Oxidation of Methane to Methanol with Oxygen Catalysed by Europium Trichloride at Room Temperature

Ichiro Yamanaka,* Masanori Soma and Kiyoshi Otsuka*

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Oxidation of methane to methanol with O_2 is catalysed by an $EuCl_3$–Zn–CF_3CO_2H system at 40 °C.

Methane is the least reactive hydrocarbon in the universe. Therefore the partial oxidation of methane to methanol with O_2 under ambient conditions is a dream reaction for chemists. It is well known that methane monooxygenase catalyses the oxidation of methane to methanol in air and at room temperature.[1] Many chemists have proposed a highly efficient catalytic system based on an enzyme model,[2] methane monooxygenase, or on powerful transition metal catalysts.[3–5] However, most of the attempts were carried out under high pressures of 30–100 atm and at high temperature of 100–180 °C. Here we report the direct oxidation of methane to methanol with O_2 by using an $EuCl_3$-catalytic system under ambient conditions.

We have reported the oxidation of higher alkanes (excluding cyclohexane) and the epoxidation of alkenes (excluding propene) catalysed by an $EuCl_3$-catalytic system ($EuCl_3$, O_2, Zn powder, $MeCO_2H$, and a solvent such as CH_2Cl_2).[6] This observation, where the rare earth element acts as a catalyst for the hydrocarbon oxidation under ambient conditions, is a very rare case. We have applied this $EuCl_3$-catalytic system to the partial oxidation of methane to methanol. However, MeOH and CO_2 were produced mainly from the $MeCO_2H$. Recently we found that the use of CF_3CO_2H as a proton donor instead of $MeCO_2H$ and the elimination of the solvent, CH_2Cl_2, realise the catalytic methane oxidation [eqn. (1)] at room temperature.

$$CH_4 + O_2 + 2\,e^- \,(Zn) + 2H^+(CF_3CO_2H) \rightarrow MeOH + H_2O \quad (1)$$

The standard conditions for the $EuCl_3$-catalytic system of the reaction were $EuCl_3$ (30 µmol), CF_3CO_2H (4 ml), Zn powder (1 g), O_2 (4 atm) and CH_4 (10 atm). Only MeOH was produced in the liquid phase with no production of HCHO. The formation of CO_2 was observed in the gas phase. The turnover number (TON) based on $EuCl_3$ for the formation of MeOH (TON = mol of MeOH produced/mol of $EuCl_3$ used) was 4.0 in 1 h, corresponding to a yield of 0.8% based on CH_4. Methanol was not produced if any one of the reagents ($EuCl_3$, CF_3CO_2H, Zn powder, O_2 or CH_4) was removed from the catalytic system. Other proton donors instead of CF_3CO_2H were tested. Formation of MeOH was observed using $C_2F_5CO_2H$ (TON = 0.45 in 1 h), $(CF_3CO)_2O$ (0.22) and $(CF_3CO)_2CH_2$ (0.12). CF_3CO_2H was therefore shown to be the most suitable proton donor for this catalytic system.

Fig. 1 shows the effect of methane pressure on the TON of MeOH and CO_2. The formation of MeOH was observed even at 1 atm with a yield of 4% and a TON of 1.6 in 1 h. The TON of MeOH increased with increasing CH_4 pressure. The maximum TON of MeOH (5.3 in 1 h) was obtained at 16 atm. In contrast to the formation of MeOH, a large amount of CO_2 was produced in the absence of CH_4. However, as described earlier, MeOH was never produced in the absence of CH_4. The TON of CO_2 decreased with increasing CH_4 pressure. Thus, the selectivity to MeOH increased with increasing CH_4 pressure. These results strongly suggest that MeOH is produced only from CH_4 and CO_2 exclusively from CF_3CO_2H. When the reaction was carried out in the absence of $EuCl_3$, neither MeOH nor CO_2 was produced. These results indicate that $EuCl_3$ catalyses both the formation of MeOH from CH_4 and of CO_2 from CF_3CO_2H. Fig. 2 shows the effect of temperature on methane oxidation under a CH_4 pressure of 10 atm. Methane was oxidized with O_2 to form MeOH even at 0 °C. The TON of MeOH increased with increasing temperature. A TON of 5.3 in 1 h was obtained at 50 °C. The TON of CO_2 also increased with temperature.

Other rare earth salts and transition metal salts were tested as catalysts for the methane oxidation under the standard conditions. The results are shown in Fig. 3. All the Eu-salts and Eu-DPM [tris(2,2,6,6-tetramethyl-3,5-heptanedionato) Eu(III)] were active for the methane oxidation. Other rare earth chlorides did not show any catalytic activity. In the case of transition-metal chlorides, MeOH was formed with catalytic $FeCl_3$ and $CuCl_2$. The TON of MeOH for these catalysts, however, were quite low compared to when $EuCl_3$ was used. These results indicate that the Eu cation has a special activity for the catalytic oxidation of CH_4 to MeOH.

The partial oxidation of ethane was also tested by using the same $EuCl_3$-catalytic system under the standard conditions. Ethanol (TON = 9.2 in 1 h), acetaldehyde (1.1 in 1 h) and CO_2 (4.3 in 1 h) were formed. The sum of the TON for ethanol and acetaldehyde was twice as large than that of MeOH in the

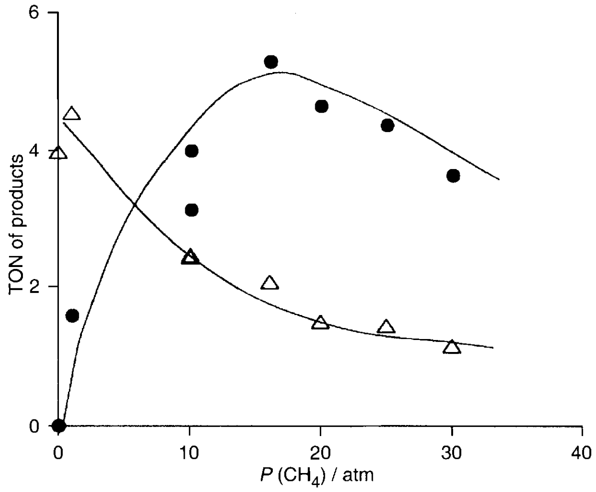

Fig. 1 Effect of methane pressure on the oxidation of methane catalysed by $EuCl_3$. (●) TON of MeOH, (△) TON of CO_2 (×0.1).†

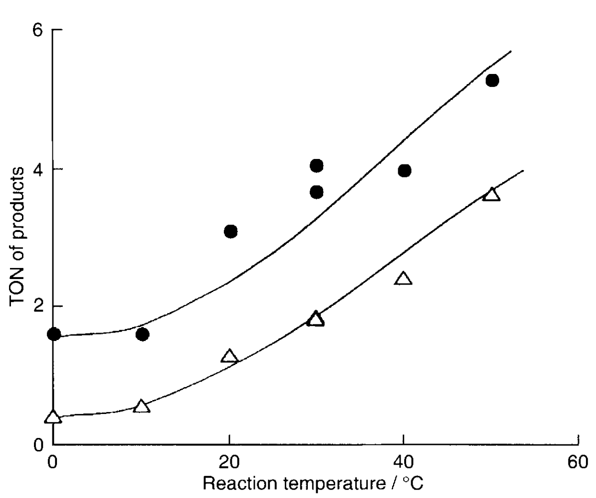

Fig. 2 Temperature dependence of the oxidation of methane catalysed by $EuCl_3$. (●) TON of MeOH, (△) TON of CO_2 (×0.1). The reaction procedure are similar to those used previously† except that $P(CH_4)$ = 10 atm. (17.3 mmol) and T = 0–50 °C.

methane oxidation. In the ethane oxidation, the catalytic formation of ethanol (0.93 in 1 h) and acetaldehyde (0.38 in 1 h) was observed when $MeCO_2H$ was used as the proton donor instead of CF_3CO_2H.

As described above, the $EuCl_3$-catalytic system ($EuCl_3$, O_2, Zn powder, CF_3CO_2H, and alkane) catalysed the oxidation of methane to methanol and ethane to ethanol and acetaldehyde at room temperature. The efficiency of the Zn powder for the oxidation of methane defined as $\phi(Zn) = 100 \times$ [amount of methanol (mol)]/[amount of Zn reacted (mol)] (%) was less than 2%. Why does only europium catalyse the methane oxidation reaction specifically? We cannot answer this question at the moment. However, it should be noted that only europium has a redox potential of RE^{3+}/RE^{2+} (−0.35 V *vs.* NHE) higher than that of Zn^{2+}/Zn^0 (−0.77 V) among the rare earth elements RE. We suggest that the divalent europium has unique catalytic ability for the monooxygenation of alkanes and alkenes under mild reaction conditions.[6]

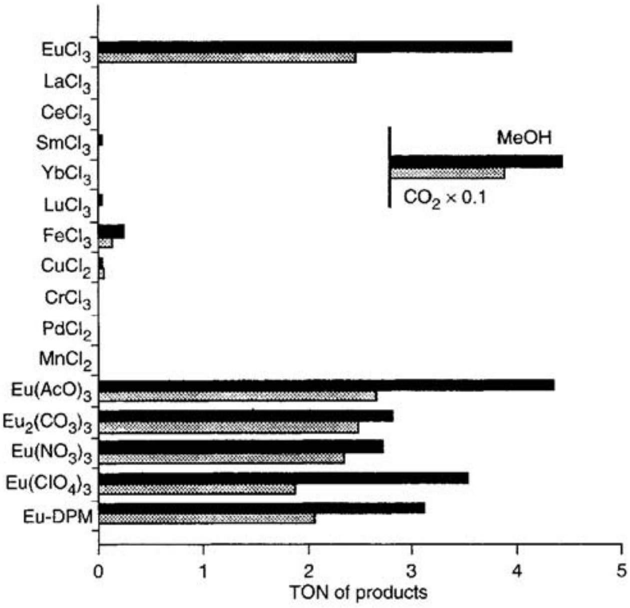

Fig. 3 The oxidation of methane by using various metal-salt catalysts. Eu(AcO) = Eu($MeCO_2$); Eu-DPM = tris(2,2,6,6-tetramethyl-3,5-heptanedionato) Eu(III). The reaction procedures are similar to those used previously† except that $P(CH_4)$ = 10 atm. (17.3 mmol) and 30 µmol of catalyst was used.

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† The reaction was carried out as follows: $EuCl_3 \cdot 6H_2O$ (30 µmol) was dissolved in CF_3CO_2H (4 ml; 13.1 mmol) in a glass-lined autoclave (47 ml). Zinc powder (1 g; 15.3 mmol) was then added to the mixture and CH_4 (0–30 atm.; 0–51.9 mmol) and O_2 (4 atm.; 6.9 mmol) were introduced. The reaction was carried out for 1 h with stirring by a magnetic spin-bar at 40 °C. The liquid products were analysed by GC after the reaction mixture was filtered and neutralised with NaOH (aq.) in the gaseous phase.

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