Catalytic performance of alkali compounds for LTMS in liquid phase over Cu-based catalyst
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Introduction

The efficiency of methanol synthesis in the industrial process is severely limited by thermodynamics because methanol synthesis is an extremely exothermic reaction ($\Delta H = -91$KJ/mol). To overcome the disadvantage, an alternative methanol synthesis method via methyl formate (MeF) at low temperatures in liquid phase had been proposed by Christiansen[1], and was widely studied by many researchers. The process involved carbonylation of methanol to methyl formate (MeF) (CH$_3$OH+CO= HCOOCH$_3$) and hydrogenolysis of MeF to methanol (HCOOCH$_3$+H$_2$=2CH$_3$OH).The two reactions proceeded in one reactor, which was so-called concurrent process. In which, the catalyst for carbonylation was usually homogeneous alkali metal methoxide, however, it can be easily poisoned by CO$_2$ and H$_2$O; the catalyst for hydrogenolysis was often modified copper solid catalyst.

In the present study, highly active system of different kinds of alkali compounds over Cu-based catalyst for low temperature methanol synthesis(LTMS) was studied.

Experimental

The catalyst was prepared by the conventional co-precipitation method. A mixed aqueous solution of copper nitrate and magnesium nitrate was used to produce the precipitate. The obtained precipitation was filtrated, washed, dried. Subsequently, the precursor was impregnated with sodium carbonate. The impregnated Cu-based catalyst was finally reduced in a stream of H$_2$ at 523K for 2h before its activity evaluation.

A flow-type semi-batch autoclave reactor with an inner volume of 85ml was employed in the experiment. The stirring speed was 1660 rpm to prevent the occurrence of the diffusion-controlled regime. All products were analyzed by two gas chromatographs, where GC-8A/TCD (Shimadzu) was used for gas products and GC353/FID(GL Science) was used for liquid products[2].

Results and discussion

Several alkali compounds were chosen as carbonylation catalysts for low temperature methanol synthesis over present Cu/MgO-Na catalyst. The standard reaction conditions were as follows: H$_2$/CO/Ar = 64.5/32.5/3, temperature=433K, pressure =5.0MPa, solvent=ethanol, W/F=12.44g.h.mol$^{-1}$, concentration of alkali compounds=0.33mol/L, reaction time=24hours. Fig.1 and Table 1 showed the function of corresponding reaction activities with time on stream.

Fig.1 Catalytic performance of alkali compounds for LTMS in liquid phase over Cu/MgO-Na catalyst

In the case of HCOONa, the initial activity was very high, however, after 4h CO conversion descended to a stable approximate 40% level unlike the conventional CH$_3$ONa, CH$_3$OH selectivity was below 90%. Main by-products contained no higher alcohols but small amount of CO$_2$, CH$_4$, MeF and EtF. It demonstrated that HCOONa was potential to act as an alternative carbonylation catalyst for LTMS. When Na$_2$CO$_3$, during the initial hours the activity was lower and then increased to a stable level; for NaHCO$_3$, the activity quickly increased to a stable level that was lowest among the four alkali compounds. Even in the case of NaOH with strong basicity, reaction activity was also exhibited. During the early hours, CO conversion was slowly increased and then reached the tendency similar to that in the case of HCOONa. After more than 20 hours, the CO conversions were almost same at about 38%. There was no doubt that the same reaction activity with HCOONa would keep from the
20th hours on. Therefore, there might exist special relationship between catalytic sites after some reaction hours when using HCOONa and NaOH.

The above experiment results made it meaningful to make clear their roles and relative inter-transformations of different sodium compounds in present system. Solid materials attained by vaporizing the final liquid sample after reaction with HCOONa, Na₂CO₃ and NaOH, respectively, were qualitatively analyzed by FTIR, shown in Fig.2. Assignments of the bands were made by analogy with the spectra of known compounds and by comparison with published literatures. For HCOONa, the bands at 1600 cm⁻¹ and 1360 cm⁻¹ were antisymmetric and symmetric stretching vibrations of carbon-oxygen bands, respectively, they were the label bands of HCOONa. Besides, the bands at 1380 cm⁻¹ and 1310 cm⁻¹ resulted from the NaHCO₃. It illuminated that some fraction of HCOONa was transformed into NaHCO₃, which resulted in the deactivation of HCOONa comparing with the reaction activity of NaHCO₃ in Fig.1. Meanwhile, some amount of HCOONa made the reaction activity with higher level than NaHCO₃. Undoubtedly, a dynamic equilibrium between HCOONa and NaHCO₃ was in function in the stable period. For Na₂CO₃, the band at 1450 cm⁻¹ was ascribed to Na₂CO₃. Moreover, the bands of HCOONa were detected out, which contributed to gradually increasing reaction activity of Na₂CO₃. For the case of NaOH, the bands at 1640 cm⁻¹, 1420 cm⁻¹ and 1380 cm⁻¹ belonged to NaHCO₃, the bands at 1600 cm⁻¹ and 1360 cm⁻¹ were attributed to HCOONa. The results demonstrated that NaOH was transformed into HCOONa and NaHCO₃ after reaction. It explained that NaOH showed comparative reaction performance of with that HCOONa[4].

Conclusions

The alternative alkali compounds like HCOONa, Na₂CO₃ and NaOH instead of conventional CH₃ONa over Cu-cased catalyst showed high performance for low temperature methanol synthesis in liquid phase. Alkali carbonate and alkali hydroxide were both transformed into alkali formates to catalyze the process, formate was the substantial species for the current process. It exploited a novel route concerning about utilization of other alkali compounds and optimization of relative transformation equilibrium for LTMS in liquid phase.

Table 1 Catalytic performance of alkali compounds for LTMS in liquid phase over Cu/MgO-Na catalyst

<table>
<thead>
<tr>
<th>Alkali compounds</th>
<th>Methanol</th>
<th>STY</th>
<th>Sel.%</th>
<th>CO₂</th>
<th>CH₄</th>
<th>MeF</th>
<th>EtF</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOONa</td>
<td>17.38</td>
<td>92.27</td>
<td>0.12</td>
<td>0.04</td>
<td>0.96</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>10.36</td>
<td>93.03</td>
<td>0.07</td>
<td>0.01</td>
<td>0.53</td>
<td>0.36</td>
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</tr>
<tr>
<td>NaHCO₃</td>
<td>4.46</td>
<td>72.28</td>
<td>0.49</td>
<td>0.13</td>
<td>1.15</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>16.16</td>
<td>92.87</td>
<td>0.13</td>
<td>0.03</td>
<td>0.37</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

Note: STY=Space time yield (mmol/g-cat.h)

Fig.2 FT-IR spectra for solid sample in liquid phase after reaction using HCOONa, Na₂CO₃, NaOH over Cu/MgO-Na catalyst

References