Efficient Oxidation of Alkane with O_2 and H_2 by Eu–Ti–Pt Catalytic System

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Alkane was efficiently oxidized to alcohol and ketone with O_2 and H_2 by $EuCl_3$–$TiO(acac)_2$–Pt/SiO_2 catalytic system with very high H_2-utilization efficiencies, 75% for adamantane and 60% for cyclohexane oxidations. ESR studies suggested that electrons originated in H_2 effectively conducted to O_2 through Pt, Eu^{3+}/Eu^{2+}, and Ti^{4+}/Ti^{3+}. Eu^{2+} and Ti^{3+} species reductively activated O_2, generating active oxygen species.

Oxidation of alkane remains an attractive topic in organic synthesis and catalysis under mild conditions. An essential point is how to catalytically generate active oxygen species. H_2O_2 is a useful and effective oxidant for the oxidation.[1] H_2O_2, however, is an expensive oxidant for production of basic chemicals. A candidate of an efficient and economic oxidant is a gas mixture of O_2 and H_2. Monooxygenase activates O_2 with NADH corresponding to H_2 and oxygenates hydrocarbons. Since an artificial model of monooxygenase P-450 (Mn-TPP, Pt-colloid, O_2, and H_2) has been reported by Tabushi,[2] several catalytic oxidation systems have been studied (Eq 1).[3]

$$\text{R–H} + O_2 + H_2(2e^-, 2H^+) \rightarrow \text{R–OH} + H_2O. \quad (1)$$

A serious problem is a large amount of H_2O formation through deep reduction of O_2 ($2H_2 + O_2 \rightarrow 2H_2O$). When H_2-utilization efficiency (*H_2-eff*) was defined by Eq 2, the *H_2-eff* values were lower than 20% in previous works.[3] In other words, 80% H_2 was uselessly consumed to H_2O formation.

$$H_2\text{-}eff = (\text{oxygenates yield})/(H_2O \text{ yield}) \times 100(\%). \quad (2)$$

Recently, we have reported the $Eu(OTf)_3$–$TiO(acac)_2$–Pt/SiO_2 catalytic system which was active for the hydroxylation of benzene to phenol with O_2 and H_2.[4] The *H_2-eff* increased with increasing $P(H_2)$ for the formation of phenol but hydrogenation of benzene to cyclohexane became dominant above 50 kPa. The positive dependence of the *H_2-eff* on $P(H_2)$ suggested that higher $P(H_2)$ would be favor for activation of O_2 by the Eu–Ti–Pt-catalytic system. Therefore, we focused in oxidation of alkanes, especially adamantane to 1-adamantanol **1**, 2-adamanatanol **2**, and 2-adamantanone **3**. Adamantane oxygenates are essential compounds for medicines of Perkinson disease, anticancer and anti-HIV. **2** and **3** are essential for the synthesis of photoresist materials with ArF laser light.[5] Therefore, we are able to expect a large demand of adamantane oxygenates, especially **2** and **3**. Adamantane oxygenates are now manufactured by the sulfuric acid-oxidation method which is not environmental friendly process.[5]

We applied the $Eu(OTf)_3$ (6 mM)–$TiO(acac)_2$ (1 mM)–1 wt% Pt/SiO_2 (0.1 g) which was active for the hydroxylation of benzene,[4] to the oxidation of adamantane (50 mM in $MeCO_2H$) with O_2 (33.8 kPa) and H_2 (67.5 kPa). Major products were **1**, **2**, **3**, and minor ones were 1,3-adamantadiol and 5-hydroxy-2-adamantanone. The sum yield of adamantane oxygenates was fairly good about 29.1%, but the *H_2-eff* of 6% was lower than that of the benzene hydroxylation (10%).

It was found that counter anion species of Eu^{3+} strongly affected the catalytic activity for the oxidation. $EuCl_3$ and $Eu(ClO_4)_3$ shows the good oxidation activities, 35.3 and 34.9% yields, and the higher *H_2-eff* of 22.3 and 22.1%, respectively. $Eu(NO_3)_3$, $Eu(OAc)_3$, and $Eu(acac)_3$ were inactive.[4] $EuCl_3$ catalyst is more favor for the oxidation because of the higher selectivity to the useful secondary oxygenate (**2** and **3**), 49% ($EuCl_3$) > 44% ($Eu_2(ClO_4)_3$) > 36% ($Eu(OTf)_3$).

After detailed studies in influences of various reaction conditions on the adamantane oxidation, it was found that lower concentrations of $EuCl_3$ and $TiO(acac)_2$ and higher $P(H_2)$ were favor for the efficient oxidation. Figure 1 shows the effects of $P(H_2)$ on the oxidation. The formation rates of **1**, **2**, **3**, and the yield of H_2O increased with increasing $P(H_2)$. The formation rates were maximum around $P(H_2) = 80$ kPa. It is to be noted that the H_2O yield sharply decreased with increasing $P(H_2) > 75$ kPa rather than decreasing in the formation rates of **1**, **2**, and **3**. Therefore, the *H_2-eff* drastically increased with $P(H_2) > 80$ kPa. The highest *H_2-eff* was 75% with 14% yield at $P(H_2) = 96$ kPa ($P(O_2) = 5$ kPa) in 1 h. This 75% *H_2-eff* is excellent to compare with the values of other oxidation system.[3] A ratio of secondary (**2** and **3**) and tertiary (**1**) oxygenate yields per a number of C–H bond (2°:3°) characterizes a nature of active oxygen species. The 2°:3° values were constant (1:2.8) at all $P(H_2)$. This fact suggests that the drastic increase in the *H_2-eff* is due to the deceleration of the deep reduction of O_2 to

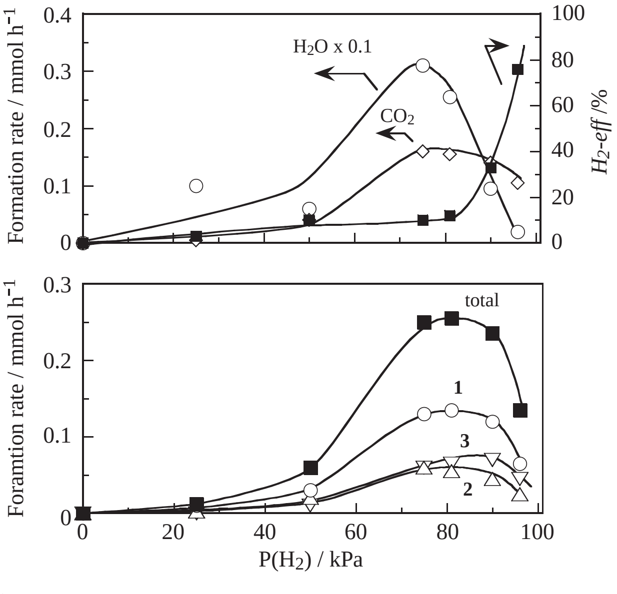

Figure 1. Effect of $P(H_2)$ on the adamantane oxidation with O_2 catalyzed by $EuCl_3$ 1 mM, $TiO(acac)_2$ 0.167 mM, and Pt/SiO_2 0.1 g at 40 °C.

H_2O and not due to changing of the reactivity of active oxygen species.

We studied kinetic curves of the adamantane oxidation at $P(H_2) = 96$ and $P(O_2) = 5$ kPa. Yields of adamantane oxygenates linearly increased with reaction times but slightly decelerated after 2 h. The *H*₂*-eff* was extrapolated to ca. 100% at early stage of the oxidation but decreased with reaction time, 46% at 3 h. When H_2O of 1 mmol corresponding to a H_2O yield at 3 h was added in the initial reaction mixture, the formation rate of oxygenates decelerated 0.6 times as slow as the standard one. This fact suggests that H_2O accumulated by equiv. 1 inhibits the oxidation activity. Dehydration treatment should be essential for the efficient continuous oxidation of adamantane.

In order to know that the significant high H_2*-eff* is peculiar to the adamantane oxidation or universal to alkane oxidation, we studied the oxidation of cyclohexane which C–H bond (2°) energy was 94 $\mathrm{kcal\,mol^{-1}}$ as strong as that for adamantane. We observed a very similar dependence of the cyclohexane oxidation on $P(H_2)$. Formation rates of cy-$C_6H_{11}OH$, cy-$C_6H_{10}O$, CO_2, and H_2O were maximum at $P(H_2) = 80$ kPa. The H_2*-eff* increased above $P(H_2) = 80$ kPa and showed the maximum of 60% at $P(H_2) = 96$ kPa. The H_2*-eff* was extrapolated to 90% at the early stage of the oxidation. These facts suggest that the $EuCl_3$–$TiO(acac)_2$–Pt/SiO_2 catalytic system can selectively activate O_2 and oxygenate alkanes.

To obtain information for the oxidation potential of the active oxygen species, oxidation of stable gaseous alkanes (propane, ethane, and methane) was carried out. A gas mixture of alkane (34 kPa), H_2 (62), and O_2 (5) was bubbled through the $EuCl_3$–$TiO(acac)_2$–$Pt/SiO_2/MeCO_2H$ mixture at 298 K. In propane oxidation (1° C–H bond: 97 $\mathrm{kcal\,mol^{-1}}$ and 2° C–H bond: 94), significant yields of 2-propanol, acetone and 1-propanol, propionaldehyde were obtained. The sum formation rates of oxygenates was 150 $\mathrm{\mu mol\,h^{-1}}$ with 10% H_2*-eff*. This value is fairly high though the concentration of propane is low. A ratio of 1°:2° was 1:7. Ethane (C–H bond: 98 $\mathrm{kcal\,mol^{-1}}$) was also oxygenated to ethanol and acetaldehyde but the formation rate of the sum of the products was only 20 $\mathrm{\mu mol\,h^{-1}}$ with a low H_2*-eff* of 1%. On the other hand, no significant formation of products was observed in the CH_4 oxidation (C–H bond: 104 $\mathrm{kcal\,mol^{-1}}$). The maximum oxidation potential of the active oxygen species is about 98 $\mathrm{kcal\,mol^{-1}}$. A low 1°:2°:3° value of 1:7:20 suggests radical character of the active oxygen species rather than electrophilic one.[6]

We carried out ESR studies to clarify oxidation states of Eu and Ti reduced with H_2 by Pt/SiO_2. In $Eu(OTf)_3$–Pt/SiO_2 system (Figure 2(1)), a broad ESR signal was observed at $g = 2.00$, which was assigned to Eu^{2+}.[7] Second, a very weak ESR signal was observed at $g = 1.95$ for $TiO(acac)_2$–Pt/SiO_2 system (2), which was assigned to Ti^{3+}.[8] This result suggests that reduction of Ti^{4+} with H_2 by Pt/SiO_2 is very slow. In the case of $Eu(OTf)_3$–$TiO(acac)_2$–Pt/SiO_2 system (3), a broad signal of Eu^{2+} and a strong signal of Ti^{3+} (around $g = 1.95$) were overlapped in the large signals. This result suggests that Ti^{4+} reduces to Ti^{3+} through a mediation of Eu^{3+}/Eu^{2+}. In other word, electrons originated H_2 conduct to Pt, Eu, and Ti. To obtain direct information for the active oxygen species, a gas mixture of O_2 and H_2 was introduced into the Eu–Ti–Pt catalytic system and quenched by liquid N_2. We could not observe any significant ESR signals. This result proposed that Eu^{2+} and Ti^{3+} species immediately react with O_2. A life of reduced oxygen species may be very short or silent for the ESR absorption.

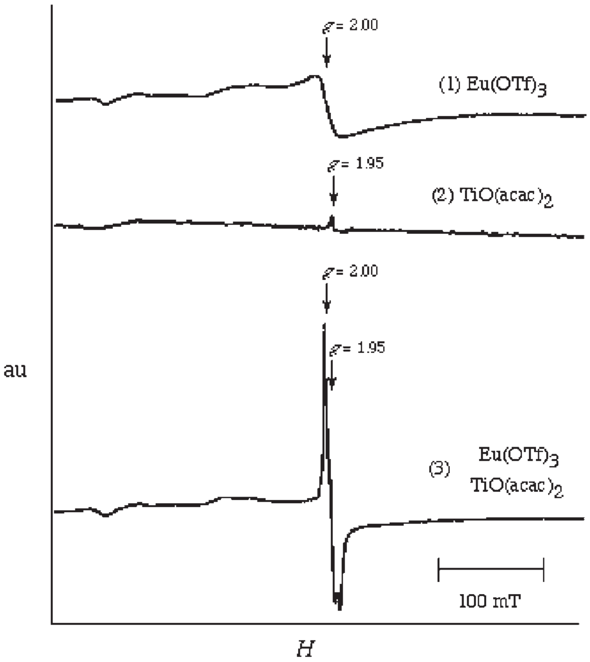

Figure 2. ESR spectra of (1) $Eu(OTf)_3$ 6 mM, (2) $TiO(acac)_2$ 1 mM, and (3) the mixture in $MeCO_2H$ after reduction with H_2 (1 atm) by Pt/SiO_2 for 30 min at 298 K and quenched by liquid N_2.

We are able to propose a model of Eu–Ti–Pt catalysis for the activation of O_2. Step 1: Pt^0 dissociatively activates H_2 to H•. Step 2: H• (e^- and H^+) reduces Eu^{3+} to Eu^{2+} over Pt^0. Step 3: Eu^{2+} reduces Ti^{4+} to Ti^{3+}. Step 4: Eu^{2+} and Ti^{3+} species should concertedly activate O_2. Step 5: The active oxygen species selectively and effectively oxygenate C–H bonds (ca. 94 $\mathrm{kcal\,mol^{-1}}$) of adamantane and cyclohexane. The active oxygen specie has radical character because of a low 1°:2°:3° value of 1:7:20. The reduction potential of H_2 ($2e^-$) finally conducts to O_2 through Pt, Eu^{3+}/Eu^{2+}, and Ti^{4+}/Ti^{3+}. The three different functions of Eu, Ti, and Pt concert and perform the efficient and selective oxidation.

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