

# Alkali compounds catalyzed low temperature methanol synthesis over Cu-based catalyst

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**Abstract:** -A novel mixed catalyst system containing alkali compounds over Cu/MgO-Na catalyst was developed to synthesize methanol from syngas via ethyl formate in a slurry reactor. The results exhibited that among the used alkali formates (HCOOM, M=Li, Na, Cs, Ca, Ba), sodium formate showed the optimizing catalytic function with Cu/MgO-Na catalyst, and high CO conversion(>80%) and methanol selectivity(~90%) with a mass space velocity of 1800L(STP)/h.kg was achieved at low temperature of 433K and 5.0Mpa. In addition, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and NaOH could catalyze the methanol synthesis through their transformation into HCOONa.

**Key-Words:** - CuMgO-Na/HCOONa catalysis system, slurry phase, low temperature methanol synthesis,

## 1 Introduction

Methanol is an industrially important chemical, it is produced at an annual rate of over 20 million tons worldwide. Methanol is widely used as a feedstock in various chemical applications and also be used as a transportation fuel or a fuel additive. It is also the raw resource for other important chemicals, such as MTBE, which is a rapidly growing octane enhancer for the automotive market.

The efficiency of methanol synthesis in the industrial process is severely limited by thermodynamics because methanol synthesis is an extremely exothermic reaction ( $\Delta H = -91\text{KJ/mol}$ ). 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) ( $\text{CH}_3\text{OH} + \text{CO} = \text{HCOOCH}_3$ ) and hydrogenolysis of MeF to methanol ( $\text{HCOOCH}_3 + \text{H}_2 = 2\text{CH}_3\text{OH}$ ). 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<sub>2</sub> and H<sub>2</sub>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.

## 2 Experimental

The catalyst was prepared by the conventional co-precipitation method. A mixing 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<sub>2</sub> at 523K for 2h before its activity evaluation.

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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].

### 3 Results and discussion

Several alkali formats were chosen as carbonylation catalysts for low temperature methanol synthesis over present Cu/MgO-Na catalyst. The standard reaction conditions here were as follows: H<sub>2</sub>/CO/Ar=64.5/32.5/3, temperature=433K, pressure =5.0MPa, solvent=ethanol, W/F=12.44g.h.mol<sup>-1</sup>, concentration of alkali compounds=0.33mol/L, reaction time=24hours. Fig.1 showed the corresponding reaction activity, formation rate of methanol and selectivity of main by-products.

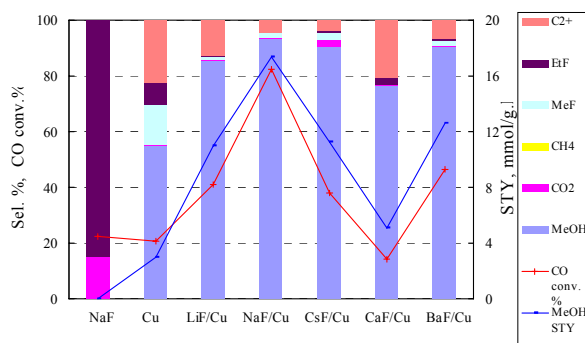


Fig.1 Alkali formates as carbonylation catalysts for low temperature methanol synthesis over Cu-based catalyst

Sodium formate exhibited low activity for carbonylation of methanol, only CO<sub>2</sub> and ethyl formate were products. Cu/MgO-Na catalyst gave a lower catalytic function for methanol synthesis under present reaction conditions, and methanol selectivity was about 56%. However, in the alkali formates/Cu catalyst systems, methanol synthesis showed higher reaction activities and methanol selectivity, like HCOOLi, HCOONa, HCOOCs. Especially, HCOONa/Cu system had a highest reaction activity among the three systems, it might attribute to the

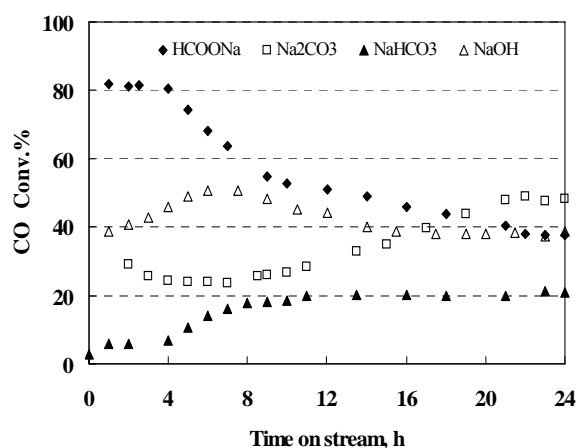


Fig.2 Catalytic performance of alkali compounds for LTMS in liquid phase over Cu/MgO-Na catalyst

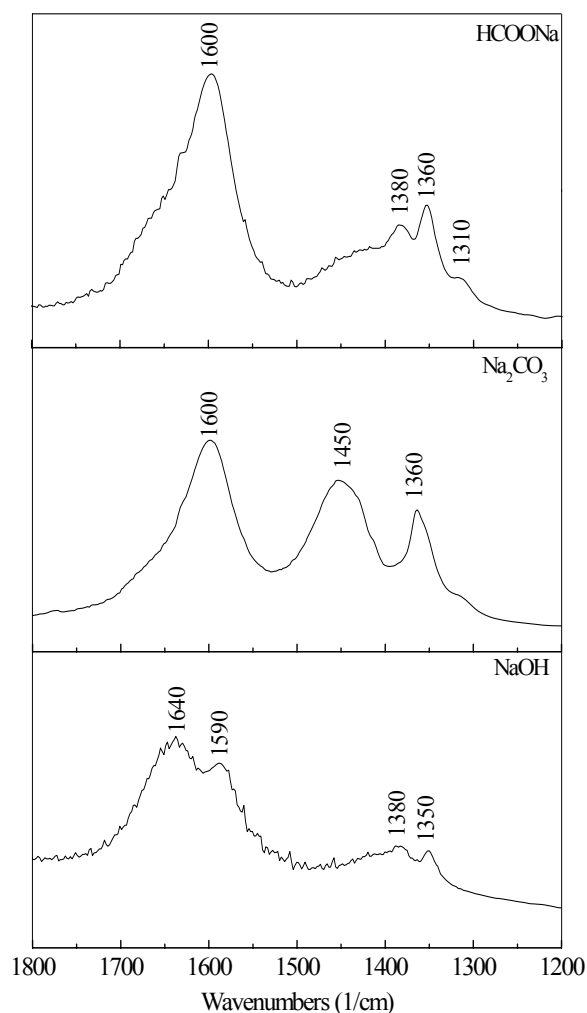


Fig.3 FT-IR spectra for solid sample in liquid phase after reaction using HCOONa, Na<sub>2</sub>CO<sub>3</sub>, NaOH over Cu/MgO-Na catalyst

dissociation activity of dissolved alkali formates and their size match degree of ions radius with Cu catalyst[3]. Differently, for II A Group formates, as shown  $\text{Ca}(\text{HCOO})_2$  and  $\text{Ba}(\text{HCOO})_2$ , the corresponding catalytic function descended. But, their stabilities were better than those of alkali formates.

Under the same reaction conditions, other several alkali compounds, like  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and  $\text{NaOH}$ , were chosen for the carbonylation catalysts. For comparison, their CO conversions function with the time on stream were shown in Fig.2. In the case of  $\text{Na}_2\text{CO}_3$ , during the initial hours the activity was lower and then increased to a stable level; in the case of  $\text{NaHCO}_3$ , the activity quickly increased to a stable level. It indicated that  $\text{NaHCO}_3$  almost had no catalytic function on present low temperature methanol synthesis. And in the case of  $\text{NaOH}$  with strong basicity, reaction activity was also showed. During the early hours, CO conversion was slowly increased and then went along the tendency similar with that in the case of  $\text{HCOONa}$ . After more than 20 hours, the CO conversions were almost same at about 38%. There was no doubt that the same reaction activity would kept from the 20th hours on. Therefore, catalytic sites should either be same or be inter-transformed into each other with a dynamic equilibrium after some reaction hours when using  $\text{HCOONa}$  and  $\text{NaOH}$ .

The results that  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  both emerged the considerable reaction activities with  $\text{HCOONa}$  made it meaningful to make clear their roles and relative inter-transformations in present system. Solid materials attained by vaporizing the final liquid sample after reaction with  $\text{HCOONa}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ , respectively, were qualitatively analyzed by FTIR, shown in Fig.3. Assignments of the bands were made by analogy with the spectra of known compounds and by comparison with published literatures. For  $\text{HCOONa}$ , the bands at  $1600\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  were antisymmetric and symmetric stretching vibrations of carbon-oxygen bands, respectively, they were the label bands of

$\text{HCOONa}$ . Besides, the bands at  $1380\text{ cm}^{-1}$  and  $1310\text{ cm}^{-1}$  resulted from the  $\text{NaHCO}_3$ . It illuminated that some fraction of  $\text{HCOONa}$  was transformed into  $\text{NaHCO}_3$ , which might result in the deactivation of  $\text{HCOONa}$  comparing with the reaction activity of  $\text{NaHCO}_3$  in Fig.1. For  $\text{Na}_2\text{CO}_3$ , the band at  $1450\text{ cm}^{-1}$  was ascribed to  $\text{Na}_2\text{CO}_3$ . Moreover, the bands of  $\text{HCOONa}$  were detected out, which contributed to gradually increasing reaction activity of  $\text{Na}_2\text{CO}_3$ . For the case of  $\text{NaOH}$ , the bands at  $1640\text{ cm}^{-1}$ ,  $1420\text{ cm}^{-1}$  and  $1380\text{ cm}^{-1}$  belonged to  $\text{NaHCO}_3$ , the bands at  $1600\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  were attributed to  $\text{HCOONa}$ . The results demonstrated that  $\text{NaOH}$  was transformed into  $\text{HCOONa}$  and  $\text{NaHCO}_3$  after reaction. It explained that  $\text{NaOH}$  showed comparative reaction performance of with that  $\text{HCOONa}$ [4].

## 4 Conclusion

The alternative alkali compounds like  $\text{HCOONa}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  instead of conventional  $\text{CH}_3\text{ONa}$  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 formate 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.

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