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The investigation of Ru based Fischer Tropsch catalyst for the production of synthetic liquid fuels derived from bio-syngas

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1. Abstract

The present research is aimed at exploring the feasibility of producing synthetic liquid fuel from bio-syngas over Ru supported on mixed oxide catalyst via Fischer-Tropsch synthesis. Attention is mainly focused on the development and improvement of Fischer-Tropsch catalysts. A series of magnesium oxide modified Ru/Al_2O_3 catalysts were prepared and characterized by BET technique. The catalytic behavior of catalysts prepared is elucidated in Fischer Tropsch reaction using transient and steady state conditions. The experiments have been carried out in a fixed bed reactor under the flow of CO/H_2 mixture over Ru/Al_2O_3 and Ru/Al_2O_3-MgO catalysts. The transient study reveals that the hydrogenation of pre-adsorbed CO using TPSR technique begins at 80°C and TPSR profile shows peak maximum at ~200°C. The steady state reaction illustrates that the production of higher hydrocarbons (C_5^+) was obtained. The modification of magnesium oxide on alumina support catalyst has an effect on the catalytic performance of Ru catalysts.

Keywords: Fischer Tropsch synthesis, Bio-syngas, Ru supported catalyst

2. Introduction

Utilization of biomass to produce gaseous, liquid and solid fuel has become the most attractive resource in Thailand. This could sustain the energy adequacy and economy stabilization at the same time. Although an indirect liquefaction of biomass via Fischer-Tropsch synthesis to produce clean liquid transportation fuels such as gasoline (C_5-C_{12}) and diesel (C_{12}-C_{20}) is extremely interesting, the program is not popular in commercial view according to a high cost of technology. However, this problem could be overcome by the development of Fischer-Tropsch catalysts and the system configurations that served the long-term with large scale production. To approach this, a present research attempts to develop the Fischer Tropsch catalyst for the production of long-chain hydrocarbons.

The most active Fischer-Tropsch catalysts are iron, cobalt, nickel and ruthenium. It is well known that CO hydrogenation on Fe, Co and Ru catalysts gives high molecular weight hydrocarbonss. Iron and cobalt are commonly used as commercial catalysts due to their low cost with high activity and selectivity towards higher hydrocarbons. However; the pretreatment of those catalysts to produce active forms are quite difficult. Cobalt and iron based catalysts are often used with high metal loading in Fischer Tropsch reaction, which make these catalysts often present as a large particle with non-uniform size distribution and predominantly they do form oxide phases with catalyst support (Zhang et al., 1999). This characteristic makes it difficult to complete reduction in pretreatment step. Among the active group VIII transition metals, ruthenium is exceptional the most active Fischer Tropsch catalyst because bulk carbide is not formed at low temperature and does not form oxide phase with catalyst supports under most preparation conditions. Ruthenium also has high extent of reduction. (Fan et al., 1997; Fujita et al., 1997; Hussain et al., 1997; Zakumbayeva et al., 1996; Haddad et al., 1995; Janardaranao, 1990) In addition, carbon monoxide dissociates easily at low temperature and specific activity for methanation and for the production of long-chain hydrocarbons have little or no oxygen content, thus simplying analysis (Anderson, 1956; Vannice, 1975).

Here, the recent research has been conducted to investigate the behavior of Ru based catalyst in Fischer-Tropsch reaction under different reaction condition. The effect of mixed metal oxide support ($MgO-Al_2O_3$) used for catalyst preparation and reaction conditions on Fischer Tropsch reaction was included in this study.

3. Experimental

3.1. Catalyst preparation and characterisation

A series of $Ru/MgO-Al_2O_3$ supported catalyst containing 1% and 10% Ru were prepared by incipient-wetness impregnation technique using a solution of $RuCl_3.6H_2O$ as a precursor. All catalysts were dried and then calcine at 400^oC for 4h. Total surface area of catalysts prepared was characterized by nitrogen adsorption at -196^oC using BET method.

3.2 Catalytic activity and selectivity measurement

Temperature-Programmed Surface Reaction (TPSR) was carried in a fixed bed reactor connected directly to FID detector fitted in gas chromatograph (Agilent 6820). Supported catalyst (0.2 g) was pretreated under pure H_2 flow at 400^oC for overnight. Then, it was flushed in a flow of helium for 20 min at the same temperature. The catalyst bed was cooled down to room temperature and the flow was switched to 10%CO/He. The catalyst was exposed to CO for 30 min following by flushing with helium. Then, hydrogenation of pre-adsorbed CO was undergone in pure H_2 flow using temperature programmed technique.

Fischer-Tropsch reaction was performed in a fixed bed reactor in the flow of H_2/CO ratio at 2:1. Prior to catalytic test, 0.2 g of supported catalyst packed in the reactor was reduced under pure H_2 flow at 400^oC for overnight. Then it was cooled down to reaction temperature. Products obtained during the reaction were directly analyzed by FID detector installed in gas chromatograph (Agilent 6890N).

4. Results and Discussion

The results obtained from the characterization of the supports show that $\gamma-Al_2O_3$ prepared gives high surface areas in the range of 253-273 m^2/g. A portion of $MgO-Al_2O_3$ support gives lower surface area of 173-200 m^2/g (Table 1). A series of $Ru/MgO-Al_2O_3$ at 1% and 10%Ru were prepared for the catalyst investigated. The catalytic activity was determined by Fischer Tropsch reaction using transient and steady state conditions.

A transient experiment was studied by temperature programmed surface reaction of pre-adsorbed CO with H_2 over $1\%Ru/MgO-Al_2O_3$. The catalytic results obtained from TPSR profile (Figure 1) reveal that hydrogenation of pre-adsorbed CO produces mainly methane. The reaction starts at 80^oC and temperature peak for the methane production (T_{max}) were observed around 200^oC for all catalysts investigated. Amount of methane produced on $1\%Ru/MgO-Al_2O_3$ (0.5:2) is much higher than that obtained from other catalysts. The addition of MgO to Al_2O_3 support at 1:2 and 2:2 molar ratio does not significant affect the hydrogenation of pre-adsorbed CO over Ru supported catalyst. The activation energy calculated based on line-shape analysis is in the range of 65-96 $kJ.mol^{-1}$.

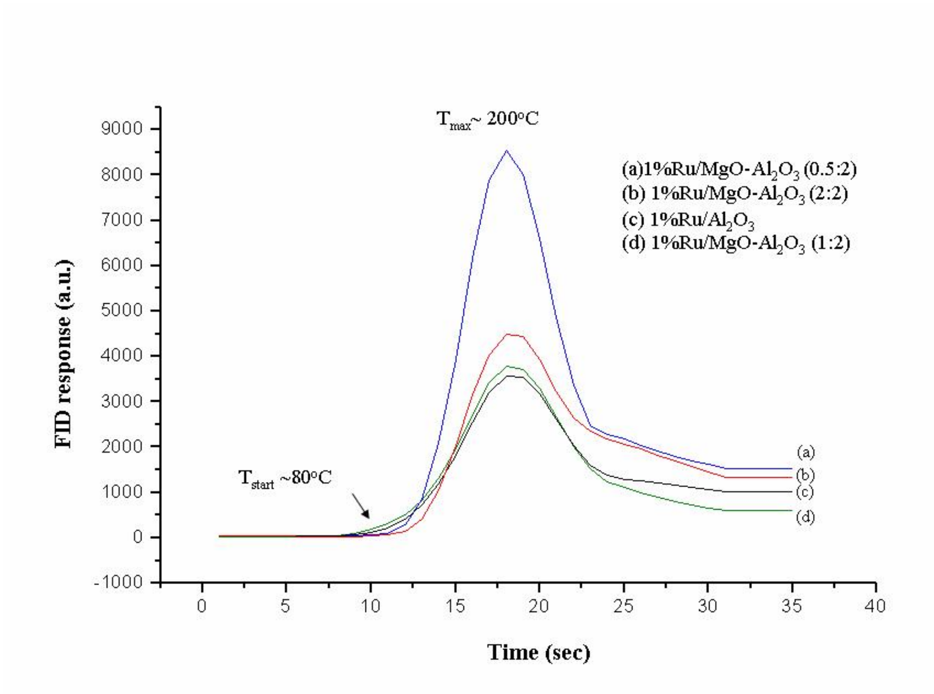

Figure 1. TPSR profile obtained from hydrogenation of pre-adsorbed CO over (a) 1%Ru/MgO-Al_2O_3 (0.5:2), (b) 1%Ru/MgO-Al_2O_3 (2:2), (c) 1%Ru/Al_2O_3 and (d) 1%Ru/MgO-Al_2O_3 (1:2), respectively.

Table 1. Characterisation of 1%Ru/Al_2O_3 and 1%Ru/ MgO-Al_2O_3 catalysts

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Peak Temperture (°C)	Activation energy (kJ mol^{-1})
1%Ru/Al_2O_3	253-273	0.130	200	66.8
1%Ru/ MgO-Al_2O_3 (0.5:2)	190	0.092	206	96.3
1%Ru/MgO-Al_2O_3 (1:2)	200	0.097	208	67.7
1%Ru/MgO-Al_2O_3 (2:2)	173	0.080	199	92.8

Fischer Tropsch reaction at different operating conditions was investigated under steady state experiment. A portion of Ru based catalyst was pretreated under a flow of pure hydrogen and then subjected to the Fischer Tropsch Reaction at different operating condition. Chromatograms obtained from Fischer Tropsch reaction over 10%Ru/Al_2O_3 at temperature of 180°C and 220°C under atmospheric pressure were illustrated in Figure 2. The chromatogram shows that the catalyst can produce hydrocarbons in the range of C_1-C_{12} and at higher temperature methane is a main product. When the reaction was carried out under higher pressure (85 psi) and low temperature (180°C), the production of higher hydrocarbons (C_5^+), especially in the range of gasoline, seems to increase (see Figure 3). This could be attributed to the limitation of chain growth of hydrocarbons at high temperature condition.

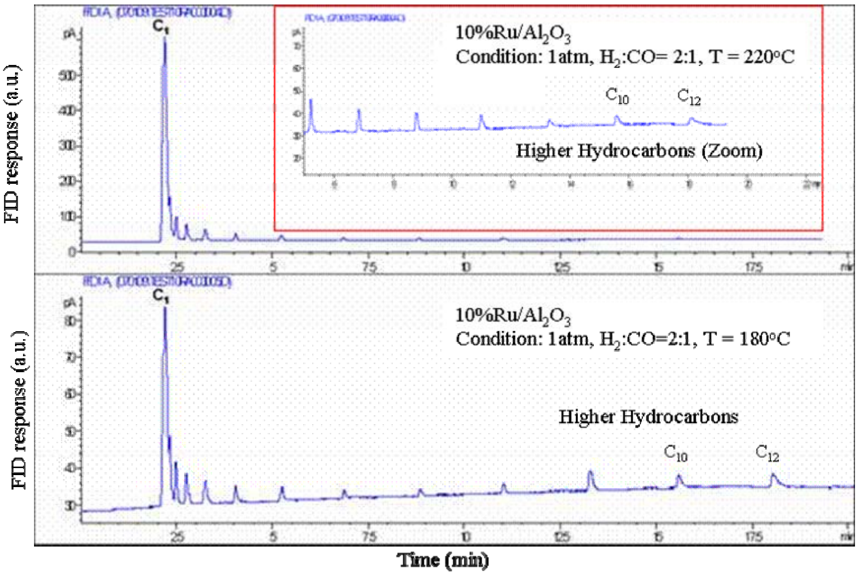

Figure 2. Chromatograms obtained from Fischer Tropsch reaction over 10%Ru/Al_2O_3 at 180°C and 220°C under atmospheric pressure.

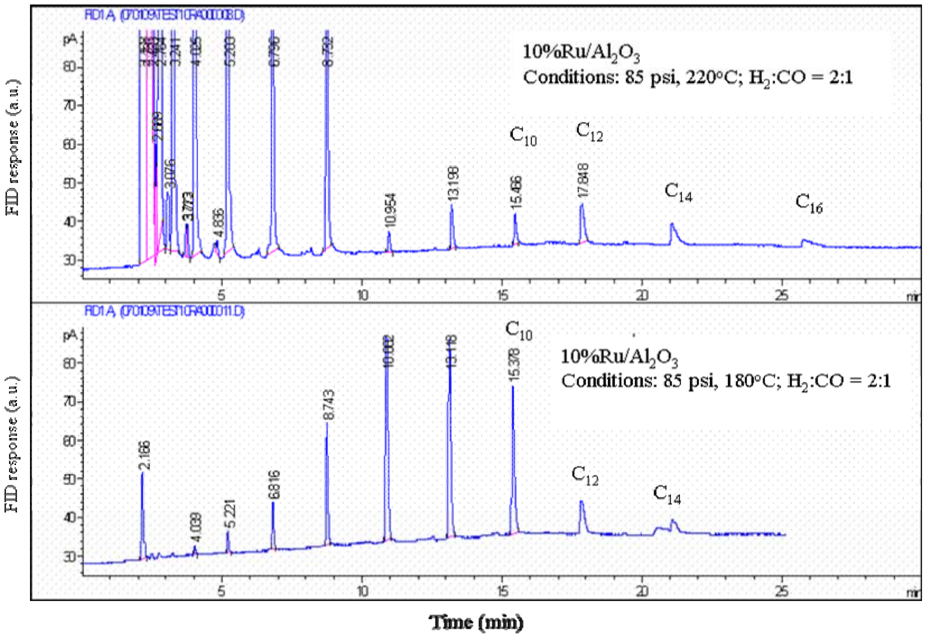

Figure 3. Chromatograms obtained from Fischer Tropsch reaction over 10%Ru/Al_2O_3 at 180°C and 220°C under pressure of 85 psi.

Figure 4 and 5 present chromatograms recorded during Fischer Tropsch reaction over 10%Ru/MgO-Al_2O_3 (0.5:2) and 10%Ru/MgO-Al_2O_3 (1:2) at 180°C, 220°C and 260°C under the pressure of 85 psi, respectively. It was observed that C_1-C_5 hydrocarbons were obtained and the reaction favors to produce methane at higher temperature for both catalysts investigated. It could be seen that modified magnesium oxide on alumina support catalyst has an effect on the catalytic performance of Ru catalysts compared to Ru/Al_2O_3 catalyst.

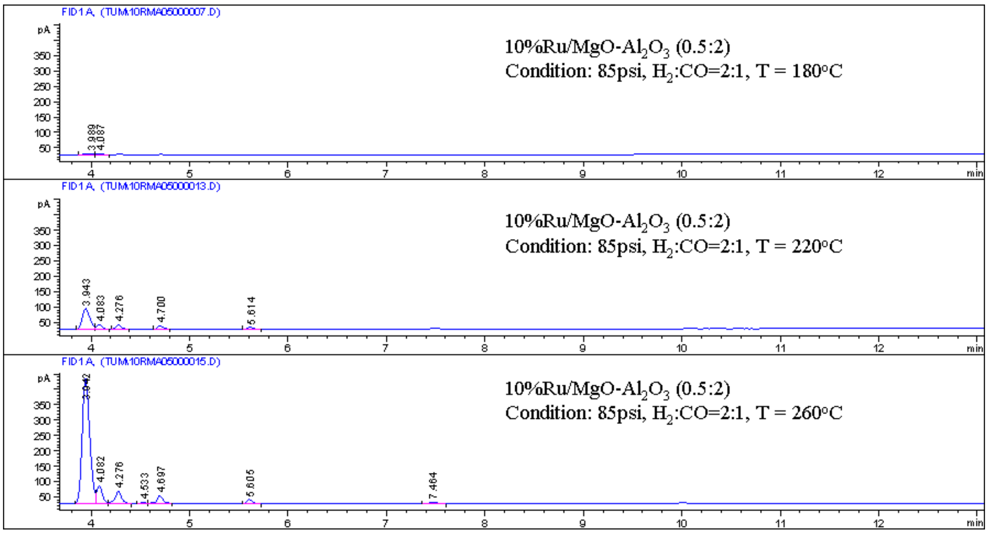

Figure 4. Chromatograms obtained from Fischer Tropsch reaction over 10%Ru/MgO-Al_2O_3 (0.5:2) at 180°C, 220°C and 260°C under the pressure of 85 psi.

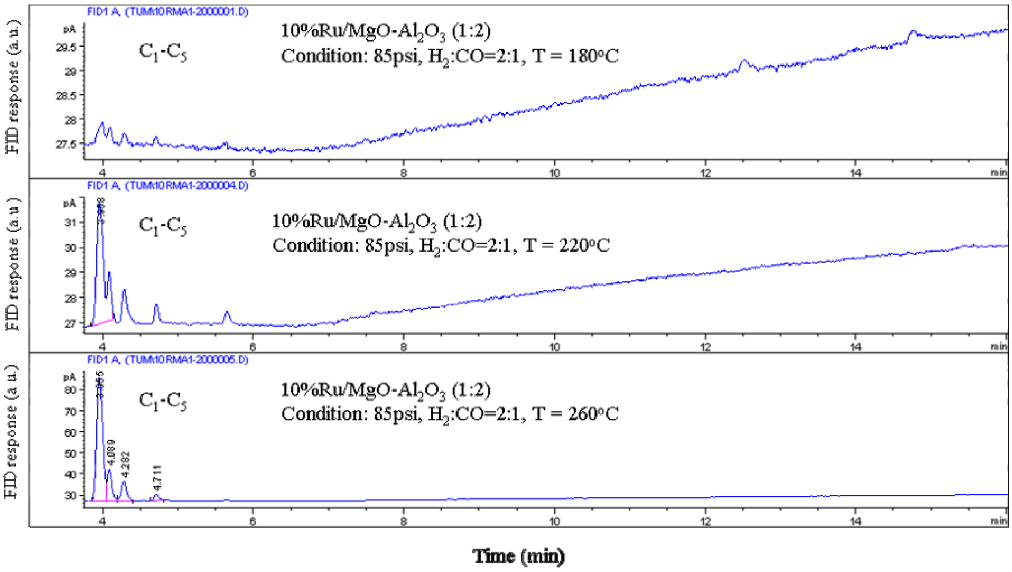

Figure 5. Chromatograms obtained from Fischer Tropsch reaction over 10%Ru/MgO-Al_2O_3 (1:2) at 180°C, 220°C and 260°C under the pressure of 85 psi.

Figure 6 presents chromatograms obtained from Fischer Tropsch reaction over 10%Ru/MgO at 180°C under atmospheric pressure. Hydrocarbons range of C_{11}-C_{20} can be formed and product selectivity of C_{11}-C_{20} is 85.39%. An enhancement in product selectivity to diesel range could be explained by the basicity of MgO support. However, it could not be elucidated in this study. Products selectivity and catalytic activity of catalysts investigated at different reaction conditions are summarized in Table 2.

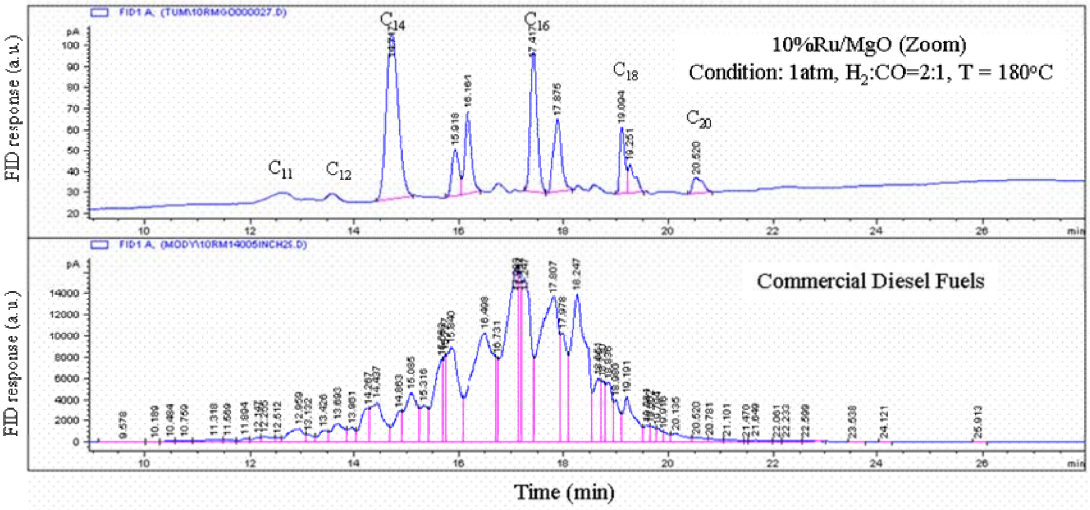

Figure 6. Chromatograms obtained from Fischer Tropsch reaction over 10%Ru/MgO at 180^oC under atmospheric pressure.

Table 2. Products selectivity and catalytic activity of catalysts investigated at different reaction conditions

Catalyst	Condition		% Selectivity				Activity (mol/sec.g of cat)			
	T (^oC)	P (psi)	CH_4	C_2-C_4	C_5-C_{12}	C_{13}-C_{24}	CH_4	C_2-C_4	C_5-C_{12}	C_{13}-C_{24}
10%Ru/Al_2O_3	180	14.7	58.37	21.66	4.78	8.54	1.38E-07	6.71E-08	1.13E-08	2.03E-08
10%Ru/Al_2O_3	220	14.7	74.62	16.74	2.83	0.74	1.52E-06	4.45E-07	5.78E-08	1.51E-08
10%Ru/Al_2O_3	180	85	8.24	16.48	30.13	28.03	1.56E-08	3.11E-08	5.69E-08	8.53E-08
10%Ru/Al_2O_3	220	85	84.62	11.79	3.44	0.15	2.50E-05	3.49E-06	1.00E-06	8.03E-09
10%Ru/MgO-Al_2O_3 (0.5:2)	180	85	38.38	41.18	7.98	0.00	9.89E-09	1.38E-08	2.06E-09	0.00
10%Ru/MgO-Al_2O_3 (0.5:2)	220	85	66.53	21.87	2.31	0.00	1.42E-07	6.64E-08	4.93E-09	0.00
10%Ru/MgO-Al_2O_3 (0.5:2)	260	85	78.01	20.76	1.23	0.00	8.57E-07	2.28E-07	1.35E-08	0.00
10%Ru/MgO-Al_2O_3 (1:2)	180	85	59.60	33.57	0.76	0.00	1.15E-08	7.67E-09	1.47E-10	0.00
10%Ru/MgO-Al_2O_3 (1:2)	220	85	60.29	32.72	1.21	0.00	1.17E-08	7.47E-09	2.35E-10	0.00
10%Ru/MgO-Al_2O_3 (1:2)	260	85	72.66	27.14	0.20	0.00	1.34E-07	5.00E-08	3.64E-10	0.00
10%Ru/MgO	160	14.7	4.06	8.95	0.00	86.99	3.19E-09	7.03E-09	0.00	7.00E-08
10%Ru/MgO	180	14.7	17.91	43.27	0.00	38.82	5.38E-09	1.31E-08	0.00	1.38E-08

5. Conclusions

The catalytic behavior illustrates that operating conditions at low pressure and high temperature, all catalysts investigated produce much methane, whereas at high pressure and low temperature, the production is selective toward higher hydrocarbons (C_5^+). This could be due to the limitation of chain propagation at high temperature. The selectivity of Ru/MgO catalyst for the production of diesel hydrocarbons observed could be attributed to the basicity of MgO, leading to the possibility of chain growth of hydrocarbons. The modification of magnesium oxide on alumina supported catalyst has an effect on the catalytic performance of Ru catalysts.

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