Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Catalysis Today 120 (2007) 90–95
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Conversion of biomass-derived syngas to alcohols and C_2 oxygenates using supported Rh catalysts in a microchannel reactor

Jianli Hu *, Yong Wang, Chunshe Cao, Douglas C. Elliott, Don J. Stevens, James F. White

Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352, United States

Abstract

The capability of a microchannel reactor for synthesis of alcohols and C_2^+ oxygenates from biomass-derived syngas was explored. Supported Rh catalysts were selected to integrate with a microchannel reactor for this study. The focus of the present research was to investigate the impact of reaction variables, including temperature, pressure, H_2/CO ratio, and activation procedures, on the activity and product selectivity of supported Rh catalysts. It was observed that the formation of undesired product, methane, can be suppressed under conditions of low temperature, high pressure, and low H_2/CO ratio. Interestingly, different catalysts responded differently to reduction–oxidation cycle (RedOx) treatment. A hybrid catalyst system containing CuZnAl and Rh-Mn/SiO_2 exhibited continued increase in activity after RedOx treatment. When Rh-Mn/SiO_2 catalyst was coated on a FeCrAlY metallic felt substrate and subsequently integrated into a microchannel reactor, a significant enhancement in specific activity was obtained, which highlights strong process intensification potential for commercial application.

Keywords: Ethanol; Methanol; C_2^+ oxygenates; Microchannel reactor; Syngas; Biomass; Rhodium catalyst

1. Introduction

With the continued climbing of crude oil price, research on alternative energy resources becomes more and more important. Biomass feedstocks, such as agriculture and forestry residues, play an important role in developing alternatives to fossil fuels [1]. While there are several methods of generating energy from biomass, gasification, in which a hydrogen–carbon monoxide gas mixture (syngas) is produced, offers several advantages. Just like petroleum products, syngas can be converted to useful chemicals and fuels via different synthetic routes including methanol synthesis, higher alcohol synthesis, Fischer-Tropsch synthesis, etc. However, an obstacle to converting biomass-derived syngas, at an economical scale, has been the decentralized nature of biomass operations. Petroleum, coal, and natural gas are high energy density materials and thus amenable to centralized, large-scale processing plants. However, biomass feedstocks with their inherently lower energy density are and will continue to be processed in geographically decentralized plants and gasification facilities. It is reported that if conventional processing technology is adopted for biomass gassification, a minimum scale of 2500 t/d would be required for production economically comparable to conventional LPG fuel [2]. Since it is difficult to supply and deliver enough biomass to satisfy this criterion using conventional technology, a more compact and efficient portable process is needed. This new process would operate under the lower limit of industrial process conditions, but with a high space time yield. It would also be compatible with both current and future bio-refinery, that is, forest product mills and corn processing facilities.

The purpose of the present research discussed here is to develop such a process capable of converting syngas generated from gasification of dispersed biomass resources. In this paper, we explore possibility of converting biomass-derived syngas to methanol, ethanol, and C_2^+ oxygenates, but preferably with high selectivity to ethanol, a product of greater value. Among the choice of supported metal catalysts, Rh appears to be the most adaptable of the elements in the transition series in terms of its properties for catalysis, particularly for syngas conversion [3–6]. Rh supported on silica and/or vanadium tends to yield alcohol synthesis catalysts with high selectivity towards ethanol [7–9]. General

---

* Corresponding author. Tel.: +1 509 376 0427; fax: +1 509 376 5106.
E-mail address: Jianli.Hu@pnl.gov (J. Hu).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.07.006

alcohol synthesis is described by Eq. (1), stoichiometrical requirement of H_2/CO ratio equals 2.

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

For ethanol synthesis, the reaction is described by Eq. (2), which is highly exothermic.

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O \quad \Delta H^\circ_{327C} = -256\,\mathrm{kJ/mol} \quad (2)$$

Considering the exothermic nature of alcohol synthesis and the small to moderate expected scale of production, we explored the feasibility of utilizing a microchannel reactor for alcohol synthesis with parallel exploration of supported Rh catalysts. It is known that microchannel reactors have the advantage of improved heat and mass transfer, which allow greater process intensification [10,11]. That is, microchannel reaction systems can be much smaller than conventional devices and still deliver high space time product yields.

2. Experimental

2.1. Methods of catalyst preparation and activation

Catalyst formulation selection is based on literature reported information [5,6]. The SiO_2 was supplied by Davison, which had been pre-calcined in air at 550 °C (BET surface area = 400 m^2/g). A rhodium nitrate solution containing 10% Rh metal purchased from Engelhard was used as precursor. Although Rh/SiO_2 itself can catalyze syngas conversion to ethanol, the use of appropriate promoters (e.g. Mn, V, etc.) is essential for the improvement of the activity and selectivity. $Mn(NO_3)_2$ (99%) and NH_4VO_3 (>98%) were obtained from Aldrich and used as precursors for Mn and V, respectively. Rh-Mn/SiO_2 catalyst was prepared by co-impregnating Rh and Mn precursors on SiO_2 support using incipient wetness technique. Final concentration of Rh and Mn were controlled at level of 6 and 1.5 wt%, respectively. After impregnation, all catalysts were subject to air calcination at 350 °C for 3 h. A methanol synthesis catalyst, F51-8PPT (Katalco Corporation) was modified by impregnating 3% Cs using incipient wetness technique. This catalyst was used as a comparison higher alcohol synthesis catalyst. Most of catalysts were tested in powdered form and only Rh-Mn/SiO_2 was tested in structured monolith type configuration. When tested in the powder form, fine particle powder catalysts were pelletized, crushed, and sieved into 70–100 mesh before placed into microchannel reactor. The purpose was to minimize pressure drop. Structured Rh-Mn/SiO_2 catalyst was prepared by wash coating technique. Powdered Rh-Mn/SiO_2 catalyst was ball-milled with water as a medium for 24 h, after which the ball-milled catalyst slurry was wash coated on FeCrAlY metallic felt. Characterization by SEM showed that the catalyst particle size on the structured catalyst varied between 0.5 and 2 μm. After wash-coating to desired weight gain, the felt catalyst (structured catalyst) was installed into a microchannel reactor equipped with active cooling functions.

All the catalysts were reduced with flowing 10% hydrogen in Helium in the 220–350 °C temperature range under atmospheric pressure. A special catalyst treatment procedure was developed where catalysts were treated by reduction–oxidation cycles (RedOx). During the RedOx treatment, catalyst is reduced first by 10% hydrogen at 350 °C for 12 h, then cooled to room temperature. After reactor was purged by nitrogen, 2% oxygen in Helium was introduced and reactor temperature was increased to 250 °C at ramping rate of 1 °C/min. The duration of oxidation is 2 h, after which reactor was cooled to room temperature under Helium gas flow. The above reduction and oxidation procedure was repeated once, and the catalyst was finally reduced by 10% hydrogen in Helium before feed gas mixture was introduced.

2.2. Microchannel reactor and operation

The experiments were carried out in a microchannel reactor (316 stainless steel), with the channel dimensions of 5.08 cm × 0.94 cm × 0.15 cm. The microchannel reactor was configured for high pressure down flow mode. The schematic diagram of the reactor system and microchannel reactor assembly was similar to those described in reference [12]. To minimize methanation reaction in the stainless steel reactor, silica (SiO_2) coated stainless steel tubing was used in the high-temperature preheating zone. Experiments were conducted at temperatures from 260 to 300 °C and pressure from 2 to 5.4 MPa. All the experiments were carried out under isothermal conditions as indicated by the uniform temperature distribution along catalyst bed.

A mixture of N_2/H_2 was fed during startup to establish steady-state flow and to heat the reactor to the desired temperature. When the catalyst bed temperature reached the target, premixed syngas at the desired ratio was fed into the reactor. The typical feed composition was $CO:H_2:CO_2:Ar = 30:62:4:4$. The presence of Ar served as the internal standard for conversion and selectivity calculation purposes. For each run using powdered catalyst, 0.20 g of catalyst were loaded into the reactor, and the volume was measured. Total feed flow rate was set to achieve the desired gas hourly space velocity (GHSV), which is measure by reactor channel volume. The reaction products were analyzed by on-line gas chromatography (HP 5890 GC) equipped with both TCD and FID detectors. GC column used was GS-Q 30 m manufactured by JW Scientific. Temperature program of 5 °C/min to 300 °C was chosen for the analysis. Liquid products were collected in a cold trap at −3 °C and were also analyzed by GC–mass spectrometry. Carbon monoxide conversion and product selectivity were calculated based on feed and product flow rates and carbon balance.

3. Results and discussion

It is well known that Rh/SiO_2 catalyst produce C_2-oxygenated compounds such as ethanol, acetaldehyde, and acidic acid from syngas with high selectivity. However, it is

Table 1
Influence reaction temperature on the activity of Rh-Mn/SiO_2 catalyst (powdered, 70–100 mesh)

Conditions	1	2	3	4
Temperature (°C)	280	300	280	265
Pressure (MPa)	5.4	5.4	5.4	5.4
GHSV (h^{-1})	3750	3750	1700	1700
H_2/CO (mol/mol)	2	2	2	2
CO conversion	24.6	40.5	38.7	25.1
Selectivities (%)				
CO_2	0.0	3.4	1.3	0
CH_4	38.4	48.1	40.2	34.2
MeOH	3.9	1.9	2.8	2.6
EtOH	56.1	44.5	53.9	61.4
C_2^+ HC and Oxy	1.6	2.1	1.8	1.8

very difficult to produce ethanol selectively without any production of other C_2-oxygenates. This is the reason why promoters are used to improve such catalyst performances. This study was not intended to explore or develop new catalyst formulations, but rather to focus on exploring the performance of supported Rh catalyst in a microchannel reactor. As a result, the selection of catalyst formulations was limited to Rh-Mn/SiO_2.

3.1. Effect of reaction temperature and pressure on performance of Rh-Mn/SiO_2 catalyst

Influence of reaction temperature, pressure, and feed compositions on catalytic activity of Rh-Mn/SiO_2 catalyst is depicted in Tables 1 and 2. Major products were comprised of methane, CO_2, MeOH, EtOH, and C_2^+ hydrocarbons and oxygenates. To study the effect of temperature, it was necessary to operate the reactor in an isothermal mode. Multiple thermocouples were installed in the catalyst bed and the furnace temperature was adjusted to control catalyst bed temperature. The temperature difference between the top and bottom of the catalyst bed was measured to be within ±2 °C, indicating excellent heat removal capability of the microchannel reactor. As illustrated in Table 1, on raising catalyst temperature from 280 to 300 °C, CO conversion increases by an increase in temperature (Conditions 1 and 2). However, methane selectivity increases from 38.4% to 48.1%, and meanwhile, selectivity to ethanol decreases remarkably. This suggests that alcohol synthesis over Rh-Mn/SiO_2 is preferred to be operated at temperatures lower than 280 °C. To further illustrate the temperature effect, experiments were conducted at lower temperature and even lower GHSV. By comparing results obtained from Conditions 3 and 4 shown in Table 1, low temperature operation results in higher selectivity to ethanol and lower methane formation. On supported Rh catalyst, methane formation is very sensitive to temperature change. This can be explained from the mechanistic consideration where hydrogenation of $(CH_x)_{ad}$ species to form methane becomes dominant at higher temperature [4]. This can also be generalized that activation energy for methanation is higher than for ethanol synthesis.

Table 2
Effect of reaction pressure and feed ratio on the performance of Rh-Mn/SiO_2 catalyst (powdered, 70–100 mesh)

Conditions	1	2	3	4
Temperature (°C)	300	300	300	300
Pressure (MPa)	5.4	3.8	3.8	3.8
GHSV (h^{-1})	3750	3750	3750	3750
H_2/CO (mol/mol)	2	2	1	3
CO conversion (mol%)	40.5	32.1	18.7	35.4
Selectivities (%)				
CO_2	3.4	2.1	8.5	1.9
CH_4	48.1	48.0	48.3	54.4
MeOH	1.9	3.2	2.1	1.9
EtOH	44.5	44.4	34.8	40.9
C_2^+ HC and Oxy	2.1	2.3	6.3	0.9

Effect of pressure on the activity of Rh-Mn/SiO_2 catalyst was studied under constant temperature of 300 °C and GHSV = 3750 h^{-1}, and results are summarized in Table 2. As the reaction proceeds from Condition 1 to 2 wherein pressure is lowered from 5.4 to 3.8 MPa, conversion decreases whereas product selectivity remains essentially unchanged. This seems to indicate that when reaction is carried out at higher temperature of 300 °C, the product selectivity is predominately controlled by reaction temperature rather than pressure, therefore changing pressure would not cause any noticeable impact on product selectivity. To further illustrate the effect of pressure on product selectivity, a reaction was carried out at relatively lower temperature of 270 °C. The reactivity results at different reaction pressures are plotted in Fig. 1. At a temperature of 270 °C, an increase in CO conversion is observed with increased pressure. There is also an increase in selectivity to total oxygenates although it is not dramatic. However, in contrast to high-temperature operation, a downward trend of methane selectivity is observed with increase in reaction pressure. Mechanistically, high pressure favors CO insertion into metal–$(CH_x)_{ad}$ surface species to form C_2^+ oxygenates, reducing the hydrogenation rate of $(CH_x)_{ad}$ for methane formation [4]. This implies that methane selectivity can be suppressed as long as the reactor is operated at

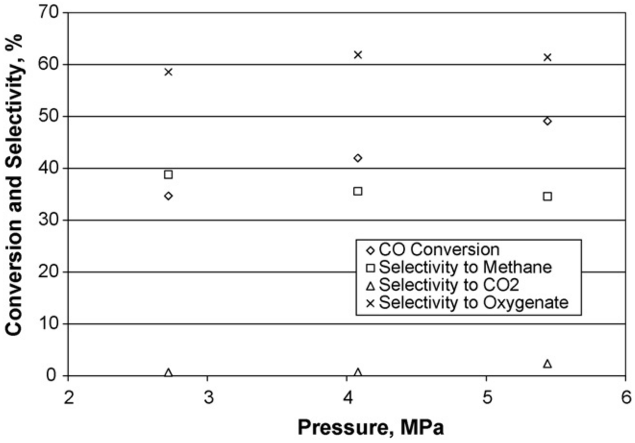

Fig. 1. Effect of reaction pressure on CO conversion and product selectivity over supported Rh catalysts (Rh-Mn-V/SiO_2 catalyst, GHSV = 1700 h^{-1}, H_2/CO = 1:1).

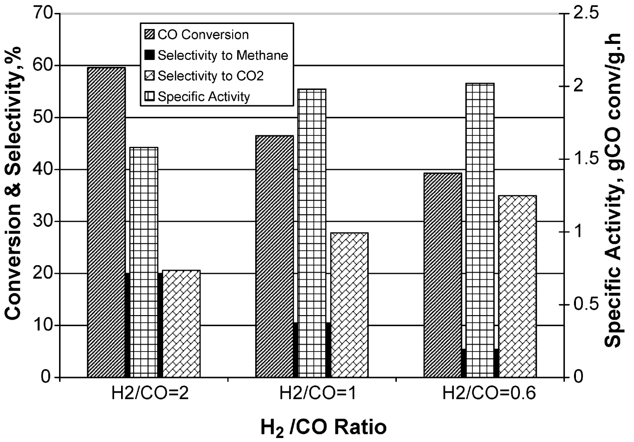

Fig. 2. Effect of H_2/CO ratio on conversion and product selectivity (Rh-Mn/SiO_2 catalyst, $P = 5.4$ MPa, $T = 280$ °C, GHSV = 3750 h^{-1}).

temperature lower than about 270 °C. The catalytic activity of Rh-Mn/SiO_2 catalyst was very steady, during 72 h time on stream operation, no catalyst deactivation was observed.

3.2. *Effect of H_2/CO ratio on product selectivity*

For ethanol synthesis, stoichiometry requirement of H_2/CO ratio is 2. However, the gasifier for biomass can achieve different ratio of H_2/CO. As a result, the impact of H_2/CO ratio on the process performance was studied. Table 2 illustrates the effect of varying H_2/CO ratio on the conversion and selectivity (Conditions 3–5). Experiments were carried out at 300 °C, 3.8 MPa and GHSV = 3750 h^{-1}, respectively. When H_2/CO ratio is reduced from 2 to 1 (Table 2, Conditions 2–3), CO conversion decreases sharply, and CO_2 selectivity increases, implying that water-gas-shift reaction becomes significant at lower H_2/CO ratio. Selectivity to ethanol is also reduced while undesired products C_2^+ hydrocarbons are increased. Changing from Condition 3 to 4 where H_2/CO ratio is raised from 1 to 3, CO conversion increases and CO_2 selectivity decreases as anticipated. A slight increase in ethanol selectivity is observed. However, undesired product methane selectivity increases as well. It seems that on Rh-Mn/SiO_2 catalyst, high-temperature and/or low pressure operation does not favor ethanol formation. Therefore, alcohol synthesis is limited to a narrow range of H_2/CO ratio. As a result, experiments were carried out to operate under high pressure but low temperature. The objective was to reveal the impact of H_2/CO on product selectivity under conditions favorable to alcohol formation. Fig. 2 clearly presents the responses of CO conversion, methane selectivity, CO_2 selectivity as well as specific activity to the change in H_2/CO ratio. On decreasing H_2/CO ratio from 2 to 0.6, CO conversion decreases, selectivity to CO_2 increases while methane selectivity decreases considerably. The specific activity, in terms of mmol CO converted per gram of catalyst per hour, increases with the decrease in H_2/CO ratio. Because GHSV was kept constant during these experiments, although total CO conversion dropped, actual carbon conversion rate increased.

3.3. *Effect of RedOx cycle treatment*

The procedures employed to activate catalysts strongly influence activity of supported Rh catalysts. Different treatment procedures may result in different extent of Rh dispersions on the surface of SiO_2 support. The influence of the dispersion on the activity and product selectivity of supported Rh catalyst had been the subject of several investigations [13,14]. The present investigation was undertaken in an effort to demonstrate the important catalyst activation procedures. One of the activation techniques adopted is called reduction–oxidation cycle, which is described in Section 2. Practically in industrial process, e.g. gasoline reforming, this procedure has been adopted to activate supported noble metals to achieve high metal dispersion and stability.

Two catalysts, Rh-Mn/SiO_2 and Rh-Mn-V/SiO_2, were treated by RedOx procedure and results are summarized in Tables 3 and 4. Interestingly, in comparing with regular hydrogen reduction treatment, RedOx treated Rh catalyst exhibits much higher initial conversion. During the initial stage (TOS less than 12 h), change of selectivity to methane is within 1% for both catalysts. Although the RedOx treatment enhances overall conversion, it has no beneficial effect on methane formation. Consequently, under steady-state operation (TOS = 72 h), CO conversion for RedOx treated catalysts is still 4% higher than regularly treated, while methane selectivity is increased by about 2% as well.

A hybrid catalyst system consisted of Cu-based methanol synthesis catalyst and supported Rh catalyst was also treated by RedOx. The hybrid catalyst system was prepared by physically

Table 3
Effect of reduction–oxidation cycle treatment on the performance of Rh-Mn/SiO_2 catalyst (powdered, 70–100 mesh)

	Regular reduction		RedOx cycle treatment	
	Initial activity, TOS = 12 h	Steady-state activity, TOS = 72 h	Initial activity, TOS = 12 h	Steady-state activity, TOS = 72 h
CO conversion (mol%)	58.9	52.9	65.3	56.6
Selectivity (%)				
CH_4	33.0	32.9	34.0	35.2
CO_2	0.0	0.3	1.3	1.1
C_2^+ HC	0.9	1.2	1.4	1.5
Alcohols and C_2^+ Oxy	66.1	65.6	63.4	62.1

GHSV = 1700 h^{-1}, $P = 5.4$ MPa, $T = 270$ °C, H_2/CO = 2:1.

Table 4
Effect of reduction and oxidation cycle treatment on the performance of Rh-Mn-V/SiO_2 catalyst (powdered, 70–100 mesh)

	Regular reduction		RedOx cycle treatment	
	Initial activity, TOS = 12 h	Steady-state activity, TOS = 72 h	Initial activity, TOS = 12 h	Steady-state activity, TOS = 72 h
CO conversion (mol%)	49.1	42.4	55.3	46.4
Selectivity (%)				
CH_4	34.6	34.8	35.2	37.1
CO_2	2.4	1.4	2.4	1.1
C_2^+ HC	1.6	1.7	1.7	1.7
Alcohols and C_2^+ Oxy	61.4	62.1	60.7	60.1

GHSV = 1700 h^{-1}, P = 5.4 MPa, T = 270 °C, H_2/CO = 2:1.

mixing the two catalysts of the same mesh sizes. The reason of using such a hybrid catalyst system was under the expectation that methanol precursors (C_1 species) produced on Cu catalyst might facilitate chain growth to yield C_2 oxygenate intermediates, favoring ethanol formation. After RedOx treatment, the time on stream performance of the hybrid catalyst system was monitored. Results are illustrated in Fig. 3. Surprisingly, after RedOx treatment, CO conversion continues to increase and does not level off until after 200 h operation. Meanwhile, CO_2 selectivity exhibits an upward trend and levels off after 200 h time on stream. The formation of CO_2 is expected which is mainly attributed to the well known water gas shift function of Cu-based catalyst. As the run proceeds, methane selectivity decreases from 20% to 10%. On the absolute basis, selectivity to methane on the hybrid catalyst is much lower than on supported Rh catalyst alone. During the entire 250 h operation, variation of selectivity to oxygenates (containing mainly methanol and ethanol) is actually moderate, approaching a constant level at TOS = 100 h. The phenomena observed here are too complicated to explain. A systematic catalyst characterization should be conducted in order to understand how RedOx treatment changes the surface property of the hybrid catalyst system. Implications from these findings are the possibility of further improving the performance of such a catalyst system by optimizing the ratio of the two catalysts.

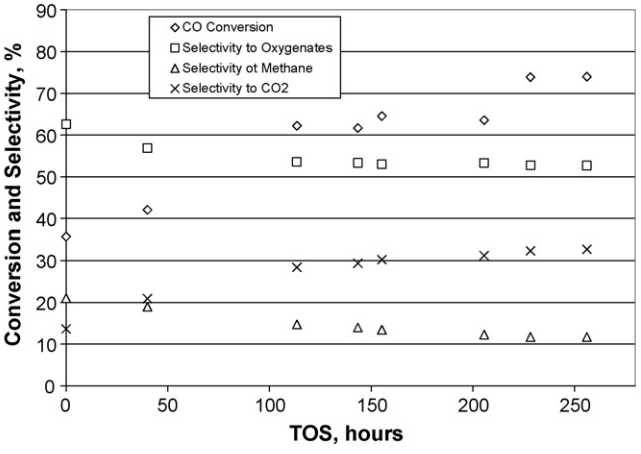

Fig. 3. Effect of RedOx treatment on the performance of hybrid catalyst system (CuZnAl and Rh-Mn/SiO_2 mixed at ratio of 1:2, P = 5.4 MPa, GHSV = 3750 h^{-1}, T = 280 °C).

3.4. Effect of adding alkali metal

Potassium was added to Rh-Mn/SiO_2 catalyst in an attempt to inhibit methane formation and boost ethanol selectivity. It is well known that alkali metals promote chain growth on Cu based catalyst. Table 5 shows that adding Cs to methanol synthesis catalyst causes increase in selectivity towards C_2^+ alcohols. However, it has not been demonstrated clearly in the literature that whether alkali metal will promote C_2^+ alcohols on supported Rh catalysts. As shown in Table 5, when 3% K is added to Rh-Mn/SiO_2, CO conversion is decreased as expected. The negative impact of adding K or other alkali metals on CO conversion has been commonly observed in many other catalyst systems used for syngas conversion. Compared with baseline Rh-Mn/SiO_2 catalyst, the addition of K results in significant decrease in methane selectivity. Although combined selectivity to methanol and ethanol increases as a result of decrease in methane selectivity, selectivity to ethanol alone decreases. The net gain is the methanol yield. The presence of K does not seem to promote chain growth on supported Rh catalyst, which is different from Cu-based catalyst. This is probably because the reaction pathways on Cu and Rh based catalyst systems are significantly different.

3.5. Performance of structured catalyst under high throughput

The ultimate goal of this study is to develop a compact reaction system effective for syngas conversion to ethanol. A major objective is to obtain a space time yield that may not be achieved with conventional reactors. As described in Section 2,

Table 5
Performance comparison of different alcohol synthesis catalysts (powdered, 70–100 mesh)

	Rh-Mn/SiO_2	Rh-Mn-K/SiO_2	Cu-Zn-Al-Cs
CO conversion (mol%)	24.6	15.6	35.2
Selectivity (%)			
CH_4	38.4	27.4	0.3
CO_2	0.0	0.0	0
MeOH	3.9	27.8	56.8
EtOH	56.1	44.3	30.0
Other HC and oxygenates	1.6	0.5	12.9

T = 280 °C, P = 5.4 MPa, GHSV = 3750 h^{-1}, H_2/CO = 2:1.

Table 6
Performance comparison of structured Rh-Mn/SiO_2 catalyst with identical powdered form in a microchannel reactor

Run numbers	Run EC-02	Run ET 32
Catalyst configuration	Rh-Mn/SiO_2 coated on FeCrAlY felt	Powdered Rh-Mn/SiO_2
GHSV (h^{-1})	20,000	2700
Conversion (mol%)	20.4	22.7
Selectivity (%)		
CH_4	36.5	31.1
CO_2	2.3	4.7
C_2^+ HCs	3.2	1.7
Alcohols and C_2^+ Oxy	58.0	62.4
Specific activity (mmol CO converted/g h)	46.0	26.8

Note 1: H_2/CO = 1:1, $T = 300$ °C.
Note 2: For engineered catalyst, specific activity was measure based on powder catalyst coated on the felt.

a structured catalyst was prepared and tested to compare with identical powdered catalyst to fully explore the capability of a microchannel reactor. The structured catalyst was coated on highly heat conducting material, a thin FeCrAlY metallic felt. The structured catalyst is closely attached to reactor channel wall where active cooling can be effective. The control run (reference run) was conducted using identical Rh-Mn/SiO_2 catalyst in the powdered form, and operated in a microchannel reactor of the same geometry. As shown in Table 6, in Run EC-02 using the structured catalyst, reaction can be carried out at GHSV = 20,000 h^{-1} to achieve the same conversion level as the control run (Run ET-32) operated at GHSV seven times slower. Due to the use of structured catalyst and active heat removal, reaction temperature and methane selectivity did not ‘‘run away’’ at high throughput. High productivity is strongly associated with the improvement in mass transport. The enhancement in mass transport may be due to reduced particle size of 0.5–2 μm on structured catalyst. Such a small particle size is not achievable with powdered catalyst testing as pressure drop will be tremendous. The implication from this finding is the potential positive process intensification by utilizing a microchannel reactor system.

4. Conclusions

The present investigation indicates that the catalytic performance of supported Rh catalysts is strongly influenced by reaction temperature, pressure, feed composition, and especially catalyst activation processes. Under reactions conditions of relatively low temperature, high pressure and low H_2/CO ratio, formation of undesired product, methane, can be suppressed. Different catalysts respond to RedOx treatment procedure differently. For certain catalyst systems such as a hybrid catalyst consisting of CuZnAl and Rh-Mn/SiO_2, the RedOx treatment can enhance overall CO conversion while still maintain product selectivity. Evidence suggests that chain growth mechanism on supported Rh catalyst system is different from that of commonly known on Cu-based higher alcohol synthesis catalysts. The unique design of the microchannel reactor enables highly exothermic CO hydrogenation reaction to be operated in an isothermal mode to achieve high productivity. Integration of structured catalyst in a microchannel reactor allows syngas to be converted to alcohols at high throughput and high space time product yield. The improvement in process performance in a microchannel reactor is attributed to effective heat removal capacity, leading to a more isothermal process, reduced mass transport limitation and minimized back mixing.

Acknowledgement

This study was funded by the U.S. Department Energy, Office of Biomass Program, under Contract DE-AC06-76RL01830.

References

[1] C. Franco, F. Pinto, I. Gulyurtlu, I. Cabrita, Fuel 82 (2003) 835–842.
[2] Y. Adachi, M. Komoto, I. Watanabe, Y. Ohno, K. Fujimoto, Fuel 79 (2000) 229–234.
[3] H. Arakawa, T. Fukushima, M. Ichikawa, S. Natsushita, K. Takeuchi, T. Matsuzaki, Y. Sugi, Chem. Lett. (1985) 881–884.
[4] P. Gronchi, E. Tempesti, C. Mazzocchia, Appl. Catal. A: Gen. 120 (1994) 115–126.
[5] S. Ishiguro, S. Ito, K. Kunimori, Catal. Today 45 (1998) 197–201.
[6] J. Fu, J. Liu, J. Xu, H. Wang, K. Tsai, J. Xiamen Univ. 3 (1992) 387–391.
[7] G. Van der Lee, A. Bastein, J. Van der Boogert, B. Schuller, H. Luo, V. Ponec, J. Chem. Soc., Faraday I 83 (1987) 2103.
[8] A. Kiennemann, R. Breault, J. Hindermann, J. Chem. Soc., Faraday I 83 (1987) 2119.
[9] M. Bowker, Catal. Today 15 (1992) 77–100.
[10] J. Hu, Y. Wang, C. Cao, D.C. Elliott, D.J. Stevens, J.F. White, Ind. Eng. Chem. Res. 44 (2005) 1722–1727.
[11] J. Hu, Y. Wang, D.P. VanderWiel, Y. Chin, D.R. Palo, R. Rozmiarek, R.A. Dagle, J.D. Holladay, E.G. Baker, Chem. Eng. J. 93 (2003) 55–60.
[12] C. Cao, G. Xia, J. Holladay, E. Jones, Y. Wang, Appl. Catal. Gen. 262 (2004) 19–29.
[13] S. Ichikawa, J. Mol. Catal. 53 (1989) 53–65.
[14] W.M. Sachtler, M. Ichikawa, J. Phys. Chem. 90 (1986) 4752–4758.