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Role of Pt nanoparticles on TiO_2 in the photocatalytic cross-coupling between THF and cyclohexane

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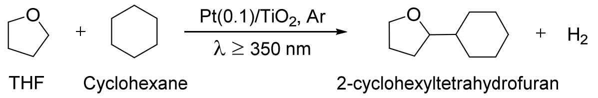
1 Introduction

Titanium oxide catalyzed organic reactions is an emerging field to develop sustainable techniques for chemical synthesis.[1] Recently, we reported a photocatalytic cross-coupling between tetrahydrofuran (THF) and cyclohexane to give 2-cyclohexyltetrahydrofuran with Pt loaded TiO_2 (Pt/TiO_2) photocatalysts (Scheme 1).[2] We also clarified the role of Pt nanoparticles in the photocatalytic reaction. For this, we performed the reaction with either Pt/TiO_2 or a physical mixture of TiO_2 and Pt/Al_2O_3 catalyst. Pt/TiO_2 photocatalyst gave a larger product yield than the physical mixture of the two catalysts.

To investigate the relationship between the state of Pt nanoparticles on the two supports and their catalytic activity, they were analyzed by XAFS.



Scheme 1 Direct cross-coupling reaction between THF and cyclohexane with Pt/TiO_2 photocatalyst

2 Experiment

The Pt/TiO_2 (ST01, Catalyst Society of Japan JRC-TIO-8) photocatalyst was prepared by a photodeposition method. The Pt/Al_2O_3 (JRC ALO-7) catalyst was prepared by an impregnation method. The loading amount of Pt was fixed to 0.1 weight% in both catalysts. The reaction between THF and cyclohexane was carried out using these catalysts and the samples were recovered after the reaction. The recovered samples were analysed by measuring Pt L_{III}-edge XAFS. A Pt foil and PtO_2 were measured in the transmission mode, while the samples were measured in the fluorescence mode.

3 Results and Discussion

Fig. 1 shows the result of the normalized XANES of Pt L_{III}-edge in the recovered samples, Pt foil, and PtO_2. The analysis revealed that the Pt nanoparticles on TiO_2 were similar to Pt foil and different from PtO_2 (Fig.1, a, b, and d). On the other hand, Pt nanoparticles on Al_2O_3 were closer to PtO_2 and quite different from Pt foil (Fig.1, a, c, and d).

So, it can be proposed that Pt nanoparticles on TiO_2 could work as an electron receiver to accept the electrons from the conduction band of TiO_2, thus becoming electron rich. However, in the physical mixture of TiO_2 and Pt/Al_2O_3, the Pt nanoparticles could not function as electron receiver. So, they remain electron deficient.

Thus, the primary role of Pt nanoparticles was proposed to be an electron receiver to reduce the recombination of electron and hole on TiO_2. Due to decreased recombination, the holes are available for the oxidation of tetrahydrofuran and cyclohexane, to generate their corresponding radicals and protons. The radical can combine to give the cross-coupling product while the protons are reduced to hydrogen radicals and ultimately to hydrogen gas.

Thus, the XAFS measurements clarified the role of Pt nanoparticles on TiO_2 in the photocatalytic cross-coupling reaction between THF and cyclohexane.

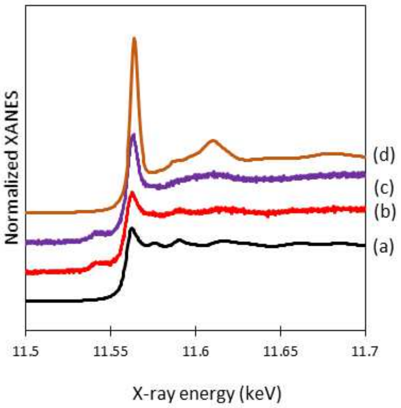


Fig. 1: Normalized XANES spectra of Pt-L_{III} edge. (a) Pt foil (b) Pt(0.1)/TiO_2-AR, (c) Pt(0.1)/Al_2O_3-AR, and (d) PtO_2

References

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