

Methanol synthesis from syngas in the homogeneous system

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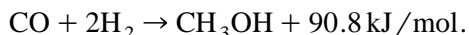
Abstract

Homogeneous synthesis of methanol from synthetic gas was carried out in the $\text{Ni}(\text{CO})_4/\text{KOME}$ catalytic system. The influence of various factors, such as the reaction temperature, the concentration of potassium methoxide, the concentration of nickel tetracarbonyl and the reaction pressure on the catalytic activity, was discussed, respectively, and the most preferred conditions were obtained. The results showed that methanol could be prepared from carbon monoxide and hydrogen under mild reaction conditions. The catalytic reactions were operated most preferably at 378 K and 1.8 MPa. The activity of catalyst characterized by space–time yield (STY) is about 4 mol/l h. The effect of additives containing N-, O-, S-elements on the catalytic activity was also investigated. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Methanol; Homogeneous synthesis; Nickel catalyst; Low temperature; Additives

1. Introduction

Methanol is one of the basic chemicals which is manufactured at an annual rate of 10,000,000 ton. It is a clean-burning fuel with versatile applications. As a combustion fuel, it provides extremely low emissions. Methanol can also be used as a primary transportation fuel or a fuel additive and especially as a raw material for methyl *t*-butyl ether. Another potential future use of methanol is as a peaking fuel in coal gasification combined cycle power stations, e.g., in integrated gasification combined cycle (IGCC). Methanol is produced from the mixture of carbon monoxide and hydrogen according to the following equation, which is highly exothermic:



One of the most important measures to realize this process is to remove from the system the heat of reaction. So it is thermodynamically favorable at lower reaction temperatures. More recent traditional systems are operated at temperatures from 483 to 553 K and at low pressures (about 5 MPa) using Cu/Zn/Al catalysts. Conversion of syngas to methanol is limited by chemical equilibrium and the high temperature sensitivity of the catalyst, so the syngas conversion per pass is generally adjusted to be very low, and recycling of cooled unreacted syngas is employed to regulate the reaction temperature.

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The process of methanol synthesis in liquid phase can effectively remove the reaction heat at a high syngas conversion. In this process, the feed syngas is introduced in an inert liquid medium which contains a solid (heterogeneous) or a liquid (homogeneous) catalyst. As a liquid medium has a greater heat capacity than gas, it is easy to remove the reaction heat by cooling the liquid.

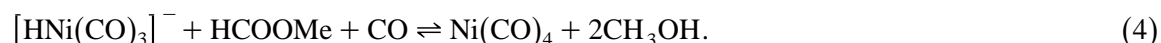
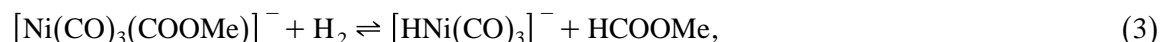
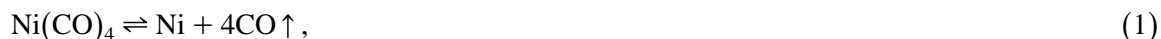
There were some reports about the synthesis of methanol from syngas by using liquid catalysts in the literatures [1–3]. In this work, the preparation of nickel tetracarbonyl will be at first studied; secondly, the effect of temperature, ratio of H_2/CO in the syngas, total pressure, concentration of nickel tetracarbonyl and potassium methoxide will be discussed, respectively, in order to obtain the preferred operated reaction conditions for the synthesis of methanol in homogeneous system.

2. Results and discussions

2.1. Catalytic performance in the $Ni(CO)_4/KOMe$ system

All experiments were carried out in a 250 cm³ zirconium autoclave. After catalysts and a solvent (100 cm³) were added into the reactor, it was purged with syngas. The syngas with a stoichiometric ratio for methanol synthesis ($H_2/CO = 2$) was employed as feed. All the reactions at different conditions took 1 h. After the run, the liquid phase was analyzed by GC-8810 gas chromatography (GC), and its peak areas were determined by a SSC-921 chromatointegrator. $Ni(CO)_4$ was prepared from nickel powder and carbon monoxide without oxygen at 333 K [4]. Potassium methoxide was prepared from methanol and potassium.

From Figs. 1–5, we can conclude the most preferred reaction conditions: $CO/H_2 = 0.49$, $T = 378$ K, $P_t = 1.8$ MPa, $[KOMe] = 0.8$ mol/l, $[Ni(CO)_4] = 0.04$ mol/l. These are the following chemical reactions in this process [5]:



When the temperature is excessively higher, according to reaction (1), the reaction equilibrium shifts to the right side, $Ni(CO)_4$ decomposes. Then the amount of catalyst decreases, the space–time yield (STY) decreases. $[HNi(CO)_3]^-$ is considered as the catalytic active species. According to reactions (2) and (3), when total pressure, concentration of $Ni(CO)_4$ and KOMe rise, respectively, the reaction equilibrium favors the formation of more $[HNi(CO)_3]^-$, which catalyzes the hydrogenolysis of methyl formate to methanol, so the reaction rate increases. The preferred reaction conditions have been determined through the variations of the reaction rate with these factors.

2.2. Effect of additives on the catalytic activity

All experiments were carried out in a 500-cm³ autoclave. We found that additives always had an effect on the reaction rate. Both the N-containing additives such as 2-amino-4-methylpyridine (2A4MPy), triethyl amine, pyridine and acetonitrile, and the O-containing additives such as DMSO, 2-hydroxybenzothiazole (2HBTZ) were studied. Table 1 shows that STY of methanol increases at

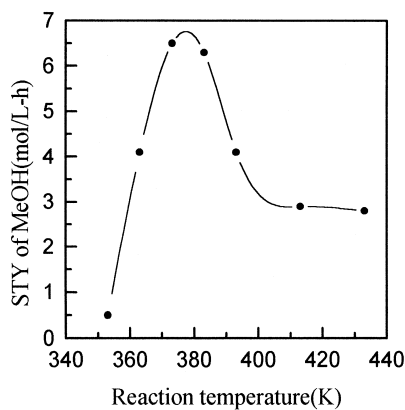


Fig. 1. Effect of the reaction temperature on the catalytic activity. Reaction conditions: $P_t = 2.0$ MPa, $r = 300$ r/min, $[\text{Ni}(\text{CO})_4] = 0.06$ mol/l, $[\text{KOME}] = 0.8$ mol/l, $t = 1$ h.

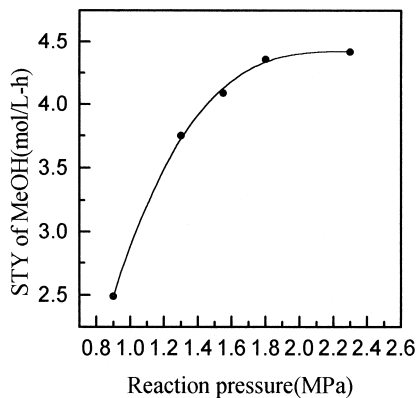


Fig. 2. Effect of the reaction pressure on the catalytic activity. Reaction conditions are same as in Fig. 1, except that $T = 373$ K and pressure varied.

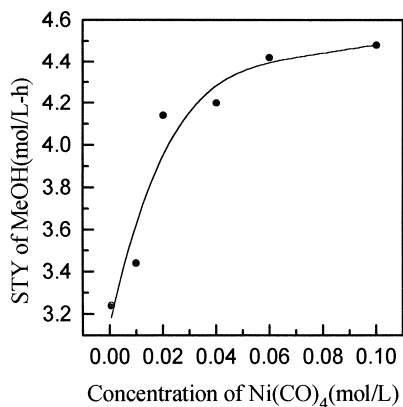


Fig. 3. Variation of the catalytic activity with $\text{Ni}(\text{CO})_4$ concentration. Reaction conditions are same as in Fig. 1, except that $T = 373$ K and $\text{Ni}(\text{CO})_4$ concentration varied.

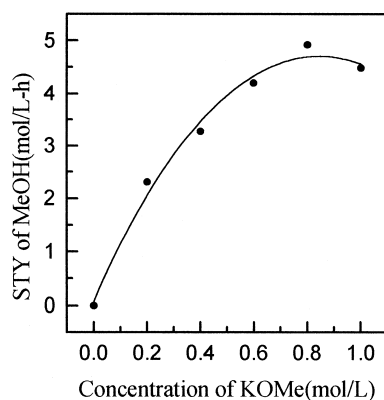


Fig. 4. Variation of STY with KOMe concentration. Reaction conditions are same as in Fig. 1, except that $T = 373$ K and KOMe concentration varied.

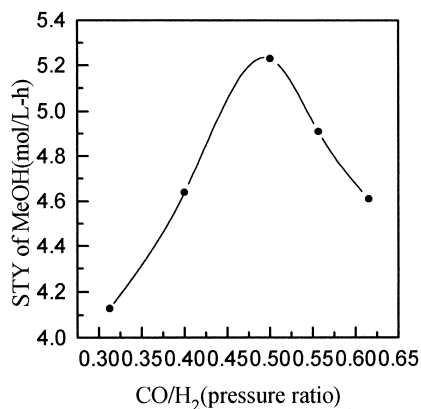


Fig. 5. Variation of STY with feed CO/H₂ ratio. Reaction conditions are same as Fig. 1, except that $T = 373$ K and CO/H₂ ratio varied.

some extent when DMSO, triethyl amine, pyridine and 2-hydroxybenzothiazole (2HBTZ) are added, respectively. Fig. 6 shows that STY of methanol decreases with increase in of 2-amino-4-methylpyridine (2A4MPy). There is no catalytic activity in methanol synthesis with acetonitrile. So the sequence of additives catalytic activities in the formation of methanol is as follows:

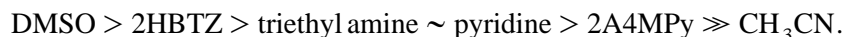


Fig. 7 shows that STY of methanol rises when the concentration of 2-hydroxy-benzothiazole (2HBTZ) increases. It reaches the most value when the concentration of 2HBTZ is 0.016 mol/l. When the concentration of 2HBTZ continues to rise, STY of methanol decreases. This is because $[\text{HNi}(\text{CO})_3]^-$ can react with 2HBTZ and produce **I**

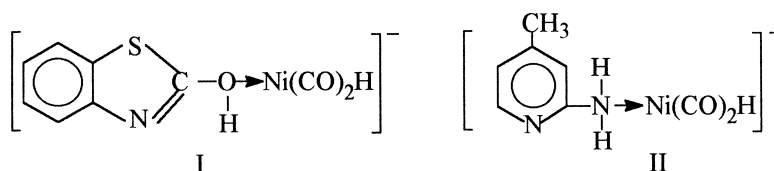


Table 1
Effect of additives on the catalytic activity

Additive	Preferred concentration of additive (mol/l)	STY (mol/l h)
–	–	2.75
DMSO	0.67	3.14
2HBTZ	0.016	2.97
Triethyl amine	0.50	2.82
Pyridine	2.16	2.82

Reaction conditions: $M_{\text{KOMe}} = 0.4 \text{ mol/l}$, $M_{\text{Ni}(\text{CO})_4} = 0.02 \text{ mol/l}$, $T = 373 \text{ K}$, $P_t = 2.0 \text{ MPa}$, $t = 1 \text{ h}$.

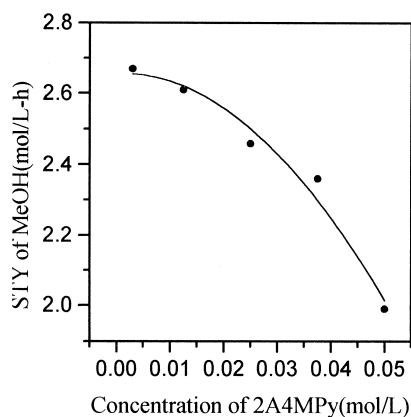


Fig. 6. Effect of 2-amino-4-methylpyridine on the catalytic activity. Reaction conditions are same as in Table 1.

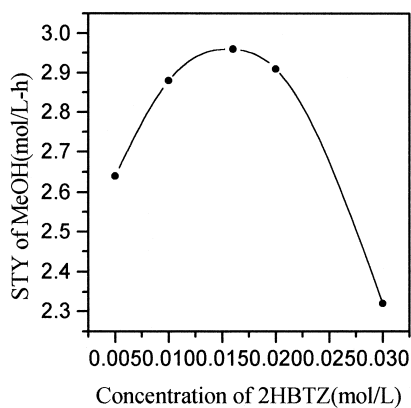
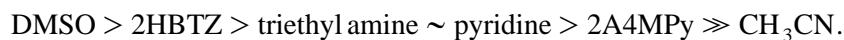


Fig. 7. Effect of 2-hydroxybenzothiazole on the catalytic activity. Reaction conditions are same as in Table 1.

which can make the catalytic active species more stable due to conjugate effect. So the reaction rate rises and the reaction activity increases. When excessive 2HBTZ is added into the reaction system, the catalytic activity is affected by space steric hindrance. But from Fig. 6, we can conclude that STY of methanol decreases with the addition of 2A4MPy which can react with $[\text{HNi}(\text{CO})_3]^-$ and generates **II**; the reaction rate decreases because of space steric hindrance of the methyl group in **II**. There is no methanol produced when acetonitrile is added, because acetonitrile can substitute all carbonyls in $\text{Ni}(\text{CO})_4$, so the catalytic reaction has no activity. STY of methanol rises with the addition of DMSO, triethyl amine and pyridine. Their polarities are favorable for the nucleophilic addition of potassium methoxide to nickel tetracarbonyl and beneficial to produce the reaction active species $[\text{HNi}(\text{CO})_3]^-$, then to quicken the reaction rate.

3. Conclusions

Finally, the overall results lead us to conclude that methanol can be prepared under mild reaction conditions ($T = 373 \text{ K}$, $P_t = 1.8 \text{ MPa}$) in the homogeneous $\text{Ni}(\text{CO})_4/\text{KOME}$ catalytic system. The most preferred reaction conditions were obtained: $\text{CO}/\text{H}_2 = 0.49$; $M_{\text{Ni}(\text{CO})_4} = 0.04 \text{ mol/l}$; $M_{\text{KOME}} = 0.8 \text{ mol/l}$; $T = 378 \text{ K}$; $P_t = 1.8 \text{ MPa}$. The effect of additives on the catalytic activity in the formation of methanol indicated the following sequence:



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