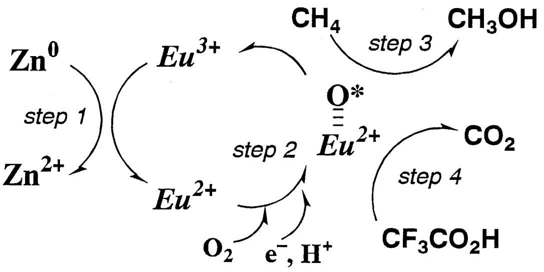
Enhancing Effect of Titanium(II) for the Oxidation of Methane with O_2 by an $EuCl_3$-Zn-CF_3CO_2H-Catalytic System at 40 °C

Ichiro Yamanaka,* Masanori Soma, and Kiyoshi Otsuka*
Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received March 11, 1996)

Bis(2,4,-pentanedionate)TiO and TiO_2 enhanced markedly the activity of the $EuCl_3$-Zn^0-CF_3CO_2H-catalytic system for the CH_4 oxidation to MeOH with O_2 at 40 °C. It is suggested that Ti(II) species generated from Ti(IV) by the reduction with Zn^0 and CF_3CO_2H is responsible for this enhancement.

Recently, we have reported the oxidation of CH_4 to MeOH with O_2 using an $EuCl_3$-Zn^0-CF_3CO_2H-catalytic system at room temperature.[1] The maximum turnover number obtained in this system was 5.3 in 1 h for the formation of MeOH based on $EuCl_3$. In this letter, we intend to improve the activity of this $EuCl_3$-catalytic system by the addition of promoters. We speculate that the oxidation of CH_4 proceeds through *steps 1-4* in Scheme 1; *step 1*, reduction of Eu^{3+} to Eu^{2+} with Zn^0; *step 2*, reductive activation of O_2 with e^- (from Eu^{2+} or Zn^0) and H^+ (from CF_3CO_2H); *step 3*, oxidation of CH_4 to MeOH by the activated oxygen on Eu-catalyst; *step 4*, formation of CO_2 from CF_3CO_2H with the activated oxygen. The *step 1* and *step 2* were already confirmed by electrochemical studies for the cyclohexane oxidation.[2] The *step 3* and *step 4* were also confirmed in the previous report.[1] We expect that the addition of promoters may accelerate the electron transfer reactions (*steps 1* and *2*) or the activation of CH_4 to MeOH (*step 3*).



Scheme 1. Model of the reaction mechanism for the methane oxidation in $EuCl_3$-catalytic system at room temperature.

A combination of Zn and carboxylic acid as a reductant has already been reported by Gif(IV) system.[3] The Gif-system is not effective for oxidation of CH_4 and C_2H_6.[3] Moreover, the $EuCl_3$-catalytic system catalyses the epoxidation of propylene and the hydroxylation of benzene[2] but the Gif-system does not.[3]

The standard condition of the oxidation of CH_4 was $EuCl_3$ (0.03 mmol), additives (0.03 mmol on the cation bases), CF_3CO_2H (13.1 mmol), Zn (15.3 mmol), CH_4 of 10 atm (51.9 mmol), O_2 of 4 atm (6.9 mmol), T = 40 °C and reaction time = 1h. Both the solutions before and after the reaction were homogeneous.

When a reaction mixture of the oxidation of CH_4 was directly analyzed by GC without the neutralization with NaOH (aq.), the product in the mixture was trifloroacetic acid methyl ester (CF_3CO_2Me). In a separate experiment, a mixture of CF_3CO_2H and MeOH immediately converted to the ester. It was reported that a C-H bond of CF_3CO_2Me is less reactive for an electrophilic attack than that of CH_4 as an effect of strong electron-withdrawing by CF_3CO_2-group.[4] Thus, MeOH (CF_3CO_2Me) accumulates in the reaction mixture not proceeding a successive oxidation to CO_2. Figure 1 shows the influences of the addition of some metal salts, complexes and oxides on the CH_4 oxidation under the standard conditions. The turnover numbers (TON) in this figure were based on $EuCl_3$. The results in Figure 1 indicate that bis(2,4,-pentanedionate)TiO (TiO•AA) and TiO_2 enhanced the oxidation of CH_4 (TON > 10 in 1 h) most appreciably. The TON observed here were more than twice of that of the standard $EuCl_3$-catalytic system.[1] It may be unusual that a complex (TiO•AA) and a solid oxide (TiO_2) exhibit similar enhancement of the oxidation. However, it should be noted that TiO_2 was not observed after the reaction. This suggests that TiO_2 has been reductively dissolved by CF_3CO_2H and Zn^0 through eqn. 1.

$$TiO_2 + 4H^+ + e^- = Ti^{3+} + 2\,H_2O \quad (-0.666\ \mathrm{V}\ vs.\ \mathrm{NHE}) \quad (1)$$

The Ti^{3+} thus formed could be reduced to Ti^{2+} with Zn^0 by taking account the redox potentials ($Ti^{3+/2+}$ = -0.368 V > $Zn^{2+/0}$ = -0.77 V > $Ti^{2+/0}$ = -1.63 V *vs.* NHE). Therefore, the TiO_2 added must have been dissolved as Ti^{2+} in CF_3CO_2H.

MeOH (CF_3CO_2Me) was not produced if any one of the elements (CF_3CO_2H, Zn^0, O_2 or CH_4) had been removed from the $EuCl_3$-TiO•AA-catalytic system. However, a large amount of CO_2

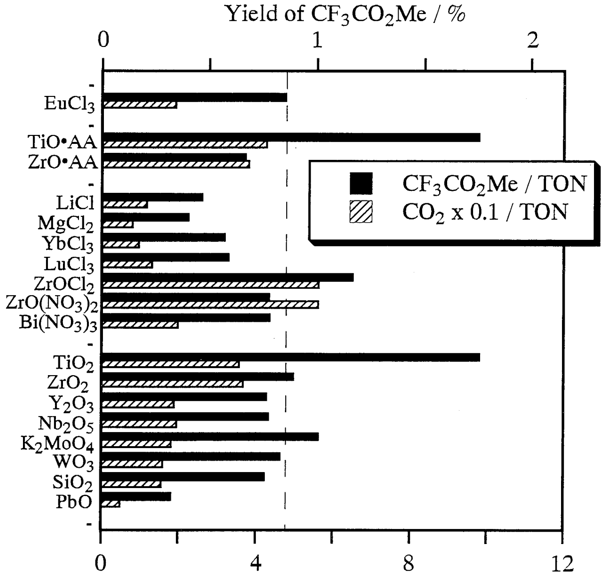


Figure 1. Influences of various additives as sub-catalyst on the oxidation of methane catalyzed by $EuCl_3$.
TiO•AA: bis(2,4,-pentanedionato)TiO.
ZrO•AA: bis(2,4,-pentanedionato)ZrO.

(TON of CO_2 = 39.5) was produced when CH_4 was not added to this $EuCl_3$-TiO•AA-catalytic system. These results suggest that MeOH is produced only from CH_4 and CO_2 is produced mainly from CF_3CO_2H, which is quite similar to the results obtained in the $EuCl_3$-catalytic system without Ti-compounds (Scheme 1). Although TiO•AA catalysed the formation of MeOH (TON = 0.6 in 1h) under the standard condition without $EuCl_3$, most of the MeOH produced by the $EuCl_3$-TiO•AA-catalytic system in Figure1 may be ascribed to the catalytic function of europium promoted by Ti^{2+}. Some additives in Figure 1, LiCl, $MgCl_2$, $YbCl_3$, $LuCl_3$ and PbO, decreased the activities of MeOH formation. The agglomeration of Zn powder was observed after the reaction with these additives. Other additives did not affect the activity of MeOH formation.

Figure 2 shows the effect of the amounts of TiO•AA added to the $EuCl_3$-catalytic system on the CH_4 oxidation. A small amount of TiO•AA (~0.005 mmol) is enough to enhance the formation rate (TON) of CF_3CO_2Me. TON of CF_3CO_2Me was almost constant at the amounts of TiO•AA > 0.005 mmol. TON of CO_2 was also enhanced by TiO•AA. The selectivity to MeOH did not depend on the amount of TiO•AA added. This result suggests that Ti compounds accelerate the formation rate of the active oxygen generated in the $EuCl_3$-catalytic system, but do not change the selectivity to the formations MeOH and CO_2. The amount of Zn^0 reacted was not influenced by the addition of TiO•AA or TiO_2. The efficiency of Zn^0 for the formation of CF_3CO_2Me, i.e., the ratio of the amount of CF_3CO_2Me (mol) and that of Zn^0 reacted (mol), [1,2] was increased twice from 1% to 2% by the addition of TiO•AA or TiO_2 (> 0.005 mmol), suggesting the enhancement in *step 1* or *2* in Scheme 1.

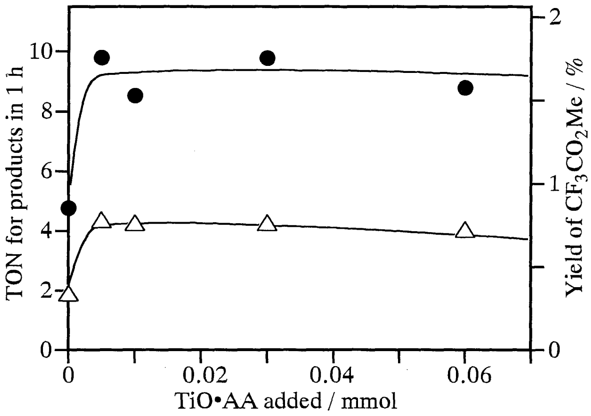


Figure 2. Effect of the amount of TiO•AA added on the oxidation of methane catalyzed by $EuCl_3$.
● CF_3CO_2Me / TON, △ CO_2 x 0.1 / TON.

Figure 3 shows the effect of the amounts of $EuCl_3$ on the CH_4 oxidation in the presence and absence of TiO•AA (0.03 mmol). The yield of CF_3CO_2Me increased with increasing the amount of $EuCl_3$ in the in the presence of TiO•AA. The maximum yield of CF_3CO_2Me was 2.7% at the $EuCl_3$-addition of 0.12 mmol. It should be note, the yields of CO_2 were roughly constant at the $EuCl_3$-addition > 0.03 mmol. Thus, the selectivity to CF_3CO_2Me increased with increasing the amount of $EuCl_3$. For the standard $EuCl_3$-catalytic system, the maximum yield of CF_3CO_2Me (1.1%) was obtained at an $EuCl_3$-addition of 0.06 mmol. The TON of CO_2 were roughly constant at the amounts of $EuCl_3$ > 0.06 mmol similar to the observation in the presence of TiO•AA. In other words, the active oxygen species and reaction mechanism must be common for the catalytic systems with and without Ti-compounds. The role of Ti compounds in the $EuCl_3$-catalytic system is to promote the formation of active oxygen on $EuCl_3$ catalyst by enhancing the rate of *step 1* or *2* or both.

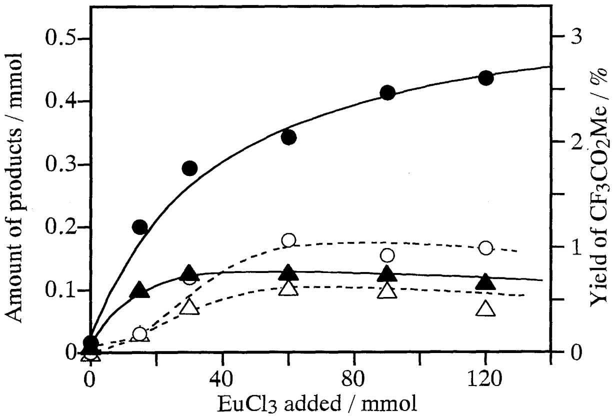


Figure 3. Effect of the amount of $EuCl_3$ on the methane oxidation in $EuCl_3$-TiO•AA- and $EuCl_3$-catalytic systems.
● CF_3CO_2Me / mmol, ▲ CO_2 x 0.1 / mmol in $EuCl_3$-TiO•AA-system.
○ CF_3CO_2Me / mmol, △ CO_2 x 0.1 / mmol in $EuCl_3$-system.

The enhancing effect of TiO•AA and TiO_2 was observed for the oxidation of C_2H_6 to EtOH and MeCHO. The TON for the sum of EtOH and MeCHO in $EuCl_3$-catalytic system was enhanced from 8.0 to 14.8 in 1h by the TiO•AA addition and to 16.9 by the TiO_2 addition. The maximum efficiency of Zn used for the C_2H_6 oxidation in $EuCl_3$-TiO_2-catalytic system was 5%. Thus, most of the Zn consumed was not used for the oxidation of CH_4 and C_2H_6. Probably, most of the Zn powder are consumed through eqn. 2, producing H_2O.

$$O_2 + 4\,CF_3CO_2H + 2\,Zn \rightarrow 2\,H_2O + Zn(CF_3CO_2)_2 \qquad (2)$$

How do Ti compounds accelerate the formation rate of MeOH and EtOH ? At this moment, we can not answer this question because the mechanisms of reaction *steps 1* and *2* in Scheme 1 have not been clarified.[1,2] However, the redox of $Ti^{4+/3+}$ and $Ti^{3+/2+}$ may be deeply concerned with the oxidations because these standard redox potentials are between those of $Zn^{2+/0}$ and $Eu^{3+/2+}$.

References

1 I. Yamanaka, M. Soma, and K. Otsuka, *J. Chem. Soc., Chem. Commun.*, **1995**, 2235.
2 I. Yamanaka, K. Nakagaki, and K. Otsuka, *J. Chem. Soc., Chem. Commun.*, **1995**, 1185; I. Yamanaka, K. Nakagaki, T. Akimoto, and K. Otsuka, *J. Chem. Soc., Perkin Trans. 2,* submitted for publication.
3 D. H. R. Barton, E. Csuhai, D. Doller, N. Ozbalik, and N. Senglet, *Tetrahedron Lett.*, **31**, 3097 (1990).
4 E. G. Thomas, F. Oliver, and A. Sen, *J. Am. Chem. Soc.*, **109**, 8109 (1987).