

Production of synthetic alcohol from syngas using $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$

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Abstract: This study examined the transformation of the biomass gasification synthesis gas (syngas, CO and H_2) to liquid fuels and chemicals via the high pressure fixed packed bed (HPFPB). The $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was packed in the packed bed (PB) to enhance the selectivity (S) and yield (Y) products. The effect of reaction temperature (T), pressure (P_{ST}), gas flow rate (Q_{G}) and H_2/CO (vol./vol.) ratio on the system performance were investigated. Typical reaction conditions unless otherwise specified were as follows: $T = 423, 473, 523$ and 573 K, $P_{\text{ST}} = 3$ MPa, $Q_{\text{G}} = 300 \text{ cm}^3 \text{ min}^{-1}$, and mass of catalyst (m_{S}) = 30 g.

The main products include CH_4 , C_2H_6 and $\text{C}_2\text{H}_5\text{OH}$ (EtOH) that EtOH being the target product. The results indicate that with packing $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst in PB, the conversion of CO (X_{CO}) and alcohol production rate (R) are highly depended on T. At $T = 573$ K, $X_{\text{CO}} = 8.19\%$, R of CH_4 (R_{CH_4}) = 194.1 mg h^{-1} and selectivity of CH_4 (S_{CH_4}) = 34.57%. For the production rate of $\text{C}_2\text{H}_5\text{OH}$ (R_{EtOH}), the maximum R_{EtOH} of 134.25 mg h^{-1} takes place at $T = 523$ K while $X_{\text{CO}} = 8.10\%$ and $S_{\text{EtOH}} = 51.98\%$. As T increase to 573 K, the EtOH is further decomposed into simple hydrocarbons (HCs) such as C1-C3 alkanes. Thus, for producing more alcohols and less alkanes, the optimal temperature condition is 523 K. For the case of varying H_2/CO ratio, the values of X_{CO} are about 7.55 to 8.32% at 523 K with H_2/CO ratios of 1 to 4, indicating no significant variation. However, the optimal ratio of H_2 and CO to produce EtOH is 2 with maximum $R_{\text{EtOH}} = 134.25 \text{ mg h}^{-1}$ and $S_{\text{EtOH}} = 51.98\%$ while $X_{\text{CO}} = 8.10\%$, $R_{\text{CH}_4} = 56.05 \text{ mg h}^{-1}$ and $S_{\text{CH}_4} = 10.85\%$. Hence, increasing the H_2/CO ratio to 3 to 4 is not beneficial for the formation of EtOH. The results also show that a higher PST of HPFPB yields more products. For the EtOH production, the maximum R_{EtOH} (= 156.65 mg h^{-1}) occurs at $P_{\text{ST}} = 3.6$ MPa with corresponding $S_{\text{EtOH}} = 51.16\%$, $X_{\text{CO}} = 9.57\%$, $R_{\text{CH}_4} = 70.31 \text{ mg h}^{-1}$ and $S_{\text{CH}_4} = 12.46\%$. Among various Q_{G} of 300, 450, 600 to 900 mL min^{-1} of HPFPB tested, the best X_{CO} is at $Q_{\text{G}} = 300 \text{ mL min}^{-1}$ with $X_{\text{CO}} = 8.10\%$, $R_{\text{CH}_4} = 56.05 \text{ mg h}^{-1}$ and $S_{\text{CH}_4} = 10.85\%$. Also, the maximum Y_{EtOH} take place at $Q_{\text{G}} = 300 \text{ mL min}^{-1}$ with corresponding $S_{\text{EtOH}} = 51.98\%$. It shows that a low flow rate gives a longer residence time for reaction of the syngas and thus enhances the yield of products. However, there's no advance for S_{EtOH} .

For the production of EtOH from syngas, the Y_{EtOH} , S_{EtOH} and R_{EtOH} are key factors for the success of process. The results of this study shows that $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst can give satisfactory S_{EtOH} and R_{EtOH} , especially the Y_{EtOH} high selectivity.

Keywords: Reforming of syngas; Synthesis of alcohol; $\text{MoS}_2/\text{Al}_2\text{O}_3$; catalytic synthesis; alcohol; alkane

1. Introduction

Energy crisis has been a great concerned issue in recent years. With the continued climbing of crude oil price, studies on alternative energy become more and more essential. The use of biomass, such as agriculture residues and woody waste, to provide energy and chemicals is receiving increasing interest because these resources can supplement the existing supplies of raw materials while have less net environmental impact [1]. The biomass of agriculture and the biomass fibers of municipal solid waste (MSW) are among the suitable bio-energy sources that can be used for generation energy [1-2].

Gasification technologies have been developed for the possible replacement of traditional combustion technologies because of their higher power generation efficiency while lower environmental pollution [2]. Gasification is a thermochemical process yielding major product of synthesis gas (syngas) consisting of CO and H_2 . Syngas can be used to produce hydrocarbons such as ethanol (EtOH) via Mo-based catalytic reaction and other high-value-added fuels via the Fischer-Tropsch process. Although the syngas has been also used as fuel gas, however, its storage, stabilization and transportation exhibit some problems. On the other

hand, alcohols converted from syngas have high heating value with small volume and are stable as liquid phase. Moreover, the use of EtOH as a part of the automobile fuel offers the same chemical energy as that of gasoline. Besides, ethanol is a good additive for improving gasoline octane value and burning efficiency [3].

In this study, a high pressure fixed packed bed (HPFPB) with continuous flow was used to synthesize the syngas yielding alcohols. A $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst was packed in the bed to enhance the production. The MoS_2 based catalysts, such as $\text{K}_2\text{CO}_3/\text{MoS}_2$ and $\text{Ni-K}_2\text{CO}_3/\text{MoS}_2$, have been already verified as effective catalysts in the synthesis of mixed alcohols [4-7]. The distinct points of this study were the use of HPFPB and preparation method of MoS_2 on the $\gamma\text{-Al}_2\text{O}_3$ support with high surface of catalyst. The production rates (R), yield (Y) and selectivity (S) of alcohols and conversion of CO (X_{CO}) were examined and elucidated.

2 Materials and Methods

2.1 Preparation of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$

The MoS_2 was loaded on $\gamma\text{-Al}_2\text{O}_3$ pellet ($\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$). In preparation, about 30 g $\gamma\text{-Al}_2\text{O}_3$ ($\phi = 3 \text{ mm}$) were soaked in 200 mL solution containing 5% ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) with the adjustment of $\text{pH} < 2$ using nitric acid for adsorbing ionic Mo on the alumina surface for 12 h. It was then sintered at 773 K with N_2 for 3 h to form $\text{Mo}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$. The resulted $\text{Mo}_x\text{O}_y/\gamma\text{-Al}_2\text{O}_3$ was further reduced and sulfurized in the mixed gas stream of $\text{H}_2\text{S}/\text{H}_2$ with volume ratio of 5/95 at 673 K for 2 h to produce $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst [8]. The $\gamma\text{-Al}_2\text{O}_3$, MoS_2 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ were supplied by First Chemical (Taipei, Taiwan), ProChem (Miaoli, Taiwan) and J.T. Baker (Phillipsburg, New Jersey, USA), respectively.

2.2 HPFPB system

The HPFPB system (Fig. 1) was carried out via continuous flow type operation. The synthesis reaction proceeded in a high pressure. Two packing materials of $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ and spherical glass beads were used and tested in the packed bed. The polar organic products such as alcohols and acids were collected by DI water (4 °C) in a condenser. The syngas was simulated with H_2/CO mole ratio of 2. The HPFPB system was operated under the conditions with mass flow rates of H_2 and CO (dmH_2/dt and dmCO/dt) of 1070.4 and 7492.8 mg h^{-1} , gas flow rate of syngas (Q_G) = 300 mL min^{-1} , temperature (T) = 423-573 K, mass of catalyst (m_S) = 30 g, flow rate (Q_G) = 300-900 mL min^{-1} , gas hourly space velocity (GHSV) = 600-1800 $\text{cm}^3 \text{gcat}^{-1} \text{h}^{-1}$, and pressure (P_{ST}) = 1.5-3.6 Mpa (reading at 298 K).

2.3 Products analysis

The analyses of gaseous organic compounds were performed using the gas chromatography/flame ionization detector (GC/FID, 6890 GC, Agilent Technologies, Santa Clara, CA, USA) with AB-5 column (30m \times 0.53mm \times 5.00 μm , Abel Industries, Pitt Meadows, BC, Canada) to separate the organic products. A purge-and-trap sample concentrator (Model 4560, OI Analytical, College Station, TX, USA) was used to purify and inject liquid samples into GC/FID for analyses.

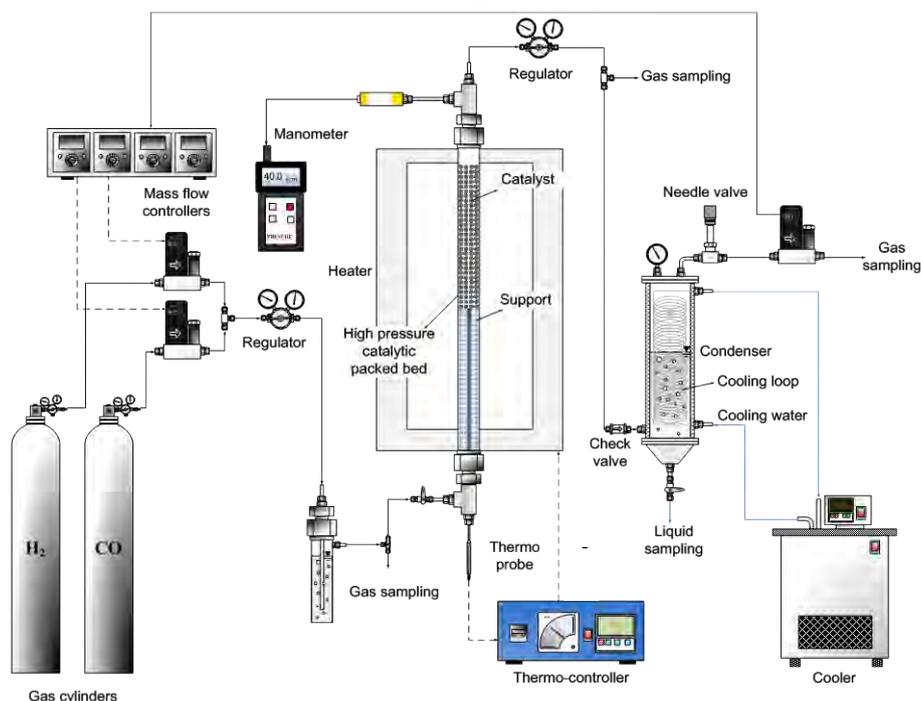


Fig. 1. Schematic diagram of HPFPB system.

3 Results and discussion

3.1 Properties of catalyst and support

The $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst used is spherical with 3 mm diameter and bulk density of 3.2055 g cm^{-3} . The MoS_2 was loaded on the surface of porous Al_2O_3 pellet. The BJH (Barrett-Joyner-Halenda) average pore sizes obtained by adsorption and desorption are 70.404 and 57.841 Å, respectively, indicating mesoporous nature of catalyst. The corresponding BET surface area is $210.345 \text{ m}^2 \text{ g}^{-1}$. The XRD (X-ray diffraction) spectrum of catalyst surface is shown in Fig. 2, exhibiting significant specific characteristics of MoS_2 at $2\theta = 14.5^\circ$, 39.6° and 60.18° .

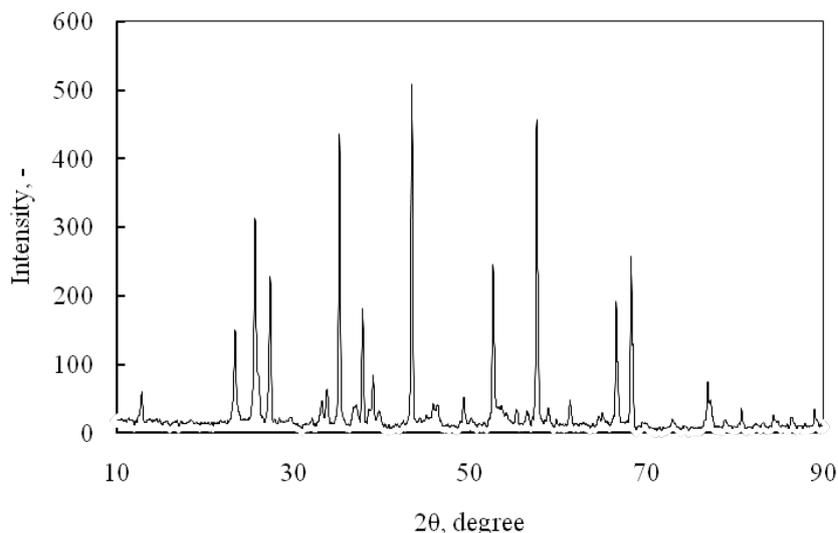


Fig. 2. XRD spectrum of $\text{MoS}_2/\text{Al}_2\text{O}_3$.

3.2 Effect of temperature

As shown in Fig. 3a, the production rate R of alkane via $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ synthesis increases with increasing reaction temperature, especially when T reaches 573 K. For the (b) alcohol products, the productions were not effected as the regular pattern as the increase T for the alkane products.

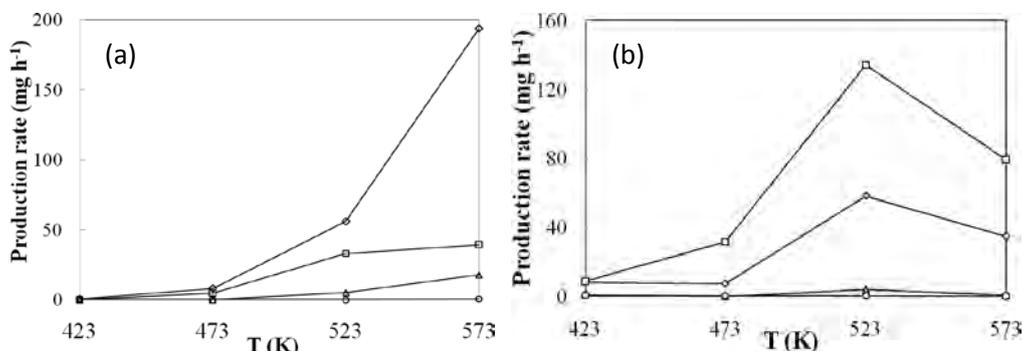


Fig. 3. Production rates of (a) alkane and (b) alcohol products at various temperatures via HPCPB- MoS_2 process. \diamond , \square , \triangle , \circ : C1, C2, C3, C4.

Table 1 illustrates the conversion of CO (X_{CO}) and selectivities (S) of synthesis products at the four different temperature conditions. Setting the reaction at the conditions of $T = 473$ K, $P_{\text{ST}} = 3$ MPa, $\text{H}_2/\text{CO} = 2$, $Q_G = 300$ $\text{cm}^3 \text{min}^{-1}$, and $\text{GHSV} = 600$ $\text{cm}^3 \text{gcat}^{-1} \text{h}^{-1}$, the selectivities of synthesis products shows the highest forming favourable $S_{\text{EtOH}} = 54.02\%$ within four different temperatures and accompanies with lower forming $S_{\text{CH}_4} = 2.09\%$. Since X_{CO} is also a meaningful efficiency index, the best X_{CO} is 8.19% while the condition at $T = 573$ K.

Table 1. Conversion of CO and selectivities of products at various temperatures.

T (K)	Conversion (%)	Selectivity (%)								
		CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_3CHO	MeOH	EtOH	PrOH	BuOH
423	0.59	1.19	0.74	-	-	31.12	16.69	36.43	6.53	7.30
473	2.09	6.88	8.06	-	-	22.50	6.38	54.02	0.30	1.86
523	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
573	8.19	34.57	14.06	9.58	0.48	6.28	6.21	28.28	0.39	0.16

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

At first appearance, the highest S_{EtOH} and the best X_{CO} seem to be well performances. In fact, they still could not represent the optimal condition because of their uncompleted well-performances which comparing these with the condition at $T = 523$ K. Setting the reaction T at 523 K is the optimal set point which not only yields more alcohol products, especially for higher S_{EtOH} , but also restrains the amount of alkanes formed.

3.3 Effect of H₂/CO ratio

Besides the temperature factor, the H₂/CO feed ratio is also a key adjustable variable affecting the conversion of syngas to ethanol or higher alcohols. The H₂/CO could be adjust to maximize S_{EtOH} and restrain methane forming that because methane is the most thermodynamically favored product, however, its economical value is less than alcohols [9]. The reactions of ethanol and methane are as the showing in following equations:



$$\Delta H_r = -61.20 \text{ kcal/mol}; \Delta G_r = -29.32 \text{ Kcal/mol}$$



$$\Delta H_r = -49.27 \text{ kcal/mol}; \Delta G_r = -33.97 \text{ Kcal/mol}$$

According the ratio of H₂/CO from the above equations, it is obvious to understand that higher ratio (eq. 2) is more favourable to produce methane than producing ethanol (eq. 1). As the shown in fig. 4, the productions present desired results which are higher production of alcohols accompany with lower production of alkanes when setting H₂/CO ratio as 2.

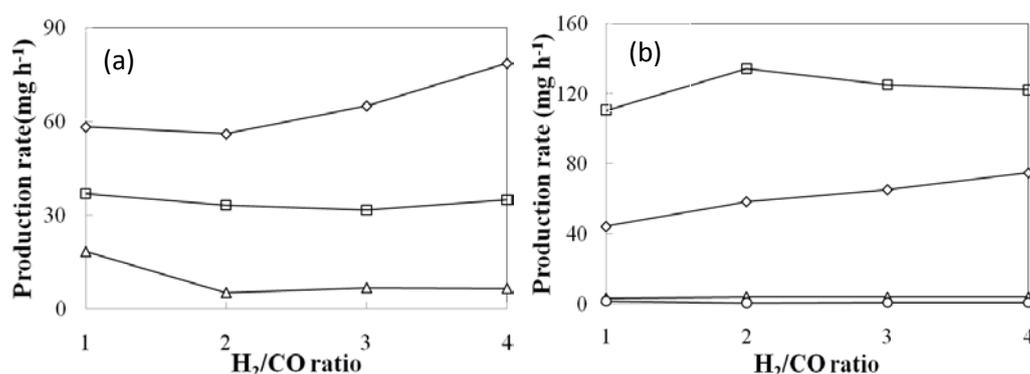


Fig. 4. Production rates of (a) alkane and (b) alcohol products at various H₂/CO ratios via HPCPB-MoS₂ process. ◇, □, △, ○: C1, C2, C3, C4.

Table 2. Conversion of CO and selectivities of products at various H₂/CO ratios.

H ₂ /C O	Conversion (%)	Selectivity (%)								
		CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	CH ₃ CHO	MeOH	EtOH	PrOH	BuOH
1	7.55	11.84	15.01	11.21	-	5.09	8.97	44.9	1.82	1.16
2	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
3	8.01	12.67	12.34	3.94	-	6.97	12.69	48.73	2.13	0.53

4 8.32 14.67 13.05 3.67 - 6.52 13.94 45.57 2.05 0.53

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

Table 2 illustrates X_{CO} and S of synthesis products at the four different H_2/CO ratios. Setting the reaction at the conditions of $T = 523$ K, $P_{ST} = 3$ MPa, $Q_G = 300$ cm³ min⁻¹, and $GHSV = 600$ cm³ gcat⁻¹ h⁻¹, X_{CO} is 8.10% and S_{EtOH} and S_{CH_4} are 51.89% and 10.85%, respectively. In these conditions, MoS₂ catalyst shows obvious favour for EtOH and slight restraint for CH₄. For this reason, the results of the shown at $H_2/CO = 2$ are desired and acceptable even if the conversion of CO is not the highest performance.

3.4 Effects of pressure

Increasing pressure is equal to increase the providing raw materials and the equilibrium concentration of products from the hydrogenation of CO [1]. As the shown in fig. 5, both of the productions of alkane and alcohol products increase as the increasing reaction pressure. Therefore, the effects of reaction pressure appear as though Le Chatelier's Principle.

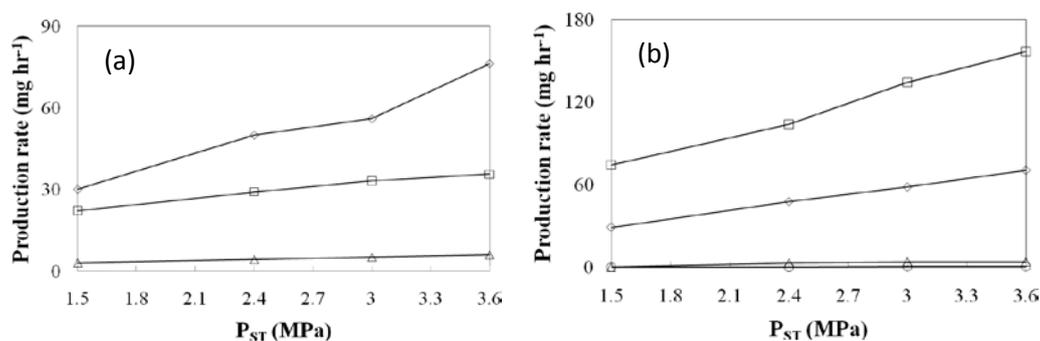


Fig. 5. Production rates of (a) alkane and (b) alcohol products at various pressures via HPCPB-MoS₂ process. \diamond , \square , \triangle , \circ : C1, C2, C3, C4.

Table 3. Conversion of CO and selectivities of products at various pressures.

P_{ST} (MPa)	Conversion (%)	Selectivity (%)								
		CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	CH ₃ CHO	MeOH	EtOH	PrOH	BuOH
1.5	4.6	11.84	15.01	11.21	-	-	9.93	50.92	2.47	-
2.4	6.48	12.05	14.04	3.08	-	7.27	11.29	50.00	2.27	-
3.0	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
3.6	9.57	12.46	12.63	2.96	-	3.71	13.94	51.16	2.86	0.28

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

Table 3 illustrates X_{CO} and S of synthesis products at the four different reaction pressures (reading at 298 K). Setting the reaction at the conditions of $T = 523$ K, $H_2/CO = 2$, $Q_G = 300$ cm^3 min^{-1} , and $GHSV = 600$ cm^3 $gcat^{-1}$ h^{-1} . As the increased pressure in this study, there are only increasing effects for X_{CO} as the shown in table 3, however, the selectivities of both alkane and alcohol products are not affected by changing the reaction pressures.

3.5 Effects of flow rate

A high flow rate into the reactor gives a higher space velocity through the fixed catalytic bed, which is equivalent to change the volume of catalyst in the reactor. As the shown in fig. 6, increasing the flow rate also means more reactants input, enhancing the production rates for both of alkanes and alcohols.

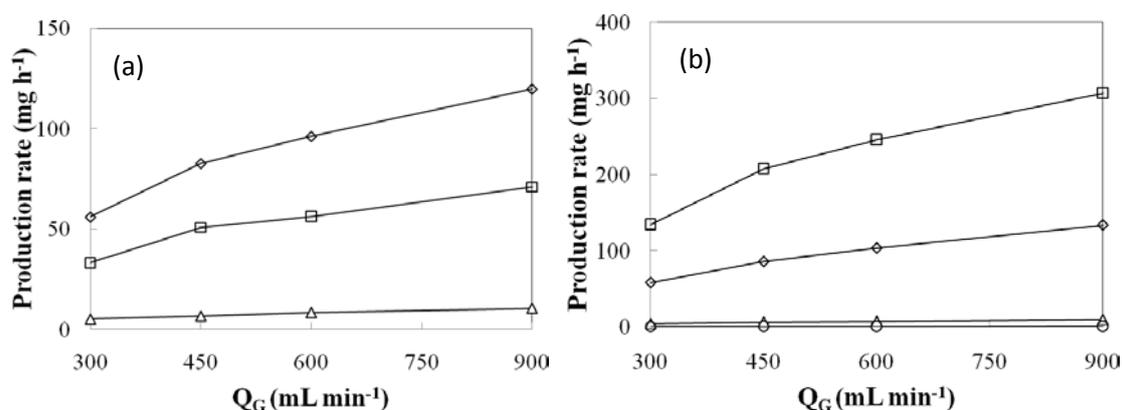


Fig. 6. Production rates of (a) alkane and (b) alcohol products at various flow rates via HPCPB-MoS₂ process. \diamond , \square , \triangle , \circ : C1, C2, C3, C4.

Table 4 illustrates the conversion of CO and selectivities of synthesis products at the four different flow rates. Setting the reaction at the conditions of $T = 523$ K, $H_2/CO = 2$, $P_{ST} = 3$ MPa, and $GHSV = 300$ cm^3 min^{-1} . As the shown in table 4, increasing the flow rate obviously decrease X_{CO} because the retention time is too small to finish more number of completed reactions. The increase of space velocity results in a slight decrease in selectivity of alkanes while an insignificant increase of alcohols in the reaction products. Besides, the effects of changing flow rate are similar with those of the changing of reaction pressures.

Table 4. Conversion of CO and selectivities of products at various flow rates.

Q_G ($mL\ min^{-1}$)	Conversion (%)	Selectivity (%)								
		CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	CH ₃ CHO	MeOH	EtOH	PrOH	BuOH
300	8.10	10.85	12.84	3.00	-	7.48	11.29	51.98	2.27	0.29
450	5.44	10.54	12.95	2.52	-	7.54	10.91	52.91	2.37	0.26
600	4.83	10.41	12.18	2.70	-	7.82	11.16	53.14	2.34	0.25
900	4.12	10.25	12.14	2.68	-	8.38	11.39	52.50	2.40	0.26

MeOH: methanol; EtOH: ethanol; PrOH: propanol; BuOH: butanol.

4. Conclusions

In HPFPB system, the main organic products of alkane and alcohols of MoS₂/γ-Al₂O₃ catalytic synthesis are ethanol and methane, respectively. From the previous results shown, ethanol selectivity decreases at all temperatures when methane is the major product. For this reason, setting the reaction temperature at T = 523 K is the optimal set point which not only yields more alcohol products, especially for higher S_{EtOH}, but also restrains the amount of alkanes formed. Furthermore, it could increase S_{EtOH} versus CH₄ while setting the H₂/CO feed ratio as 2. Considering the effects of P_{ST} and Q_G, there are similar trends for both of alkane and alcohol products besides of the trend for the conversion of CO. Increasing the flow rate would decrease X_{CO} because the retention time is too small to finish more number of completed reactions.

Taken together, these observations suggest that setting the parameter as T = 523 K, H₂/CO = 2, higher pressure, and lower flow rate to reach the purpose of obtaining higher X_{CO} and outstanding S_{EtOH}.

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