Influencing factors for catalytic oxidation of mine gas to methanol in liquid phase

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Abstract   The influencing factors for liquid phase catalytic oxidation of mine gas to methanol (in form of CH_3COOCH_3) are studied using the self-established experimental apparatus. The results show that CH_3COOCH_3 (target product) is obtained by using CH_3COOH as reaction solvent, and the yield of target product increases with the increasing of reaction temperature, gas pressure and reaction time. In the mine gas-$Pd(OAc)_2$-CH_3COOH system, the yield of CH_3COOCH_3 increases with the increasing of addition of $Pd(OAc)_2$ which is redox catalyst for mine gas conversion. The yield of CH_3COOCH_3 will be greatly improved by composite additional oxidant which is obtained by equimolar mix of p-benzoquinone with NO_2.

Key words   mine gas; liquid phase; methanol; influencing factor

1 Introduction

Mine gas, containing methane and air, is hazard for underground mining coal. Every year, a large amount of mine gas is vented into the atmosphere during coal mining, causing casualties and loss. So, a new technology for mine gas utilization is urgently demanded.

Methanol is regarded as an optimal product for conversion of methane (Chen, 2010), and can be synthesized using mine gas as raw material because mine gas is a mixture of methane and air. It is of extremely vital significance for developing this technology to prevent gas accidents, reduce greenhouse effect caused by gas emissions, and utilize the coal bed methane.

A variety of oxidants, such as H_2O_2, $K_2S_2O_8$ and $KMnO_4$, can oxidize methane to methanol (Zhang et al., 2008). O_2 is preferred for environmental protection purposes. However, the research of using O_2 as oxidant is still in infancy. In CF_3COOH solvent, methane reacts with O_2 at 80℃ to selectively generate methanol using $Pd(OAc)_2$ as catalyst (Kao et al., 1991; Lin et al., 1992). Yamanaka et al. (1995) have found that methane can be converted to methanol in the presence of O_2 by $EuCl_3$–Zn catalyst in CF_3COOH solvent. Thus, reaction of methane (1.0 MPa) with O_2 (0.4 MPa) at 40℃ generates methanol with yield of 0.8% in CF_3COOH medium. Fan et al. (2010) have discovered that the precious metal-metallophthalocyanine composite catalysts have catalytic activity for methane

oxidation with O_2 as oxidant.

We prepared the simulating mine gas by the compounding of CH_4, O_2 and N_2 in a certain proportion. In this paper, the experiment on catalytic oxidation of simulating mine gas to methanol was carried out in liquid phase, and influencing factors on the simulating mine gas conversion were examined according to the yield of target product.

2 Reagents and experimental procedures

2.1 Reagents

CH_4 (99.9%), O_2 (99.99%) and N_2 (99.999%) were furnished by Harbin Liming Gases Co.Ltd., Harbin, China. Pd $(OAc)_2$(AR), $H_3PO_4\cdot12$ MoO_3 (AR), p-benzoquinone (CP) and copper (CP) were obtained from Sinopharm Chemical Reagent Co.Ltd., Shanghai, China. CH_3COOH (AR) was purchased from Tianjin Ruijinte Chemical Co. Ltd., Tianjin, China. CF_3COOH (AR) was gained from Beijing Xingjin chemical works, Beijing, China. HNO_3 (AR) was provided by Beijing chemical works, Beijing, China.

2.2 Experimental procedures

All tests were carried out using the self-established experimental apparatus (Xu and Zhu, 2012). The 50 mL solvent and a certain amount of catalyst were put into the reactor, sealed, and flushed

with the N_2 for three times. After N_2, O_2 and CH_4 were pressurized into the reactor in turn, the reactor was heated to the enactment value in stirring condition. Then, the reaction was performed at the above temperature. After the reaction, the products of the oxidation reaction were analyzed by a gas chromatography (FULI9790) when the reactor was cooled to room temperature. At the end of the reaction, the gas was collected in a gas sampling bag, and tested by TCD detector and TDX-01 packed column (2 m×4 mm). The liquid product, i.e., CH_3COOCH_3, was analyzed with FID detector and KB-5 capillary column (50 m× 0.25 μm×0.25 μm) by external standard method.

3 Results and discussion

3.1 Selection of reaction solvent

At 130℃, the partial oxidation performance of mine gas with Pd (OAc)$_2$ as catalyst was examined in different solvents, and the results are listed in Table 1. As shown in the table, the mine gas can be converted to methanol. Because CF_3COOH and CH_3COOH are excessive in reaction system, the methanol synthesized can react with them, and give CF_3COOCH_3 and CH_3COOCH_3. So, the target product is given in the form of CF_3COOCH_3 or CH_3COOCH_3. Table 1 indicates that the amount of target product is higher when CF_3COOH is used as solvent. Considering the experimental cost and equipment protection, we chose CH_3COOH as solvent.

3.2 Quantity of Pd (OAc)$_2$ addition

At 130℃, the effect of quantity of Pd(OAc)$_2$ addition on selective oxidation of mine gas is studied in the presence of 3.2 MPa CH_4, 0.4 MPa O_2, 0.4 MPa N_2, and the results are shown in Fig.1. As shown in Fig.1, CH_3COOCH_3 is not formed without Pd(OAc)$_2$. When Pd(OAc)$_2$ is added into the reaction system,
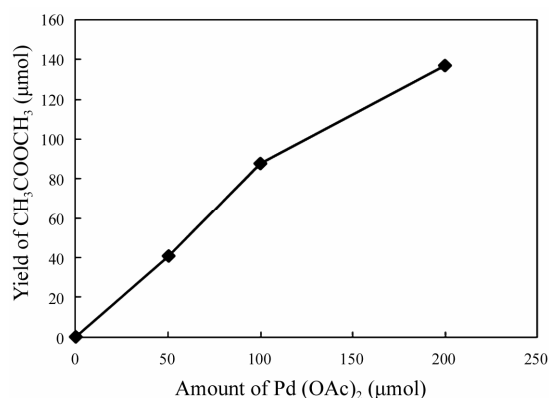
CH_3COOCH_3 is determined in solution after the reaction finished. This indicates that Pd(OAc)$_2$ is redox catalyst of methane conversion in the mine gas-Pd(OAc)$_2$-CH_3COOH system. The experiment result, the yield of CH_3COOCH_3, increases with the increase of Pd (OAc)$_2$ addition quantity, showing that the regeneration of catalyst can not happen under this condition due to the absence of an oxidant which is able to perform the conversion of Pd^0 to Pd^{2+}.

3.3 Additional oxidant

To improve performance of the catalyst, we need to constitute a new catalyst system to regenerate catalyst. So, it is necessary to choose an oxidant which is able to perform the conversion of Pd^0 to Pd^{2+}. The study of p-benzoquinone oxidizing Pd^0 to Pd^{2+} was reported by Yoshihiko et al. (1978) and Stefanie et al. (1999). P-benzoquinone is reduced into hydroquinone while it oxidizing Pd^0. The hydroquinone formed may be oxidized to p-benzoquinone by O_2 in mine gas. However, the slow regeneration rate of p-benzoquinone results in the decrease of catalytic activity of the reaction system (An, 2008). The oxidants, which can oxidize hydroquinone to p-benzoquinone rapidly, are required in order to increase the catalytic activity of the reaction system. The hydroquinone can be converted to p-benzoquinone by NO_x (Eric Bosch et al., 1994). Hence, NO_2 is chosen as the oxidant of regenerating p-benzoquinone. The composite additional oxidant is obtained by equimolar mix of p-benzoquinone with NO_2. At 130℃, the effect of additional oxidant on conversion reaction of mine gas was investigated in the presence of 100 μmol Pd(OAC)$_2$, 3.2 MPa CH_4, 0.4 MPa O_2, 0.4 MPa N_2, and the results are shown in Fig. 2. As shown in Fig. 2, the addition of additional oxidant increases greatly the yield of CH_3COOCH_3. However, the yield shows a downward trend while the addition of additional oxidant exceeds 2000 μmol, which might be that the excessive NO_2 causes deep oxidation of target product.
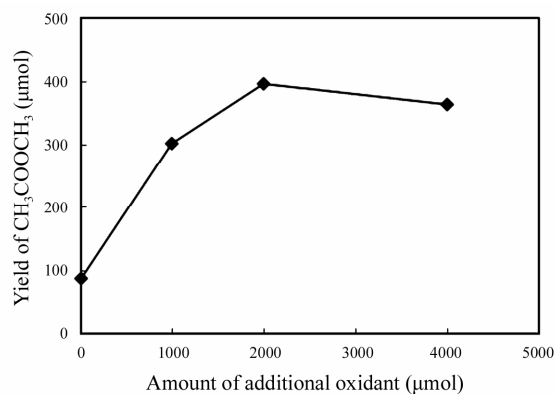

Fig. 1. Effect of Pd (OCA)$_2$ amount on thereaction.

Fig. 2. Effect of additional oxidant on thereaction.

Table 1   Effect of solvent on selective oxidation of mine gas

Entry	Solvent	Addition quantity of Pd(OAc)$_2$ (μmol)	Pressure of CH$_4$ (MPa)	Pressure of N$_2$ (MPa)	Pressure of O$_2$ (MPa)	Yield of target product	
						CF$_3$COOCH$_3$ (μmol)	CH$_3$COOCH$_3$ (μmol)
1	CF$_3$COOH	100	3.2	0.4	0.4	96	——
2	CH$_3$COOH	100	3.2	0.4	0.4	——	88

3.4 Temperature

The effect of temperature on selective oxidation of mine gas was studied in the presence of 100 μmol Pd (OAc)$_2$, 2000 μmol additional oxidant, 3.2 MPa CH$_4$, 0.4 MPa O$_2$, and 0.4 MPa N$_2$. The experimental results are shown in Fig. 3. Because high temperature helps to increase the number and percentage of active molecules, as well as the transforming of methane, the yield of target product increases with the increase of reaction temperature in the range of the experimental temperature. Considering the deep oxidation of methane under the condition of high temperature, the experimental temperature should not be too high. The selected experiment temperature is 130℃ in this paper.
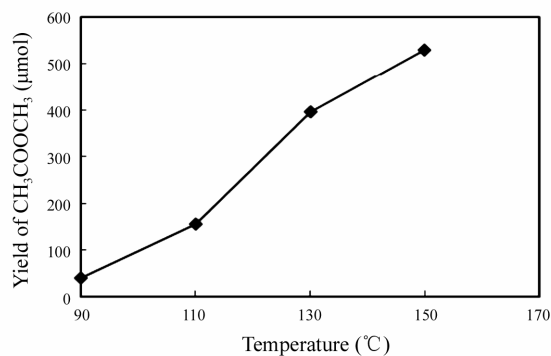

Fig. 3. Effect of temperature on thereaction.

3.5 Methane pressure

At 130℃, the effect of methane pressure on the yield of CH$_3$COOCH$_3$ was examined in the presence of 100 μmol Pd(OAc)$_2$, 2000 μmol additional oxidant, 0.4 MPa O$_2$, and 0.4 MPa N$_2$, and the results are shown in Fig. 4. The results indicate that higher gas pressure is, more yield of target product, whose reason is that the yield of target product is related with the gas solubility in solvent for liquid phase reaction. At the same temperature, there is positive correlation between the gas solubility in solvent and the pressure of gas. So, the yield of CH$_3$COOCH$_3$ increases with the increase of gas pressure.

3.6 Reaction time

At 130℃, the effect of reaction time on the yield of CH$_3$COOCH$_3$ is observed in the presence of 100 μmol Pd(OAc)$_2$, 2000 μmol additional oxidant, 3.2 MPa CH$_4$, 0.4 MPa O$_2$, and 0.4 MPa N$_2$. As shown in Fig. 5, the yield of CH$_3$COOCH$_3$ increases by basic linearity with the increase of reaction time in 7 hours.
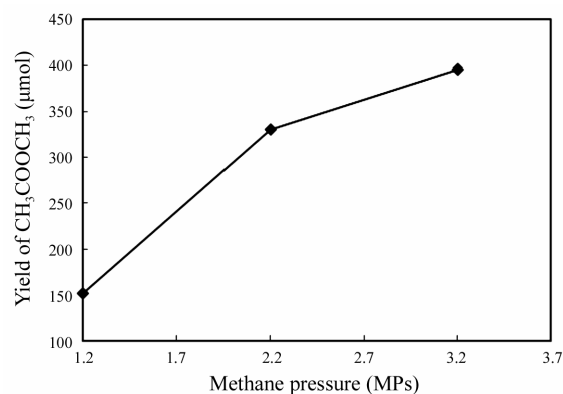

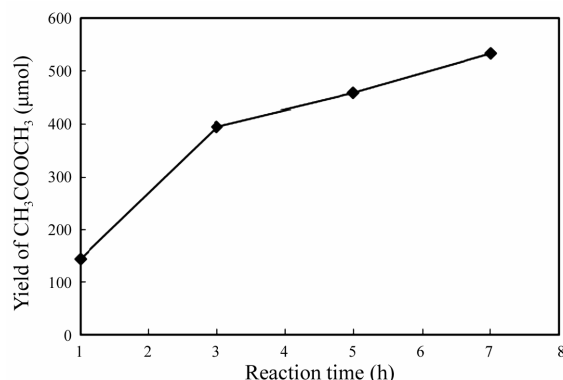Fig. 4. Effect of methane pressure on thereaction.

Fig. 5. Effect of reaction time on thereaction.

4 Conclusions

The influencing factors for liquid phase catalytic oxidation of mine gas to methanol are investigated. The following main conclusions are obtained.

(1) CH$_3$COOH can be used as solvent for catalytic oxidation of mine gas to methanol.

(2) Pd (OAc)$_2$ is redox catalyst of methane conversion in the mine gas-Pd (OAc)$_2$-CH$_3$COOH system. And the yield of CH$_3$COOCH$_3$ increases with the increase of Pd (OAc)$_2$ amount.

(3) The yield of CH$_3$COOCH$_3$ can be increased greatly by the composite additional oxidant which is obtained by equimolar mix of p-benzoquinone with NO$_2$. At 130℃, the optimum additive quantity of the additional oxidant is 2000 μmol in the presence of 100 μmol Pd(OAc)$_2$, 3.2 MPa CH$_4$, 0.4 MPa O$_2$, and 0.4 MPa N$_2$.

(4) The yield of CH$_3$COOCH$_3$ increases with the increase of reaction temperature, gas pressure and reaction time. However, considering the deep oxidation of methane under the condition of high temperature, the experimental temperature should not be too high.

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