



Oxidation of alkane using Pt/Eu₂O₃/TiO₂/SiO₂ catalyst with O₂ and H₂ in acetic acid under mild conditions

Ichiro Yamanaka*, Yuta Suzuki, Masashi Toida

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-S1-43 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

ARTICLE INFO

Article history:
Available online 25 February 2010

Keywords:
Oxidation
Europium catalysis
Titanium catalysis
Platinum catalysis
Active oxygen
Alkane

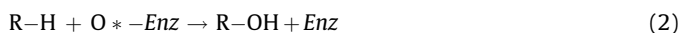
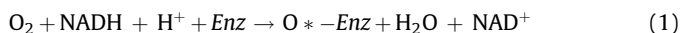
ABSTRACT

A new solid catalyst of Pt/Eu₂O₃/TiO₂/SiO₂ for oxidation of alkane was developed. Oxidation of adamantane using the multi-components supported catalyst with O₂ and H₂ was studied in acetic acid at 313 K. Several multi-components supported catalysts were prepared and tested the oxidation activity. It is found that loading order of Eu₂O₃, TiO₂ and Pt on the SiO₂ support strongly affected the oxidation catalysis. The active catalysts model was proposed from TEM-EDS analysis that very small Pt particles well dispersed on amorphous Eu₂O₃ and TiO₂ on the SiO₂ support. Eu and Ti oxides concertedly activated O₂ with electrons supplied from H₂ on Pt, and active oxygen species efficiently oxidized adamantane and other alkanes to oxygenated compounds. Active oxygen species could not be identified but its reactivity was studied. It showed radical nature for oxidation of alkanes and a cleavage of C–H bond was the rate-determining step during the oxidation.

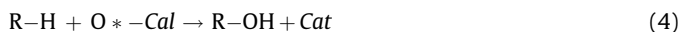
© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Oxidation of hydrocarbons under mild conditions remains an attractive topic in organic synthesis and catalysis. An essential point is how to generate active oxygen species. Monooxygenase (*Enz*) activates O₂ using NADH (2e⁻, H⁺) and H⁺, and generates active oxygen species (O*, intermediate), as indicated in Eq. (1). The *Enz* oxygenates hydrocarbon with O* to alcohol, aldehyde and so on (Eq. (2)). The reductive activation of O₂ is very powerful method for the oxidation.



An analogy of combination of NADH (2e⁻, H⁺) and H⁺ is H₂. If we can choose suitable catalyst (*Cat*), the reductive activation O₂ will perform (Eq. (3)) and produces oxygenated compounds (Eq. (4)).



Prof. Tabushi first reported application of the reductive activation of O₂ with H₂ for epoxidation of cyclohexene [1], then other researchers reported various catalyst systems for hydroxylation of aromatics, oxidation of alkanes, and epoxidation of alkenes under mild conditions [2–7]. Fairly good oxidation activity was

performed but oxidation efficiency was not enough for previous catalyst system [1–7]. To evaluate oxidation efficiency, a H₂-utilization efficiency (*H₂-Eff*) was defined in Eq. (5).

$$H_2\text{-Eff}(\%) = \frac{\text{oxygenates yield}}{\text{H}_2\text{O yield}} \times 100 \quad (5)$$

If the reductive activation of O₂ to O* (Eq. (3)) and the oxygenation of hydrocarbon with O* (Eq. (4)) are completely proceeded, equal amounts of oxygenates and H₂O will form and the *H₂-Eff* is 100%. The *H₂-Eff* values were lower than 10% in previous works [1–7].

We have also reported that Eu(OTf)₃-TiO(acac)₂-Pt/SiO₂ catalyst was active for hydroxylation of benzene to phenol with O₂ and H₂ [8] but the *H₂-Eff* of 10% was as low as other catalytic system. We improved the catalyst (EuCl₃-TiO(acac)₂-Pt/SiO₂) and reaction conditions for oxidation of adamantane and achieved a significant higher *H₂-Eff* of 75% [9]. The EuCl₃-TiO(acac)₂-Pt/SiO₂ catalyst has very unique catalysis and reactivity; however, it was complicate reaction system of homogeneous EuCl₃ and TiO(acac)₂ catalysts and heterogeneous Pt/SiO₂ catalyst. In addition, the separation of the former components from reaction mixtures is difficult, which is the disadvantage for an industrial application. Thus, we improved the homo/heterogeneous EuCl₃-TiO(acac)₂-Pt/SiO₂ catalyst to a solid catalyst of Pt/Eu₂O₃/TiO₂/SiO₂ and studied its catalysis in this work.

2. Experimental

We prepared a solid catalyst of Pt/Eu₂O₃/TiO₂/SiO₂ using a successive loading method as follows: first, impregnation of TiO(acac)₂/CH₂Cl₂ on SiO₂ and calcination in air at 573 K (TiO₂/

* Corresponding author. Tel.: +81 3 5734 2144; fax: +81 3 5734 2144.
E-mail address: yamanaka@apc.titech.ac.jp (I. Yamanaka).

SiO₂); second, impregnation of Eu(NO₃)₃/H₂O on TiO₂/SiO₂ and the calcination in air at 573 K (Eu₂O₃/TiO₂/SiO₂); third, impregnation of H₂PtCl₆/H₂O on TiO₂/Eu₂O₃/SiO₂ and the calcination in air at 573 K (PtO/TiO₂/Eu₂O₃/SiO₂). We can control loading order of three components on the SiO₂ support and prepared several catalysts. Pre-reduction of the catalysts with H₂ was not conducted; however, color of all catalysts changed from white to gray or dark gray within 5 min after oxidation started by introduction of a gas mixture of O₂ and H₂. This indicated that PtO reduced to Pt with H₂ in the working state; therefore, we indicated PtO/TiO₂/Eu₂O₃/SiO₂ as Pt/TiO₂/Eu₂O₃/SiO₂. Loadings of each component are, respectively, Pt 1.0 wt%, Eu₂O₃ 2.0 wt%, TiO₂ 2.4 wt%. We usually prepared the solid catalyst of 1 g at a time.

In oxidation of adamantane, the solid catalyst (0.1 g) was added in the reaction solutions of adamantane (50 mM) and acetic acid (20 mL). A gas mixture of O₂ (96 kPa) and H₂ (5 kPa) was introduced into the reaction mixture and the total flow rate was 20 mL min⁻¹. Oxidation was started by stirring with a magnetic spin-bar for 1–10 h at 313 K. We filtrated the reaction mixture and separated the solution and the solid after the oxidation. We neutralized the reaction solution using NaOH aq. and extracted oxygenated products using CH₂Cl₂ solvent at three times. Oxygenated products were identified by GC-Mass and yields were determined using GC (FID) and HPLC (UV–vis) techniques.

To evaluate reactivity of adamantane by the catalysts, selectivity to secondary oxygenates (2°-Sel) was defined in Eq. (6). In addition, 2-adamantanol and 2-adamantanone are much useful rather than 1-adamantanol in the current chemical industry [9]; therefore, the 2°-Sel value is important.

$$2^{\circ}\text{-Sel}(\%) = \frac{2\text{-adamantanol} + 2\text{-adamantanone}}{\text{sum of adamantane oxygenates}} \times 100 \quad (6)$$

3. Results and discussion

We prepared various solid catalysts supported Pt, Eu₂O₃, and TiO₂ on SiO₂ by changing preparation procedures and tested these for oxidation of adamantane with O₂ (5 kPa) and H₂ (96 kPa) in acetic acid, as shown in Fig. 1. Major products were 1-adamantanol, 2-adamantanol, 2-adamantanone, and CO₂. We found that the loading order of the three elements of Pt, Eu₂O₃, and TiO₂ on the SiO₂ support strongly affected on the product yields and the H₂-Eff. The catalysts could separate two groups, active and inactive catalysts. The former was Pt/Eu₂O₃/TiO₂/SiO₂, TiO₂/Pt/Eu₂O₃/SiO₂ and Pt/Eu₂O₃/TiO₂/SiO₂ and the latter was TiO₂/Eu₂O₃/Pt/SiO₂, Eu₂O₃/TiO₂/Pt/SiO₂ and Eu₂O₃/Pt/TiO₂/SiO₂. We noticed a common feature between the two groups. Pt was loaded on after Eu₂O₃ loading in the active catalyst group; on the other hand, Pt was loaded before Eu₂O₃ loading in the inactive catalyst group. This fact suggests that Pt on Eu₂O₃ may be important for the oxidation catalysis. In addition, we tested Pt/Eu₂O₃/SiO₂ and Pt/TiO₂/SiO₂ catalysts for the oxidation of adamantane, and the formation rates of sum of products were very low, 10 and 5 μmol h⁻¹, respectively. Synergy of Eu₂O₃ and TiO₂ was essential for the oxidation. The Pt/Eu₂O₃/TiO₂/SiO₂ catalyst showed the highest formation rate of products and a higher H₂-Eff of 13% among the catalysts in Fig. 1.

Fig. 2 shows effects of P(H₂) on products yields of the oxidation of adamantane using the Pt/Eu₂O₃/TiO₂/SiO₂ catalyst (P(H₂) + P(O₂) = 1 atm) for 1 h at 313 K. We observed no oxidation of adamantane at P(H₂) = 0 kPa (P(O₂) = 101 kPa) and significant yields of the oxidation product at higher P(H₂) > 68 kPa (P(O₂) < 35 kPa). The yields of 1-adamantanol, 2-adamantanol and 2-adamantanone increased with increasing P(H₂) and showed the maximum at P(H₂) = 96 kPa (P(O₂) = 5 kPa). We did not pre-

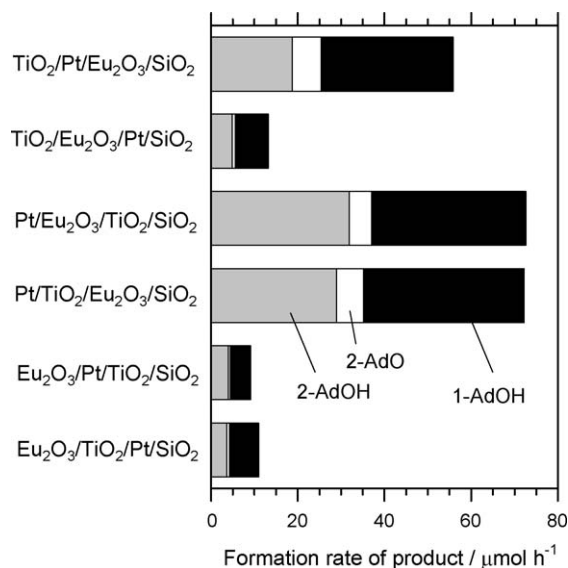


Fig. 1. Oxidation of adamantane using various Pt–Eu₂O₃–TiO₂ solid catalysts with O₂ and H₂ at 313 K. Catalyst 0.1 g; loadings: Eu₂O₃ 2.0 wt%, TiO₂ 2.4 wt%, Pt 1.0 wt%, adamantane (50 mM) and acetic acid (20 mL). P(O₂) 5 kPa, P(H₂) 96 kPa, total flow rate 20 mL min⁻¹.

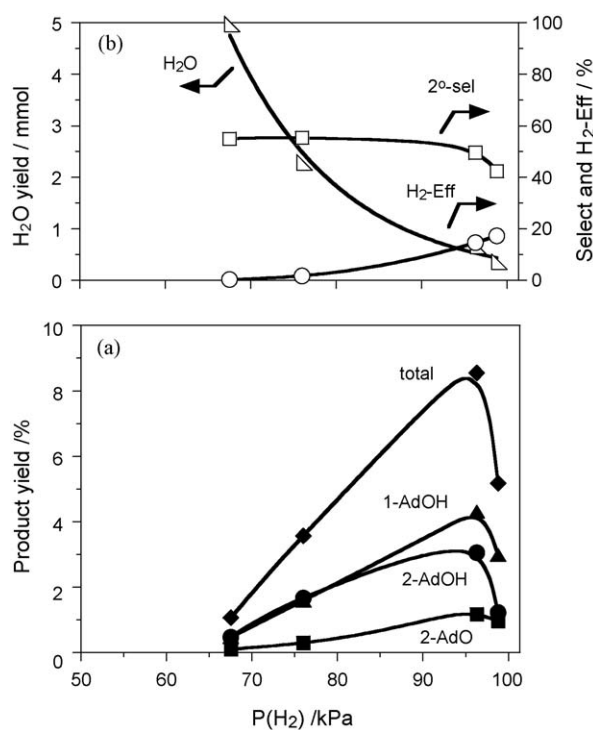


Fig. 2. Effect of P(H₂) on the oxidation of adamantane using the Pt/Eu₂O₃/TiO₂/SiO₂ catalyst with O₂ and H₂ at 313 K. Reaction time 1 h, catalyst 0.1 g; loadings: Eu₂O₃ 2.0 wt%, TiO₂ 2.4 wt%, Pt 1.0 wt%, adamantane (50 mM) and acetic acid (20 mL). P(O₂) + P(H₂) = 101 kPa, total flow rate 20 mL min⁻¹.

reduce the prepared catalyst (PtO/Eu₂O₃/TiO₂/SiO₂) with H₂ before the oxidation in the standard experimental procedures; therefore we tested the pre-reduction of the catalyst with H₂ at 423 K, and obtained very similar data to that without the pre-reduction, even at lower P(H₂). PtO reduced to Pt under the reaction conditions, as mentioned in Section 2. Higher P(H₂) conditions are suitable for the oxidation by the Pt/Eu₂O₃/TiO₂/SiO₂ catalyst.

To evaluate reactivity of adamantane by the catalysts, a selectivity to secondary oxygenates (2°-Sel) was plotted in

Download English Version:

<https://daneshyari.com/en/article/56233>

Download Persian Version:

<https://daneshyari.com/article/56233>

[Daneshyari.com](https://daneshyari.com)