Chapter 8
Advances in Catalytic Conversion of Syngas to Ethanol and Higher Alcohols

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ABSTRACT

Ethanol and higher alcohols (C2+OH) have attracted much attention owing to their wide applications. They can be produced from syngas using homogeneous and heterogeneous catalysts. Although homogeneous catalysts exhibit high productivity and selectivity of C2+OH, difficulties in separating and recycling homogeneous catalysts remain challenging. Among heterogeneous catalysts, Rh-based catalysts show promising higher selectivity of C2+OH. However, prohibitive cost of Rh metal hinders its large-scale application. Non-noble metal based heterogeneous catalysts include modified methanol synthesis catalysts, modified Fischer-Tropsch (F-T) synthesis catalysts, and Mo/MoS2-based catalysts. Compared with the modified F-T synthesis catalysts and Mo/MoS2-based catalysts, production of undesired byproducts on modified Cu-based catalysts can be well suppressed. Here, the influences of additives and supports on catalytic activity of modified Cu-based catalysts are discussed. Reaction mechanism and development of novel reactors are also included.

INTRODUCTION

Ever since 1970s, energy crisis has been one of the hottest topics (Forzatti, Tronconi, & Pasquon, 1991). Recent nuclear disaster in Japan in 2011 has pulled the trigger on the reconsideration of the security of nuclear energy, leading to perpetual termination of several nuclear power plants in Europe (Benichou & Mayr, 2014). Meanwhile, increasing demand of crude oil has triggered a sharp decline to the oil reserves worldwide, leading to accelerated search for alternative fuels. Recent advancement in the shale gas in the United States will accelerate the transformation in energy resource structure to decrease the severity of current oil dependence ("The shale revolution," 2009).

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Integrated utilization of coal, natural gas and biomass has received increasing attention recent years. Abundant reserves of coal and natural gas can be converted into syngas. In South Africa and some other countries that are short of oil, the technology for gasification of coal has been well developed for decades (van Dyk, Keyser, & Coertzen, 2006). Syngas can be obtained from oil residues, some solid and/or liquid carbonaceous wastes and non-food biomass, as well (Göransson, Söderlind, He, & Zhang, 2011; He et al., 2009). Large reserves of biomass, especially abundant non-food based lignocelluloses (e.g. weed, bark and wheat-straw etc.), could be converted to syngas through gasification process and subsequent purification so that the obtained syngas could satisfy the specific requirements for ethanol and higher alcohol ($C_{2+}OH$) production (Göransson et al., 2011; Higman & Tam, 2013). The process of direct gasification includes low temperature gasification and high temperature gasification (Göransson et al., 2011). Low temperature gasification process can be performed under 900 °C within a fixed-bed reactor or a fluidized-bed reactor with flowing air or other oxidizing agent, while the high temperature gasification are conducted above 1300 °C in an fluidized gasifier which has already been adopted to industrial production in some coal-fired power stations.

As schematically shown in Figure 1, Syngas can be converted into various chemicals, such as methanol, ethanol, higher alcohols, alkanes (F-T process) etc. (Corma, 2014) Production of methanol has been industrialized for decades worldwide, basically using Cu/ZnO-based heterogeneous catalysts at 220-270 °C and 5-15 MPa (Behrens et al., 2012). Based on methanol, various value-added chemicals can be obtained, e.g. dimethyl ether (DME) and lower olefins etc. Different from methanol, $C_{2+}OH$ can be supplied to combustion engine as fuel directly or be added into gasoline to improve the octane value as fuel additives in place of methyl tert-butyl ether (MTBE) (Subramani & Gangwal, 2008). Compared with alkane products (mainly as fuel) obtained through conventional F-T synthesis process, $C_{2+}OH$ are much more versatile products. Ramayya et al. studied the dehydration process of several alcohols (e.g. ethanol, propanol etc.) catalyzed by Arrhenius acids (such as H_2SO_4 and HCl) in supercritical water (Ramayya, Brittain, DeAlmeida, Mok, & Antal Jr, 1987). It was reported that high selectivity of lower olefins ($\geq$ 97%) was obtained within 1-2 min when catalyzed by 0.05 M HCl. When the dehydration process of higher alcohols was catalyzed heterogeneously using Al_2O_3 and/or zeolites, it was suggested that the selectivity of lower olefins was 97-100% under mild reaction condition (Bi, Guo, Liu, & Wang, 2010; G. Chen, Li, Jiao, & Yuan, 2007). Zhang et al. reviewed recent advances in dehydration of ethanol to ethylene (Zhang & Yu, 2013). They suggested that this process was more economically feasible over activated Al_2O_3-based catalysts considering the stability of catalysts, the process of which had already been applied in the industrial plant. In addition, ethanol is environmentally friendly and relatively easier to store. Hence, it has also been selected as one promising candidate to store and transport hydrogen (Davidson et al., 2014). Steaming reforming of $C_{2+}OH$ can provide on-site hydrogen source for fuel cell and/or some small-sized and scattered chemical processes (Ferencz et al., 2014; Wei, Sun, Li, Datye, & Wang, 2012).

From a commercial viewpoint, both the yield/selectivity of higher alcohols, and the cost of catalysts should be considered in evaluating different catalysts. The required syngas conversion should be as high as 5-10% with alcohol productivity of about 0.2-0.5 g/(g_{cat}•h) in order to ensure economic viability (Knifton, Lin, Storm, & Wong, 1993). Since 1980s, plenty of patents focusing on higher alcohol synthesis from syngas have been filed by some famous chemical companies and institutes, such as Dow Chemical and Institut Francais du Petrole (IFP) etc. (Subramani & Gangwal, 2008; Xiaoding, Doesburg, & Scholten, 1987). Up to date, commercial success has not been realized in this field because of the low yield of higher alcohols from syngas and the decline in oil prices recent years. However, with increasing con-