

Selective oxidation of low-concentration coal mine gas to methanol in oleum over PbSO₄ catalyst

Feng Xu, Fan Li, Li-Hua Zhu and Yang Wu

College of Safety Engineering, Heilongjiang University of Science and Technology, Harbin 150022, China

E-mail: xufeng79_79@163.com

Abstract. Selective oxidation of low-concentration coal mine gas to methanol was carried out over PbSO₄ catalyst in a concentration of 20% oleum. The effects of reaction temperature, reaction pressure, reaction time and catalyst dosage on the conversion of methane in gas as well as the yield of methanol were studied. What is more, the reaction mechanism of selective oxidation of low-concentration coal mine gas was also investigated. The results showed that the optimal reaction conditions are determined under the reaction temperature of 180°C, the reaction pressure of 5MPa, the reaction time of 3h, and the PbSO₄ dosage of 300μmol for selective oxidation of low-concentration coal mine gas to methanol by PbSO₄ catalyst in oleum. Under this technological condition, the conversion ratio of methane in gas is 8.56% while the methanol selectivity is 78.59%. Mechanism research showed that methane in gas is transformed into methyl bisulfate firstly. Besides, the methyl bisulfate is hydrolyzed into methanol. The selective oxidation of low-concentration coal mine gas is following the mechanism of electrophilic substitution.

1. Introduction

Coal mine gas is a kind of unconventional natural gas. Methane, as the main component of coal mine gas, can be utilized to serve as chemical material[1,2]. On the situation of the energy shortage and the severity of work safety conditions, it is important to research preparation of methanol with coal mine gas, especially low-concentration coal mine gas as raw materials[3]. In 1993, by using concentrated sulfuric acid as both the solvent and the oxidant, Periana et al.[4]succeeded in converting methane to methanol with an HgSO₄ catalyst. In this system, methane in gas was transformed into methyl bisulfate (CH₃OSO₃H), which was immediately hydrolyzed to methanol:



In 1998, a solvent oleum was proposed to replace concentrated sulfuric acid with the conversion of methane by Periana et al.[5], and the conversion of methane and selectivity of methanol was developed further. In this system, the oxidant is SO₃. Since then, researchers have studied in depth on selective oxidation of methane in oleum. Moreover, gratifying progress has been made[6-12]. It has been shown that some catalysts, such as Pt(bpym)Cl₂, Hg₂SO₄, Pd₂SO₄ and iodine compounds, could achieve high methane conversion and yield of methanol[5,13-16]. On the basis of the above references, this paper investigated the liquid-phase selective oxidation of low-concentration coal mine



gas to methanol. Furthermore, selective oxidation of low-concentration coal mine gas to methanol was carried out over PbSO₄ catalyst in oleum. At the meanwhile, the mechanism of reaction was also discussed.

2. Experimental

2.1 Chemicals and apparatus

The low-concentration coal mine gas ($\varphi(\text{CH}_4)=25\%,\varphi(\text{O}_2)=5\%,\varphi(\text{N}_2)=70\%$) was purchased from Harbin Chunlin Gases Co., Ltd.. Oleum (AR, 20% SO₃) was produced by Shanghai Waigang Farm. Nickel sulfate (AR) and cadmium sulfate (AR) were obtained from Tianjin Zhiyuan Chemical Reagent Co. Ltd. Lead sulfate (AR) was provided by Beijing Chemical Reagent Co. Ltd. Zirconium sulfate (AR) was produced by Tianjin Guangfu Fine Chemical Research Institute.

The catalytic oxidation of low-concentration coal mine gas was carried out in a high pressure reactor. The reactor was made by Dalian Sanling Power Electronic Instrument Factory. The effective volume of the reactor was 20 milliliters. A polytetrafluoroethylene liner was placed inside of the reactor in order to separate the oleum from the reactor wall.

2.2 Catalytic reactions

A certain amount of sulfate catalyst and oleum were added into the reactor. The reactor was closed and purged with experimental mine gas for three times. The reactor was thereafter sealed with experimental gas under the desired pressure. The contents of the reactor were heated at the reaction temperature, and reacted for a certain reaction time under agitation conditions. After the end of reaction, the reactor was cooled until the room temperature.

The gas mixture in the reactor was collected and analyzed by gas chromatograph. The liquid sample in the reactor was diluted for 20 times with distilled water, and the resulting solution was hydrolyzed for 3 h at 90°C. After the hydrolysis, the solution was analyzed by gas chromatograph.

2.3 Product analysis

The gas mixture in the reactor was analyzed by a GC9790II gas chromatograph equipped with a packed column(TDX-01, 2m×4mm). Carbon monoxide, carbon dioxide and methane were tested by FID detector, and oxygen and nitrogen were tested by TCD detector. Methanol, as the product of hydrolysis of the liquid sample in the reactor, was analyzed by a GC9790 gas chromatograph equipped with a packed column (GDX-102, 2m×3mm) and a FID detector. The external standard method was used for the analyses of the above products. The selectivity of carbon monoxide, carbon dioxide and methanol as well as the conversion of methane can be calculated after carbon balance. Moreover, these formulas are defined as follows:

$$CH_4 \text{ conversion} = \frac{\frac{P_2V}{RT_2}(x_{CO} + x_{CO_2}) + n_{CH_3OH}}{\frac{PV_1}{RT_1}x_{CH_4}} \times 100\%$$

$$\text{Selectivity of CO} = \frac{\frac{P_2V}{RT_2}x_{CO}}{\frac{P_2V}{RT_2}(x_{CO} + x_{CO_2}) + n_{CH_3OH}} \times 100\%$$

$$\text{Selectivity of CO}_2 = \frac{\frac{P_2V}{RT_2}x_{CO_2}}{\frac{P_2V}{RT_2}(x_{CO} + x_{CO_2}) + n_{CH_3OH}} \times 100\%$$

$$\text{Selectivity of CH}_3\text{OH} = \frac{n_{CH_3OH}}{\frac{P_2V}{RT_2}(x_{CO} + x_{CO_2}) + n_{CH_3OH}} \times 100\%$$

where P_1 and P_2 are gas pressure before and after the reactions respectively, Pa; V is the volume of gas phase inside the reactor, m^3 ; T_1 and T_2 are temperatures before and after the reactions respectively, K; R is universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$; x_{CH_4} is mole fraction of CH_4 in gas before the reactions, %; x_{CO} and x_{CO_2} are mole fractions of CO and CO_2 in gas after the reactions, %; n_{CH_3OH} is the amount of substance of CH_3OH , mol.

3. Results and discussion

3.1 Catalyst selection

The catalytic activity of several sulfate compounds for activation of low-concentration coal mine gas in oleum was researched, and the results of catalytic tests are given in Table 1. It can be seen that the $NiSO_4$, $CdSO_4$ and $ZrSO_4$ have no catalytic activity in the oxidation of low-concentration coal mine gas to methanol. However, $PbSO_4$ has the capacity to catalytically convert low-concentration coal mine gas to methanol.

Table 1. Activity of sulfate compounds for low-concentration coal mine gas activation in oleum

Catalyst	Catalyst dosage / μmol	Conversion of methane/%	Selectivity of methanol/%	Conversion of oxygen/%
None	0.00	0.00	0.00	0.00
$NiSO_4$	100	0.00	0.00	0.00
$CdSO_4$	100	0.00	0.00	0.00
$ZrSO_4$	100	0.00	0.00	0.00
$PbSO_4$	100	2.96	76.90	0.00

Reaction conditions: $P=3MPa$, $T=180^\circ C$, $t=2h$, Stirring rate 300r/min.

Table1 shows that the concentration of oxygen in mine gas has not changed after the reactions. It means that oxygen has not participated in selective oxidation of methane. For the selective oxidation of low-concentration coal mine gas in oleum, the oxidant is SO_3 .

3.2 Effect of reaction temperature

The products of the selective oxidation of low-concentration coal mine gas were mainly CH_3OH , CO and CO_2 . The typical distribution of products as a function of temperature is shown in Figure1.

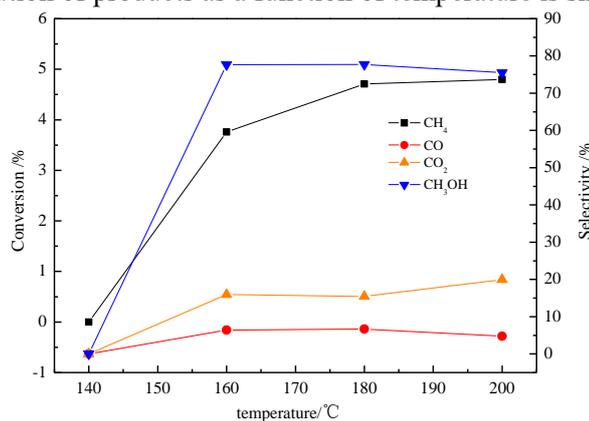


Figure 1. Effect of reaction temperature on the partial oxidation of gas (reaction conditions: 200 μmol of $PbSO_4$, 2h , 300r/min, 3MPa of mine gas)

When the reaction temperature was raised to above $140^\circ C$, the selective oxidation of mine gas started in oleum(20% SO_3) in the presence of $PbSO_4$. At a temperature range of 160-180 $^\circ C$, the conversion ratio of methane in gas rose with the increasing of reaction temperature. When the reaction temperature was reached to $200^\circ C$, the conversion ratio of methane decreased. This shows that the reaction temperature is a key factor influencing the selective oxidation of mine gas. At a temperature range of 160-200 $^\circ C$, the increase in the temperature resulted in a slight decrease in CH_3OH selectivity.

Because the methanol is more active than the methane, the deep oxidation to carbon dioxide is easily occurred. Based on the methane conversion and the selectivity of CH_3OH , it was concluded that the temperature of 180°C should be the optimum operating temperature for low-concentration coal mine gas transformation into methanol.

3.3 Effect of catalyst dosage

Figure 2 shows the effects of catalyst dosage on the selective oxidation of low-concentration coal mine gas. The methane conversion rose with the increasing of PbSO_4 dosage. However, as the PbSO_4 dosage researches up to $300\mu\text{mol}$, the methane conversion sharply increases. When PbSO_4 dosage was increased, the selectivity of CO_2 decreased while the selectivity of CO had not changed significantly. The selectivity of CH_3OH obtained its maximal value with the PbSO_4 dosage of $300\mu\text{mol}$. Data in Figure 2 indicate that the increase in the PbSO_4 dosage has positive effects on the formation of CH_3OH . What is more, it is verified that the optimum dosage of PbSO_4 is $300\mu\text{mol}$.

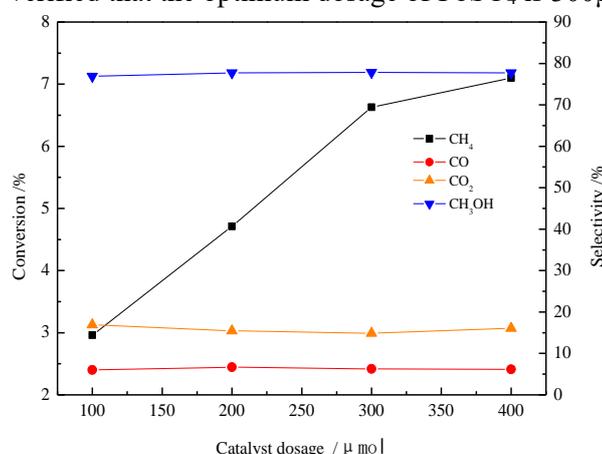


Figure 2. Effect of catalyst dosage on the partial oxidation of gas (reaction conditions: 180°C , 2h, 300r/min, 3MPa of mine gas)

3.4 Effect of reaction time

Figure 3 shows the effects of reaction time on the selective oxidation of low-concentration coal mine gas. When the reaction time increased from 1h to 2h, the methane conversion sharply rose from 3.52% to 6.63%. Once the time is above 2h, the conversion of methane began to slow down. The methane conversion gradually increased from 6.63% to 7.23% if the reaction time rose from 2h to 4h. Such results might indicate that the reaction of selective oxidation of low-concentration coal mine gas is basically completed 2h later. Methane is deeply oxidized to CO and CO_2 with a further increase in the reaction time. The increase in the reaction time resulted in a slight decrease in CH_3OH selectivity.

3.5 Effect of reaction pressure

The reaction pressure plays a major role in the selective oxidation of low-concentration coal mine gas. In order to observe the effects of the reaction pressure on the methane conversion and the selectivity of products formed from mine gas oxidation, the pressure of mine gas was varied in the range of 2-5MPa and the corresponding results are given in Figure 4. The conversion of methane was found to be faster when the reaction pressure was below 5MPa. With the increase of pressure, selectivity of CH_3OH increased. At the pressure of 5MPa, the selectivity of CH_3OH reached to the maximum of 78.59%. Generally, in the liquid-phase reaction, the product formation is highly dependent on the solubility of reactive gas in the solvent. The solubility of mine gas in solvent rose with the increasing of the pressure of gas in the reactor. Thus, more mine gas would get to the PbSO_4 catalyst, consequently increasing methane conversion and methanol selectivity. On the basis of these studies, it was found that the reaction pressure of 5MPa should be the optimum operating pressure for low-concentration coal mine gas transformation into methanol.

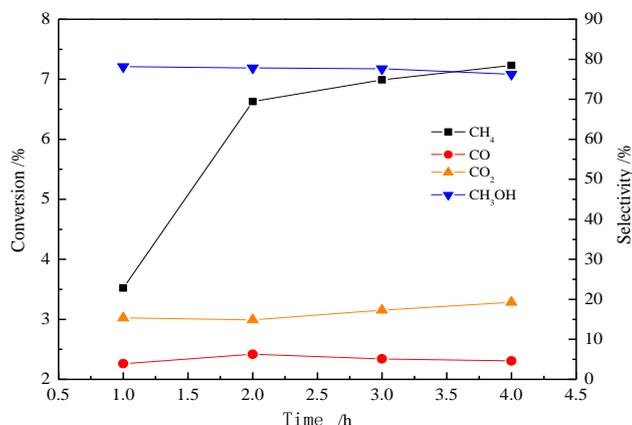


Figure 3. Effect of reaction time on the partial oxidation of gas (reaction conditions: 300 μ mol of PbSO₄, 180°C, 300r/min, 3MPa of mine gas)

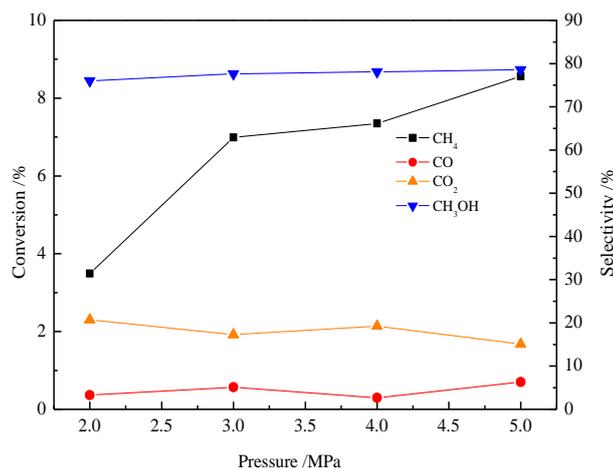


Figure 4. Effect of reaction pressure on the partial oxidation of gas (reaction conditions: 300 μ mol of PbSO₄, 180°C, 300r/min, 3h)

3.6 Reaction mechanism

The mechanism of electrophilic substitution is most popular for selective oxidation of methane in Oleum[17,18]. Therefore, it is concluded that the mechanism of electrophilic substitution is also followed by the selective oxidation of low-concentration coal mine gas in Oleum. In the liquid phase oxidation of low-concentration coal mine gas, Pb²⁺, as an electrophilic reagent, makes an electrophilic attack on methane in gas, generating the metal complex of CH₃-Pb²⁺. Furthermore, the CH₃-Pb²⁺ is transformed into stable intermediate product of CH₃OSO₃H by H₂SO₄. Pb⁰ is then oxidized to Pb²⁺ by SO₃. CH₃OSO₃H can be hydrolyzed into methanol. Based on the above analysis, the reaction mechanism for selective oxidation of low-concentration coal mine gas was shown in Figure5.

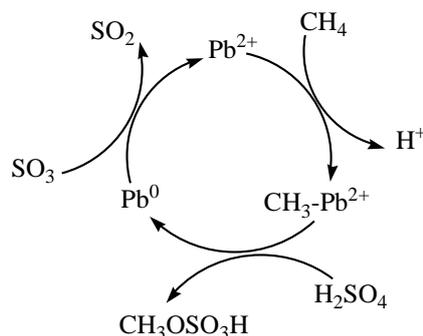


Figure5. Reaction mechanism for the partial oxidation of low-concentration coal mine gas catalyzed by $PbSO_4$

4. Conclusions

The catalytic activity of several sulfate compounds for activation of low-concentration coal mine gas in oleum medium was studied in this paper. The results show that $PbSO_4$ has the ability to catalytically convert low-concentration coal mine gas into methanol. However, $NiSO_4$, $CdSO_4$ and $ZrSO_4$ have no catalytic activity in the oxidation of low-concentration coal mine gas to methanol. The influence of reaction conditions (including reaction temperature, reaction pressure, reaction time and catalyst dosage) on selective oxidation of low-concentration coal mine gas was investigated in a concentration of 20% oleum medium with $PbSO_4$ catalyst. These results indicate that the optimal reaction conditions are determined under the reaction temperature of $180^\circ C$, the reaction pressure of 5MPa, the reaction time of 3h, and the $PbSO_4$ dosage of $300\mu mol$ for selective oxidation of low-concentration coal mine gas to methanol by $PbSO_4$ catalyst in oleum. Under this technological condition, the conversion ratio of methane in gas is 8.56% while the methanol selectivity is 78.59%. It is concluded that the mechanism of electrophilic substitution is followed by the selective oxidation of low-concentration coal mine gas in Oleum.

Acknowledgments

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