Catalytic production of 1-butanol from ethanol over alkaline earth metal-doped Ni-Mo/C catalyst under supercritical conditions

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Ethanol, one of major products obtained from biomass conversion, can be converted to 1-butanol by catalytic reactions, such as Guerbet reaction [1]. As a fuel, 1-butanol has much higher value than ethanol since it can be blended well with gasoline fuels due to its physico-chemical properties similar to those of gasoline [2]. Recently, the catalytic conversion of ethanol to 1-butanol over heterogeneous catalysts have received many attentions [3, 4]. However, many researches suffer from poor selectivity to 1-butanol, higher reaction temperatures above 400 ºC and long reaction times [5].

In our study, the catalytic synthesis of 1-butanol from ethanol was conducted over alkaline earth metal-doped Ni-Mo/C catalysts under supercritical conditions. Mg, Ca, Sr and Ba were added into Ni-Mo/C catalysts in order to investigate the effect of catalyst basicity on the conversion of ethanol to 1-butanol. The catalysts were prepared by a wet impregnation method, followed by calcination and reduction.

As shown in Figure 1, the conversion of ethanol is proportional to reaction temperature, indicating that the higher reaction temperature is favorable for the ethanol conversion. On the other hand, the yield of 1-butanol significantly increases until 300 °C, however, the yield sharply decreases from 0.89 to 0.52 mol/L when the reaction temperature rises from 300 to 380 °C. This suggests that 1-butanol is unstable in the reaction condition and thus converted to higher alcohols, such as 1-hexanol and 1-octanol, evidenced by GC-MS analysis.

Table 1 shows that the conversion of ethanol and the yield of 1-butanol dramatically increase after the reaction at 350 °C over 2 g of catalyst (Ethanol: 50 g), which indicates that Mg-Ni-Mo/C catalyst accelerates the conversion of ethanol to 1-butanol. On the other hand, the water content in ethanol is unlikely to be very influential in the ethanol conversion and the 1-butanol yield, which is advantageous for technical commercialization, since there is no need to separate water from ethanol completely via expensive separation processes, although biomass-derived ethanol inevitably contains small amounts of water.

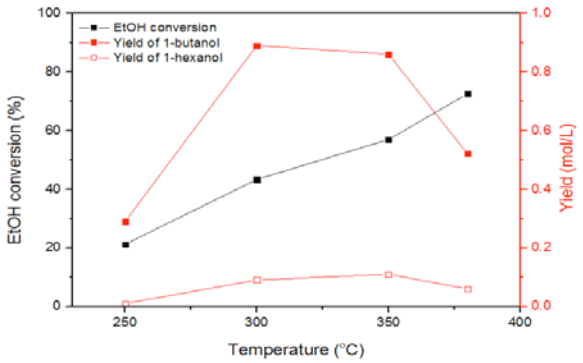

Fig.1 Ethanol conversion and yields of 1-butanol and 1-hexanol at different reaction temperatures (reaction time: 60 min).

Table 1. Effect of catalyst and water content in ethanol on ethanol conversion and 1-butanol production (reaction temperature: 350 °C, reaction time: 60 min).

Catalyst amount (Mg-Ni-Mo/C) (g)	Conversion of ethanol (%)	Yield of 1-butanol (mol/L)
0	18.1	0.08
2	56.9	0.86
Water content in ethanol (wt%)	**Conversion of ethanol (%)**	**Yield of 1-butanol (mol/L)**
0	56.9	0.86
5	57.1	0.89
10	55.3	0.66

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