Liquid-phase Oxidation of Methane into Methane Oxygenates

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Abstract: The liquid-phase oxidation of methane into methane oxygenates with hydrogen peroxide was performed using different catalyst systems including transition metal (Cu and Fe) sulfates and/or Pd/C catalyst. The significant amounts of methane oxygenates were obtained in the presence of $FeSO_4$ and Pd/C, which implies that both catalysts have a synergistic effect on methane oxidation. The presence of acid such as sulfuric acid also has a positive effect on this reaction.

Keywords: Methane, Methane oxygenates, Hydrogen peroxide, Iron sulfate, Pd/C

1. Introduction

Recent upsurge of shale gas promotes the chemical conversion of methane which is currently just used as an energy source. Since there is no economic process for the utilization of methane in a small scale, about 35% of methane is just burnt away in the United States [1]. Therefore, the technology development for the efficient chemical transformation of methane is highly demanded. Recently, Hutchings and his coworkers [2] reported that the direct conversion of methane into methanol could be achieved in a liquid phase using heterogeneous catalysts such as Cu-promoted Fe/ZSM-5. This can compete with the present methanol synthesis process in which methane is first transformed into synthesis gas through high-temperature reforming process as long as hydrogen peroxide can be produced cheaply or replaced with dioxygen.

Motivated by their works, we tried to carry out the same reaction using the homogeneous catalysts composed of $CuSO_4$ and/or $FeSO_4$. We have found out that the addition of Pd/C and sulfuric acid can enhance the methane oxygenates yield significantly as long as $FeSO_4$ is used as the homogeneous catalyst.

2. Experimental

The liquid-phase partial oxidation of methane with hydrogen peroxide was carried out in an autoclave with a glass liner. The reaction temperature was fixed at 50 ^oC and reaction time was 1 h with vigorous stirring at 1500 rpm. The volume of liquid was 30 mL and volume of gas was 95 mL. In the liquid phase, the glass liner was charged with 15 mM H_2SO_4 and the concentration of hydrogen peroxide was 0.94 wt.%. The amount of each homogeneous catalyst was adjusted to be 10 μmol. 50 mg of 1 wt.% Pd/C was added for some experiments. The gas phase was composed of 15 bar of methane and 13 bar of nitrogen. After the reaction, the reactor was cooled and products were extracted if needed. The liquid phase products were analyzed with ^{1}H-NMR and HPLC.

3. Results and discussion

Table 1 shows the result of each experiment. It is confirmed that no methane oxygenates can be formed in the absence of any catalyst (entry 1). Each $CuSO_4$ or $FeSO_4$ does not show any catalytic activity for this reaction (entries 2 and 3). However, a small amount of formic acid was detected in the presence of both $CuSO_4$ and $FeSO_4$ (entry 4). This implies that there is a synergistic effect between $CuSO_4$ and $FeSO_4$. As an additional catalyst component, Pd/C was added to the homogeneous catalyst system. No methane oxygenates was observed in the presence of Pd/C and $CuSO_4$ (entry 5). However, significant amounts of formic acid were formed in the presence of Pd/C and $FeSO_4$ (entries 6 and 7). Contrary to the pure homogeneous catalyst system, no synergistic effect between $CuSO_4$ and $FeSO_4$ was observed in the presence of Pd/C (entry 7). The separate experiment confirms that Pd/C does not have any catalytic activity for this reaction (entry 8). Finally, the same reaction was also carried out in the absence of any acid to find out any effect of acid on this

Table 1. The catalytic performance for methane oxidation with hydrogen peroxide with different catalyst systems[a].

Entry	*Catalyst*	*Medium*	*H_2O_2 conversion (%)*	*MeOH (μmol)*	*HCOOH (μmol)*	*Total (μmol)*
1	No catalyst	15mM H_2SO_4	20	n.d.	n.d.	n.d.
2	$CuSO_4$	15mM H_2SO_4	2	n.d.	n.d.	n.d.
3	$FeSO_4$	15mM H_2SO_4	23	n.d.	n.d.	n.d.
4	$CuSO_4$ + $FeSO_4$	15mM H_2SO_4	34	n.d.	27	27
5	$CuSO_4$ +1%Pd/C	15mM H_2SO_4	97	n.d.	n.d.	n.d.
6	$FeSO_4$ +1%Pd/C	15mM H_2SO_4	99	n.d.	278	278
7	$CuSO_4$ + $FeSO_4$ +1%Pd/C	15mM H_2SO_4	100	n.d.	190	190
8	1%Pd/C	15mM H_2SO_4	96	n.d.	n.d.	n.d.
9	$FeSO_4$ +1%Pd/C	H_2O	100	12	14	26

[a] n.d.: not detected

reaction. The total yield to methane oxygenates decreased significantly in the absence of sulfuric acid (entry 9). However, the formation of methanol was observed. Therefore, it can be said that the addition of sulfuric acid can promote the catalytic activity for this reaction resulting in the predominant formation of formic acid. It is worth mentioning that the conversion of hydrogen peroxide increases noticeably in the presence of Pd/C.

4. Conclusions

In the liquid-phase partial oxidation of methane with hydrogen peroxide, a mixture of $CuSO_4$ and $FeSO_4$ can produce formic acid in the presence of sulfuric acid. This reaction rate can be enhanced significantly in the presence of Pd/C which also accelerates the conversion of hydrogen peroxide. In the absence of sulfuric acid, the formation of methanol was detected but the total yield to methane oxygenates decreased significantly compared with the case in the presence of sulfuric acid.

References

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