

Pd(OAc)₂ and chloranil-catalyzed oxidation of low-concentration coal mine gases to methanol

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Abstract: A self-made experimental system was used to study the catalytic oxidation of low-concentration coal mine gases to methanol in acetic acid solution. With Pd(OAc)₂ as catalyst, addition of *p*-benzoquinone or chloranil in the reaction system provides a beneficial environment for activation of methane, and chloranil shows a more positive effect. Chloranil amount and reaction temperature and pressure are the key factors influencing the catalytic properties. The target product yield has a positive relationship with these three factors. CH₃OH is formed from the reaction of generated H₂O₂ and CH₄. CH₃COOCH₃ is generated via two routes; one is direct oxidation of Pd²⁺ and CH₄, the other is esterification of CH₃OH and CH₃COOH.

Key words: palladium acetate; chloranil; mine gases; methanol

Although mine gases, as one of coal accessories, may cause destructive disaster for coal mines and severe air pollution, they can be used to serve as clean energy and manufacture chemicals^[1–3]. The mine gases explosion accident is often avoided by enhancing their extraction. However, this makes the extracted mine gases with low concentration of CH₄ (<30%), thus, majority of which are directly discharged into air due to lack of economic utilization technology. This not only leads to severe air pollution, but also waste significant amounts of carbon resource^[4,5]. Therefore, it is necessary and important to utilize these low-concentration mine gases. An interesting approach is to convert them into methanol by liquid-phase catalytic oxidation^[6,7]. Liquid-phase catalytic oxidation allows the reaction to be conducted under mild conditions by means of solvation. It has been shown that noble metal catalysts, such as Pt, Pd and Rh, give high methane conversion in acidic medium^[8–11]. Mukhopadhyay et al^[12] synthesized CH₃SO₃H by reacting SO₂ and CH₄ in H₂SO₄ solution in the presence of PdCl₂-CuCl₂ catalyst. Periana et al^[13] obtained a high yield of methanol through liquid-phase partial oxidation of methane in oleum by using SO₃ and Pt(bpy)₂Cl₂ as oxidant and catalyst respectively. The catalytic effect of metallic palladium dissolved in oleum on the conversion of methane was investigated by Michalkiewicz et al^[14]. With the biological oxidation knowledge, An et al^[15] proposed an electron-transfer loop with Pd²⁺ as active site for

oxidation of methane in CF₃COOH. In this way, methane was selectively oxidized to methanol at 80°C and 5.5 MPa. Yuan et al^[16] found that methane can also be selectively oxidized to methanol in CF₃COOH with Pd(OAc)₂/benzoquinone/H₅PMo₁₀V₂O₄₀ as catalyst. Xu et al^[17–20] preliminarily studied the liquid-phase oxidation of methane or mine gases to methanol over Pd(OAc)₂ or Pd-CuPc/Y catalyst in CH₃COOH solution. However, the above studies center on the conversion of pure methane or mine gases with high concentration of methane. Liquid-phase catalytic oxidation of mine gases having low content of methane has not been reported yet. Thus, catalytic oxidation of mine gases with low concentration of methane (20%) to methanol over palladium acetate and chloranil are studied here.

1 Materials and methods

1.1 Materials

The model mine gases ($\varphi(\text{CH}_4) = 20\%$, $\varphi(\text{O}_2) = 5\%$, $\varphi(\text{N}_2) = 75\%$) were purchased from Tongda Industrial Gas Sales Department, Lanxi County, Heilongjiang Province. Carbon monoxide (CO, 99.999%) was bought from Harbin Liming Gas Group. Palladium acetate (AR) and chloranil (AR) were purchased from Sinopharm Chem. Reagent Co., Ltd.. Acetic

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acid (AR) and 3% Pd/C were ordered from Tianjin Regent Chem. Co., Ltd. and Shaanxi Kaida Chem. Eng. Co., Ltd. respectively. Chloranil (98%) was provided by Aladdin Ind. Co..

1.2 Experimental apparatus

The self-made experimental apparatus for liquid-phase catalytic oxidation of model mine gases is shown in Figure 1. The effective volume, agitation speed, and maximum working temperature and pressure of the reactor are 100 mL, 0–1000 r/min, and 230°C and 15 MPa. The agitation torque is 1.2 Nm.

1.3 Experimental

First, a certain amount of palladium acetate or 3% Pd/C, stoichiometric *p*-benzoquinone or chloranil, and 30 mL of acetic acid were added and sealed into the reactor. Then, it was purged with model mine gases for three times. After that, 0.1 MPa carbon monoxide was filled. This was followed by filling model mine gases until reaching the required pressure. Finally, the reaction mixture was heated to the designed temperature, and reacted for 3 h under agitation conditions. After reaction, the reactor was cooled to room temperature. The gas product was analyzed by a GC9790 gas chromatograph equipped with a packed column (TDX-01) and a thermal conductivity detector (TCD). The liquid product was analyzed by another GC9790 gas chromatograph equipped with a capillary column (KB-5, 50 m × 0.25 μm × 0.25 μm) and a flame ionization detector (FID). The external standard method was used for analyses.

2 Results and discussion

2.1 Effects of *p*-benzoquinone and chloranil

In the Pd(OAc)₂-catalyzed reaction system, *p*-benzoquinone is a co-oxidant. This is supported by our result obtained in the acetic acid system that *p*-benzoquinone is an indispensable additional oxidant for liquid-phase catalytic oxidation of methane to methanol^[17,20].

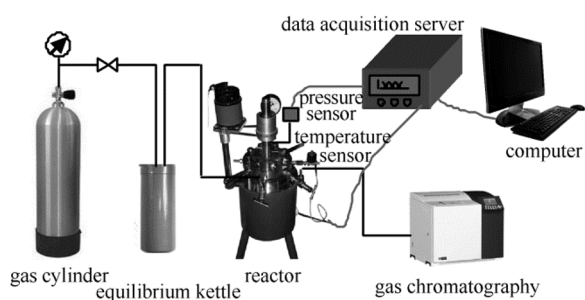


Fig. 1 Schematic diagram of experimental apparatus

An et al^[21] found that chloranil was more stable than *p*-benzoquinone in the acidic system, and also beneficial to the catalytic conversion of methane. To investigate the effects of *p*-benzoquinone and chloranil on the catalytic oxidation of low-concentration mine gases, the reaction was carried out with two palladium catalysts, viz. 3% Pd/C and Pd(OAc)₂, under the following conditions: reaction temperature of 140°C, reaction time of 3 h, 1000 μmol of *p*-benzoquinone or chloranil, 100 μmol of Pd(OAc)₂ or 2 g of 3% Pd/C, and gas pressure of 4 MPa. Table 1 summarizes the catalytic results. CH₃COOCH₃ and CH₃OH were detected in the liquid product. The target product was expressed in the form of CH₃OH as CH₃COOCH₃ can be hydrolyzed into equivalent amounts of CH₃OH. Thus, the CH₃OH yield displayed in Table 1 includes both CH₃COOCH₃ and CH₃OH.

Table 1 shows that selective oxidation of low-concentration mine gases to methanol can occur in all the four reaction systems, and chloranil has more positive effect than *p*-benzoquinone regardless of the used catalyst.

2.2 Effect of chloranil amount

Figure 2 shows the methanol yield obtained in the Pd(OAc)₂-chloranil-CO reaction system containing different amounts of chloranil. In the experimental range, the methanol yield increased with increasing amount of chloranil. This may be because chloranil provide a beneficial environment for activation of methane.

2.3 Effect of gas pressure

Figure 3 shows the methanol yield obtained in the Pd(OAc)₂-chloranil-CO reaction system filled with different amounts of mine gases. Generally, in the liquid-phase reaction, the target product yield is highly dependent on the solubility of reactive gas in the solvent. The solubility of mine gases in solvent increases with increasing their partial pressure. Thus, more mine gases would approach the catalyst, consequently increasing methanol yield.

2.4 Effect of reaction temperature

Table 1 CH₃OH yield obtained over the Pd(OAc)₂ and 3%Pd/C in the oxidation of mine gases

Entry	Reaction system	CH ₃ OH yield <i>m</i> /μmol
1	3%Pd/C- <i>p</i> -benzoquinone-CO	105
2	3%Pd/C-chloranil-CO	120
3	Pd(OAc) ₂ - <i>p</i> -benzoquinone-CO	352
4	Pd(OAc) ₂ -chloranil-CO	385

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