**	82

examined in an argon atmosphere. Therefore, it was found that both PtNPs/TiO$_2$ and light are indispensable for this reaction to take place.

Next, the wavelength of the emitted light was examined (Table 3). When we performed the control experiments irradiated at a wavelength of 365 nm, which is higher in energy than the bandgap energy of titanium oxide, the yield of **2a** decreased to 22%. Since it was confirmed that the aldehyde compound was produced in a yield of 45% or more under these experimental conditions, it was considered that the alcohol was oxidized by the holes formed in titanium oxide. Furthermore, when we performed the control experiments irradiated with light at 400 nm wavelength, the yield of **2a** further decreased to 35%, and when the wavelength was extended to 470 nm, the

yield of **2a** dropped significantly, the reaction hardly proceeded, and the starting material **1a** was recovered. Therefore, light with a wavelength of 420 nm is optimal for this reaction, and we decided to use this light in subsequent experiments.

The generality of this reaction was examined under the optimum conditions obtained above. First, an unsubstituted benzyl alcohol **1b**, substrates **1c** and **1g–1i** with an alkyl group as a substituent, substrates **1d** and **1e** with a halogen atom, and substrate **1f** with a nitro group, which is a strong electron-withdrawing group, were examined. When unsubstituted **1b** and 4-tBu derivative **1c** were used, corresponding ethers **2b** and **2c** were obtained (Table 4). It is considered that the yield of **2i** was higher than that of **2g** and **2h** due to the presence of three electron-donating groups. In addition, the reaction hardly
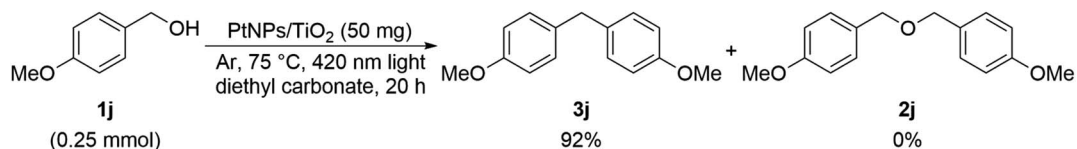
Scheme 4 Reaction of 4-methoxybenzyl alcohol **1j**.
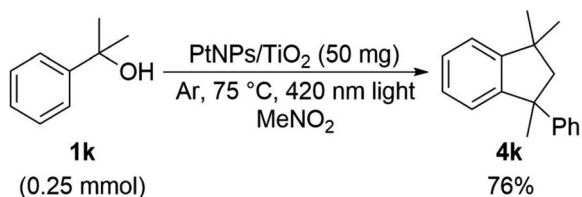
Scheme 5 Reaction of 2-phenyl-2-propanol **1k**.
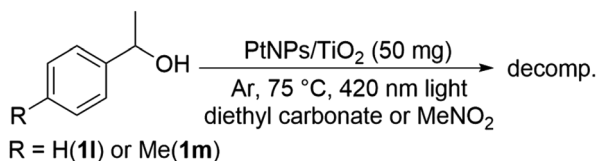
Scheme 6 Reaction of 1-phenyl-1-ethanol **1l** and 1-*p*-tolyl-1-ethanol **1m**.

proceeded on the substrates **1d** and **1e** with a halogen atom each, and the reaction did not proceed at all on the substrates **1f** that had a nitro group. From these results, it was found that an electron donating group, such as methyl group is imperative for this reaction to proceed with good yield.

Subsequently, the experiment was continued using the 4-OMe derivative **1j**. As a result, the corresponding ether **2j** was not obtained at all, instead a diphenylmethane compound **3j** was obtained (Scheme 4).[15]

Furthermore, the experiment was continued using a substrate having a substituent at the benzyl position. When 2-phenyl-2-propanol **1k**, which is a tertiary alcohol, and 1-phenyl-1-ethanol **1l** and 1-*p*-tolyl-1-ethanol **1m**, which are secondary alcohols, were used as substrates and diethyl carbonate was used as a solvent, reaction was resulted in a complex mixture. When nitromethane was used as the solvent, 1,1,3-trimethyl-3-phenylindane **4k**, in which the substrate was dimerized, was obtained only in the case of **1k** (Scheme 5), but the reaction was resulted in a complex mixture again with secondary alcohols (Scheme 6).

The experimental results obtained so far suggest that the reaction mechanism and products differ depending on the substrate. First, in order to investigate the reaction mechanism, the following reaction was examined using 4-methylbenzyl alcohol **1a** and 4-methoxybenzaldehyde **5j**. As a result, although
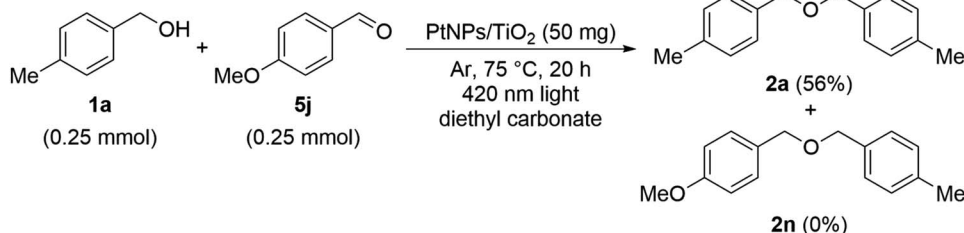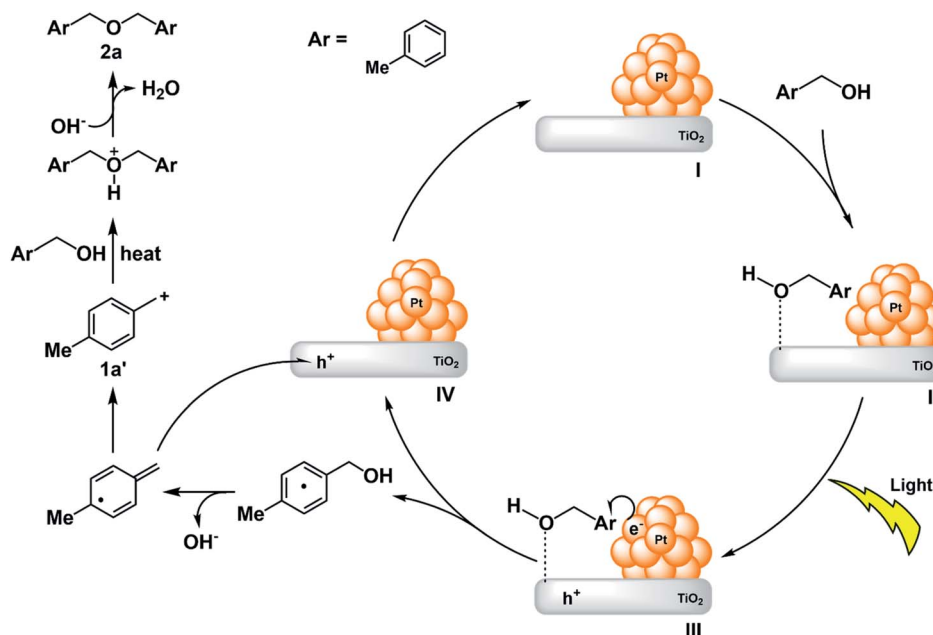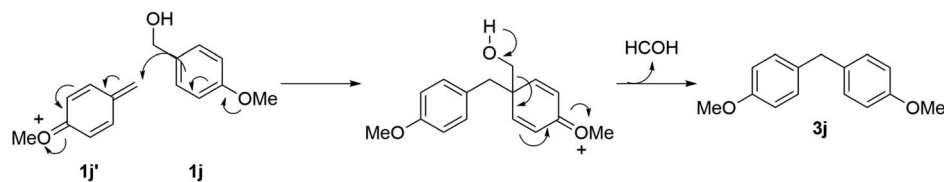

Scheme 7 Cross-over reaction of alcohol **1a** and aldehyde **5j**.

Fig. 3 Plausible reaction mechanism to give ether derivatives from benzyl alcohol derivatives.

Scheme 8 Plausible reaction mechanism of 4-methoxybenzyl alcohol **1j**.

the reactivity was lowered, dibenzyl ether derivative **2a** was obtained in a yield of 56% same as before, and compound **2l** in which the methyl and methoxy forms were coupled was not obtained at all. Therefore, it was clarified that this reaction does not pass through aldehyde **5j** as a reaction intermediate (Scheme 7).

Since the existence of TiO$_2$ and PtNPs as well as irradiation with wavelength of 420 nm were essential (Tables 2 and 3), the following reaction mechanism was estimated (Fig. 3). First, the irradiation of light causes electrons to move from titanium oxide to Pt. Alternatively, electrons move from platinum to titanium oxide. In the latter case, it is considered to take place due to the surface plasmon resonance of Pt. Here, it is assumed that electrons have moved from titanium oxide to Pt. 4-Methylbenzyl alcohol **1a**, which is a substrate, approaches the surface of titanium oxide, and electrons on Pt, generated by irradiation with light, move onto the benzene ring of the substrate. Then, the hydroxyl group is desorbed, electrons are deprived of the holes formed on titanium oxide, and simultaneously, a benzyl cation intermediate **1a′** is generated, and another 4-methylbenzyl alcohol **1a** nucleophilically attacks the benzyl cation intermediate **1a′** to afford ether **2a**.

When the substrate is 4-methoxybenzyl alcohol **1j**, it is considered that the ipso-position Friedel–Crafts reaction between the benzyl cation intermediate **1j′** and another 4-methoxybenzyl alcohol **1j** proceeded to give **3j**. In this case, formic acid is considered to be eliminated (Scheme 8).

As shown in Scheme 5, 1,1,3-trimethyl-3-phenylindane **4k** was obtained when **1k** of tertiary alcohol was used as a substrate. Since α-methylstyrene **6k** was considered as an intermediate in the reaction mechanism of this compound, it was confirmed that this reaction proceeds using **6k** as a substrate. As a result, 1, 1, 3-trimethyl-3-phenylindane **4k** was obtained in 77% yield (Scheme 9), and it was suggested that α-methylstyrene **6k** or an equivalent thereof was used as an intermediate.

In summary, we have prepared Pt nanoparticle catalysts closely located on a semiconductor photocatalyst titanium oxide, PtNPs/TiO$_2$, and found its unprecedented catalytic activity on the etherification reaction under the irradiation of 420 nm. All compositions of PtNPs, TiO$_2$ and irradiation of 420 nm are indispensable in this reaction. The as-prepared PtNPs/TiO$_2$ can be handled stably even in air.

Author contributions

Conflicts of interest

There is no conflict of interest to declare.

## Note added after first publication

This article replaces the version published on 23 Jun 2021, which contained errors in Scheme 2 and Figure 1. The correct versions are now shown.

Acknowledgements

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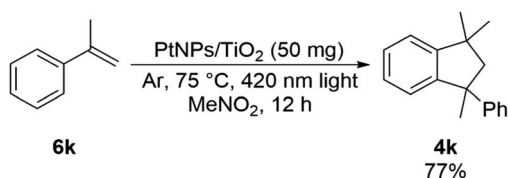
Scheme 9 Identification of intermediates derived from phenylindane derivative **4k**.

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14 Although we repeatedly used the catalyst, we have not succeeded in its repeatedly use until now.

15 When we used the **2j** as the starting material under the optimized conditions, we couldn't get the **3j** as the product and just recovered **2j**.