Tetrahedron xxx (2016) 1–4

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# Aerobic oxidation of alcohols in visible light on Pd-grafted Ti cluster

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ARTICLE INFO

*Article history:*
Received 10 May 2016
Received in revised form 12 July 2016
Accepted 29 July 2016
Available online xxx

*Keywords:*
Titanium cluster
Photoactive
Heterogeneous catalysis
Visible light
Aerial oxidation
Palladium nanoparticle

ABSTRACT

The titanium cluster with the reduced band gap has been synthesized having the palladium nanoparticles over the surface, which not only binds to the atmospheric oxygen but also catalyzes the oxidation of alcohols under visible light.



## 1. Introduction

The increasing focus on the utilization of visible light energy is due to its abundant nature and its impeccable tolerance towards the environment.[1] Harvesting visible light and performing chemical transformations with it in a concerted process is a high priority chemical research area.[2] Most of the photo-catalysts, especially based on titanium oxide, are active under ultra-violet light (UV);[3] visible light mediated reactions have not received similar attention.[4] There are many photoactive materials available in the literature[4] and a vast majority of them has received casual attention in academic publications due to low activity and/or limited applicability. Titanium-based materials have received maximum consideration as a photoactive material, the major limitation being their wider band gaps, which make it active only under UV irradiation conditions. The activity specific to UV light diminishes its role as a photoactive material, which can utilize solar energy in chemical reactions. Therefore, it becomes imperative to reduce the band gap in titanium materials in order to bring its activity into the visible spectrum of electromagnetic radiation.[5]

Titanium material in combination with metals and other doping elements have been used to reduce the band gap, therefore, sunlight could be utilized for the reaction.[6] Nitrogen doping in titanium oxide has been known to reduce band gap to a great extent.[7] However, the reaction of *N*-doped titanium oxide is uncontrollable in visible light due to its high activity; complete decomposition or mineralization of the organic matter is common occurrence in environmental remediation studies[8] thus rendering this catalyst incongruous in organic synthesis.[9] On the other hand, titanium oxide has been used as a support for the immobilization of transition metals and its application in oxidation chemistry is growing.[10] Hong and co-workers have immobilized palladium and gold combination over the surface of $TiO_2$ but they lost the ethos of $TiO_2$ as a photoactive material when the reaction was performed under thermal heating using oxygen atmosphere.[11] In this reaction, gold adsorbs the oxygen in the reaction media and transfers into the reactant via the bimetallic interaction with palladium. The use of titanium oxide becomes irreverent, as its photoactivity has not been utilized. Similarly, Li et al. utilized biosynthesized Au/Pd-$TiO_2$ supported nanoparticle in the oxidation reaction.[12] We strived to utilize the core property of titanium as photoactive material along with structural modification to create the cluster which can adsorb the atmospheric oxygen and transfer to the reactant in an oxidation process. Accordingly, we prepared nitrogenous titanium cluster, immobilized the palladium to develop photoactive gold-free catalyst, and demonstrated its application in selective oxidation of alcohols; titanium cluster performs the dual task by providing required activation energy and transmitting oxygen in the oxidation step.

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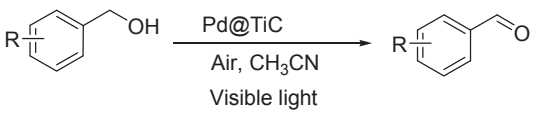
http://dx.doi.org/10.1016/j.tet.2016.07.070

## 2. Result and discussion

In continuation of our desire to develop benign methods for environmental remediation and green synthesis,[13] herein, we report a photoactive palladium-grafted titanium cluster and demonstrated its application in selective oxidation of alcohols to the corresponding carbonyl compounds. Generally, oxidation chemistry is conducted using transition metals along with a supporting co-oxidant.[14] Often, co-oxidants comprise homogenous mix of reagents and catalysts with occasional use of oxygen. However, the utility of oxygen as co-oxidant comes with various detriments that include addition of oxygen absorbing material or metals that can bind oxygen in the reaction such as gold. The main objective here is the adsorption and transmission of the required oxygen for the catalytic process.[15] However, our titanium cluster based catalyst does not require any of these additives and the reaction can be conducted under visible light using oxygen from the atmosphere. The first step in developing the active catalyst was the synthesis of titanium cluster with the significant reduction in the band gap. It has been accomplished by treating titanium (IV) isopropoxide with 4-aminobenzoic acid in isopropanol at 120 °C for 72 h;[16] shiny crystals of titanium clusters ensued which settled down at the bottom of the reaction vessel and were separated by decanting and centrifugation. The Ti-cluster was then suspended in isopropanol and treated with palladium nitrate at 80 °C; palladium salt was reduced and Pd (0) deposited over the cluster. The palladium grafted titanium cluster (Pd@TiC) was separated and its application has been evaluated in the selective oxidation of alcohols (Scheme 1).




**Scheme 1.** Pd@TiC catalyzed oxidation of alcohols.

The Pd@TiC catalyst was characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD). The percentage of palladium was determined using inductive coupled plasma atomic emission spectroscopy (ICP-AES) analysis. The SEM images of Ti-cluster and Pd@TiC catalyst illustrate the immobilization of palladium (Pd) nanoparticles (Fig. 1) with the apparent changes in the surface morphology. The immobilization of Pd was further established by XRD (Fig. 2) and the concentration confirmed to be 4.88% by ICP-AES analysis.

The activity of Pd@TiC was evaluated in the aerial oxidation of alcohols under visible light irradiation with benzyl alcohol as a model substrate. The preliminary results obtained during the screening and reaction optimization are summarized in Table 1. The

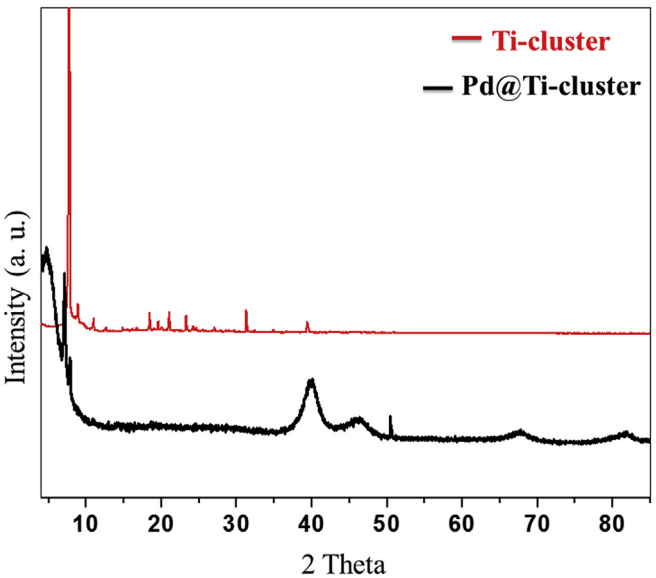



**Fig. 2.** XRD of Ti-Cluster and Pd@TiC.

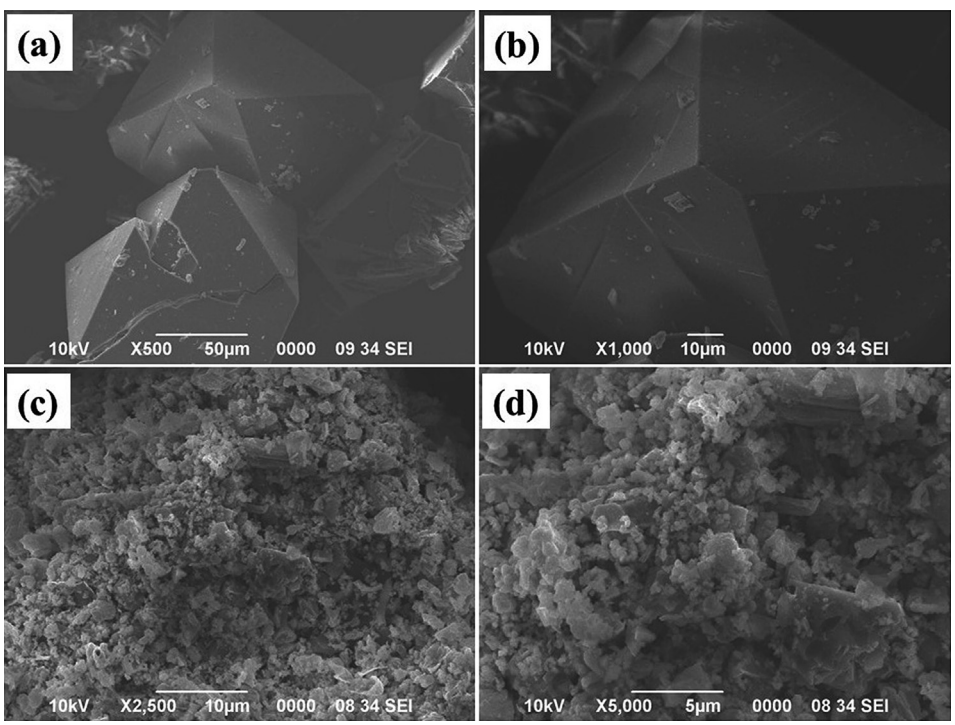



**Fig. 1.** SEM images of Ti-Cluster (a) Pyramid-like structure and (b) Close view of pyramid; (c) and (d) SEM images of Pd@TiC.

Please cite this article in press as: Verma, S.; et al., Tetrahedron (2016), http://dx.doi.org/10.1016/j.tet.2016.07.070