CHAPTER 6

CONCLUSIONS and RECOMMENDATIONS

From the experiments that have been carried out, the following conclusion and recommendations may be drawn:

1. A set of experimental apparatus that can withstand up to 100 atg at 400°C has been fabricated and tested for gas leakage. An electrict furnace has been made and tested for axial temperature uniformity. Then three types of catalysts have been prepared and a sizable number of experiments carried out on synthesis of the ethanols and other alcohols.

2. From the results that are summarized in **Appendix C**, the $Rh_1Mn_1Fe_{0.1}/SiO_2$ catalyst has been found to give the best result in $STY_{tot.alc.}$, namely, 4.975 mole/lit.cat.-hr (based on the moles of products), at the working pressure 80 atg, GHSV 8,000 hr^{-1}, 340°C and the feed ratio of $CO:H_2 = 1:2$. Under the same conditions a maximum STY_{EtOH} is also obtained at the value 2.85 mole/lit.cat.-hr (based on the moles of products). The $STY_{tot.alc.}$ and STY_{EtOH} increase monotoniclly with temperature within the whole range studied at $P = 80$ atg and GHSV 2,000 hr^{-1} and above, while at a lower pressure, there exists an optimum temperature around 310°C.

3. When the feed ratio of $CO:H_2$ is fixed at 1.25:1, the $Rh_1Mn_1Fe_{0.1}/SiO_2$ catalyst gives the best $STY_{tot.alc.}$ at 40 atg, GHSV 2,000 hr^{-1}, 340°C. And the $STY_{tot.alc.}$ increases monotonically up to the maximum investigated temperature. While at an higher pressure, i.e. 80 atg, there exists an optimum temperature at 280°C for GHSV 2,000 hr^{-1} and above.

4. The effect of the feed ratio of $CO:H_2$ shows that at an higher reaction pressure and higher GHSV result in an higher

$STY_{tot.alc.}$ and STY_{EtOH} when the feed ratio of $CO:H_2$ = 1:2. While at the feed ratio $CO:H_2$ = 1.25:1, a moderate pressure (namely, 60 atg) yields an higher $STY_{tot.alc.}$ than the highest pressure.

5. For the $Co_1Ba_{0.05}Ag_{0.1}/SiO_2$ catalyst, if the abnormal result at 250°C, 60 atg and GHSV 2,000 hr^{-1} is discarded, the maximum $STY_{tot.alc.}$ and STY_{EtOH} are obtaind at 310°C, GHSV 2,000 hr^{-1}, at 40 atg and 80 atg, respectively. Note that the feed ratio is $CO:H_2$ = 1.25:1. By the way at the highest pressure, i.e. 80 atg, an optimum temperature is found at 310°C GHSV 2,000 hr^{-1} for $STY_{tot.alc.}$ and at 310°C GHSV 2,000 hr^{-1} for STY_{EtOH}.

6. For the IFP-type catalyst, the $STY_{tot.alc.}$ and STY_{EtOH} is found to increase with temperature at 40 atg, GHSV 2,000 hr^{-1}. Whereas at a higher pressure, i.e. 60 and 75 atg, there exists an optimum temperature at 310°C. The best $STY_{tot.alc.}$ is obtained at 75 atg GHSV 2,000 hr^{-1} and 310°C. While the maximum STY_{EtOH} at 60 atg and 75 atg are both found at 310°C and nearly equal.

7. The $Rh_1Mn_1Fe_{0.1}/SiO_2$ catalyst gives a significantly better $STY_{tot.alc.}$ and STY_{EtOH} when the feed ratio of $CO:H_2$ = 1:2.

8. It should be noted that the IFP-type catalyst is comparable to the rhodium catalyst at the same feed ratio of CO to H_2 and the nearly same working pressure, around 80 atg, GHSV 2,000 hr^{-1}, temperature 310°C and 280°C, respectively. A further study on the IFP-type catalyst is warranted both for the synthesis of ethanol and mixed alcohols.

9. It should be emphasized that the above conclusions are based on the results that are derived from the definition stated in **Appendix B.** The effects of temperature on the trends of $STY_{tot.alc.}$ and STY_{EtOH} are quite complex, and depending on the pressure and GHSV.

To see the effect of reaction conditions on the alcohol product distribution, it is worthwhile here to define the Space

Time Yield in terms of g-atom of Carbon in the product per litre of catalyst per hour. The STY values based on this new definition are shown in **Appendix E.** for the three catalysts. **Tables E.1-E.2** summarize the results for the $Rh_1Mn_1Fe_{0.01}/SiO_2$ catalyst when the feed ratio of $CO:H_2 = 1:2$ and $CO:H_2 = 1.25:1$, respectively. **Tables E.3-E.4** summarize the results of $Co_1Ba_{0.05}Ag_{0.1}/SiO_2$ catalyst and the IFP-type catalyst, respectively.

Based on the results shown **Appendix E**, a few additional conclusions may be drawn:

10. In the case of the $Rh_1Mn_1Fe_{0.01}/SiO_2$ catalyst with the feed ratio $CO:H_2 = 1:2$, the alcohols detected are MeOH, EtOH and higher alcohols, especially i-PrOH. Meantime, the detected hydrocarbons are methane, ethane, propane. As the reaction temperature increases, the combustion reaction becomes important. Compared to the feed ratio of $CO:H_2 = 1.25:1$, the synthesis gas that is richer in hydrogen appears to give better alcohols synthesis and give lower hydrocarbons, also give lower combustion.

11. In the case of the $Co_1Ba_{0.05}Ag_{0.1}/SiO_2$ catalyst, generally at a lower temperature, i.e. 250-280°C, the major alcohols are MeOH and EtOH. At an higher temperature, more higher alcohols are synthesized. Meanwhile, the major hydrocarbons are methane, ethane and propane. At an higher temperature, more higher hydrocarbons are observed but the three hydrocarbons all increase sharply. Generally the combustion reaction increases with the temperature but less compared to Rh-catalyst. The desired alcohol products are generally less than those of the other two catalysts at the same conditions.

12. For the IFP-type catalyst, the alcohols detected generally are MeOH, EtOH and PrOH. The higher alcohols such as i-PrOH generally increase as temperature increases and become more abundant. Like the other two catalysts, the detected hydrocarbons are methane, ethane and propane, but their amounts are

comparatively lower than those of the other catalysts. At a lower pressure, e.g. 40 atg, more combustion products are observed than the other catalysts. Again the combustion products increase with the temperature, except at 60 atg, when an optimum temperature of combustion at 310°C exists.

13. Of all the three catalysts, the $Rh_1Mn_1Fe_{0.01}/SiO_2$ catalyst gives the highest STY in alcohols synthesis. And the global optimum conditions are : feed ratio of $CO:H_2 = 1:2$, 40 atg, GHSV = 2,000 hr^{-1}, 340°C.

The **Recommendation** IFP-type catalyst at the feed ratio of $CO:H_2 = 1:2$ should be further investigated. Furthermore certain modification of the catalyst composition is also worth investigating. One metal that might be considered for addition is Fe.