

Oxidation of methane and benzene with oxygen catalyzed by reduced vanadium species at 40°C

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Received 23 June 1997; accepted 20 November 1997

Abstract

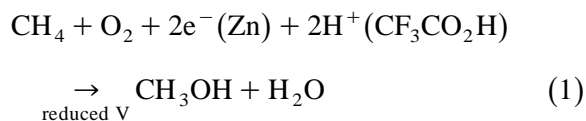
Hydroxylation of CH₄ to MeTFA was performed by NH₄VO₃⁻ or VO·(Acac)₂-O₂-Zn⁰-CF₃CO₂H-systems at 40°C. Reduced vanadium species produced from V⁵⁺ or V⁴⁺ by the reduction with Zn⁰ work as a catalyst for reductive activation of O₂ and the hydroxylation of CH₄. This vanadium species also catalyze hydroxylation of benzene to PhOH. The active oxygen species generated in V-system has strong radical character and weak electrophilicity compared with that of the EuCl₃-O₂-Zn⁰-CF₃CO₂H system. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxylation; Methane; Benzene; Methanol; Phenol; Vanadium

1. Introduction

We have recently reported the oxidation of CH₄ to MeOH by using the EuCl₃-O₂-Zn⁰-TFAH-catalytic system (TFAH: CF₃CO₂H) [1]. Eu(II), together with e⁻ and H⁺, was suggested to be responsible for the activation of O₂ and the hydroxylation of CH₄ and other hydrocarbons [1–5]. Among rare earth elements, only europium has the standard redox potential (Eu³⁺/Eu²⁺ = -0.35 V vs. NHE) above zinc (Zn²⁺/Zn⁰ = -0.77). The catalytic activities of some cations tested were very low (TON; FeCl₃ 0.24, CuCl₂ 0.03, CrCl₃ < 0.01). These cations reduced with Zn⁰ but may be reduced into zero-valence state. While, europium cation

should not be reduced to metal by Zn⁰. Therefore, we have suggested that the redox of Eu³⁺/Eu²⁺ in the presence of Zn⁰ is a key factor for the hydroxylation of CH₄. This primitive concept suggests that other cations, whose redox potentials are higher than that of Zn²⁺/Zn⁰ but their lower valence cations are not reduced to metals, may be catalysts for the hydroxylation of CH₄. For example, candidate metal elements are V, Ti and Nb [6]. Actually, we tested these metal compounds and other compounds of 4A–5A group (Zr, Mo, and W). We have found that V-compounds catalyze the hydroxylation of CH₄ to MeOH (Eq. (1)). Details will be described in this report.



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2. Experimental

The reaction was carried out as below: catalysts (0.03 mmol) were dissolved in $\text{CF}_3\text{CO}_2\text{H}$ (TFAH) of 4 ml in an autoclave with glass liners (47 ml in volume). After Zn powder of 1 g was added to the mixture, CH_4 of 10 atm and O_2 of 4 atm were introduced. Reaction was carried out for 1 h by stirring with a magnetic spin-bar at 40°C . Products were analyzed by GC. Products were MeOH with no production of HCHO in the liquid phase and CO_2 in the gas phase. It was determined that MeOH in the mixture was present as ester, $\text{CF}_3\text{CO}_2\text{CH}_3$ (MeTFA). In a separate experiment, a rapid conversion of MeOH to MeTFA was observed in this reaction mixture. Oxidations of higher hydrocarbons (benzene, cyclohexane, and 1-hexane) were carried out using a mixture of MeCO_2H and CH_2Cl_2 instead of TFAH at atmosphere of O_2 [2–4]. Products were analyzed by capillary-GC with a FID detector and HPLC with an UV–Visible detector.

3. Results and discussion

Fig. 1 shows the activities of oxidation of CH_4 with O_2 catalyzed by some typical-metal

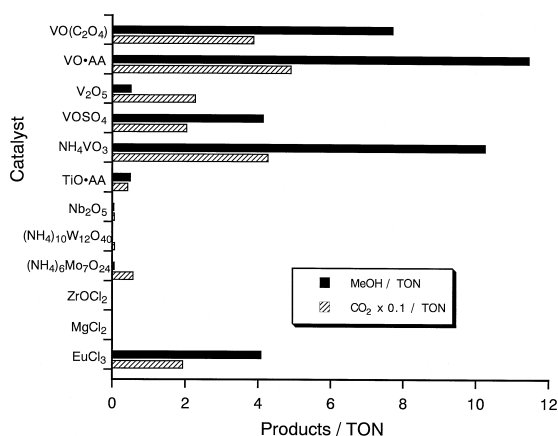


Fig. 1. The hydroxylation of CH_4 with O_2 catalyzed by various typical metal compounds at 40°C . $\text{VO}(\text{Acac})_2$: bis(2,4-pentanedionate) VO, $\text{TiO}(\text{Acac})_2$: bis(2,4-pentanedionate)TiO.

cation compounds at 40°C . All V-compounds in Fig. 1 catalyzed the hydroxylation of CH_4 to MeOH (MeTFA). NH_4VO_3 and bis(2,4-pentanedionate)VO ($\text{VO}\cdot(\text{Acac})_2$) were especially active for the formation of MeTFA, $\text{TON} > 10$ in 1 h. These catalytic activities are twice that of the standard EuCl_3 -system [1] and as well as the improved EuCl_3 -system enhanced by Ti compounds [5]. MeTFA was not produced if any one of the elements (catalysts, TFAH, Zn^0 , O_2 or CH_4) had been removed from NH_4VO_3 - and $\text{VO}\cdot(\text{Acac})_2$ -catalytic systems. There are not much difference between the catalytic activities of V^{5+} (NH_4VO_3) and V^{4+} ($\text{VO}\cdot(\text{Acac})_2$) in Fig. 1. This fact implies that the active forms of both catalysts are similar under the reaction condition. The standard redox potentials for V^{5+} and V^{4+} ($\text{VO}_2^+/\text{VO}^{2+} = +1.00$, $\text{VO}^{2+}/\text{V}^{3+} = +0.337$, $\text{V}^{3+}/\text{V}^{2+} = -0.255$) propose that vanadium may be reduced with Zn^0 to V^{2+} or V^{3+} . Actually, the change of the color of the solution from purple (V^{4+}) to orange (V^{2+}) was observed [6]. While, just $\text{TiO}\cdot(\text{Acac})_2$ [5] shows a very low catalytic activity for the hydroxylation of CH_4 among other compounds except for V-compounds. The enhancement effect of co-addition of $\text{TiO}\cdot(\text{Acac})_2$ was not observed in NH_4VO_3 - and $\text{VO}\cdot(\text{Acac})_2$ -systems [5].

Effect of pressure of CH_4 on the formation of MeTFA and CO_2 was studied for NH_4VO_3 -system. The formation of MeTFA was observed at 1 atm with a yield of 7% and a TON of 4.0 in 1 h. The TON for MeTFA formation increased with increasing the pressure of CH_4 . The maximum TON for formation of MeTFA (11 in 1 h) was obtained at 15 atm. In contrast to the formation of MeTFA, a large amount of CO_2 was produced in the absence of CH_4 . However, as described earlier, MeTFA was never produced in the absence of CH_4 . The TON of CO_2 decreased with increasing the pressure of CH_4 . When the reaction was carried out in the absence of V-catalysts, neither MeTFA nor CO_2 was produced. These results suggest that reduced V species catalyses both formations of

MeOH (MeTFA) from CH₄ and of CO₂ from TFAH. These observations are similar to that for the EuCl₃-system [1,5].

When hydroxylation of benzene was carried out using VO·(Acac)₂-O₂-Zn⁰-AcOH-CH₂Cl₂-system, phenol (7.6 TON in 1 h), hydroquinone (0.89), catechol (0.24), and biphenyl (0.12) were produced. Products were present as free form, e.g., phenol but not phenyl acetate, in the reaction mixture. The yield of phenol was more than twice larger than that for EuCl₃-system [2–4]. In hydroxylation of toluene, products were benzyl position oxygenates, benzyl alcohol (2.17 TON in 1 h) and benzaldehyde (0.09), and benzene ring oxygenates, *o*- (3.51), *m*- (1.51), and *p*-cresol (1.45). The ration of the total amounts of benzyl position oxygenates and that of cresols, Bz:Cr, was 1.0:2.9 in V-system that is almost the same as that of Eu-system (1.0:2.6) [2–4]. The selectivity of *o*-: *m*-: *p*- in cresols per C–H bonds was 2:1:2 in V-system that is very different from that of 13:1:16 in Eu-system [2–4]. Then, product selectivities in the oxidation of 1-hexene were very different between VO·(Acac)₂- and EuCl₃-systems. The major product was pentanal (67% selectivity) in the VO·(Acac)₂-system but the selectivity to 1,2-epoxyhexane was just 6%. The epoxide is major product (> 70%) in EuCl₃-system [2–4]. These results suggest that active oxygen species in V-system have stronger radical character than that of EuCl₃-system.

A kinetic isotope effect (KIE) in the oxidation of a mixture of cy-C₆H₁₂ and cy-C₆D₁₂ (1:1 (mol)) was 2.0 in VO·(Acac)₂-system. Cyclohexanol (92%), not cyclohexyl acetate, as the main product and cyclohexanone (8%) were formed in the oxidation of cyclohexane. A regioselectivity to secondary and tertiary C–H bonds (2°/3°) per number of C–H bonds in the adamantane oxidation was 2.7. These results of the KIE and the 2°/3° are the same as those of the last version of the Gif-system [7,8]. However, some different reactivities for the oxidation in Gif-system were observed to compare with that for the V-system, (i) the hydroxyl-

ations of CH₄ and benzene and the oxidation of alkene do not proceed, (ii) cyclohexanone (~ 92% selectivity) is the main product, and (iii) pyridine derivatives are essential component. These facts suggested that the active oxygen species in our V-system are different from that of the Gif-system.

Very recently, Nizova et al. and Shul'pin and Suss-Fink reported oxidation of CH₄ to MeOOH and cyclohexane to cy-C₆H₁₁OOH with H₂O₂ and O₂ catalyzed by [NBu₄]VO₃-pyrazine-2-carboxylic acid in MeCN [9,10]. They said that HO· initiates the cleavage of C–H bonds of CH₄ and cyclohexane. It is important that the active oxygen species in our V-system is HO· or not. As mentioned above, KIE = 2.0 for the cyclohexane oxidation in our V-system is different from KIE = 1.1 observed for HO· [11,12] and MeOH (MeTFA) is only product from CH₄ in our V-system. These facts suggest that the active oxygen species in our V-system are not likely to be HO· (Shul'pin's V-system [9,10]).

It is well known that V⁴⁺ or V⁵⁺ catalyses the oxidation of hydrocarbons with various oxidants (H₂O₂, *tert*-BuOOH, etc.) [9,10,13,14] or with a combination of O₂ and reductants [15,16]. In our system, it is suggested that reduced vanadium species, V²⁺ or V³⁺, that was generated by reduction with Zn⁰, work as catalyst for activation of O₂ and hydroxylation of CH₄ and benzene.

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