Selective cross-coupling between pyridine and cyclohexane through a photoexcitation of pyridine surface complex on titanium oxide

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Abstract: Direct selective cross-coupling between pyridine and cyclohexane proceeded over metal loaded titanium oxide photocatalyst (M/TiO_2) under visible light irradiation (λ > 400 nm). A new absorption band appeared around 360 nm in wavelength on the DR UV-vis spectrum of the pyridine-adsorbed TiO_2 photocatalyst. It was suggested that the reaction proceeds selectively when only the surface complex consisting of the TiO_2 surface and adsorbed pyridine is excited under visible light irradiation.

Keywords: Pyridine-adsorbed titanium oxide, Photocatalysis, Cross-coupling.

1. Introduction

Titanium oxide (TiO_2) is one of the most practical photocatalysts with many applications including photocatalytic organic synthesis.[1] One of the problems of TiO_2 photocatalyst is difficulty in selective oxidation because of its strong oxidation ability that arises from the high potential of its valence band. In this regard, some recent studies have revealed that adsorption of molecules on TiO_2 surface leads to the formation of surface complexes that can be excited by visible light to promote various reactions.[2] In these systems, selective oxidation can be achieved by the hole, which results from electron excitation from a new energy level generated by molecular adsorption on the surface of TiO_2. In this study, we employed pyridine as an adsorbate to form the surface complex and found that a selective C–C bond formation reaction takes place through a photoexcitation of a new surface complex on the TiO_2 photocatalyst under visible light irradiation.

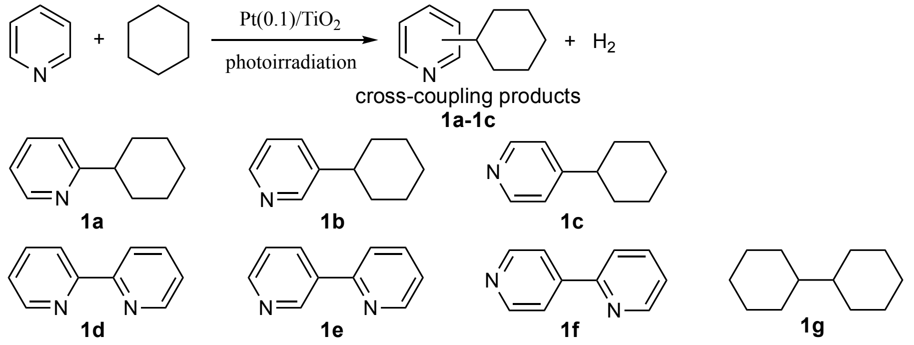
2. Experimental

Typical catalytic test was carried out as follows. A solution of pyridine (1.2 mmol) in cyclohexane (18 mmol) and a 0.1 wt% Pt loaded TiO_2 photocatalyst (0.1 g) prepared by photodeposition method were added to the test tube, followed by sealing and bubbling with a flow of argon gas for 10 min. Then the contents were stirred under irradiation for 2 h. The irradiation wavelength was limited by a long-pass filter. GC-TCD and GC-MS were used to analyze the gaseous and liquid products, respectively.

3. Results and discussion

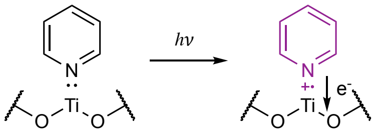
Table 1 shows the result of the cross-coupling reaction between pyridine and cyclohexane under the irradiation of both UV and visible light (entry 1) or visible light (entries 2 and 3). The reaction gave 2-cyclohexylpyridine (**1a**), 3-cyclohexylpyridine (**1b**) and 4-cyclohexylpyridne (**1c**) as the cross-coupling products as well as the homo-coupling products from pyridine and cyclohexane (**1d**, **1e**, **1f** and **1g**). The selectivity under visible light was almost two times higher than that under UV and visible light. Figure 1 shows DR UV-vis spectra of the TiO_2 sample with and without a small amount of pyridine. A new absorption band was observed around 360 nm in the difference spectrum due to the introduction of pyridine to the TiO_2 sample (Figure 1c). This absorption band can be attributed to the excitation of the surface complex between pyridine and TiO_2 (scheme 1). Isotopic experiment indicated that the rate determining step is C–H bond cleavage in cyclohexane regardless of the irradiation wavelength, and both oxidation of pyridine and cyclohexane proceed competitively under photoirradiation including UV light, but not competitively under visible light. Thus, it was suggested that the reaction path was different with the irradiation wavelength. Under the light including UV (λ > 350 nm), both pyridine and cyclohexane are oxidized by the holes generated by the photoexcitaion of TiO_2 to form their radical species, allowing the homo-coupling of these two molecules as well as cross-coupling. Under visible light (λ > 400 nm), pyridine is oxidized first by the photoexcitation of the surface complex, and this could suppress the homo-coupling, leading to the selective cross-coupling.

Table 1. Results of the reaction tests under photoirradiation with different wavelength[a]



Entry	λ / nm	Products / µmol				Selectivity (%)[b]	
		1a+1b+1c	**1d+1e+1f**	**1g**	others[c]	S_{Py}	S_{Cy}
1	>350	8.7	7.6	8.8	0.15	37	33
2	>400	5.5	1.3	0.47	0.17	68	78
3[d]	>400	9.7	1.7	1.2	0.27	74	79

[a] Reaction conditions were the same as described in experimental section. The light intensity was 130 mW cm^{-2} measured at 415 ± 55 nm. [b] Cross-coupling selectivity. Selectivity based on pyridine was calculated as: $S_{Py} = [100 \times (\mathbf{1a} + \mathbf{1b} + \mathbf{1c})\ (\mu mol)]/[\mathbf{1a} + \mathbf{1b} + \mathbf{1c} + 2 \times (\mathbf{1d} + \mathbf{1e} + \mathbf{1f})\ (\mu mol)]$; selectivity based on cyclohexane as: $S_{Cy} = [100 \times (\mathbf{1a} + \mathbf{1b} + \mathbf{1c})\ (\mu mol)]/[\mathbf{1a} + \mathbf{1b} + \mathbf{1c} + 2 \times \mathbf{1g} + \text{others}\ (\mu mol)]$. [c] Cyclohexanone and cyclohexanol. [d] Reaction time was 3 h and the light intensity was 160 mW cm^{-2}.



(Scheme 1)

4. Conclusion

Direct cross-coupling reaction between pyridine and cyclohexane proceeded selectively over metal loaded TiO_2 photocatalyst by photoexcitation of the surface complex between TiO_2 and pyridine under visible light irradiation. It was suggested that the high selectivity to cross-coupling under visible light irradiation could be due to selective first oxidation of pyridine by surface complex excitation, which is different from simultaneous oxidation of both pyridine and cyclohexane by TiO_2 excitation.

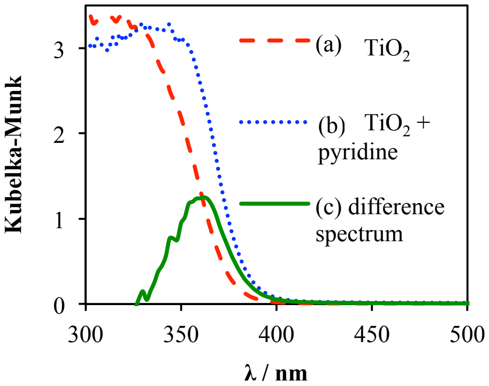


Figure 1. DR UV vis spectra of the TiO_2 sample (a), the pyridine-adsorbed TiO_2 sample (b), and the difference spectrum (c).

References

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