

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Yamamoto, T. Ohara and H. Yoshida, *Catal. Sci. Technol.*, 2018, DOI: 10.1039/C7CY02566A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/catalysis

Journal Name

COMMUNICATION



Visible-light-induced Photocatalytic Benzene/Cyclohexane Crosscoupling Utilizing a Ligand-to-metal Charge Transfer Benzene Complex Adsorbed on Titanium Oxides

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1059/X0XX00

www.rsc.org/

The cross-coupling reaction of benzene and cyclohexane molecules proceeded selectively over Pd-modified titanium dioxide photocatalysts under visible light. A ligand-to-metal charge transfer surface complex of benzene adsorbed on a titanium oxide was proposed as the key species for the selective formation of the cross-coupling product.

A. Yamamoto,*^{ab} T. Ohara,^a and H. Yoshida*^{ab}

Titanium dioxide (TiO_2) photocatalysts promote various reactions such as water splitting,¹ the decomposition of harmful organic and inorganic molecules,² and synthesis of organic compounds.³ However, in several cases, organic synthesis using TiO₂ photocatalysts exhibits poor selectivity, possibly because photo-generated holes in the TiO₂ valence band, owing to their deep oxidation potential, oxidize molecules indiscriminately. Thus, improvement of selectivity in photocatalytic reactions remains challenging.

Recently, photocatalytic reactions for the selective formation of chemical compounds have been reported.⁴ One of these successful approaches employs ligand-to-metal charge transfer (LMCT) from the adsorbed molecule to the TiO₂ conduction band using visible light (in-situ doping).⁵ Using this approach, selective photocatalytic reactions were reported, for example, photooxidation of alcohols⁶ and amines,⁷ photoactivation of ammonia,⁸ where molecules adsorbed onto the photocatalyst surface by chemical bonding exhibited high selectivity towards the desired products under visible light.

Although several LMCT surface complexes have been

reported,^{5b} only a few studies have dealt with non-chemically bonded molecules (*e.g.*, benzene) onto a TiO_2 surface.⁹ Moreover, the mechanism in these cases is unclear, possibly owing to the weak interactions. Herein, we demonstrate a selective cross-coupling reaction between benzene and cyclohexane molecules via the C–H bond activation using the LMCT surface benzene complex on a TiO₂ photocatalyst. In addition, the origin of the selectivity improvement was discussed in terms of the C–H bond dissociation energy (BDE).

Metal co-catalysts were photodeposited on a TiO₂ sample (JRC-TIO-8, anatase, 338 m² g⁻¹).⁺ The catalyst is referred to as M/TiO₂ (M = Rh, Pt, Au, Pd, Ag, Ni, and Co). The reaction was carried out in a closed reactor under Ar atmosphere at room temperature with a 300 W xenon lamp using a long pass filter (light wavelength, λ > 350 or 400 nm) (ESI).⁺

The coupling reaction of benzene and cyclohexane over metal (M)-modified TiO₂ photocatalysts (M = Rh, Pt, Au, Pd, Ag, Ni, and Co; 0.1 wt%) under UV-light irradiation afforded both cross-coupling [phenylcyclohexane (PCH)] and homo-coupling [bicyclohexyl (BCH) and biphenyl (BP)] products (Table 1). The reaction did not proceed in the dark or in the absence of a photocatalyst. Moreover, no product was generated with a Pd/Al₂O₃ sample under visible light. These results indicate that the reaction proceeded with the aid of TiO_2 photocatalysis. The formation of the three products (Table 1, entry 3) suggests that cyclohexyl and benzyl radicals were generated under these conditions¹⁰ and the coupling afforded the three products (eq. 1–6). By comparison between the pristine TiO_2 and M/TiO₂ samples, noble metal co-catalysts improved the photocatalytic activity to PCH (entries 1-9). The Rh/TiO₂ and Pt/TiO₂ samples displayed the high activity leading to the PCH formation after 1 h. However, comparable amounts of the homo-coupling products were also formed. Conversely, the $\ensuremath{\text{Pd}/\text{TiO}_2}$ sample exhibited relatively high selectivity towards PCH formation, where BCH formation was drastically suppressed. Thus, Pd was selected as the co-catalyst for this reaction. Unfortunately, the homo-coupling reactions also proceeded to some extent, even in the Pd/TiO_2 sample. In

^a Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Yoshida Nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan.

^{b.} Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8520, Japan.

E-mail: yamamoto.akira.2a@kyoto-u.ac.jp (AY), yoshida.hisao.2a@kyoto-u.jp (HY) † Electronic supplementary information (ESI) available: experimental details, Pd-K edge XAFS spectra of Pd/TiO₂ samples, and free energy calculation method. See DOI: 10.1039/x0xx00000x

COMMUNICATION

Published on 12 January 2018. Downloaded by Fudan University on 12/01/2018 13:47:04

DOI: 10.1039/C7CY02566A Journal Name

addition, compared to the total amount of PCH, BCH, and BP, a large amount of hydrogen evolution was observed in the Pt/TiO₂, Au/TiO₂ and Pd/TiO₂ samples (Table 1, entry 3–5). This low mass-balance between the hydrogen and the coupling products suggests that unfavorable reactions (*e.g.*, dehydrogenative polymerization) would occur in parallel under UV light.

Table 1 Photocatalytic coupling reaction of cyclohexane and benzene^{*a*}.

$() + () \longrightarrow $									
	-			PCH		BCH		BP	
	Entry	Catalyst	t ^b	Product amount / μmol Selec. ^c (%					^c (%)
			/ h	PCH	BCH	BP	H ₂	Sc	SB
	1	TiO2 ^d	1	0.7	4.2	n.d. ^e	06	7.4	>99
	2	Rh/TiO2 d	1	5.7	2.4	0.6	05	53	83
	3	Pt/TiO ₂ ^d	1	5.6	3.6	0.3	34	40	90
	4	Au/TiO2 ^d	1	4.9	3.3	1.0	26	42	71
	5	Pd/TiO ₂ ^d	1	3.7	0.5	1.1	23	78	64
	6	Ag/TiO2 ^d	1	2.2	1.7	0.2	03	38	83
	7	Ni/TiO ₂ ^d	1	0.5	0.7	n.d. ^e	01	13	>99
	8	Co/TiO ₂ ^d	1	0.3	0.3	n.d. ^e	n.d. ^e	35	>99
	9	Pd/TiO ₂ ^f	1	0.6	n.d. ^e	n.d. ^e	02	>99	>99
	10	Pd/TiO ₂ ^f	3	2.3	n.d. ^e	n.d. ^e	02	>99	>99
	11	Pd/TiO ₂ ^f	6	3.4	0.4	n.d. ^e	01	81	>99
	13	Pt/TiO ₂ ^f	6	1.1	0.3	n.d. ^e	01	65	>99
	14	TiO ₂ ^f	6	0.3	0.1	n.d. ^e	n.d. ^e	55	>99

^{*a*} Catalyst amount: 0.20 g, metal loading: 0.1 wt%, Ar atmosphere. Cyclohexane (2 mL) and benzene (2 mL) were used for the reaction. ^{*b*} Reaction time under irradiation, ^{*c*} Selectivity to phenylcyclohexane (PCH) based on cyclohexane (S_c) and benzene (S_b) consumed in the reaction test (the detail is shown in ESI⁺), ^{*d*} Wavelength of light λ > 350 nm, ^{*e*} not detected, ^{*f*} λ > 400 nm.

$TiO_2 + h\nu \rightarrow e_{cb} + h_{vb}^+$	(1)
$h^+_{vb} + C_6H_6 \rightarrow TiO_2 + \cdot C_6H_5 + H^+$	(2)
$h^{+}_{vb} + C_6 H_{12} \rightarrow TiO_2 + \cdot C_6 H_{11} + H^+$	(3)
$\cdot C_6H_5 + \cdot C_6H_5 \rightarrow C_6H_5 - C_6H_5 \text{ (BP)}$	(4)
$\cdot \mathbf{C}_{6}\mathbf{H}_{5} + \cdot \mathbf{C}_{6}\mathbf{H}_{11} \rightarrow \mathbf{C}_{6}\mathbf{H}_{5} - \mathbf{C}_{6}\mathbf{H}_{11} \text{ (PCH)}$	(5)
$\cdot C_6 H_{11} + \cdot C_6 H_{11} \rightarrow C_6 H_{11} - C_6 H_{11}$ (BCH)	(6)
$e_{cb}^{-} + H^{+} \rightarrow H$	(7)
$\cdot H \rightarrow 1/2 H_2$	(8)

We next performed the reaction experiment using a different wavelength using the Pd/TiO₂ sample, which is known to affect the activity and selectivity of the reaction.¹¹ As illustrated in Table 1, a higher selectivity towards PCH was observed under visible light ($\lambda > 400$ nm, entries 9–11) than UV-light ($\lambda > 350$ nm, entry 3) . Surprisingly, BP formation was completely suppressed by limiting the light wavelength. The state of Pd co-catalysts after the reactions under UV-visible and visible light were similar each other by X-ray adsorption fine structure (XAFS) spectroscopy as shown in Fig. S1 (ESI).⁺ Thus, the deference in selectivity strongly suggests that the reaction proceeded via a different mechanism when only visible light was applied.

To investigate the light-absorbing species under visible light, UV-Vis diffuse reflectance spectra (DRS) were recorded in the presence of benzene and cyclohexane (Fig. 1). An edge shift was observed after benzene was added to the TiO₂ sample; on the other hand, this shift was not observed when cyclohexane was added instead of benzene. The upper panel illustrates the difference spectrum (b-a), and a clear band appeared by the addition of benzene. These results indicate that the emerged absorption after the benzene addition was due to the benzene species adsorbed onto the TiO₂ surface.^{9a} Similar phenomena were also reported for several molecules such as catechol, alcohol, amine, ammonia.⁸ In these studies, the molecules were adsorbed via chemical bonding, and the resultant absorption bands were attributed to LMCT excitation from the adsorbed molecules to the TiO₂ conduction band.¹² On the other hand, it was reported that the absence of dissociative reactivity between the benzene molecules and the pristine TiO_2 (110) surface due to the little hybridization between TiO_2 and benzene electronic states.¹³ Furthermore, the emerged band position was close to that of an electron donor-acceptor complex of benzene (π electron donor) and TiCl₄ (electron acceptor),¹⁴ where the complex was converted to the radical pair $[ArH^+, TiCl_4^-]$ form by LMCT excitation with visible light. Thus, the adsorption band could be attributed to the π interaction between the benzene complex and the TiO₂ surface (eqs. 9, 10), which was also proposed in toluene-Nb₂O₅ system^{9b} recently.



Published on 12 January 2018. Downloaded by Fudan University on 12/01/2018 13:47:04

(13)



Fig. 1 UV-Vis DR spectra of the TiO_2 sample without adsorbate (a), with benzene (b), and with cyclohexane (c), and the action spectrum (green circle, left axis). Upper panel shows the difference spectrum (b-a).

$$C_6H_6 + TiO_2 \rightarrow C_6H_6-TiO_2$$
 (surface complex) (9)

$$C_6H_6$$
-TiO₂ (surface complex) $\rightarrow C_6H_6^+$ + TiO₂ (e⁻) (10)

To investigate the reaction mechanism, we next measured the apparent quantum yield (AQY) for the reaction by applying eq. 11 using various monochromatic lights.[†]

$$AQY(\%) = \frac{\text{Total amounts of PCH, BCH, and BP}}{\text{Number of incident photons}}$$
(11)

The AQY was 1.5% at 360 nm, and decreased with the wavelength of the light as shown in Fig.1B. The trend, i.e., the action spectrum, coincided with the absorption spectrum of the adsorbed benzene molecules on the TiO_2 surface, supporting the LMCT mechanism from the adsorbed benzene molecule to the TiO_2 conduction band (eq. 10).

The formation of BP was markedly suppressed under visible light when compared to UV light (entries 5 and 11, Table 1). The formation of benzene radical cation intermediates provides us a reasonable explanation of the suppression of BP formation based on the C–H BDEs¹⁵ of benzene (472.2 kJ mol⁻¹) and cyclohexane (416.3 kJ mol⁻¹). The change in Gibbs energy $(\Delta G^{\circ}=19 \text{ kJ mol}^{-1})$ of the benzyl radical formation by the benzene radical cation (eq. 12) was calculated from the BDE and the one-electron oxidation potential of benzene (2.48 V vs SCE)¹⁶ and hydrogen radicals (-1.87 V vs SCE)¹⁷ (ESI)⁺. The positive value for benzene indicates that the reaction hardly proceeds at room temperature because of the thermodynamic limitation. Conversely, the reaction between the benzene and radical cation cyclohexane (eq. 13) was thermodynamically favorable ($\Delta G^{\circ} = -37 \text{ kJ mol}^{-1}$). Thus, the formed benzene radical cation activates cyclohexane more easily than benzene.

$$C_6H_6^+ + C_6H_6 \to C_6H_6 + \cdot C_6H_5 + H^+$$
 (12)

$$C_6H_6^+ + C_6H_{12} \rightarrow C_6H_6 + \cdot C_6H_{11} + H^+$$

Our previous studies demonstrated that Pd co-catalysis promoted the addition of photo-generated radical species to an aromatic benzene ring over the Pd-modified TiO₂ photocatalyst.^{10b, 18} The significant promotion effect of the Pd co-catalyst, compared to pristine TiO₂ and Pt/TiO₂, was also observed (entries 11-13) in the present study. It is likely that the Pd co-catalyst promotes the attack of the cyclohexyl radical to the benzene molecule. Isotope experiments were carried out to evidence the radical addition mechanism (Table 2). When cyclohexane- d^{12} was employed, the $k_{\rm H}/k_{\rm D}$ value was determined as 1.0 and kinetic isotope effect (KIE) was not observed while slightly lower than unity values were obtained with benzene- d° (inverse KIE). These results indicate that the dissociation of the C-H bond of cyclohexane and benzene was not the rate-determining step of the reaction. The inverse KIE suggests that the reaction proceeds via a cyclohexyl radical addition into benzene (eq. 14) and the addition step is the rate-determining step. The radical attacks result in hybridization of benzene carbon from sp^2 to sp^3 , and the change would lead to the inverse kinetic effect due to the change of these zero point energies,¹⁹ and the phenomenon was also observed in our previous papers.^{18a} The consideration of the rate-determining step is also supported by the positive effect of Pd loading on the activity because the Pd co-catalyst would accelerate the radical addition to benzene.^{10b, 18} Moreover, a small amount of the homo-coupling product of cyclohexane was also generated in the Pd/TiO₂ sample under visible light, which indicating that cyclohexyl radical formation (eq. 13) and its homo-coupling (eq. 6) occurred during the reaction under visible light. These reactions are consistent with the proposed mechanism. On the other hand, the photogenerated electron reduces the proton on the Pd site into the hydrogen atom (eq. 7), and the hydrogen atoms formed in eqs. 7 and 15 desorb as a molecular hydrogen (eq. 8).

$$\cdot C_6 H_{11} + C_6 H_6 \to \cdot C_6 H_6 - C_6 H_{11}$$
(14)

$$C_6H_6 - C_6H_{12} \rightarrow C_6H_5 - C_6H_{11} (PCH) + H.$$
 (15)

Table 2 Isotope experiment in the photocatalytic coupling reaction.^a

Entry	Reactants		Pro	Product amount / µmol				
Entry			PCH	BCH	BP	H_2		
1	C_6H_{12}	C_6H_6	0.80	n.d. ^b	n.d. ^b	0.95	-	
2	C ₆ D ₁₂	C_6H_6	0.78	n.d. [#]	n.d. [#]	1.00	1.00	
3	C_6H_{12}	C_6D_6	1.10	n.d. ^b	n.d. ^b	0.56	0.75	

^{*a*} Catalyst: 0.1wt% Pd/-TiO₂ samples (0.10 g), Ar atmosphere. Cyclohexane (1 mL) and benzene (1 mL) were used for the reaction, reaction time: 1 h, λ > 400 nm. ^{*b*} $k_{\rm H}/k_{\rm D}$ = (PCH amount in entry 1)/(PCH amount in entry 2 or 3), ^{*c*} not detected.

In summary, reaction mechanisms for the cross-coupling reaction between benzene and cyclohexane under UV and visible light are proposed (Fig. 2). In the UV-irradiated Pd/TiO_2 system (Fig. 2a), holes in the TiO_2 valence band react with

COMMUNICATION

benzene and cyclohexane to form the corresponding radicals. The radical coupling provides three products: PCH, BCH, and BP. On the other hand, visible light excitation of the LMCT complex of benzene adsorbed on TiO₂ (Fig. 2b) and the resulting benzene radical cation selectively activates cyclohexane to form cyclohexyl radical. The cyclohexyl radical attacks benzene molecule via the addition-elimination route to form PCH (eqs. 14, 15). The selective formation of cyclohexyl radical completely suppresses the homo-coupling of benzene. Furthermore, acceleration of the addition of the cyclohexyl radical to benzene by a Pd co-catalyst suppresses the formation of BCH. Thus, the selective formation of crosscoupling products was achieved via the surface-benzenecomplex-mediated LMCT mechanism with the aid of Pd metal catalysis.



Fig. 2 Schematic illustration of the reaction mechanism under visible light and UV-light.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number JP16K14477 as Grant-in-Aid for Challenging Exploratory Research. The XAFS experiments were performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2016G643).

Conflicts of interest

The authors declare no competing financial interest.

Notes and references

- 1. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37.
- a) A. Fujishima, T. N. Rao and D. A. Tryk, J. Photochem. Photobiol., C, 2000, 1, 1–21; b) T. Ochiai and A. Fujishima, J. Photochem. Photobiol. C, 2012, 13, 247.
 a) M. Fagnoni, D. Dondi, D. Ravelli and A. Albini, Chem. Rev., 2007, 107, 2725; b)
- D. Friedmann, A. Hakki, H. Kim, W. Choi and D. Bahnemann, *Green Chem.*, 2016, 18, 5391.
- a) Y. Shiraishi and T. Hirai, J. Photochem. Photobiol. C, 2008, 9, 157–170; b) H. Yoshida, H. Yuzawa, M. Aoki, K. Otake, H. Itoh and T. Hattori, Chem. Commun., 2008, 4634; c) H. Yuzawa and H. Yoshida, Chem. Commun., 2010, 46, 8854–8856;

d) T. Shishido, K. Teramura and T. Tanaka, *Catal. Surv. Asia.*, 2011, **15**, 240; e) H. Yuzawa, S. Yoneyama, A. Yamamoto, M. Aoki, K. Otake, H. Itoh and H. Yoshida, *Catal. Sci. Technol.*, 2013, **3**, 1739; f) X. Lang, X. Chen and J. Zhao, *Chem. Soc. Rev.*, 2014, **43**, 473; g) X. Lang, J. Zhao and X. Chen, *Angew. Chem. Int. Ed.*, 2016, **55**, 4697; h) J. Kou, C. Lu, J. Wang, Y. Chen, Z. Xu and R. S. Varma, *Chem. Rev.*, 2017, **117**, 1445; i) A. Tyagi, A. Yamamoto, T. Kato and H. Yoshida, *Catal. Sci. Technol.*, 2017, **7**, 2616.

- a) T. Shishido, K. Teramura and T. Tanaka, *Catal. Sci. Technol.*, 2011, **1**, 541–551;
 b) G. Zhang, G. Kim and W. Choi, *Energy Environ. Sci.*, 2014, **7**, 954–966; c) M. Fukui, A. Tanaka, K. Hashimoto and H. Kominami, *Chem. Commun.*, 2017, **53**, 4215.
- a) T. Shishido, T. Miyatake, K. Teramura, Y. Hitomi, H. Yamashita and T. Tanaka, J. Phys. Chem. C, 2009, 113, 18713–18718; b) S. Higashimoto, N. Suetsugu, M. Azuma, H. Ohue and Y. Sakata, J. Catal., 2010, 274, 76; c) S. Higashimoto, K. Okada, T. Morisugi, M. Azuma, H. Ohue, T.-H. Kim, M. Matsuoka and M. Anpo, Top. Catal., 2010, 53, 578; d) S. Furukawa, T. Shishido, K. Teramura and T. Tanaka, Chemphyschem, 2011, 12, 2823; f) S. Furukawa, T. Shishido, K. Teramura and T. Tanaka, Chemphyschem, 2014, 15, 2665.
- a) X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji and J. Zhao, *Chem. Eur. J.*, 2012, **18**, 2624; b) S. Furukawa, Y. Ohno, T. Shishido, K. Teramura and T. Tanaka, *J. Phys. Chem. C*, 2013, **117**, 442.
- S. Yamazoe, K. Teramura, Y. Hitomi, T. Shishido and T. Tanaka, J. Phys. Chem. C, 2007, 111, 14189–14197.
- a) A. Ramakrishnan, S. Neubert, B. Mei, J. Strunk, L. Wang, M. Bledowski, M. Muhler and R. Beranek, *Chem. Commun.*, 2012, 48, 8556–8558; b) K. Tamai, K. Murakami, S. Hosokawa, H. Asakura, K. Teramura and T. Tanaka, *J. Phys. Chem. C*, 2017, 121, 22854.
- a) H. Yuzawa, J. Kumagai and H. Yoshida, J. Phys. Chem. C, 2013, 117, 11047–11058; b) H. Yoshida, Y. Fujimura, H. Yuzawa, J. Kumagai and T. Yoshida, Chem. Commun., 2013, 49, 3793.
- 11. S. Fukuzumi and K. Ohkubo, Chem. Sci., 2013, 4, 561.
- a) Y. Wang, K. Hang, N. A. Anderson and T. Lian, J. Phys. Chem. B, 2003, 107, 9434–9440; b) S. Varaganti and G. Ramakrishna, J. Phys. Chem. C, 2010, 114, 13917–13925.
- J. Zhou, S. Dag, S. D. Senanayake, B. C. Hathorn, S. V. Kalinin, V. Meunier, D. R. Mullins, S. H. Overbury and A. P. Baddorf, *Phys. Rev. B*, 2006, 74, 125318.
- 14. K. Brueggermann, R. S. Czernuszewicz and J. K. Kochi, J. Phys. Chem., 1992, 96, 4405.
- Y.-R. Luo, in Comprehensive Handbook of Chemical Bond Energies, CRC Press, 2007, pp. 19.
- 16. P. B. Merkel, P. Luo, J. P. Dinnocenzo and S. Farid, J. Org. Chem., 2009, 74, 5163.
- a) E. Baciocchi, T. Del Giacco and F. Elisei, J. Am. Chem. Soc., 1993, 115, 12290; b)
 E. Baciocchi, T. Del Giacco, O. Lanzalunga, P. Mencarelli and B. Procacci, J. Org. Chem., 2008, 73, 5675.
- a) A. Tyagi, T. Matsumoto, T. Kato and H. Yoshida, *Catal. Sci. Technol.*, 2016; b) E. Wada, T. Takeuchi, Y. Fujimura, A. Tyagi, T. Kato and H. Yoshida, *Catal. Sci. Technol.*, 2017, 7, 2457.
- A. Streitwieser, R. H. Jagow, R. C. Fahey and S. Suzuki, J. Am. Chem. Soc., 1958, 80, 2326.

Catalysis Science & Technology Accepted Manuscript

Table of Contents

High selectivity was achieved in photocatalytic cross-coupling of benzene and cyclohexane by photoexcitation of benzene surface complex

