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Gasoline and Diesel Production via Fischer-Tropsch Synthesis over Cobalt based Catalyst

N. Choosri, N. Swadchaipong, T. Utistham, and U. W. Hartley

***Abstract*—**Performance of a cobalt doped sol-gel derived silica (Co/SiO_2) catalyst for Fischer–Tropsch synthesis (FTS) in slurry-phase reactor was studied using paraffin wax as initial liquid media. The reactive mixed gas, hydrogen (H_2) and carbon monoxide (CO) in a molar ratio of 2:1, was flowed at 50 ml/min. Braunauer-Emmett-Teller (BET) surface area and X-ray diffraction (XRD) techniques were employed to characterize both the specific surface area and crystallinity of the catalyst, respectively. The reduction behavior of Co/SiO_2 catalyst was investigated using the Temperature Programmmed Reduction (TPR) method. Operating temperatures were varied from 493 to 533K to find the optimum conditions to maximize liquid fuels production, gasoline and diesel.

***Keywords*—**Fischer Tropsch synthesis, slurry phase, Co/SiO_2, operating temperature.

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I. Introduction

FISCHER –Tropsch synthesis (FTS) is a well-known method for producing liquid hydrocarbons such as paraffins, olefins and other chemicals. FTS has drawn great interest in the past decade since it is believed that synthetic liquid fuels produced from this process can solve the shortage of liquid transport fuels. The FTS efficiency and product distribution depend on variables such as reactor type, operating conditions and the nature of the catalyst used [1]. The operating conditions are keys in the control of product distribution during FTS. Proper selection of reaction conditions such as temperature plays an important role in the catalytic activity and the selectivity of the reactions [2], [3]. The low temperature Fischer-Tropsch (LTFT) is run at temperatures of 493 to 533K. Cobalt based-catalysts are normally employed for production of long chain hydrocarbons and small olefins [4]-[6]. Farias and coworkers showed that liquid hydrocarbon product distribution of iron based catalyst was dependent on the operating pressure and temperature [7]. Tian and coworkers found that increasing both reaction temperature and inlet H_2/CO ratio improved the selectivity to low molecular hydrocarbons, while decreasing total pressure favoured selectivity to high molecular hydrocarbons [8]. De la Osa [2] showed that CO conversion and selectivity to hydrocarbon chains of 5 or more (C_5^+) was influenced by addition of promoters and variation of operating condition such as space velocity, H_2/CO ratio and reaction temperature.

Cobalt and iron catalysts have been applied to industrial-scale FTS process. However, cobalt-based catalysts for FTS have received the most attention due to their high selectivity to linear hydrocarbon products, high resistance to deactivation and low activity towards occurrence of the water gas shift reaction (WGS) [9]-[11].

In general, porous inorganic oxides are doped with cobalt via the wetness impregnation method using the solution of various salts [6], [12], [13]. Suitable inorganic oxides as a support should possess a high surface area such as SiO_2, aluminium oxide (Al_2O_3) and Titania (TiO_2). Khodakov, Diehl and Viana de Sousaa investigated supported Co based catalysts with a view to maximizing the FTS efficiency by improving the dispersion ability and reducibility of the catalysts [5],[14],[15]. Khodakov and Oh found that the support influenced several important catalytic properties, including reducibility, dispersion ability, mechanical and chemical strength [6], [16]. SiO_2 is commonly utilized for supporting Co in the FTS process due to its weak interaction with Co leading to good reducibility of Co oxides [17]. The effects of the SiO_2 support textural properties on FTS catalytic performance has been studied in a number of publications [18]-[20]. Liu studied the effect of the textural properties of SiO_2 supports on catalyst performance. The pore size of the SiO_2 support was shown to strongly influence the catalytic activity of Co/SiO_2 for FTS [21]. Investigations of the morphological properties of the SiO_2 support have not received as much attention. On the other hand, catalyst modification for the purpose of maximizing the efficiency of the FTS had been researched widely. The catalytic properties of SiO_2 can be adjusted to the most favorable condition for FTS [22].

Judicious election of the catalyst, support and the reaction conditions are significant for the FTS performance with respect to FTS activity and product distributions. In this paper, an experimental investigation of reaction temperature for Co

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doped sol-gel derived SiO_2 catalysts was carried out to optimize catalytic activity and product distribution to maximize gasoline (C_5-C_{12}) and/or diesel (C_{13}-C_{23}).

II. Experimental

A. Catalyst Preparation

Silica was prepared by the sol-gel method. A solution of ethanol and tetraethyl orthosilicate (TEOS, Aldrich) were mixed and stirred vigorously for 15 min. De-ionized water and hydrochloric (Aldrich, 37%) acid were added to the mixture of TEOS and ethanol then continuously stirred for a further 1 hour (h) at 303 K. The final solution was heated in an oven at 338 K for 24 h. The gel sample was collected and calcined in air at 773 K for 6 h. The calcined sample was then ground using a pestle and mortar and sieved to collect only fine particles (297–840 μm) of Co/SiO_2.

Cobalt (II) nitrate ($Co(NO_3)_2{\cdot}6H_2O$, Ajax Finechem) solution was impregnated into the sieved silica supports by an incipient wetness method to obtain cobalt metal loading of 13 wt.%. The impregnated catalyst was dried in an oven at 393 K for 12 h, and then calcined at 723 K for 4 h in air.

After calcination, the catalyst was activated in a stainless steel fixed bed reactor by flowing pure hydrogen flowing over 10 h at 673 K followed by passivation using 1% O_2/N_2 for 1 h at room temperature.

B. Catalyst Characterization

The catalyst surface area and crystallinity were characterized. The surface area, pore size and pore volumes of the catalyst were measured by a standard BET method using N_2 physisorption, the data were collected at its boiling point (77 K) on a Quanta chrome apparatus model Autosorb-1.

Diffractograms of SiO_2 and Co/SiO_2 were obtained by XRD analysis using a Bruker AXS, D8 Advance diffractometer (Germany) with Cu(Kα) radiation and operating parameters of 40 kV and 30 mA. Diffraction patterns were acquired using a step scanning technique from 10° to 80° in 2θ. The diameter of the Co_3O_4 crystalline size was calculated from Scherrer equation as shown in the equation (1) [23].

$$L = \frac{K\lambda}{\Delta(2\theta)\cos\theta_0} \quad (1)$$

where L is the crystalline size (nm)
K is a Scherrer constant (K = 0.9 – 1.1)
λ is the wavelength of X-ray (Cu(Kα) = 0.154 nm)
$\Delta(2\theta)$ is the width of the peak at half height (radian)

The reduction behavior of the cobalt oxide (Co_3O_4) component in the lab-prepared catalyst was investigated using the hydrogen temperature-programmed reduction (H_2-TPR) technique. Prior to the H_2-TPR experiment, the catalyst was pretreated with helium at 473 K, then cooled down to room temperature. The reducing gas, 5% H_2 /Ar, was fed through the calcined catalyst at a heating rate of 10 K/min from ambient temperature to 1123 K. The thermal conductivity detector (TCD) signal indicated hydrogen consumption at different temperatures. The result was recorded on-line by computer.

C. Fischer-Tropsch Synthesis

Catalytic FTS were carried out in a slurry-phase reactor (Parr reactor model 4848) with a volume 0.25 L at temperature ranging from 493 to 533 K. CO conversion and product distribution were determined at each temperature to find the optimum operating temperature to maximize the desired yields of gasoline and diesel. 2 g of passivated catalyst was loaded into the reactor and suspended in 65 g of molten paraffin wax (the start-up medium). 50 ml/min of reactant gas, H_2:CO at a molar ratio of 2, was introduced into the reactor. The total pressure was maintained at 2 MPa. The ratio of catalyst weight to reactant gas flow rate (W/F) and gas hourly space velocity (GHSV) were fixed at 15 g-cat.h/mol and 1.5 l(STP)/g/h, respectively. The effluent gas was passed through a hot trap (433K), followed by a cold trap (293K) then back-pressure regulator, before analysis by gas chromatography using a thermal conductivity detector (GC-TCD). Qualitative and quantitative gas analyses were performed on a Shimadzu gas chromatograph GC-8A. The products analyzed were H_2, CO, carbon dioxide (CO_2) and methane (CH_4). The gas mixture was carried in as a mobile phase and passed through the stationary phase of a Porapak Q column. The outlet of the column was connected directly to a TCD, which responded in proportion to the concentration of the components in the sample stream. The liquid products were analyzed by combined gas chromatograph connected to a mass spectrometer (GC-MS).

III. Result and Discussion

A. Characterization of Catalyst

Cobalt content, specific surface area and crystallinity of the catalysts were characterized by XRF, BET and XRD techniques, respectively. The Table I shows the structural properties of the sol-gel derived SiO_2 support and the Co/SiO_2 catalyst before exposure to FTS. After Co impregnation, the surface area and pore volume of the doped catalyst were found to be reduced, compared to the undoped SiO_2. This may be due to formation of large Co_3O_4 particles on the catalysts surface that were detected by XRD. Co_3O_4 coagulation occurred on the catalyst's surface and partly penetrated the supports inner pores resulting in a drop of surface area and pore volume [24].

Fig. 1 shows XRD patterns of the lab-prepared SiO_2 and Co/SiO_2. The Co/SiO_2 diffractogram indicates the presence of Co_3O_4 as a minor crystalline phase. The diameter of the Co_3O_4 particle was measured as 4.5 nm. The large Co_3O_4 particles could be formed by a weak interaction between SiO_2 and Co oxide species resulting in a low dispersion of Co on the SiO_2 [16], [25].

TABLE I
PHYSICAL PROPERTIES OF FTS CATALYSTS

Sample	Co content (wt.%)	BET surface area (m^2/g)	Total pore volume (ml/g)	Average pore diameter (nm)	Co_3O_4 particle size (nm)
SiO_2	-	376	0.20	2.15	-
Co/SiO_2	13	284	0.14	1.84	45

Fig. 2 shows the H_2-TPR profile of the FTS catalyst, demonstrating the reducibility of Co_3O_4 to Co^0, Co in the zero oxidation state being the active site for FTS. In Fig. 2, two major peaks were seen at 634 and 648 K, corresponding to the two major mechanisms of the reduction process [26]-[28]. The low temperature sharp peak, detected between room temperature and 634 K, could be assigned to the partial reduction of Co_3O_4 to CoO. The second broad peak at medium temperature of 648 K could be ascribed to the subsequent reduction of CoO particle to the Co^0 species [29]. However, the third peak at 1073 K probably occurred due to reduction of undesired cobalt silicate phase that could reduce the catalyst's activity towards FTS [30]. A small shoulder peak at about 625 K was also found. This peak is attributed to the decomposition of residual nitrate ions (from the cobalt (II) nitrate precursor) which decomposes completely above 673 K [26], [31].

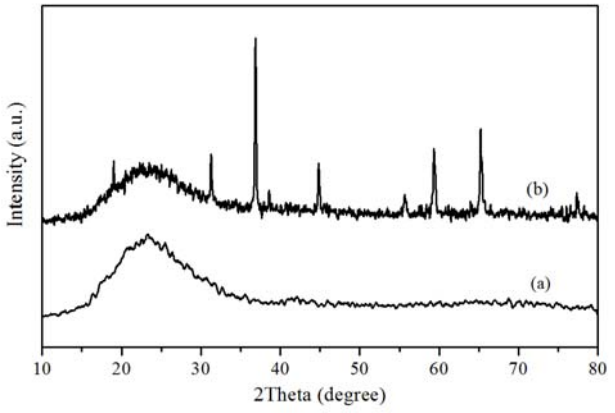


Fig. 1 The XRD patterns of the (a) sol-gel derived silica (SiO_2) support and (b) cobalt doped on sol-gel derived silica support (Co/SiO_2) catalyst

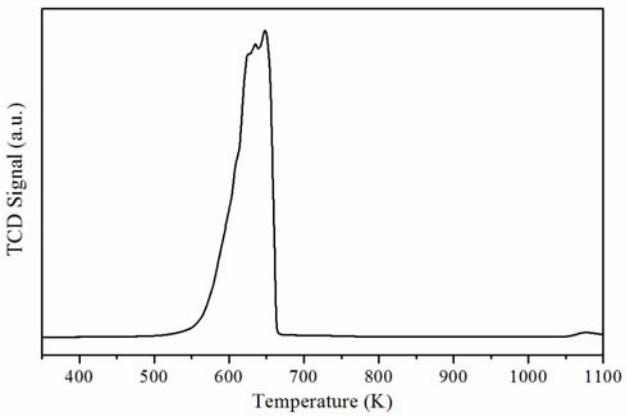


Fig. 2 The H_2-TPR profile of the Co/SiO_2 calcined catalyst

B. Fischer-Tropsch synthesis

In order to study the performance of the synthesized catalyst and to find the optimum operating temperature for the highest yields of hydrocarbon liquid fuels, the experiments were performed at different temperature. The CO conversion, FTS activity, product selectivity and distribution were determined after 24 h exposure of the catalyst to FTS as shown in Table II.

The CO conversion (%) was calculated from the amount of CO used minus the CO that remained in the tail gas as:

$$\text{CO conversion}\,(\%)=\frac{(\text{Moles of CO})_{\text{in}}-(\text{Moles of CO})_{\text{out}}}{(\text{Moles of CO})_{\text{in}}}\times 100 \quad (2)$$

TABLE II
CATALYTIC PERFORMANCES OF THE CATALYST WITH THE VARIOUS REACTION TEMPERATURES IN SLURRY-PHASE FTS

Reaction temperature (K)	CO conversion (%)	CH_4 selectivity (%)	CO_2 selectivity (%)
493	7.40	2.02	
513	11.05	3.75	
533	23.17	8.86	0.52

CO conversions as function of time on stream (TOS) of the Co/SiO_2 catalyst under temperatures of 493, 513 and 533 K are shown in Fig. 3. The CO conversion at 513 K was slightly higher than the CO conversion at 493K through the time on stream. The highest CO conversion, 23.17%, occurred at 533 K. From Table II, CO_2 is a minority product indicating the water-gas shift reaction (WGS) was efficient. This indicates that the CO has reacted with water generating CO_2 and H_2. Cobalt based catalysts is low activity in WGS [32]. Presumably, increased temperature caused an increase in CO_2 and CH_4 formation via the WGS and methanation. These are endothermic reactions, thermodynamically favored at high temperature [33]. The result is in agreement with previous works. CO dissociation was promoted by increased temperatures and provided more surface C atoms leading to the release of hydrocarbons. Additionally, methane formation was promoted due to feed gas ratio enrichment within the reactor at increased operating temperatures [8],[34],[35].

The liquid products collected and analyzed by GC-MS showed n-paraffins as a main product with trace amounts of oxygenates.

Fig. 4 shows the number of carbons in the liquid hydrocarbon produced in the experiments. Long chain hydrocarbons with carbon chains ranging from $C_{10} - C_{16}$, $C_{10} - C_{21}$ and $C_7 - C_{23}$ were produced at 493K, 513K and 533K,

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respectively.

These findings are in agreement with previous studies reported by other researchers [7]. However, C_5 and C_6 n-paraffins were not detected. This might be due to the space limitation inside the catalyst pores. Increased operating temperature apparently increases the spread of longer and shorter chain hydrocarbons using this catalyst. Fig. 5 represented amount of total liquid fuels (mg) produced by FTS at temperatures of 493K, 513K and 533K. This result is consistent with the earlier results from Table II and Fig. 4 which showed that, at 533 K, the highest CO conversion and highest amount of gasoline and diesel were obtained, respectively.

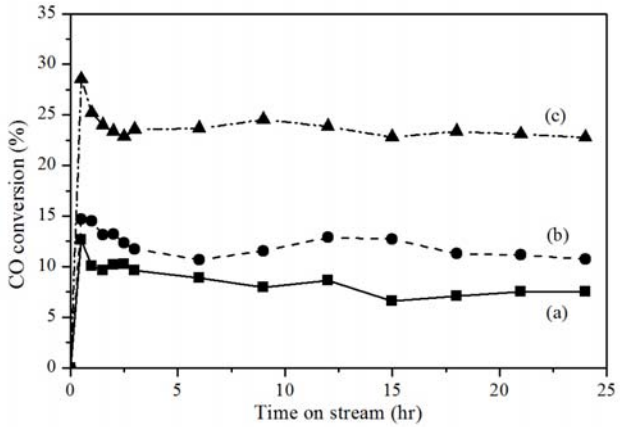


Fig. 3 Catalytic performances with time courses for FTS over Co/SiO_2 catalyst at different reaction temperature as (a) 493 K, (b) 513 K, and (c) 533 K

IV. Conclusion

Large particles of Co_3O_4 were found as a minor crystalline phase in the lab-prepared cobalt doped sol – gel derived amorphous silica, Co/SiO_2 catalyst. Co_3O_4 aggregated and formed on the surface of the catalyst resulting in a drop of the surface area and pore volume. However, this catalyst displayed a good performance towards the FTS in slurry-phase reactor.

The Co/SiO_2 possesses good selectivity towards hydrocarbons liquid fuels in the C_5 to C_{23} range for LTFT.

The operating temperature of the reaction strongly influenced the performance of the catalyst towards FTS.

Increased temperatures resulted in greater CO conversion to hydrocarbon product, while similarly, the yield of the liquid products and the spread of carbon chain length numbers were influenced by the temperature with a higher temperature producing a greater spread.

The maximum CO conversion and liquid products yield was obtained at 533 K for Co/SiO_2 catalyst in a slurry-phase reactor.

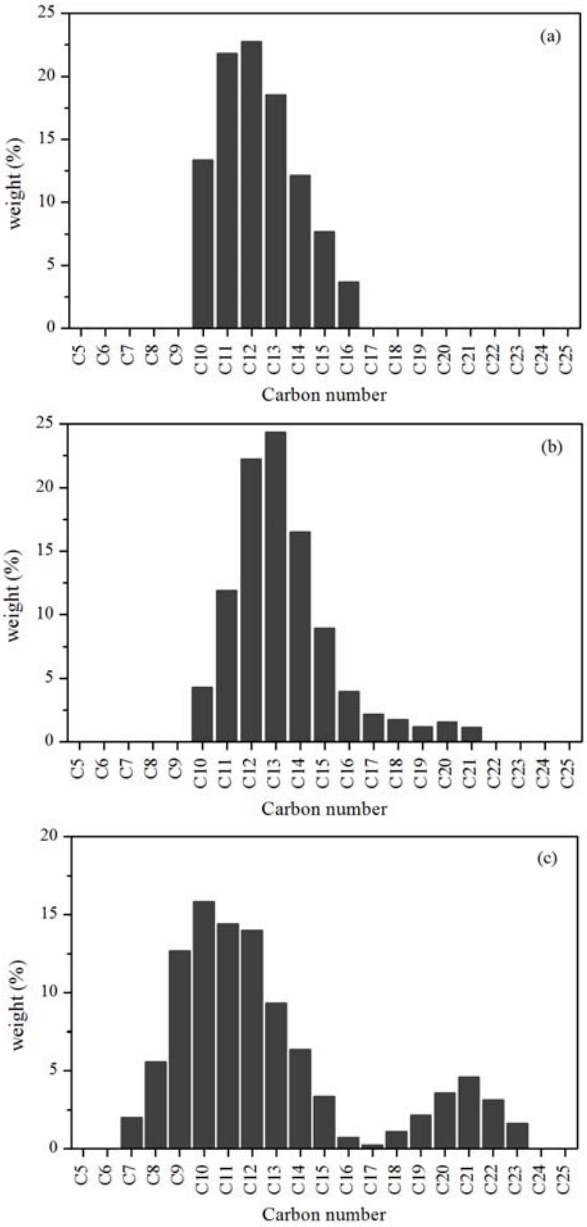


Fig. 4 Percentage of weight of each carbon number in hydrocarbon liquid products which was detected as the n-paraffins for (a) 493K, (b) 513K, and (c) 533K

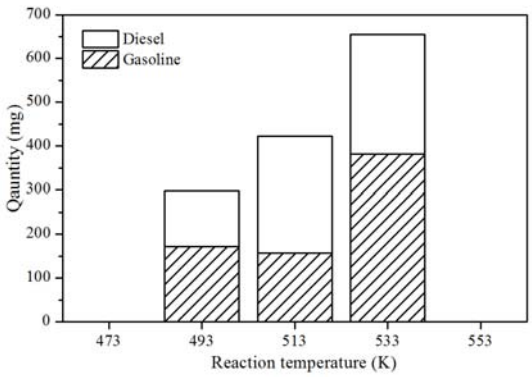


Fig. 5 Quantity of liquid fuels products obtained from FTS over Co/SiO_2 catalyst

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REFERENCES

[1] M.E. Dry, "Fischer-Tropsch reactions and the environment," Applied Catalysis A: General, vol. 189, pp. 185-190, Dec.1999.

[2] A.R. de la Osa, A. De Lucas, A. Romero, J.L. Valverde, and P. Sanchez, "Fischer–Tropsch diesel production over calcium-promoted Co/alumina catalyst: Effect of reaction conditions," *Fuel* , vol. 90, pp. 1935–1945, May 2011.

[3] K.J. Woo, S.H. Kang, S.M. Kim, J.W. Bae, and K.W. Jun, "Performance of a slurry bubble column reactor for Fischer–Tropsch synthesis: Determination of optimum condition," *Fuel Processing Technology*, vol. 91, pp. 434–439, Apr. 2010.

[4] B. Jager, "Development in Fischer-Tropsch technology," *Stud. Surf. Sci. Catal*, Vol. 119, 1998.

[5] Andrei Y. Khodakov," Fischer-Tropsch synthesis: Relations between structure of cobalt catalysts and their catalytic performance," *Catalysis Today* vol. 144, issue 3-4, pp. 251–257, Jun. 2009.

[6] A.Y. Khodakov, W. Chu, P. Fongarland . "Advance in the development of Novel Cobalt Fischer-Tropsch catalyst for Synthesis of Long-Chain Hydrocarbons and clean Fuels," *Chem. Rev.*,vol. 107, pp. 1692-1744, Jul.2007.

[7] F.E.M. Faris, F.R.C. Silva, S.J.M Cartaxo, F.A.N. Fernades and F.G. Sales, "Effect of operating conditions on Fischer-Tropsch liquid products," *Latin American Applied Research*, vol. 37, no. 4, pp.283-287.Oct.2007.

[8] L. Tian, C.F. Huo, D.B. Cao, Y. Yang, and et al., "Effects of reaction conditions on iron-catalyzed Fischer–Tropsch synthesis: a kinetic Monte Carlo study," *Theochem*, vol .941, pp.30–35. Feb. 2010.

[9] P.J. Van Berge and R.C.Everson. Studies in Surface Science and Catalysis (Natural Gas Conversion IV). pp.207, 1997.

[10] M.A. Vannice, "The catalytic synthesis of hydrocarbons from H_2/CO mixtures over the Group VIII metals V. The catalytic behavior of silica-supportedmetals," *Journal of Catalysis*, vol. 50, issue 2, pp. 228-236. Nov. 1997.

[11] H. Schulz, "Short history and present trends of Fischer–Tropsch synthesis," *Applied Catalysis A: General*, vol. 186, pp. 3–12, Oct. 1999.

[12] M.E. Dry, "The Fischer–Tropsch process: 1950–2000" *Catalysis Today*, vol. 71, pp.227-241, Jan. 2002.

[13] R. Oukaci, A.H. Singleton, J.G. Goodwin, "Comparison of patented Co F–T catalysts using fixed-bed and slurry bubble column reactors" *Applied Catalysis*, vol. 186, issue 1-2, pp.129-144, Oct. 1999.

[14] F. Diehl, and A.Y. Khodakov, "Promotion of Cobalt Fischer-Tropsch Catalysts with Noble Metals: a Review," *Oil Gas Sci. Technol.-Rev. IFP* vol. 64, no.1, pp.11–24, Nov. 2008.

[15] B. Viana de Sousaa, M. ucia Freire Rodriguesa, Leonardo Andres Canob, and et al., "Study of the effect of cobalt content in obtaining olefins and paraffins using the Fischer-Tropsch reaction," *Catalysis Today*, vol. 172, pp.152– 157. Aug. 2011.

[16] J.H. Oh, J.W. Bae, S.J. Park, P.K. Khanna and K.W. Jun, " Slurry-Phase Fischer-Tropsch Synthesis Using Co/γ-Al_2O_3, Co/SiO_2 and Co/TiO_2: Effect of Support on Catalyst Aggregation," *Catal Lett,* vol.130, pp.403-409. May 2009.

[17] A. Martinez, C. Lopez, F. Marquez, and I. Diaz, "Fischer–Tropsch synthesis of hydrocarbons over mesoporous Co/SBA-15 catalysts: the influence of metal loading, cobalt precursor, and promoters," *Journal of Catalysis*. Vol. 220, pp.486–499, Dec. 2003.

[18] L. Shi, D. Li, B.Hou, Y.Wang, and Y. Sun, "The modification of SiO_2 by various organic groups and its influence on the properties of cobalt-based catalysts for Fischer–Tropsch synthesis," *Fuel Processing Technology*, vol. 91, pp.394–398. Apr. 2010.

[19] Y. Zhang, M. Koike, R. Yang, S. Hinchiranan, and et al., 'Multi-functional alumina–silica bimodal pore catalyst and its application for Fischer-Tropsch synthesis," *Applied Catalysis A:* General: vol. 292, pp. 252–258. Sep. 2005.

[20] Y. Zhang, Y. Liu, G. Yang, Y. Endo, and N. Tsubaki, "The solvent effects during preparation of Fischer–Tropsch synthesis catalysts: Improvement of reducibility, dispersion of supported cobalt and stability of Catalyst," *Catalysis Today*, vol.142, pp. 85–89. Apr. 2009.

[21] Y. Liu, T. Hanaoka. M. Tomohisa, M., Kazuhisa, and et al., "Fischer – Tropsch synthesis in slurry-phase reactors over Mn- and Zr-modified Co/SiO_2 catalysts," *Fuel Processing Technology*, vol. 90, issues 7–8, pp. 901–908, Jul. 2009.

[22] B.C. Dunn, P. Cole, G.C. Turpin, Z. Ma, and et al., "Silica Aerogel Supported Catalysts for Fischer - Tropsch Synthesis," Applied Catalysis A: General, vol. 278, pp. 233-238, Jan. 2005.

[23] Cullity B.D. Elements of X-ray Diffraction, Addison-Wesley, London. 1978.

[24] X. Zhou, Q. Chen, Y. Tao, and H. Weng, "Effect of vacuum impregnation on the performance of Co/SiO_2 Fischer-Tropsch catalyst," *Journal of Natural Gas Chemistry*, vol. 20, pp. 350-35, Jan. 2011.

[25] X. Sun, X. Zhang, Y. Zhang,and N. Tsubaki, "Reversible promotional effect of SiO_2 modification to Co/Al_2O_3 catalyst for Fischer–Tropsch synthesis," *Applied Catalysis A: General*, vol. 377, pp.134–139, Jan. 2010.

[26] W. Chu, P.A. Chernavskii, L. Gengembre, G.A. Pankina, and et al., "Cobalt species in promoted cobalt alumina-supported Fischer–Tropsch catalysts" Journal of Catalysis, vol. 252, issue 2, pp.215-230, Dec. 2007.

[27] P. Arnoldy, and J.A. Moulijn, "Temperature-programmed reduction of CoO/Al_2O_3 catalysts," *Journal of Catalysis*, vol. 93, pp. 38-54, May. 1985.

[28] D.I. Enache, M. Roy-Auberger, and R. Revel "Differences in the characteristics and catalytic properties of cobalt-based Fischer–Tropsch catalysts supported on zirconia and alumina," *Applied. Catalysis A: General*, vol. 268, issue 1-2, pp. 51-60. Aug. 2004.

[29] S. Yuvaraj, L.F.Yuan, C. T. Huei, and Y. C.Tih, "Thermal Decomposition of Metal Nitrates in Air and Hydrogen Environments," *J. Phys. Chem. B,* vol. 107, pp.1044-1047. Jan. 2003.

[30] A. H. Kababji, B. Joseph, and J. T. Wolan, "Silica-Supported Cobalt Catalysts for Fischer–Tropsch Synthesis: Effects of Calcination Temperature and Support Surface Area on Cobalt Silicate Formation," *Catal Lett*, vol.130, pp. 72-78, Mar. 2009.

[31] E. van Steen, G.S. Sewel, R.A. Makhothe, C. Micklethwaite, and et al., **"**TPR Study on the Preparation of Impregnated Co/SiO_2 Catalysts," *Journal of Catalysis*, vol.162, pp. 220, Sep. 1996.

[32] I. Wender, "Reactions of synthesis gas," *Fuel Processing Technology*, vol. 48, issue 3, pp.189-297. Sep. 1996.

[33] C. Zhang, G. Zhao, J. Chang, H. Xiang, and Y. Li, "Factors influencing the WGS reaction in Fischer-Tropsch synthesis over iron-based catalysts," unpublished.

[34] Y. Liu, B.T. Teng, X.H. Guo, Y.Li and et al., "Effect of reaction conditions on the catalytic performance of Fe–Mn catalyst for Fischer–Tropsch synthesis," *Journal of Molecular Catalysis A: Chemical*, Vol. 272, Issues 1–2, pp.182-190, Jul. 2007.

[35] F.E.M. Farias, F.G. Sales, and F.A.N. Fernandes, "Effect of operating conditions and potassium content on Fischer–Tropsch liquid products produced by potassium-promoted iron catalysts," *Journal of Natural Gas Chemistry*, vol.17, issue 2, pp. 175-178. Jun.2008.