Catal Lett (2013) 143:126–129
DOI 10.1007/s10562-012-0931-0

Partial Oxidation of Methane with the Catalysis of Palladium(II) and Molybdovanadophosphoric Acid Using Molecular Oxygen as the Oxidant

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Received: 3 September 2012 / Accepted: 16 October 2012 / Published online: 7 November 2012

Abstract With the catalysis of K_2PdCl_4 and $H_5PMo_{10}V_2O_{40}$ in CF_3COOH, methane can be oxidized into CH_3COOH and CF_3COOCH_3 using molecular oxygen as the oxidant at a low temperature. $H_5PMo_{10}V_2O_{40}$ is a reversible oxidant that allows to retain Pd(II) in CF_3COOH and thus to complete a two-step catalytic cycle of oxidation of methane by molecular oxygen; in addition, it can catalytically oxidize methane into CH_3COOH and CF_3COOCH_3.

Keywords Homogeneous catalysis · C–H bond activation · Partial oxidation · Methane · Molecular oxygen

1 Introduction

The activation of methane has attracted much attention due to its high abundance in natural gas and its low activity. Current technologies for the activation of methane proceed by generation of carbon monoxide and hydrogen (syngas), followed by converting syngas into liquid products through Fischer–Tropsch chemistry. However, the production of syngas is an energy-intensive and cost-intensive process. In contrast, direct, low-temperature, partial oxidation of methane becomes promising.

Although methane can be oxidized into methanol and chloromethane with $PtCl_6^{2-}$ as the oxidant and with $PtCl_4^{2-}$ as the catalyst in an aqueous solution, the yield and selectivity of methanol are very low [1]. Periana et al. [2, 3] have reported that high conversion of methanol derivatives from methane could be obtained with the catalysis of Hg(II) or Pt(II) in concentrated sulfuric acid. The metal ion M(II) (M=Hg, Pt) reacts with methane by an electrophilic displacement mechanism to produce CH_3MOSO_3H which can readily decompose to CH_3OSO_3H and the reduced metal species. The catalytic cycle is completed by the reoxidation of the reduced metal species with concentrated sulfuric acid to regenerate M(II) [2, 3]. Pt(II) is more efficient than Hg(II) during the catalysis reaction, however, it will be irreversibly reduced in bulk metal, which results in fast deactivation of catalysts and steep decrease of selectivity [2]. In order to inhibit the irreversible reduction, Periana et al. [3] further developed a stable platinum ligand (bpym)$PtCl_2$, which could directly oxidize methane into a methanol derivative with higher yield and selectivity. About 90 % methane conversion and 81 % selectivity could be obtained at 220 °C for 2.5 h [3]. Although Hg(II) and Pt(II) salts can give high catalytic activity, Hg(II) salt is high toxic, and (bpym)$PtCl_2$ is too expensive, which hinders their industrial application.

In addition, the oxidation of methane to acetic acid catalyzed by Pd^{2+} in 96 wt% sulfur acid has been described by Periana et al. [4], in which the selectivity of liquid-phase product, acetic acid and methyl bisulfate, is as high as 90 %. However, Pd^{2+} is also reduced irreversibly to Pd black, which leads to the deactivation of catalyst. In order to regenerate the catalyst, Zerella et al. [5] have suggested to reoxidize palladium black by oxygen and sulfur acid.

Molybdovanadophosphoric acid (HPA) was reported to have good catalytic activity in the partial oxidation of

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methane by H_2O_2 or $K_2S_2O_8$ [6–8]. With the catalysis of $H_4PVMo_{11}O_{40}$, 33.0 % conversion of methane could be obtained at 80 °C in $(CF_3CO)_2O$ using H_2O_2 as the oxidant [6, 7].

Besides catalysts, the oxidants are crucial to the partial oxidation process. Strong oxidants, such as concentrated sulfuric acid, H_2O_2 and $K_2S_2O_8$, are necessary in transition metal catalytic systems or in HPA catalytic systems. Molecular oxygen is an environmentally friendly, inexpensive oxidant; however, due to its relatively poor oxidation capacity, there are only a few reports on partial oxidation of methane using molecular oxygen as the oxidant. In addition to the above mentioned catalytic system suggested by Bell et al., An et al. developed a catalytic system for the one-pot aerobic oxidation of methane with the combination of the three redox couples Pd(II)/Pd(0), p-benzoquinone (BQ)/hydrobenzoquinone (H_2Q), NO_2/NO in CF_3COOH [9]. However, methane conversion is too low in this catalytic system [9].

Pd(II)/HPA/O_2 system is very important in homogeneous catalysis of organic synthesis [10]. In this system, HPA is a reversible oxidant that allows to retain Pd(II) in the solution and thus to complete a two-step catalytic cycle of oxidation of the substrates by molecular oxygen [10]. In order to develop an efficient method for partial oxidation of methane using molecular oxygen as the oxidant, $K_2PdCl_4/H_5PMo_{10}V_2O_{40}$ catalytic system is suggested in this study.

2 Experimental

2.1 Materials

K_2PdCl_4 and CF_3COOH were purchased from Shanghai Jingchun Reagent Co. Ltd., P. R. China. BQ was purchased from Sinopharm Chemical Reagent Co. Ltd., P. R. China. Methane, oxygen and nitrogen were obtained from Beijing Huayuan Gas Co. Ltd., P. R. China. $H_5PMo_{10}V_2O_{40}$ was prepared from H_3PO_4, MoO_3, and V_2O_5 [11]. H_3PO_4, MoO_3 and V_2O_5 were from Beijing Chemical Factory, P. R. China. All of the chemical reagents are at analytic reagent grade.

2.2 Partial Oxidation of Methane

K_2PdCl_4 and $H_5PMo_{10}V_2O_{40}$ were dissolved in CF_3COOH before methane oxidation reaction. In addition, NaCl was also introduced into CF_3COOH, and the molar ratio of NaCl to K_2PdCl_4 is 50.

Methane oxidation in 10 ml of CF_3COOH was conducted in a 50 ml cylindrical stainless steel autoclave with a Teflon liner inside. Mild stirring was provided by a magnetic stirring bar coated with Teflon. The reactor was three times purged with 1.0 MPa of methane and then pressurized with methane and oxygen. It was heated to 80 °C in an oil bath and kept under stirring. After the reaction, the reactor was cooled in ice/water mixture to 3 °C, thus the pressure was slowly reduced.

The products were analyzed by gas chromatography-mass spectroscopy (GC–MS) and ^{1}H-NMR (Brucker AV600, Swiss). The gas phase was analyzed by a gas chromatograph (GC 4000A, East & West Analytical, PRC) with TDX-01 column, and the liquid was qualified by a gas chromatograph with a Porapak QS column.

2.3 Preparation of the Nascent Pd(0)

The nascent Pd(0) powders were prepared by the reduction of $Pd(OAc)_2$. pH value of $Pd(OAc)_2$ aqueous solution was adjusted to about ten by adding ammonia solution, then hydrazine hydrate was added into the solution, thus the nascent Pd(0) sediment formed. The black sediment was cleaned by distilled water for times in order to remove the residual Pd^{2+} ions.

2.4 Oxidation Reaction of the Nascent Pd(0) by $H_5PMo_{10}V_2O_{40}$ in CF_3COOH

0.0044 g of $H_5PMo_{10}V_2O_{40}$ powders was firstly dissolved in 25 ml of CF_3COOH, then 20 ml of $H_5PMo_{10}V_2O_{40}$ solution were used to oxidize 0.0022 g of the nascent Pd(0). At the same time, 1 ml acetic acid was also added to provide acetate ions. Concentration of Pd^{2+} in the samples at various intervals was analyzed by colorimetric method using 5-Cl-PADAB as the developer at wavelength of 570 nm.

3 Results and Discussion

3.1 Partial Oxidation of Methane

The results of Gretz et al. [12] implied that Pd(II) could oxidize methane selectively to CF_3COOCH_3 in CF_3COOH at 80 °C. In that process, Pd(II) did not act as a catalyst because it was stoichiometrically converted to Pd(0) [13]. In order to regenerate Pd(II), we chose $H_5PMo_{10}V_2O_{40}$ to oxidize Pd(0), and molecular oxygen as the terminal oxidant to regenerate $H_5PMo_{10}V_2O_{40}$.

Table 1 lists a series of typical reaction results for partial oxidation of methane in CF_3COOH catalyzed by $H_5PMo_{10}V_2O_{40}$ or $K_2PdCl_4/H_5PMo_{10}V_2O_{40}$. It shows in Table 1 that Pd^{2+} can stoichiometrically oxidize methane into CF_3COOCH_3 in CF_3COOH, which is consistent with the previous results [9, 13]. Using molecular oxygen as the

Table 1 Results of the partial oxidation of methane using molecular oxygen as the oxidant[a]

Entry	K_2PdCl_4 (mM)	$H_5PMo_{10}V_2O_{40}$ (mM)	CH_4 (MPa)	O_2 (MPa)	CF_3COOCH_3 (mM)	CH_3COOH (mM)
1	0.05	0	3.0	0.5	0.05	0
2	0	0.050	3.0	0.5	0.16	58.46
3	0.05	0.050	3.0	0.5	3.38	150.73
4	0.05	0.025	3.0	0.5	0.11	70.61
5	0.05	0.050	3.0	1.0	3.88	180.93
6	0.05	0.050	3.0	1.5	4.05	208.34
7	0.05	0.050	2.0	1.5	0.98	103.18
8	0.05	0.050	2.5	1.5	2.81	160.66

[a] Conditions: CF_3COOH, 10 ml; molar ratio of NaCl to K_2PdCl_4, 50; 80 °C; 8 h

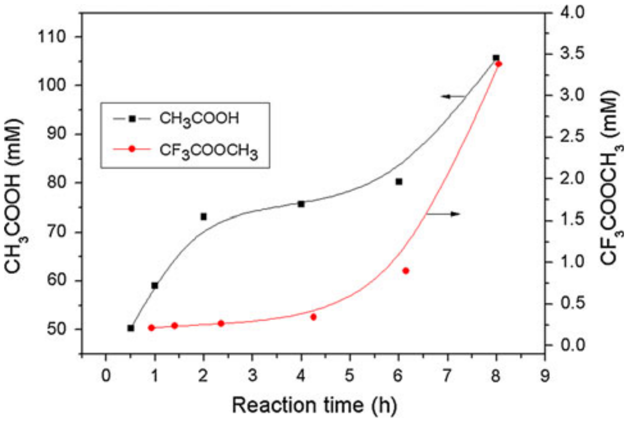

Fig. 1 The concentration of CH_3COOH and CF_3COOCH_3 as a function of reaction time. (Conditions: CF_3COOH, 10 ml; molar ratio of Cl^- to K_2PdCl_4, 50; 80 °C; K_2PdCl_4, 0.05 mM; $H_5PMo_{10}V_2O_{40}$, 0.050 mM; CH_4, 3.0 MPa; O_2, 0.5 MPa.)

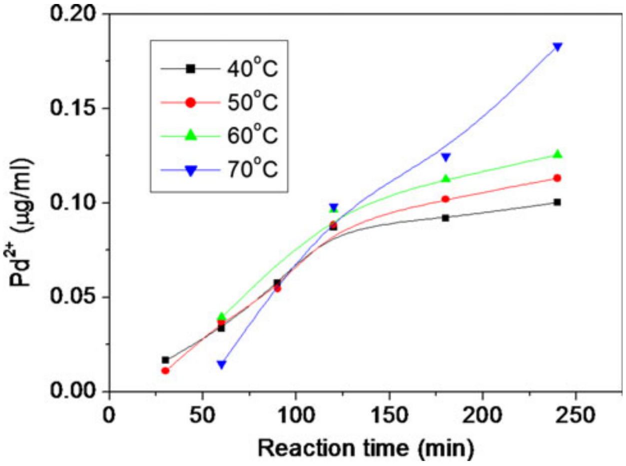

Fig. 2 Oxidation rate of the nascent Pd(0) by $H_5PMo_{10}V_2O_{40}$ in CF_3COOH at various temperatures. (Conditions: the nascent Pd(0), 0.0022 g; $H_5PMo_{10}V_2O_{40}$, 0.0035 g; HOAc, 1 ml; CF_3COOH, 20 ml)

oxidant, methane can be oxidized into CH_3COOH and CF_3COOCH_3 with the catalysis of $H_5PMo_{10}V_2O_{40}$ or $K_2PdCl_4/H_5PMo_{10}V_2O_{40}$, and CH_3COOH is the major product. In addition, the yield in $K_2PdCl_4/H_5PMo_{10}V_2O_{40}$ binary-component system is more than the yield sum in single-component system (Table 1, entry 1, 2 and 3), indicating $K_2PdCl_4/H_5PMo_{10}V_2O_{40}$ binary-component catalyst exhibits good activity. Moreover, higher concentration of $H_5PMo_{10}V_2O_{40}$ in $K_2PdCl_4/H_5PMo_{10}V_2O_{40}$ catalysts leads to higher conversion (Table 1, entry 3 and 4). Higher concentration of $H_5PMo_{10}V_2O_{40}$ can improve the activity of Pd(II); however, limited by the solubility of $H_5PMo_{10}V_2O_{40}$ in CF_3COOH, it is difficult to increase its concentration further.

The yield of CH_3COOH and CF_3COOCH_3 increases with increasing partial pressure of oxygen (Table 1, entry 3, 5 and 6), since the regeneration rate of HPA increases with partial pressure of oxygen [12]. In addition, the yield of CH_3COOH and CF_3COOCH_3 increases with increasing partial pressure of methane (Table 1, entry 6, 7 and 8).

In $Pd(OAc)_2/BQ/NO_2/O_2$ system, CF_3COOCH_3 is the only product [9]. In contrast, CH_3COOH is the major product when using $K_2PdCl_4/H_5PMo_{10}V_2O_{40}$ as catalysts. With the increase of reaction time, the concentration of CH_3COOH and CF_3COOCH_3 increases (Fig. 1). At 8 h, the conversion of methane adds up to 10.85 %, higher than the results in $Pd(OAc)_2/BQ/NO_2/O_2$ system [9].

3.2 Possible Mechanism

Periana et al. [3] tried to prevent the reduction of Pd(II) by the addition of HPA in concentration sulfuric acid but failed. It is probably because concentration sulfuric acid could not regenerate HPA. Once HPA is reduced, it cannot oxidize Pd(0) to Pd(II), which results in catalyst deactivation.

Although it is well known that HPA can oxidize Pd(0) into Pd(II) in aqueous solution [14, 15], there has been no reports on the oxidization of Pd(0) in CF_3COOH. Figure 2 shows oxidation rate of the nascent Pd(0) by $H_5PMo_{10}V_2O_{40}$ in CF_3COOH at various temperatures. It can be seen from Fig. 2 that $H_5PV_2Mo_{10}O_{40}$ can oxidize Pd(0) powders into

Pd(II) in CF_3COOH, and the increase of reaction temperature can enhance the oxidation rate. That indicates that $H_5PMo_{10}V_2O_{40}/O_2$ system can inhibit the deactivation of Pd(II).

The partial oxidation of methane with Pd(II)/$H_5PMo_{10}V_2O_{40}$ as the catalysts and with molecular oxygen as the oxidant might occur in the following routes: (1) Pd(II) oxidizes methane into CF_3COOCH_3, then is regenerated with $H_5PMo_{10}V_2O_{40}$ and oxygen; (2) $H_5PMo_{10}V_2O_{40}$ abstracts H· from CH_4 to form a methyl radical ($CH_3\cdot$) which would be oxidized by $H_5PMo_{10}V_2O_{40}$ to a methyl cation (CH_3^+), then CH_3^+ combines with COO^- from CF_3COOH into CH_3COOH, and with CF_3COO^- into CF_3COOCH_3 [8, 16].

4 Conclusion

Methane can be partially oxidized into CH_3COOH and CF_3COOCH_3 with the catalysis of K_2PdCl_4 and $H_5PMo_{10}V_2O_{40}$ using molecular oxygen as the oxidant at a low temperature. $H_5PMo_{10}V_2O_{40}$ is a reversible oxidant that allows to retain Pd(II) in CF_3COOH and thus to complete a two-step catalytic cycle of oxidation of methane by molecular oxygen; in addition, it can catalytically oxidize methane into CH_3COOH and CF_3COOCH_3.

Acknowledgments This work was supported by the National Natural Sciences Foundation of China (Grant No. 20776013), Beijing Natural Science Foundation (Grant No. 2102034) and the Special Fund of Basic Research in Central Universities (Grant No. JD1107).

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