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Personal Review:

Research on ethanol synthesis from syngas[*]

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Abstract: It is a very fine substitutable energy technology to synthesize ethanol from biomass-derived syngas. This paper summarized the development of preparing ethanol from syngas, and especially elaborated on the research status of catalysts for the process. Based on the relative researches on the reaction mechanism, structure and performance of the catalysts, the optimum design of catalysts with high activity was presented in this review, which set the theoretical and application foundation for the industrial production of ethanol from syngas.

Key words: Syngas, Catalyst, Ethanol, Biomass, Promoter
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INTRODUCTION

With continuous climbing of crude oil price, research on alternative energy resources becomes more and more important (Hu *et al.*, 2007). Biomass feedstock, such as inexpensive agriculture and forestry residues, plays an important role in developing alternatives to fossil fuels (Hu *et al.*, 2007). Development of liquid biofuel based on these low-cost raw materials has several benefits. First, fuels from renewable sources, such as agricultural crops, can reduce the dependence of imported oil. Second, oxygenated fuels, such as ethanol, burn more cleanly than fossil fuels, alleviating environmental concerns such as net atmospheric CO_2 content, greenhouse effect, and noxious CO emissions. Other advantages include the development of the rural economy by creating employment opportunities and utilizing marginal lands to cultivate crops as feedstock for biofuel production (Rajagopalan *et al.*, 2002). While there are several methods of generating energy from biomass, gasification, in which syngas is produced, possesses several advantages. Just like petroleum products, syngas can be converted into useful chemicals and fuels via different synthetic routes including methanol synthesis, higher alcohol synthesis, Fischer-Tropsch synthesis (FTS), etc.

In the past decade, use of inexpensive agricultural crops and residues for producing ethanol has received considerable attention. Ethanol is a good additive for improving gasoline octane value and burning efficiency, and is projected as an alternative to gasoline or methyl tertiary butyl ether (MTBE) (Rajagopalan *et al.*, 2002). There are two methods for the production of ethanol from syngas. One is to separate ethanol from originally obtained alcohols; the other is directly to prepare ethanol with high selectivity catalysts. The production of higher alcohols from syngas has been an active area of research for more than fifty years (Roberts *et al.*, 1997), and has been thoroughly developed during 1930~1945 (Tien-Thao *et al.*, 2007a). Comparatively, there are still many difficulties for synthesizing ethanol from syngas exclusively. Fortunately, these by-products share value as commercial chemicals, fuel additives, or potentially fuels in their own right.

The catalyst with specific structure is critical for ethanol production, which should be paid more at-

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tention to. Though commonly used Mn-Rh-based catalysts endow with satisfactory performance, they are too expensive to be commercialized. Therefore the K-MoS_2-based or K-Cu-Zn-based catalysts become the focus of research. Moreover, it is significant to take advantage of the nano-catalyst for its exclusively excellent catalytic performance. Finally, it is expected that the present research is useful to develop a process capable of converting biomass-derived syngas into ethanol in large scale, to replace limited petroleum and grain resources.

CATALYSTS

Types of catalysts

There are still many difficulties for directly converting syngas into ethanol. Although it is necessary to exploit new type catalysts with high selectivity, the commonly used method is to separate ethanol from originally obtained alcohols. Methanol and higher alcohols can be simultaneously produced from syngas with many different types of catalysts. The catalysts can be classified into three categories: modified FTS catalysts, Groups VI~VIII metal-based catalysts, and modified methanol synthesis catalysts (Kulawska and Skrzypek, 2001). However, the required catalysts are mostly utilized in severe conditions with complex compositions. The products are mixture of either branched or linear primary alcohols ranging from methanol to hexanol (Tien-Thao *et al*., 2007a). Types of catalysts that have been studied are summarized as follows.

1. Rh-based catalysts

Among the choice of supported transition metal catalysts, Rh appears to be the most adaptable element in terms of its properties for catalysis, particularly for syngas conversion (Hu *et al*., 2007). Rh-based catalysts tend to be more selective for C_2-oxygenates (Luo *et al*., 2001; Ojeda *et al*., 2004). Rh/SiO_2 is the baseline catalyst used for alcohols synthesis from syngas and shows high selectivity towards ethanol (Hu *et al*., 2007). The addition of V to it obviously promotes the activity and selectivity to C_2-oxygenates. Vanadium ions of lower valence have a good capacity of hydrogen storage, and this can enhance the hydrogenation ability of the catalyst and promote the formation of ethanol. Furthermore, the Rh-Mn/SiO_2 catalyst promoted with potassium species could be used to inhibit methane formation (Lou *et al*., 2001).

2. Cu-Zn-based and Zn-Cr-based catalysts (Breman *et al*., 1995; Kieffer *et al*., 1997; Kulawska and Skrzypek, 2001; Nowicki, 2005; Roberts *et al*., 1997; Tien-Thao *et al*., 2006; 2007a; 2007b)

These catalysts include high-temperature-pressure Zn-Cr-based and low-temperature-pressure Cu-Zn-based catalysts (Tien-Thao *et al*., 2007a). Adding alkali promoters to these kinds of methanol synthesis catalysts causes increase in selectivity towards ethanol.

3. Modified FTS catalysts (Tien-Thao *et al*., 2007a; Kieffer *et al*., 1997; Nowicki, 2005)

Among transition metals, cobalt is known to be very active for FTS while copper tends to form alcohols. This leads to the assumption that Co-Cu mixed oxide with definite structure such as perovskite or spinel could be a promising catalyst for syngas conversion into alcohols and hydrocarbons. Furthermore, these catalysts show better selectivity to higher alcohols if a proper amount of alkali promoters are introduced.

4. Alkaline metal doped transition metal sulfide catalysts (sulfur tolerant catalysts) (Koizumi *et al*., 2004; Iranmahboob *et al*., 2003; Ma *et al*., 2006; Jiang *et al*., 1994; Iranmahboob *et al*., 2002)

MoS_2-based, Co-Mo-S-based or Ni-Mo-S-based catalysts promoted with alkali promoters having excellent sulfur tolerance can be utilized not only to yield a homolog of linear primary alcohols and hydrocarbons (Tien-Thao *et al*., 2007a), but also to simplify the conventional, huge and complex process by leaving out the desulphurization unit (Koizumi *et al*., 2004; Iranmahboob *et al*., 2003). It is dependent of their compositions and structures as well as the reaction conditions to make full play of the catalysts. It requires higher reaction pressures (usually above 10 MPa) for ethanol synthesis compared with Cu-based catalysts. It is also worthy to note that CO hydrogenation activities of transition metal sulfides except for Mo and W sulfides have not been investigated yet (Koizumi *et al*., 2004).

5. Fe-based catalysts (Koizumi *et al*., 2004; Xu *et al*., 2004)

Fe-based catalysts are primarily used for catalytic liquefaction of coal, and can be used to prepare ethanol from syngas after modified by certain promoter. For the FTS reactions using CO-rich syngas, Fe-based catalysts are more suitable than Co-based catalysts for their water-gas shift activities (Koizumi *et al*., 2004). Besides, the addition of appropriate amount of Mn oxides (MnO) to these sulfur resistance Fe-based catalysts is found to improve the sulfur tolerance much more effectively (Koizumi *et al*., 2004). Moreover, the incorporation of iron resulted in substantial changes in both structure properties and catalytic performances in multi-component Fe-Cu-Mn/ZrO_2 catalysts, leads to better dispersibility and stabilization of Cu (Xu *et al*., 2004).

Catalytic activity influencing factors

The catalyst activity is closely related with its composition, structure and reaction conditions such as temperature, pressure, solvent, syngas feedstock, reactor, catalyst preparation and activation methods, etc. The catalysts with various compositions, configurations and activities could be prepared by many different methods. For example, two types of $LaCo_{0.7}Cu_{0.3}O_3$ perovskite catalysts are synthesized by reactive grinding and citrate complex method (Tien-Thao *et al*., 2007a), respectively. The ground sample shows a rather high surface area with nano-scaled size. This nanocrystalline perovskite precursor shows a better catalytic performance in comparison to the citrate-derived sample in terms of both alcohol selectivity and productivity (Tien-Thao *et al*., 2007a). In addition, in multi-component Fe-Cu-Mn/ZrO_2 catalysts, the effect of iron is greatly influenced by the catalyst preparation methods. It is found that for the catalyst prepared by co-precipitation method, iron species act as structural promoter. As a result, the introduction of iron by co-precipitation method is favorable to synthesis of methanol and branched products. Comparatively, for the catalyst prepared by wetness impregnation method, the iron oxide-support interaction is relatively weak. The iron oxide could be partially reduced, which led to increase of the interaction between highly dispersed copper and iron. Such interaction is in favor of chain growth to form higher alcohols (Xu *et al*., 2004). Thirdly, good temperature control is important to the reaction selectivity and catalyst life considering the exothermic nature of alcohol synthesis. Fourthly, there is an optimum content of alkali promoter in the catalyst (Roberts *et al*., 1997). Finally, the activity results of a series of vulcanized K-MoO_3/γ-Al_2O_3 catalysts indicate that with Mo loading increase the total CO conversion into mixed alcohols, hydrocarbons and the selectivity to mixed alcohols are significantly changed (Bian *et al*., 1998). This exactly illustrates the fact that the catalyst activity is influenced by its compositions.

In conclusion, presently, ethanol is mainly separated from the originally obtained alcohols. Though provided with relatively catalytic specificity, the traditional Rh-based catalysts are too expensive to apply. It is necessary to explore and utilize some economic, efficient catalysts including modified Fe-based, Mo-based, FTS and methanol synthesis catalysts. Generally, there are structural and electronic promoters for catalysts. The alkali promoter is vital for ethanol synthesis from syngas. Besides, appropriate incorporation of a minor amount of multi-walled carbon nanotubes (CNT) into vulcanized $Co_iMo_jK_k$ leads to a significant increase in CO conversion and the selectivity for ethanol. The water-gas-shift (WGS) side reaction is also inhibited to a great extent over it (Ma *et al*., 2006). Commonly, the presence of residual Na is responsible for coking and deactivating of the catalysts (Kieffer *et al*., 1997). The promotional effects are found to be dependent of the promoters' contents and physicochemical properties such as electronic structure, electronegativity, radius, etc. (Tien-Thao *et al*., 2007b). For example, the chain growth probability factors of products are correlated with the alkali metal's electronegativity. The catalyst surface area varies with the cationic radius of the alkali metals used (Roberts *et al*., 1997). Noticeably, in view of its excellent catalytic performance, the nano-catalyst should be particularly emphasized.

REACTION MECHANISMS

Ascertaining the mechanisms of alcohol synthesis from syngas is essential for the structure design of catalysts, reactors, etc. The general alcohol synthesis reaction is described by Eq.(1):

$$nCO+2nH_2\rightarrow C_nH_{2n+1}OH+(n-1)H_2O. \qquad (1)$$

For ethanol synthesis, the reactions are described by Eqs.(2)~(5), which is highly exothermic, more exothermic than methanol one (Roberts *et al.*, 1997).

$$2CO+4H_2\rightarrow C_2H_5OH+H_2O,\quad \Delta H_{327\ ^\circ C}=-256\ \text{kJ/mol}, \tag{2}$$

$$6CO+3H_2O\rightarrow C_2H_5OH+4CO_2, \tag{3}$$

$$6H_2+2CO_2\rightarrow C_2H_5OH+3H_2O, \tag{4}$$

$$6CO+6H_2\rightarrow 2C_2H_5OH+2CO_2. \tag{5}$$

With CO alone as the sole substrate carbon source, one-third of the carbon from CO can theoretically be converted into ethanol (Eq.(3)). For an equimolar mixture of H_2 and CO, two-thirds of the carbon from CO can theoretically be converted into ethanol as shown in Eq.(4) (composed of Eqs.(3) and (4)). Obviously, the theoretical yield of ethanol is associated with the composition of syngas (Rajagopalan *et al.*, 2002).

The formation of higher alcohols is generally assumed to be a combination of hydrogenation and carbon-carbon bonding via aldol reaction and CO insertion reaction (Tien-Thao *et al.*, 2007a). For example, in the Co promoted Cu-$La_2Zr_2O_7$ methanol catalysts, the mechanistic results are in good accordance with a CO insertion mechanism. The chain growth step can be attributed to the insertion of a C_1 oxygenated species (CO was mainly derived from the feed or formed previously from CO_2) into a metal-alkyl bond (Kieffer *et al.*, 1997). In the Rh-Mn/Al_2O_3 catalysts, the presence of oxidized $Rh^{\delta+}$ sites near the Rh-MnO interface favors the CO insertion reaction (Ojeda *et al.*, 2004). Besides, evidence suggests the presence of K does not seem to promote chain growth on supported Rh-based catalyst, which is different from commonly known Cu-based catalysts. This is probably because the reaction pathways or chain growth mechanisms on Cu-based and Rh-based catalysts systems are significantly different (Hu *et al.*, 2007; Luo *et al.*, 2001). Furthermore, it indicates that the K-Mo-S species in K-Mo-S/γ-Al_2O_3 catalysts are active for the formation of alcohols from CO hydrogenation, while the Mo coordinatively unsaturated sites [Mo (CUS) sites] could be responsible for the formation of hydrocarbons. It maybe concludes that the formation of alcohols and hydrocarbons occurred independently on different types of active sites (Nowicki, 2005). For example, at high K loadings, the unaggregated KCl has preferential coverage on the Mo (CUS) sites and results in a large increase in alcohol selectivity. The other research shows that the high C_2^+OH/C_1OH ratio in alcohol product distribution could be attributed to the substantial amount of SH groups present on the supported sulfide samples (Jiang *et al.*, 1994).

In multi-component Fe-$CuMnZrO_2$ catalysts, iron species could act as structural promoter, which increase copper dispersion and improve the formation of a homogeneous copper phase. On the other hand, the iron oxide could be partially reduced if the iron oxide-support interaction is relatively weak, which leads to reinforcing the interaction between highly dispersed copper and iron. Such interaction is in favor of chain growth to form higher alcohols (Xu *et al.*, 2004). Activity results and structural studies of vulcanized K-MoO_3/γ-Al_2O_3 catalysts indicate that the dispersion state of the active species and the content of unreduced Mo species influence the total CO conversion but the acidity of the catalyst controls the selectivity to mixed alcohols (Bian *et al.*, 1998). In the K_2CO_3/Co-MoS_2/clay catalysts, cobalt lies on the edge of MoS_2 slabs in the form of "Co-Mo-S" phase. The formation of H_2S over the alkali-promoted Co-MoS_2 catalyst may enhance the higher alcohol synthesis (HAS) under appropriate conditions (Iranmahboob *et al.*, 2002). In the $LaCo_{1-x}Cu_xO_{3-\delta}$ perovskites catalysts, Cu in close proximity to Co sites in perovskite lattice plays an important role in the promotion of cobalt reducibility and the production of higher alcohols (Tien-Thao *et al.*, 2006). Accordingly, one might expect that a close contact between cobalt and copper phases (e.g. perovskite systems) may yield an active component for higher alcohol synthesis (Tien-Thao *et al.*, 2007a). Secondly, the reduced forms of $LaCo_{0.7}Cu_{0.3}O_3$ perovskites are very active for the conversion of syngas into higher alcohols and hydrocarbons (Tien-Thao *et al.*, 2007a). However, such catalysts are inferior for their less specific surface area (Tien-Thao *et al.*, 2007a). It indicates that nanocrystalline Co-Cu-based perovskite precursors may be promising catalysts for the synthesis of higher alcohols from syngas (Tien-Thao *et al.*, 2007a).

PROCESS PARAMETERS

The catalysts performances, product distributions and yields are closely related to the catalysts and reaction conditions such as temperature, pressure, H_2/CO ratio, gaseous hourly space velocity (GHSV), reactor, etc. Syngas is a major building block for fuels and chemicals (Younesi *et al.*, 2005). There are H_2-rich or CO-rich syngas with different sulfur content produced from different raw materials by various methods. It has been generally assumed that catalysts for CO hydrogenation are poisoned by a small amount of sulfur compounds in the feed (Koizumi *et al.*, 2004). Fortunately, the biomass-derived syngas is rich in H_2 and contains smaller amount of sulfur compounds, compared with coal and heavy oil (Koizumi *et al.*, 2004; Iranmahboob *et al.*, 2003; McCutchen *et al.*, 1996). To avoid sulfur poisoning, conventional plants are equipped with a huge desulfurizing installation to remove the sulfur compounds almost completely from the feed (usually below 1×10^{-6}) (Koizumi *et al.*, 2004). Otherwise, the optimum design of the reactor, equipped with effective heat removal capacity and reduced mass transport limitation and minimized back mixing, enables the highly exothermic CO hydrogenation reaction to be operated in an isothermal mode with high yield (Hu *et al.*, 2007). Owing to their inherently isothermal nature, slurry reactors are the subject of considerable research and development for ethanol synthesis from syngas. The general advantages of slurry reactors are displayed as follows (Roberts *et al.*, 1997): (1) essentially isothermal; (2) small catalyst particles minimizing mass and heat transfer effects; (3) liquid vaporization removing heat; (4) greater flexibility in catalyst design.

CONCLUSION

Presently, ethanol is mainly separated from the originally obtained alcohols. The utilized catalysts can be classified into three categories: modified FTS catalysts, Groups VI-VIII metal-based catalysts and modified methanol synthesis catalysts. Among the choice of the catalysts, Rh appears to be one of the most adaptable elements in transition metal series, and tends to yield alcohol synthesis catalysts with high selectivity towards ethanol, but these catalysts are too expensive to apply. Contrarily, those K-doped Cu-Zn-based, Zn-Cr-based, Cu-Co-based, Fe-based, Mo-based catalysts or modified FTS, methanol synthesis catalysts should be preferentially selected in view of their performances and costs. Generally, there are structural and electronic promoters for ethanol synthesis catalysts. More emphasis should be given to the alkali metal promoters. The function is dependent on the promoter's content and physicochemical property such as electronic structure, electronegativity, radius, and so on (Tien-Thao *et al.*, 2007b). Moreover, considering the highly exothermic nature of alcohol synthesis reaction (Roberts *et al.*, 1997) and the scale production, it is necessary for the structured catalyst coated on highly heat conducting material (e.g., FeCrAlY metallic felt (Ojeda *et al.*, 2004)) to develop a compact reaction system which is effective for syngas conversion into ethanol. Thirdly, in contrast to those conventional metallic catalysts, an alkaline metal-promoted sulfur tolerant catalyst (e.g., Fe, Co, Mo or Ni sulfide-based catalyst) not only preserves its initial activity for the synthesis of mixed alcohols for a long period even in the presence of H_2S 50×10^{-6} in concentration (Koizumi *et al.*, 2004), but also simplifies the traditional complex process by leaving out the desulphurization unit, which is quite advantageous for developing a novel on-site process that produces transportation fuels in the vicinity of small-scale and dispersed carbon resources (Koizumi *et al.*, 2004; Iranmahboob *et al.*, 2003). The performance of these catalysts is, however, not adequate since they require higher reaction pressures (usually above 10 MPa) to attain activities and selectivity for C_2^+ alcohol synthesis compared with those of Cu-based catalysts. Finally, in view of its performance, more attention should be paid to the nano-catalyst. After all, this work is part of a holistic study to produce ethanol from a wide variety of agricultural feedstock. Further study should be conducted in the near future.

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