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Catalytic upgrading nitrogen-riched wood syngas to liquid hydrocarbon mixture over a Fe–Pd/ZSM-5 catalyst

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ABSTRACT

Biomass like wood chips, switchgrass and other plant residues are first converted to syngas through gasification process using air, oxygen or steam. A downdraft gasifier is performed for syngas production in Mississippi State. The syngas from the gasifier contains up to 49% (vol) N_2. High-level nitrogen-containing (nitrogen can be up to 60%) synthesis gas is converted to liquid hydrocarbon mixture through a one-stage catalytic process with a Fe–Pd/ZSM-5 catalyst. The Fe–Pd/ZSM-5 catalyst shows relatively high activity and selectivity in producing liquid hydrocarbons when running with nitrogen-rich syngas. The CO conversion, hydrocarbon selectivity and hydrocarbon distribution as a function of temperature, pressure, GHSV, composition of the feed, and reaction time are examined.

1. Introduction

Syngas can be converted to many fuels and chemicals by a couple of approaches [1]. Fischer–Tropsch synthesis (FTS) can upgrade syngas to liquid fuels with a wide range of liquid hydrocarbon fuels, it is a major part of gas-to-liquids (GTL) technology [1,2,3,4]. However, the FTS process is controlled by the Anderson–Schulz–Flory (ASF) polymerization kinetics, and leading nonselective products [5,6]. Another approach is first to convert syngas to methanol over a methanol synthesis catalyst and subsequently polymerize methanol to hydrocarbons over ZSM-5 [7,8]. Syngas is first converted to methanol over a copper-based hydrogenation catalyst. In the second stage, methanol is converted to gasoline over a ZSM-5 catalyst. During the recent years, many investigations have demonstrated the advantages of the one-stage processes by using bi-functional catalysts compared with the two-stage and three-stage processes of synthesis gas conversion to gasoline [9,10]. The use of a bi-functional catalyst allows for simultaneously carrying out the synthesis of methanol from syngas over the metallic function and the transformation of methanol into hydrocarbons over the acidic function. The fulfillment of both steps in the same reaction medium promotes the displacement of the thermodynamic equilibrium of methanol synthesis. Also, the shape selectivity of the acidic function provides a high selectivity that cannot be reached in the Fischer–Tropsch synthesis. Moreover, previous syngas to gasoline technologies are mostly based on using high purity syngas (mainly $CO + H_2$) or low nitrogen syngas [11,12,13], which is mainly derived from natural gas or coal, there are limited publications using nitrogen-rich syngas to produce hydrocarbons [14,15]. The existing downdraft gasifier is producing syngas from biomass. Currently, the syngas from the MSU gasifier contains about 20% hydrogen, 19% CO, 12% CO_2, 2% CH_4 and 49% N_2 [7,16]. The

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nitrogen and carbon dioxide contents are too high for the hydrocarbon synthesis if we use existing technologies including catalysts [17]. Developing high activity and high stability catalysts is the key for a better overall performance when using the bio-syngas from the gasifier [18,19].

Existing syngas to gasoline technologies are mostly based on using cleaning syngas or low level nitrogen syngas, while the biomass derived syngas from the gasifier contains N_2 up to 50%–60% (mol). Most of the catalysts for the syngas to gasoline process have low performance under such high nitrogen content. Moreover, the operation cost of the syngas compression press is a large portion of the overall invests. The purpose of the present work is to catalytic upgrade high-level nitrogen syngas to higher hydrocarbons and value-added chemicals.

2. Experimental

2.1. Catalyst preparation

9.4 g of $PdCl_2$ was dissolved in 1000 mL DI water, stirred for 2 h, then, 50 g of ZSM-5 zeolite powder was added to $PdCl_2$ solution, added several drops of H_2SO_4 until the pH of the solution became 4.0. Transferred the above mixture into a 5-L autoclave and maintained at 378–393 K for 8–20 h. Evaporating the product, and oven-dried at 383 K overnight, then the mixture was calcined at 673 K for 3 h. The obtained Pd–ZSM-5 was added to an aqueous solution containing 95 g of ferric nitrate in 1000 mL of water, kept stirred the mixture at 353 K overnight, the brown products were dried at 383 K for 5 h, then the dried mixture was calcined at 673 K for 5 h. 50 mL 2.5 wt% KOH solution was added to the resulting mixture of the Fe/Pd–ZSM-5, the promoted catalyst was calcined at 573 K for 2 h, then crushed and pelletized to tablets under 20 kN of force.

2.2. Gases used

Four different compositions of commercial compressed syngas (Airgas, Inc.) were used in this test (Table 1) :1) 50% H_2, 50% CO; 2.) 20.1% H_2, 19.9% CO, balance N_2; 3) 19% H_2, 20% CO, 12% CO_2, 2% CH_4, 47% N_2, 4) 40% H_2, 20% CO, 12% CO_2, 2% CH_4, 26% N_2.

2.3. Catalytic reaction

The synthesis gas conversion reaction was carried out in a home-built continuous flow fixed-bed reactor system. Three (3) grams of the catalyst was loaded to the reactor. The system was first purged by a helium flow for 30 min, followed by pre-reducing with a syngas mixture at 673 K for 8 h, then syngas was fed in until reaching the desired pressure with slow adjustment of the system to the desired temperature. The reaction was operated under the following conditions: 523–673 K, a gas volume hourly space velocity (GHSV) of 500–3000 h^{-1} and a pressure of 3.45–8.62 MPa.

2.4. Sample analysis

Liquid products were collected using a condenser kept at subzero temperature of 270 K, and the effluent gas from the condenser was analyzed with an on-line gas chromatograph (GC, HP 6980) equipped with thermal conductive detector (TCD) and flame ionization detector (FID). A packed Molecular Seive 5A column and an HP-1 capillary column were employed for separation of inorganic gases and light hydrocarbons. Liquid products, collected from the condenser, were separated into oil phase and water phase, and analyzed with GC–mass spectrometer (Agilent) equipped with DB-Wax capillary column for oxygenated compounds and HP-5ms capillary column for hydrocarbons [7,15].

3. Results and discussion

3.1. Effect of temperature

The temperatures studied are: 563, 573, 583, 593, 603 and 623 K, with the remaining conditions maintained at the values previously indicated. Table 2 shows the variation of CO conversion, $C_1 \sim C_5^+$ selectivity with temperature, the other variables remaining constant. Table 2 shows that the influence of temperature on CO conversion is very important. CO conversion increases from 55% at 563 K to 83% at 623 K. It clearly shows the hydrocarbon distribution changes with temperature, the light hydrocarbons being favored at higher temperatures. Higher hydrocarbons are more sensitive to temperature. Previous work has also shown that the increase of process temperature resulted in the increase of CO conversion, a shift toward products with a lower carbon number on iron catalysts [20]. Table 2 shows the liquid fuel distribution in three groups, i.e., paraffins, aromatics, and olefins. Results indicate that as the temperature evaluated from 563 K to 623 K, paraffins decreased from 48.0% to 38.0%; olefins decreased from 21.0% to 14.0%; aromatics increased from 31.0% to 48.0%. Dictor and Bell [21] also observed a decrease of the olefin selectivity with increasing temperature for unalkalized iron oxide powders.

3.2. Influence of pressure on the catalyst performances

Experiments under pressures of 3.45–8.62 MPa have been carried out. The other operating conditions are: temperature, 583 K; gas space velocity 2000 h^{-1}, with syngas of 19.0% H_2, 20.0% CO, 12.0% CO_2, 2.0 % CH_4, balance N_2. The effect of pressure on both CO conversion and process selectivity shows that when pressure increases, CO conversion increases (Table 3). Within the C_5^+ fraction, an important effect of pressure on selectivity was observed. The increase in pressure clearly favors the formation of C_5^+, while $C_1 \sim C_3$ gaseous

Table 1 – Compositions of commercial compressed syngas from Airgas, Inc.

Gas composition	H_2 (%)	CO (%)	CO_2 (%)	CH_4 (%)	N_2 (%)
Gas 1	50.0	50.0	–	–	–
Gas 2	20.1	19.9	–	–	60.0
Gas 3	19.0	20.0	12.0	2.0	47.0
Gas 4	40.0	20.0	12.0	2.0	26.0

Table 2 – Effect of temperature on (a) CO conversion, CO_2 and hydrocarbon selectivity, (b) hydrocarbon distribution, and (c) liquid hydrocarbon distribution at 6.90 MPa, with syngas of 19.0% H_2, 20.0% CO, 12.0% CO_2, 2% CH_4, balance N_2, GHSV of 2000 h^{-1}; 3 g of catalyst was used in the reaction. Time-on-stream of 48–100 h.

Reaction conditions						
Feed gas components: 19.0% H_2, 20.0% CO, 12.0% CO_2, 2% CH_4, balance N_2						
Temperature (K)	5630	573	583	593	603	623
Pressure (MPa)	6.90	6.90	6.90	6.90	6.90	6.90
GHSV (h^{-1})	2000	2000	2000	2000	2000	2000
Conversion (%)						
CO	58.2	65.4	75.4	83.3	88.9	93.2
Selectivity (%)						
CO_2	19.1	21.4	23.8	25.5	29.6	35.4
Hydrocarbons	80.9	78.6	76.2	74.5	70.4	64.6
Selectivity of hydrocarbons (%)						
CH_4	18.2	20.5	21.2	22.1	23.5	25.7
C_2H_6	8.8	8.2	9.1	10.2	10.1	11.9
C_3H_8	4.8	5.3	5.9	6.5	7.8	9.1
C_4H_{10}	11.9	12.1	10.5	11.7	9.5	6.2
C_5^+ gasoline	56.3	53.9	53.3	49.5	49.1	47.1
Liquid hydrocarbons distribution (% by weight)						
Paraffins	48.0	45.0	43.0	40.0	38.0	38.0
Olefins	21.0	20.0	20.0	18.0	15.0	14.0
Aromatics	31.0	35.0	37.0	42.0	47.0	48.0

hydrocarbons clearly decrease with increasing of pressure. An increase in total pressure will increase the equilibrium toward the product side, and increase the conversion. Furthermore, a change in total pressure will not affect the water gas shift reaction but will change the equilibrium product distribution. Table 3 also shows the liquid fuel distribution by three groups. The results show that with the increasing of the reaction pressure, paraffins were almost unchanged whereas the amounts of the aromatics increased from 33.6% to 41.5%, while olefins decreased a little bit from 22.5% to 16.4%. Some previous FTS studies also showed that the product selectivity shifts to heavier products with increasing total pressure [22].

Table 3 – Effect of pressure on (a) CO conversion, CO_2 and hydrocarbon selectivity, (b) hydrocarbon distribution, and (c) liquid hydrocarbon distribution at 310 °C, with syngas of 19.0% H_2, 20.0% CO, 12.0% CO_2, 2.0% CH_4, balance N_2, GHSV of 2000 h^{-1}; 3 g of catalyst was used in the reaction. Time-on-stream 48–100 h.

Reaction conditions				
Feed gas components: 19.0% H_2, 20.0% CO, 12.0% CO_2, 2% CH_4, balance N_2				
Temperature (°C)	583	583	583	5830
Pressure (MPa)	3.45	5.17	6.90	8.62
GHSV (h^{-1})	2000	2000	2000	2000
Conversion (%)				
CO	66.9	68.4	75.4	80.2
Selectivity (%)				
CO_2	24.6	24.1	23.8	23.5
Hydrocarbons	75.4	75.9	76.2	76.5
Selectivity of hydrocarbons (%)				
CH_4	29.7	23.5	21.2	20.1
C_2H_6	8.7	8.5	9.1	8.2
C_3H_8	4.5	5.3	5.9	4.5
C_4H_{10}	10.9	12.1	10.5	11.7
C_5^+ gasoline	46.2	50.6	53.3	55.5
Liquid hydrocarbons distribution (% by weight)				
Paraffins	43.9	44.5	43	42.1
Olefins	22.5	23	20	16.4
Aromatics	33.6	33.5	37	41.5

3.3. *Impact of space velocity on the catalyst performances*

Experiments were completed with different GHSV, 500, 1000, 2000, 2500 and 3000 h^{-1}; the remaining operating conditions have been maintained at 583 K, 6.90 MPa, $CO/H_2 = 1$. The effect of the space velocity on CO conversion and hydrocarbon distribution shows that when the space velocity increases, CO conversion decreases as expected (Table 4). At the same time, C_5^+ selectivity also decreases. It can be concluded that CO conversion decreases with the increasing of space velocity. The effect of space time on product distribution is significant. It was observed that the yields of hydrocarbons decreased with increasing of space velocity. The gasoline fraction (C_5^+) continuously decreases with increasing space velocity.

3.4. *Role of syngas composition on the catalyst performances*

Synthesis gas composition is an important parameter in higher hydrocarbon synthesis. It can affect both reaction rates and activity. It was found that the catalyst has relatively high activity and selectivity in producing liquid hydrocarbons when running with nitrogen-rich syngas (Table 5).

3.5. *Time-on-stream performance*

The effect of time-on-stream on the performance of the catalyst was studied at 583 K over a period of 120 h. The evolution of CO conversion and hydrocarbon distribution with

Table 4 – Effect of gas hourly space velocity (GHSV) on (a) CO conversion, CO_2 and hydrocarbon selectivity, (b) hydrocarbon distribution, and (c) liquid hydrocarbon distribution at 583 K, 6.90 MPa, with syngas of 19.0% H_2, 20.0% CO, 12.0% CO_2, 2.0 % CH_4, balance N_2; 3 g of catalyst was used in the reaction.

Reaction conditions					
Feed gas components: 19.0% H_2, 20.0% CO, 12.0% CO_2, 2% CH_4, balance N_2					
Temperature (K)	583	583	583	583	583
Pressure (MPa)	6.90	6.90	6.90	6.90	6.90
GHSV (h^{-1})	500	1000	2000	2500	3000
Conversion (%)					
CO	88.2	80.4	75.4	73.3	68.9
Selectivity (%)					
CO_2	28.3	25.7	23.8	20.5	21.6
Hydrocarbons	71.7	74.3	76.2	79.5	78.4
Selectivity of hydrocarbons (%)					
CH_4	14.3	17.5	21.2	22.5	23.8
C_2H_6	3.5	4.2	9.1	10.7	10.3
C_3H_8	2.1	4.7	5.9	7.5	7.1
C_4H_{10}	7.2	8.6	10.5	10.7	10.5
C_5^+ gasoline	72.9	65	53.3	48.6	48.3
Liquid hydrocarbons distribution (% by weight)					
Paraffins	40.0	43.0	43.0	42.0	45.0
Olefins	15.0	17.0	20.0	21.0	23.0
Aromatics	45.0	40.0	37.0	37.0	32.0

time-on-stream are shown in Fig. 1 for the new catalyst. The activity of the catalyst reached a steady state after a period of approximately 20 h under operating conditions. Time-on-stream results showed the catalyst was stable. CO conversion reached 74% after 20 h run at 583 K, and kept constant after 120 h run.

Table 5 – Effect of syngas composition on (a) CO conversion, CO_2 and hydrocarbon selectivity, (b) hydrocarbon distribution, and (c) liquid hydrocarbon distribution at 583 K, 6.90 MPa, GHSV of 2000 h^{-1}; 3 g of catalyst was used in the reaction.

Reaction conditions				
Feed gas	Gas 1	Gas 2	Gas 3	Gas 4
Temperature (K)	583	583	583	583
Pressure (MPa)	6.90	6.90	6.90	6.90
GHSV (h^{-1})	2000	2000	2000	2000
Conversion (%)				
CO	85.5	78.9	75.4	77.2
Selectivity (%)				
CO_2	23.5	26.8	23.8	27.7
Hydrocarbons	76.5	73.2	76.2	72.3
Selectivity of hydrocarbons (%)				
CH_4	16.5	22.3	21.2	25.5
C_2H_6	7.8	8.5	9.1	7.2
C_3H_8	4.9	4.3	5.9	6.8
C_4H_{10}	10.3	12.5	10.5	15.7
C_5^+ gasoline	60.5	52.4	53.3	44.7
Liquid hydrocarbons distribution (% by weight)				
Paraffins	41.0	44.0	43.0	47.0
Olefins	14.0	21	20.0	15.0
Aromatics	45.0	35.0	37.0	38.0

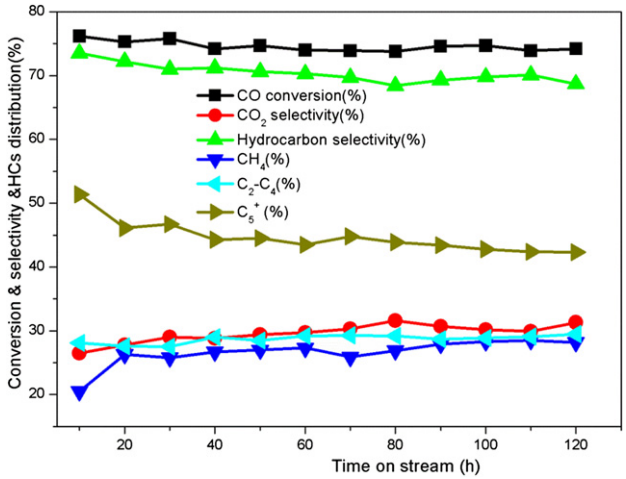

Fig. 1 – Time-on-stream of CO conversion, hydrocarbon selectivity and distribution on the Fe–Pd/ZSM-5 catalyst at 583 K, 6.90 MPa, 2000 h^{-1} with syngas of 19.0% H_2, 20.0% CO, 12.0% CO_2, 2% CH_4, balance N_2.

4. Conclusion

A bi-functional catalyst has been prepared and evaluated for catalytic converting nitrogen-riched syngas to gasoline range hydrocarbons. It was found that the catalyst has relatively high activity and selectivity in producing liquid hydrocarbons when running with nitrogen-riched syngas. The CO conversion, hydrocarbon selectivity and hydrocarbon distribution as a function of temperature, pressure, GHSV, composition of the feed, and reaction time were examined. The increase of temperature and pressure favors carbon monoxide conversion and formation of more hydrocarbons. The conversion of carbon monoxide in the syngas was 73% under a reaction temperature of 583 K, and a pressure of 6.90 MPa and 58% under a reaction pressure of 3.45 MPa when using a simulated gasifier-derived syngas. This catalyst gave higher conversion efficiency under a lower CO–H_2 pressure. The conversion into hydrocarbons reached about 70% while the conversion into carbon dioxide was about 30 mol%. The resultant hydrocarbons were hydrocarbons of the gasoline boiling point range, which contained 30–40 wt% of light hydrocarbons (C_1–C_4). According to detailed analysis, the composition of gasoline fraction contained up to 40 wt% aromatics, 15 wt% of olefins and 40 wt% of paraffins. The compositions of liquid hydrocarbon mixture products can be adjusted through the operating conditions. Time-on-stream results showed the catalyst was stable. CO conversion reached 74% after 20 h run at 583 K, and kept constant after 120 h run.

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