Effects of pH on selective oxidation of methane into methane oxygenates over Cu-Fe/ZSM-5 catalysts with hydrogen peroxide in water

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Abstract: The efficient utilization of hydrogen peroxide is critical in the direct oxidation of methane with hydrogen peroxide in water. We have found that the pH of the aqueous solution is an important factor to determine the product distribution and to control the efficiency of the hydrogen peroxide for partial oxidation of methane over Cu-Fe/ZSM-5 catalyst. The total yield to the methane oxygenates including methanol and formic acid increased with decreasing pH. The preferential formation of formic acid was observed especially at low pH below 2.

Keywords: Methane, Hydrogen peroxide, Methanol, Formic acid, Phosphoric acid.

1. Introduction

Since methane is now one of the largest hydrocarbon resources as shale gas production increases, there is a growing interest in converting methane to useful chemicals. Methanol is one of chemicals that can be produced from methane and is in increasing demand worldwide because of its wide applications in various fields. Methanol is currently synthesized from syngas, a mixture of CO and H_2, which can be produced from methane via steam reforming reaction at high temperature, which requires a lot of energy. Therefore, the partial oxidation of methane at low temperature is quite attractive.[1] The literature reports that Fe/ZSM-5 and Cu-Fe/ZSM-5 catalysts are effective in the partial oxidation of methane using hydrogen peroxide, which seems to be related to the MFI framework and Brønsted acid site of ZSM-5.[2,3] In addition, hydrogen peroxide used in the reaction is an environmentally friendly oxidant used in many industries. Furthermore, it can provide oxygen at relatively low temperatures. However, it is important to use hydrogen peroxide efficiently because hydrogen peroxide is more expensive than other oxidizing agents and is liable to decompose on contact with the catalyst. In this study, we examined the effect of pH on the partial oxidation of methane with hydrogen peroxide in water to find out the way to increase the efficiency of hydrogen peroxide for this reaction.

2. Experimental

The Cu-Fe/ZSM-5 catalyst was prepared as described in the previous work.[2] The Cu and Fe contents were intended to be 1.25 and 1.25 wt%, respectively. A high-pressure batch reactor was used to carry out the partial oxidation of methane in water using hydrogen peroxide as an oxidant. The reaction was typically performed at 70 °C for 1 h. The volume of the liquid phase and vapor phase were 30 and 95 mL, respectively. The reactor was filled with pure methane and the total pressure was set to 31 bar. 0.88 mmol of hydrogen peroxide and 50 mg of catalyst were used. After 1 h, the reactor was contacted with liquid nitrogen to quench the reaction by decreasing the temperature below 10 °C. The pH of the solution was controlled by adding different amounts of phosphoric acid. The product was analyzed by GC-FID, HPLC and ^{1}H NMR.

3. Results and discussion

During the selective methane oxidation, methanol and formic acid are determined to be main products as methane oxygenates. Fig. 1(A) shows the yields to methanol and formic acid at different pHs. As long as the pH is between 3 and 7, only methanol is obtained and there is no noticeable change in the methanol yield as a function of pH. However, as the pH decreases from 3 to 2, the methanol yield increases and reaches the maximum value at pH = ~2. As the pH decreases further from 2, the methanol yield decreases but the formic acid appears and its yield increases with decreasing pH. Generally, the total yield of methanol and formic acid increases with decreasing pH and the efficiency of hydrogen peroxide also shows a similar trend with total yield as a function of pH. When a small amount of phosphoric acid was added (pH = ~4), the efficiency of hydrogen peroxide increased even though the methanol yield was similar to that at pH = 7. This seems to be related to the stabilizing effect of phosphoric acid on hydrogen peroxide. Phosphoric acid prevents the autogeneous decomposition of hydrogen peroxide without participating in the reaction, thereby contributing to the increase of the product yield.

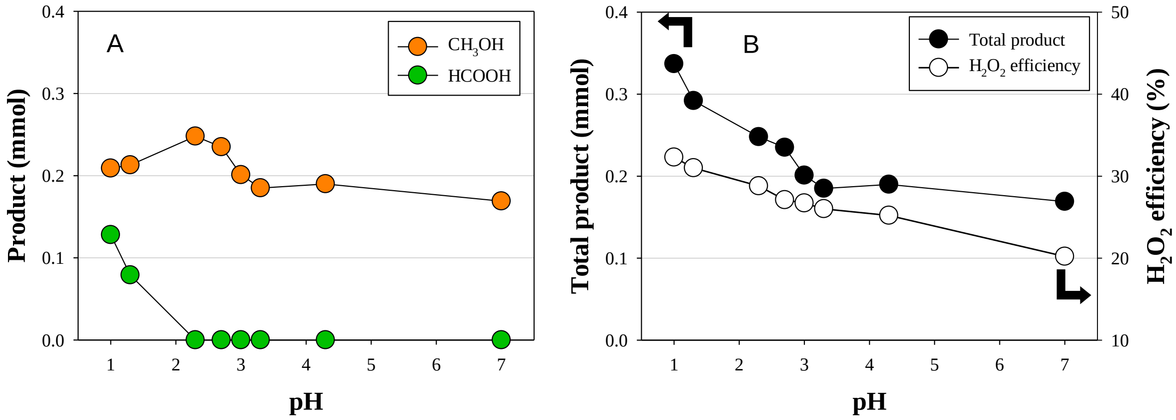

Figure 1. Yields of methanol and formic acid (A) and total yields of methane oxygenates and efficiency of hydrogen peroxide (B) at different pHs.

4. Conclusions

The addition of phosphoric acid has a positive effect on the direct oxidation of methane with hydrogen peroxide in an aqueous phase to produce methane oxygenates such as methanol and formic acid. The total yield to the methane oxygenates and efficiency of hydrogen peroxide increases with decreasing pH. The formation of formic acid can be observed especially at low pHs and the yield to formic acid increases with decreasing pH. This seems to be related to the stabilization effect of phosphoric on hydrogen peroxide.

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