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Oxidation of alkane using $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst with O_2 and H_2 in acetic acid under mild conditions

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ABSTRACT

A new solid catalyst of $Pt/Eu_2O_3/TiO_2/SiO_2$ for oxidation of alkane was developed. Oxidation of adamantane using the multi-components supported catalyst with O_2 and H_2 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 Eu_2O_3, TiO_2 and Pt on the SiO_2 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 Eu_2O_3 and TiO_2 on the SiO_2 support. Eu and Ti oxides concertedly activated O_2 with electrons supplied from H_2 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.

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 O_2 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 O_2 is very powerful method for the oxidation.

$$O_2 + \mathrm{NADH} + H^+ + Enz \rightarrow O*-Enz + H_2O + \mathrm{NAD}^+ \quad (1)$$

$$\mathrm{R{-}H} + O*-Enz \rightarrow \mathrm{R{-}OH} + Enz \quad (2)$$

An analogy of combination of NADH ($2e^-$, H^+) and H^+ is H_2. If we can choose suitable catalyst (*Cat*), the reductive activation O_2 will perform (Eq. (3)) and produces oxygenated compounds (Eq. (4)).

$$O_2 + H_2 + Cat \rightarrow O*-Cal + H_2O \quad (3)$$

$$\mathrm{R{-}H} + O*-Cal \rightarrow \mathrm{R{-}OH} + Cat \quad (4)$$

Prof. Tabushi first reported application of the reductive activation of O_2 with H_2 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 H_2-utilization efficiency (*H_2-Eff*) was defined in Eq. (5).

$$H_2\text{-}Eff(\%) = \frac{\text{oxygenates yield}}{H_2O\ \text{yield}} \times 100 \quad (5)$$

If the reductive activation of O_2 to O^* (Eq. (3)) and the oxygenation of hydrocarbon with O^* (Eq. (4)) are completely proceeded, equal amounts of oxygenates and H_2O will form and the *H_2-Eff* is 100%. The *H_2-Eff* values were lower than 10% in previous works [1–7].

We have also reported that $Eu(OTf)_3–TiO(acac)_2–Pt/SiO_2$ catalyst was active for hydroxylation of benzene to phenol with O_2 and H_2 [8] but the *H_2-Eff* of 10% was as low as other catalytic system. We improved the catalyst ($EuCl_3–TiO(acac)_2–Pt/SiO_2$) and reaction conditions for oxidation of adamantane and achieved a significant higher *H_2-Eff* of 75% [9]. The $EuCl_3–TiO(acac)_2–Pt/SiO_2$ catalyst has very unique catalysis and reactivity; however, it was complicate reaction system of homogeneous $EuCl_3$ and $TiO(acac)_2$ catalysts and heterogeneous Pt/SiO_2 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 $EuCl_3–TiO(acac)_2–Pt/SiO_2$ catalyst to a solid catalyst of $Pt/Eu_2O_3/TiO_2/SiO_2$ and studied its catalysis in this work.

2. Experimental

We prepared a solid catalyst of $Pt/Eu_2O_3/TiO_2/SiO_2$ using a successive loading method as follows: first, impregnation of $TiO(acac)_2/CH_2Cl_2$ on SiO_2 and calcination in air at 573 K (TiO_2/

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SiO_2); second, impregnation of $Eu(NO_3)_3/H_2O$ on TiO_2/SiO_2 and the calcination in air at 573 K ($Eu_2O_3/TiO_2/SiO_2$); third, impregnation of H_2PtCl_6/H_2O on $TiO_2/Eu_2O_3/SiO_2$ and the calcination in air at 573 K ($PtO/TiO_2/Eu_2O_3/SiO_2$). We can control loading order of three components on the SiO_2 support and prepared several catalysts. Pre-reduction of the catalysts with H_2 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 O_2 and H_2. This indicated that PtO reduced to Pt with H_2 in the working state; therefore, we indicated $PtO/TiO_2/Eu_2O_3/SiO_2$ as $Pt/TiO_2/Eu_2O_3/SiO_2$. Loadings of each component are, respectively, Pt 1.0 wt%, Eu_2O_3 2.0 wt%, TiO_2 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 O_2 (96 kPa) and H_2 (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 sold after the oxidation. We neutralized the reaction solution using NaOH aq. and extracted oxygenated products using CH_2Cl_2 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.

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

3. Results and discussion

We prepared various solid catalysts supported Pt, Eu_2O_3, and TiO_2 on SiO_2 by changing preparation procedures and tested these for oxidation of adamantine with O_2 (5 kPa) and H_2 (96 kPa) in acetic acid, as shown in Fig. 1. Major products were 1-adamantanol, 2-adamantanol, 2-adamantanone, and CO_2. We found that the loading order of the three elements of Pt, Eu_2O_3, and TiO_2 on the SiO_2 support strongly affected on the product yields and the *H_2-Eff*, The catalysts could separate two groups, active and inactive catalysts. The former was $Pt/Eu_2O_3/TiO_2/SiO_2$, $TiO_2/Pt/Eu_2O_3/SiO_2$ and $Pt/Eu_2O_3/TiO_2/SiO_2$ and the latter was $TiO_2/Eu_2O_3/Pt/SiO_2$, $Eu_2O_3/TiO_2/Pt/SiO_2$ and $Eu_2O_3/Pt/TiO_2/SiO_2$. We noticed a common feature between the two groups. Pt was loaded on after Eu_2O_3 loading in the active catalyst group; on the other hand, Pt was loaded before Eu_2O_3 loading in the inactive catalyst group. This fact suggests that Pt on Eu_2O_3 may be important for the oxidation catalysis. In addition, we tested $Pt/Eu_2O_3/SiO_2$ and $Pt/TiO_2/SiO_2$ 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 Eu_2O_3 and TiO_2 was essential for the oxidation. The $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst showed the highest formation rate of products and a higher *H_2-Eff* of 13% among the catalysts in Fig. 1.

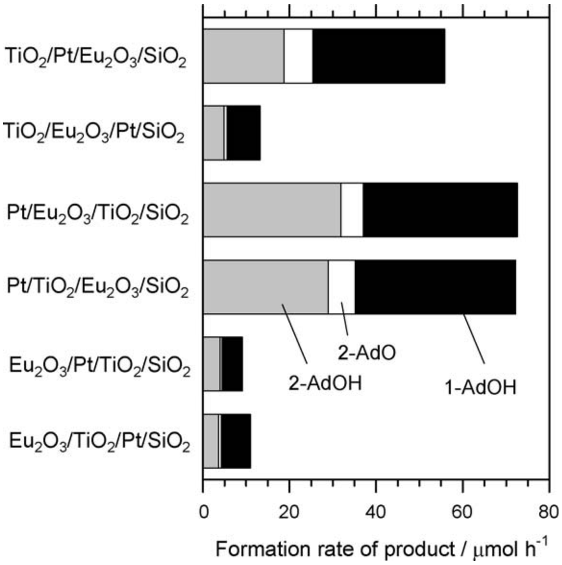

Fig. 1. Oxidation of adamantane using various $Pt–Eu_2O_3–TiO_2$ solid catalysts with O_2 and H_2 at 313 K. Catalyst 0.1 g; loadings: Eu_2O_3 2.0 wt%, TiO_2 2.4 wt%, Pt 1.0 wt%, adamantane (50 mM) and acetic acid (20 mL). $P(O_2)$ 5 kPa, $P(H_2)$ 96 kPa, total flow rate 20 mL min^{-1}.

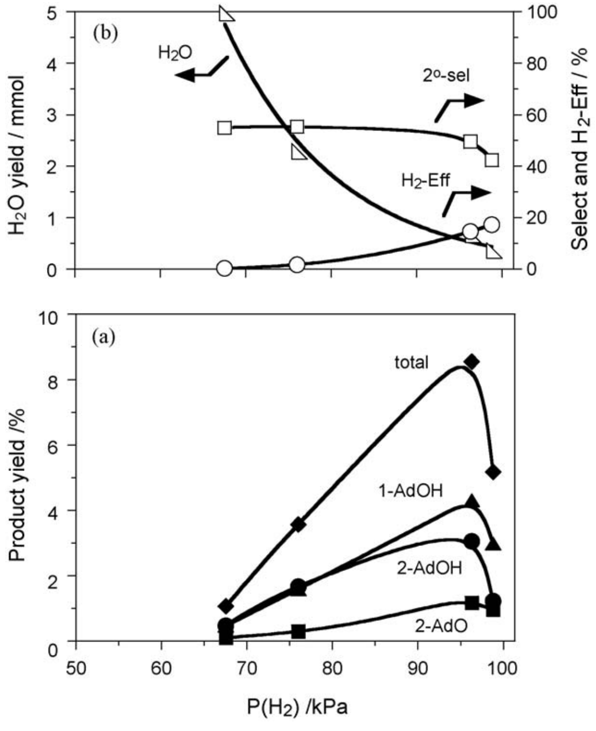

Fig. 2. Effect of $P(H_2)$ on the oxidation of adamantane using the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst with O_2 and H_2 at 313 K. Reaction time 1 h, catalyst 0.1 g; loadings: Eu_2O_3 2.0 wt%, TiO_2 2.4 wt%, Pt 1.0 wt%, adamantane (50 mM) and acetic acid (20 mL). $P(O_2) + P(H_2) = 101$ kPa, total flow rate 20 mL min^{-1}.

Fig. 2 shows effects of $P(H_2)$ on products yields of the oxidation of adamantane using the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst ($P(H_2) + P(O_2) = 1$:atm) for 1 h at 313 K. We observed no oxidation of adamantane at $P(H_2) = 0$ kPa ($P(O_2) = 101$ kPa) and significant yields of the oxidation product at higher $P(H_2) > 68$ kPa ($P(O_2) < 35$ kPa). The yields of 1-adamantanol, 2-adamantanol and 2-adamantanone increased with increasing $P(H_2)$ and showed the maximum at $P(H_2) = 96$ kPa ($P(O_2) = 5$ kPa). We did not pre-reduce the prepared catalyst ($PtO/Eu_2O_3/TiO_2/SiO_2$) with H_2 before the oxidation in the standard experimental procedures; therefore we tested the pre-reduction of the catalyst with H_2 at 423 K, and obtained very similar data to that without the pre-reduction, even at lower $P(H_2)$. PtO reduced to Pt under the reaction conditions, as mentioned in Section 2. Higher $P(H_2)$ conditions are suitable for the oxidation by the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst.

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

Fig. 2b. The 2°-*Sel* values were about 50%, except for 40% at $P(H_2) = 98$ kPa. The 2°-*Sel* values of the other active catalysts of $TiO_2/Pt/Eu_2O_3/SiO_2$ and $Pt/TiO_2/Eu_2O_3/SiO_2$ in Fig. 1 were 45% and 49%, respectively. The distributions of the products were almost constant for the active catalysts.

On the other hand, a large amount of H_2O was produced at $P(H_2) > 68$ kPa, unsuitable conditions for the oxidation of adamantane. The yield of H_2O dramatically decreased with increasing $P(H_2)$. Therefore, the H_2-*Eff* increased with increasing $P(H_2)$ from 0.3% at 68 kPa to 18% at 98 kPa. This indicated that strong reductive condition was suitable to generate oxidation catalysis of the $Pt/Eu_2O_3/TiO_2/SiO_2$. We observed a very similar nature in the previous homo/heterogeneous catalyst system ($EuCl_3$–$TiO(acac)_2$–Pt/SiO_2).

Fig. 3 shows time courses of the oxidation of adamantane using the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst with H_2 (96 kPa) and O_2 (5 kPa). The yields of 1-adamantanol, 2-adamanatanol, 2-adamantanone (Fig. 3a) and also CO_2 (Fig. 3b) increased smoothly with reaction. The total yield of adamantane oxygenates was over 19% at 3 h and the distribution of products was constant. These data indicated that oxidation of adamantane with O_2 and H_2 continuously proceeded by the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst until 3 h. However, the formation rates of adamantane oxygenate decreased after 3 h and the yields showed a plate after 10 h. A yield of CO_2 increased smoothly with reaction time for 10 h (6% based on C). We filtrated the catalyst from the reaction mixture, and re-used the catalyst for the oxidation of adamantane. We obtained a very similar experimental result to Fig. 3. This indicated that the catalyst did not deactivate in the oxidation for 10 h. Loadings of Eu_2O_3 (2.0 wt%), TiO_2 (2.4 wt%) and Pt (1.0 wt%) on SiO_2 were corresponding to 11, 30 and 5 μmol in 0.1 g of the catalyst. Turnover numbers for the formation of adamantane oxygenates are 17 TON(Eu), 6.3 TON(Ti) and 38 TON(Pt) in 3 h. The $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst efficiently promotes the oxidation of adamantane.

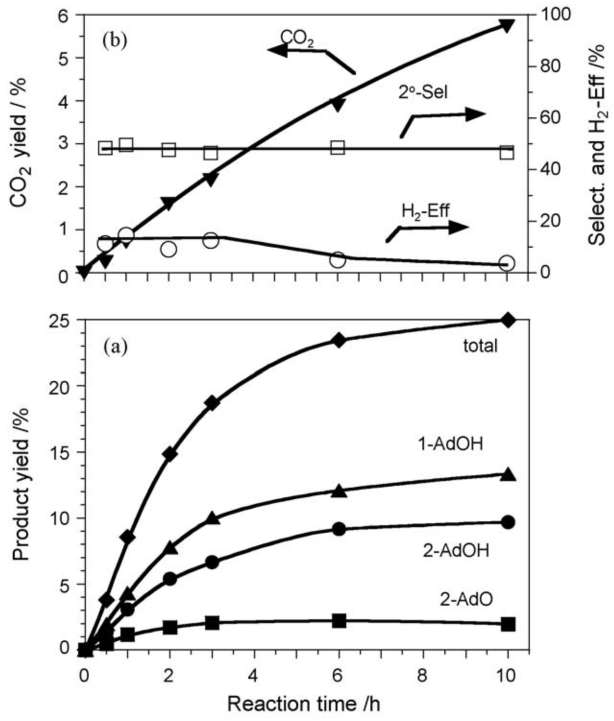

Fig. 3. Time courses of oxidation of adamantane using the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst with O_2 and H_2 at 313 K. Catalyst 0.1 g; loadings: Eu_2O_3 2.0 wt%, TiO_2 2.4 wt%, Pt 1.0 wt%, adamantane (50 mM) and acetic acid (20 mL). $P(O_2)$ 5 kPa, $P(H_2)$ 96 kPa, total flow rate 20 mL min^{-1}.

Products selectivity and the 2°-*Sel* in adamantane mono-oxygenates were constant but we observed production of significant amounts of adamantane di-oxygenates in the reaction mixture after 6 h. We could not succeed a quantitative analysis of adamantane di-oxygenates because of hard establishing quantitative analysis conditions, but successive oxidation of adamantane mono-oxygenates undoubtedly proceeded after 6 h.

The H_2-*Eff* was about 13% until 3 h but decreased to 4% at 10 h. This apparent large decrease in the H_2-*Eff* should be due to the formation of adamantane di-oxygenates after 6 h. The suppression of the successive oxidation of mono-oxygenates (1-adamantanol, 2-adamanatanol and 2-adamantanone) is essential to obtain a higher yield of the mono-oxygenates.

Significant effect of the loading order of Eu_2O_3, TiO_2, and Pt on the oxidation activity (Fig. 1) was studied using TEM observation with EDS and ESR spectroscopy. Fig. 4 shows TEM images of the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst (a: active catalyst) and the $Eu_2O_3/TiO_2/Pt/SiO_2$ catalyst (b: inactive catalyst). As you can see in Fig. 4a, we cannot observe clear particles on the image. We uniformly observed Pt, Eu and Ti elements at every different point on SiO_2 from EDS analysis. In addition, we could not obtain diffraction spectra assigned crystals of Pt, Eu_2O_3 and TiO_2 using XRD. These observations indicate Pt, Eu and Ti elements highly dispersed as amorphous or very small particle formula (<2 nm). Very similar TEM images were observed at other two active catalysts. In

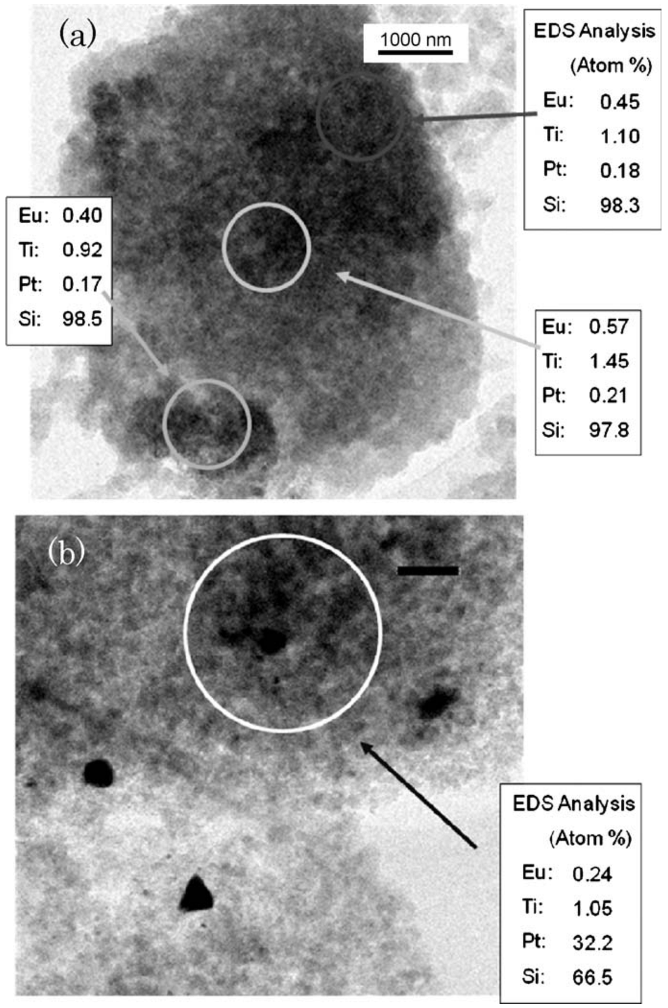

Fig. 4. TEM images of $Pt/Eu_2O_3/TiO_2/SiO_2$ (a: active catalyst) and $Eu_2O_3/TiO_2/Pt/SiO_2$ (b: inactive catalyst) with EDS analysis data. Loadings: Eu_2O_3 2.0 wt%, TiO_2 2.4 wt%, Pt 1.0 wt%, SiO_2 94.6 wt%.

Table 1
Reactivity of active oxygen species on the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst.

Entry	Reactant	Remarks
1[a]	cy-C_6D_6, cy-C_6H_6	*KIE* = 2.2 (HO$^\bullet$, *KIE* = 1.2)
2[b]	*cis*-1,2-dimethyl-cyclohexane	*cis*:*trans* = 54:46 (1-ol), *cis*:*trans* = 100:0 (3-ol, 4-ol)
3[b]	*trans*-1,2-dimethyl-cyclohexane	*cis*:*trans* = 49:51 (1-ol), *cis*:*trans* = 0:100 (3-ol, 4-ol)
4[c]	Adamantane, CCl_4	Selectivity (%): 1-AdCl(59), 2-AdCl(30), 1-AdOH(1), 2-AdOH(2), 2-AdO(8)

T = 313 K, reaction time 10 min, $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst 0.1 g; loadings: Eu_2O_3 2.0 wt%, TiO_2 2.4 wt%, Pt 1.0 wt%, reactant/acetic acid (20 mL). $P(O_2)$ 5 kPa, $P(H_2)$ 96 kPa, total flow rate 20 mL min^{-1}.

[a] cy-C_6D_6 2 mL, cy-C_6H_6 2 mL.

[b] *cis*- or *trans*-1,2-dimethyl-cyclohexane 2 mL, 1-ol: 1,2-dimethylcyclohexan-1-ol, 3-ol: 1,2-dimethylcyclohexan-3-ol and -3-one, 4-ol: 1,2-dimethylcyclohexan-4-ol and -4-one.

[c] Adamantane 50 mM/CCl_4 1 mL + AcOH 19 mL.

contrast, we observe large particles of Pt and domains of Eu and Ti on SiO_2 at the $Eu_2O_3/TiO_2/Pt/SiO_2$ inactive catalyst (Fig. 4b). We confirmed formation of Pt^0 on the used catalyst by XRD. Broad and weak X ray diffraction at $2\theta = 40^\circ$ and 47° was observed. Very similar un-uniform TEM images were observed on other two inactive catalysts. These indicated highly dispersion of well mixture of Pt, Eu and Ti elements was essential for catalysis in the oxidation.

ESR studies using various samples, the $Pt/Eu_2O_3/TiO_2/SiO_2$ active catalyst, the $Eu_2O_3/TiO_2/Pt/SiO_2$ inactive catalyst, $Pt/Eu_2O_3/SiO_2$, $Pt/TiO_4/SiO_2$ samples, were done in the gas mixture of O_2 and H_2, and in H_2. Then, we obtained a few significant ESR signals of the samples in H_2. First, ESR signals assigned to mixture of Eu^{2+} and Ti^{3+} signals were observed the sample of $Pt/Eu_2O_3/TiO_2/SiO_2$ and $AcOH/CH_2Cl_2$ solutions with introduction of H_2. The ESR signal of Eu^{2+} was also observed on the $Pt/Eu_2O_3/SiO_2$ sample with introduction of H_2 but the ESR signals of Ti^{3+} were not at the $Pt/TiO_4/SiO_2$ sample. These observations suggest that Eu^{2+} produces by reduction of Eu_2O_3 with H_2 on Pt and Ti^{3+} should produce by reduction of TiO_2 with Eu^{2+}. The ESR signals of Eu^{2+} and Ti^{3+} on the active catalyst immediately disappeared when O_2 was introduced to the ESR sample. These indicate that electron transfer reactions proceed through $H_2 \rightarrow Pt \rightarrow Eu \rightarrow Ti \rightarrow O_2$ and active oxygen species finally generate on the active catalysts [9]; therefore, the loading order of Pt, Eu_2O_3, and TiO_2 should be essential for the oxidation catalysis. Any ESR signals were not observed on the inactive catalyst. We tried to quench the active oxygen species during the oxidation with O_2 and H_2 using liquid N_2 but we could not be detected ESR active species.

To obtain information for nature of active oxygen species of the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst, several oxidations of hydrocarbons were conducted, as summarized in Table 1. Reaction time was reduced 10 min to obtain initial products selectivity.

A kinetic isotope effect (*KIE*) was 2.2 calculated from a ratio of initial conversion rates of cy-C_6D_{12} and cy-C_6H_{12} during the oxidation of the mixture (Entry 1). The KIE of 2.2 is larger than values of 1.2–1.4 observed in HO$^\bullet$. This fairly large KIE value indicates the rate-determining step is a cleavage C–H bond of cyclohexane.

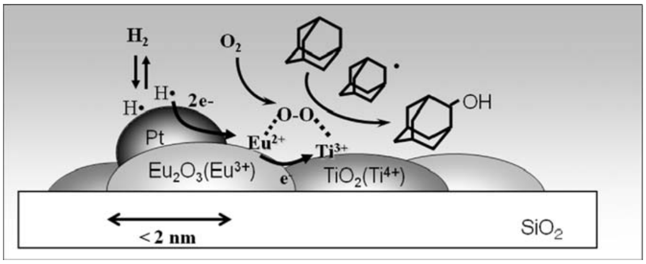

Fig. 5. Reaction mechanism model of oxidation on $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst.

In the case of oxidation of *cis*-1,2-dimethyl-cyclohexane, we obtained *cis*-compounds (1,2-dimethyl-cyclohexan-3-ol, -4-ol, -3-one, -4-one) and *cis*- and *trans*-1,2-dimethyl-cyclohexan-1-ol (Entry 2). Retention of configuration of *cis*-1,2-dimethyl cyclohexane was perfect in the former products (oxygenated at 3- or 4-positions, *cis*:*trans* = 100:0), but the configuration did not retained in 1,2-dimethyl-cyclohexan-1-ol (*cis*:*trans* = 54:46). Very similar reactivity was observed in the oxidation of *trans*-1,2-dimethyl-cyclohexane (Entry 3). The *cis*:*trans* was 0:100 for the products oxygenated at 3- or 4-positions, and that was 51:49 for the product at 1-position. These facts indicate that a cleavage of C–H bonds occurs and may form an alkyl radical intermediate during the oxidation. Therefore, the configuration of the four carbon bonds disappeared during the oxidation.

We added a radical trap reagent of CCl_4 (1 mL) to the standard mixture of adamantane oxidation (20 mL) and obtained adamantan-1-Cl (59% selectivity) and adamantan-2-Cl (30%) as the major products. Adamantan-1-Cl and adamantan-2-Cl should be produced through the trapping adamantyl radical with CCl_4. This indicates formation of alkyl radical intermediate during the oxidation.

We can propose reaction mechanisms from the experimental facts described above, as illustrated in Fig. 5. The $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst has very uniform surface and very small Pt particles (<2 nm) well dispersed on amorphous oxides of Eu_2O_3 and TiO_2 on the SiO_2 support because we could not observe clear particles and XRD diffraction. PtO easily reduce to Pt with the reaction gas mixture of O_2 and H_2 because we observed the color change of the catalyst to dark gray and no influence of the pre-reduction of the catalyst on the oxidation. H_2 activates on Pt and supplies electrons and protons. Electron reduces Eu_2O_3 to Eu^{2+} form; then, Eu^{2+} reduces TiO_2 to Ti^{3+} form because of ESR studies. Eu^{2+} and Ti^{3+} concertedly activate O_2 and the activate oxygen species should form on the catalyst; however, formula of the active oxygen species cannot be clarified. The active oxygen species attach and cleave a C–H bond of alkane generating alkyl radical intermediate; then oxygen species recombine with alkyl radical intermediate forming oxygenated products because we observed the *KIE* and radical trapping products. The rate-determining step is cleavage of C–H bond. The active oxygen species has radical character and configuration of C–H bonds does not retain during the oxidation.

4. Conclusions

We developed the $Pt/Eu_2O_3/TiO_2/SiO_2$ solid catalyst for oxidation of alkane with O_2 and H_2 in acetic acid at 313 K. Loading order of Eu_2O_3, TiO_2 and Pt on the SiO_2 support strongly affects the oxidation catalysis because electron transfer reactions from H_2 through Pt, Eu_2O_3 ($Eu^{3+/2+}$), TiO_2 ($Ti^{4+/3+}$) to O_2 are essential for the formation of active oxygen species. Active oxygen species cannot be identified but has radical character for

C–H bonds of alkane. In the oxidation of adamantane using the $Pt/Eu_2O_3/TiO_2/SiO_2$ catalyst with H_2 (96 kPa) and O_2 (5 kPa), the maximum yield sum of 1-adamantanol, 2-adamantanol and 2-adamantanone was 25% in 10 h, corresponding to 22 TON based on Eu, 8 TON based on Ti and 50 TON based on Pt, though the apparent H_2-*Eff* of 4% should be improved. To perform more efficient oxidation of adamantane and alkanes, we have to design and make nano-structure of the three essential components of Eu_2O_3, TiO_2 and Pt to improve systematic electron transfer reaction.

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