

## Effect of cobalt catalyst type and reaction medium on Fischer-Tropsch synthesis

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**Abstract**—This study covers the performance of five cobalt-based catalytic systems with different support characteristics in Fisher-Tropsch synthesis (FTS) under conventional gas-phase using syngas, and the manner in which the reaction medium is influenced by the addition of solvents such as n-hexane and squalane has been also investigated. The reaction was conducted in a fixed bed high-pressure FTS reactor setup at a reaction temperature of 220 °C to 260 °C. In terms of the effect of the reaction medium, higher CO conversion was obtained in gas phase reaction, whereas the olefin selectivity was higher in n-hexane medium than in gas phase and squalane medium. In addition, the undesired production of CH<sub>4</sub> and CO<sub>2</sub> was relatively reduced in solvent addition compared to the gas phase FTS. The reaction performance was also compared according to the type of catalyst. CO conversion by type of catalyst decreased in the following order: 20% Co/SiO<sub>2</sub>>20% Co/Al<sub>2</sub>O<sub>3</sub>>20% Co/HAS>20% Co/Si-MMS>20% Co/TiO<sub>2</sub>. However, the C<sub>5+</sub> content of products was little affected by catalyst supports.

Key words: Cobalt Catalyst, Fischer-Tropsch, Gas Phase, Reaction Medium, n-Hexane, Squalane

### INTRODUCTION

With petroleum reserves dwindling, interest has been increasing worldwide in Fischer-Tropsch (FTS) synthesis as a method of producing synthetic liquid fuels and chemicals from coal, natural gas or biomass. FTS offers the possibility of converting a mixture of hydrogen and carbon monoxide (syngas) into clean hydrocarbons, which are free from sulfur. In general, modern FT synthesis is operated through the gas phase-fixed bed system, the gas phase-fluidized bed system or the liquid phase-slurry system [1-3]. The gas-phase reaction system is inevitably accompanied by the local overheating of the catalyst surface, as well as by the production of heavy wax. Local overheating of the catalyst may lead to its deactivation and also to an increase in methane selectivity. Heavy wax may plug the micropores of the catalyst and the catalyst bed itself, which will also lead to its deactivation. The slurry phase FTS process, on the other hand, in which a slurry, composed of fine powdery catalyst and mineral oil, is used as a reaction medium, has been developed to overcome the defects of the gas-phase process. However, the diffusion of synthesis gas in the micropores of the catalyst is so slow in the slurry phase that the overall reaction rate is markedly lower than that of the gas-phase reaction. It was known that a supercritical fluid has unique characteristics such as the quick diffusion of reactant gas, effective removal of reaction heat, and the in-situ extraction of high molecular weight hydrocarbon, such as wax [4-7].

FTS is a surface-catalyzed polymerization process that utilizes methylene intermediates, formed by adsorbed CO hydrogenation, to produce hydrocarbons with a broad range of chain length and

functionality. Both the structure and the performance of cobalt catalysts depend on catalytic support. The principal function of the catalyst support is to disperse cobalt and produce stable cobalt metal particles in the catalysts after reduction. Cobalt is considered the most favorable catalyst for the formation of high molecular weight and long-chain hydrocarbons from synthesis gas, which can further produce lubricants and diesel by hydrocracking. Due to the high price of the precious metals required, the design of highly dispersed cobalt-based catalysts on porous supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> has recently been investigated. The porous structure of the support could control the sizes of supported cobalt particles. A large number of reports have focused on the effect of the support. The catalytic activity of cobalt-based catalysts as a function of the support used was found it to decline in the following order: Co/TiO<sub>2</sub>>Co/Al<sub>2</sub>O<sub>3</sub>>Co/SiO<sub>2</sub>>100% Co>Co/MgO [1,7].

In silica-supported catalysts, the interaction between the support and the cobalt is relatively weak, which usually leads to better cobalt reducibility. At the same time, cobalt dispersion is much lower in silica-supported catalysts than in alumina-supported catalysts. On the other hand, in alumina-supported catalysts, cobalt oxide strongly interacts with the support, forming relatively small cobalt crystallites. The chemical reaction of small cobalt particles with the support may result in the diffusion of cobalt active phase into alumina and the formation of stoichiometric or nonstoichiometric cobalt aluminate spinels. Cobalt reducibility is one of the most important problems of alumina-supported catalysts. Recently, novel mesostructured materials with adjustable porous networks have shown a great deal of promise for the design of heterogeneous catalysts. Pore sizes of these materials can be adjusted within the range of 2 to 30 nm at the stage of synthesis using different surfactants. The stability of the mesoporous structure in the presence of water is a crucial issue in

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the preparation of cobalt catalysts. A recent report has shown that the introduction of small amounts of cobalt via aqueous incipient wetness impregnation could result in significant modification in the MCM-41 structure and loss of hexagonal ordering [1,3].

In this study, our major aim is to obtain a deeper insight into the effect of the type of support on the reaction performance over a supported cobalt catalyst in a fixed bed reactor. This study also examined the effects of the reaction medium with the addition of a solvent such as n-hexane and squalane. Catalytic supports used were two types of alumina (high surface alumina and commercial Catapal B) and silica ( $\text{SiO}_2$  and silica-based mesoporous molecular sieve) and  $\text{TiO}_2$ .

## EXPERIMENTAL

### 1. Preparation of Catalyst

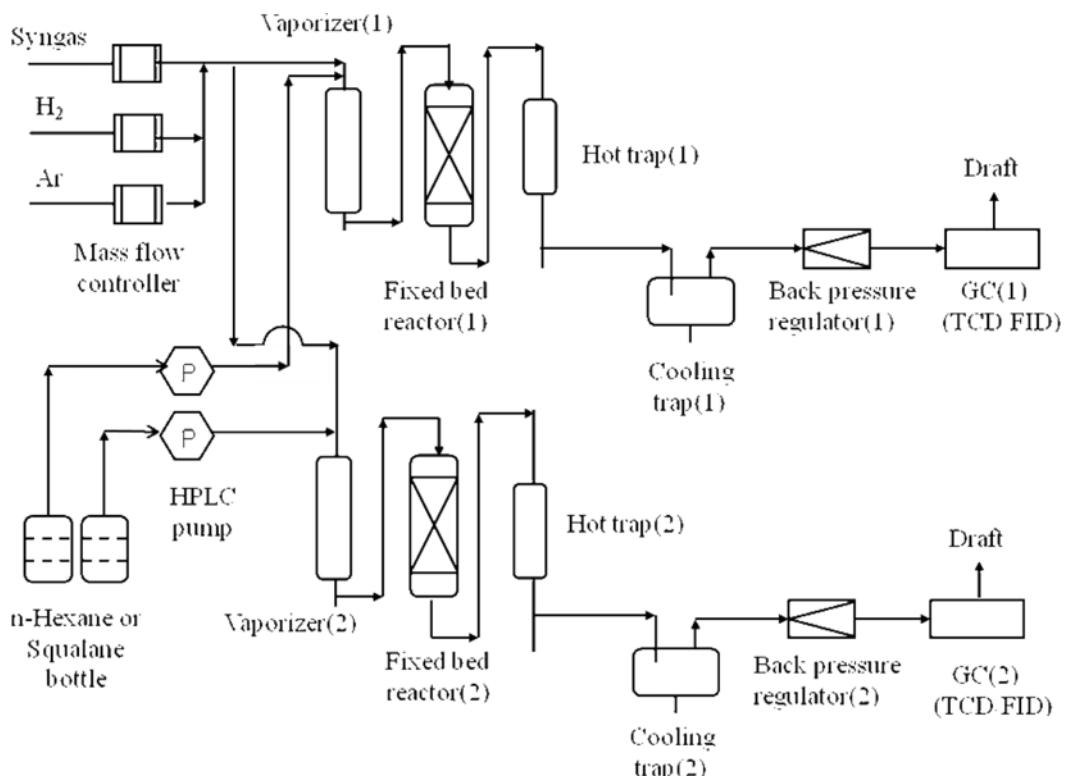
Catalysts containing 20 wt% Co were prepared through a conventional impregnation method using different supports such as high surface area  $\text{Al}_2\text{O}_3$  (HAS, 350.5  $\text{m}^2/\text{g}$ ), commercial  $\text{Al}_2\text{O}_3$  (Catapal B, 220.2  $\text{m}^2/\text{g}$ ),  $\text{TiO}_2$  (Aldrich, 96.2  $\text{m}^2/\text{g}$ ),  $\text{SiO}_2$  (Davisil 645 silica gel, 300.3  $\text{m}^2/\text{g}$ ) and Si-MMS (silica-based mesoporous molecular sieve, 993.9  $\text{m}^2/\text{g}$ ) with aqueous solutions of cobalt nitrate [3]. Especially, high surface area  $\text{Al}_2\text{O}_3$  was prepared by adopting the sol-gel method using aluminum iso-propoxide and Si-MMS was synthesized from fluorosilicon compounds in an ammonia-surfactant mixed solution [3,8]. Five different supported catalysts in the same 20% Co content were as follows: 20% Co/HAS (high surface area  $\text{Al}_2\text{O}_3$ ), 20% Co/ $\text{Al}_2\text{O}_3$  (Catapal B), 20% Co/ $\text{TiO}_2$ , 20% Co/ $\text{SiO}_2$ , 20% Co/Si-MMS (silica-based mesoporous molecular sieve).

The catalyst precursors were dried overnight at 120 °C in an air oven, after which they were calcined at 500 °C for 5 hrs to form a supported metal oxide, and crushed to a particle size below 100  $\mu\text{m}$ .

### 2. Catalyst Characterization

The BET surface area, pore volume and average pore size were estimated from nitrogen adsorption and desorption isotherm data using a constant-volume adsorption apparatus (Micromeritics, ASAP-2400). The dispersion and surface area of cobalt metal were measured by hydrogen chemisorption at 100 °C under static conditions using Micromeritics ASAP-2000 instrument equipped with a pump system providing a high vacuum of 10<sup>-6</sup> torr. Prior to the adsorption measurements, the sample (~0.5 g) was reduced in situ with hydrogen at 400 °C for 12 hrs. Hydrogen uptakes were separately determined as the difference between two successive isotherms measured at 100 °C. After the hydrogen chemisorption, the sample was reoxidized at 450 °C by 10%  $\text{O}_2$  in helium to determine the extent of reduction. The reduction degree was calculated by assuming that all metallic Co was converted to  $\text{Co}_3\text{O}_4$  [3].

Temperature programmed reduction (TPR) experiments were performed to determine the reducibility of the catalyst surface. First, the sample was pretreated in a He flow up to 350 °C, kept for 2 hrs to remove the adsorbed water and other contaminants, which was followed by cooling to 50 °C. The reducing gas containing 5%  $\text{H}_2$ /Ar mixture was passed over the samples at a flow rate of 30 ml/min with a heating rate of 10 °C/min up to 1,100 °C, and was maintained at that temperature for 30 min. The effluent gas was passed through a 5 Å molecular sieve trap to remove the generated water, and was analyzed by a GC equipped with a thermal conductive detector (TCD).



**Fig. 1. Schematic diagram of the Fischer-Tropsch reaction system.**

### 3. Apparatuses for Reaction and Product Analysis

The FTS reaction containing a gas, supercritical and liquid phase reaction was performed in a conventional, pressured, fixed-bed flow reactor system as shown in Fig. 1. The catalyst was packed into the reactor and reduced in hydrogen in argon gas flow at 400 °C for 12 hrs before the reaction. After the reduction, syngas (CO : H<sub>2</sub> : Ar=1 : 2 : 0.1 (mol ratio), Ar was used as the internal standard) in gas phase was directed to the reaction system, and the temperature and pressure of the reaction system were raised simultaneously. Once the temperature and the pressure reached the desired values, reaction time was measured. In the effect of solvent, n-hexane (C<sub>6</sub>H<sub>14</sub>, HPLC grade, Aldrich) and squalane (C<sub>30</sub>H<sub>62</sub>, 99%, Aldrich) as solvent medium were added in the gas phase reaction by a high pressure liquid pump, respectively. Typical reaction conditions were T=240 °C, P<sub>total</sub>=2.0 MPa (gas phase and squalane medium), 5.5 MPa (n-hexane medium, syngas=2.0 MPa, P<sub>n-hexane</sub>=3.5 MPa), WHSV =2,000. Argon was used as the internal standard in the feed gas.

Gaseous compounds were analyzed on-line using gas chromatographs. CO, CO<sub>2</sub>, and CH<sub>4</sub> were analyzed by using a carbosphere column with a thermal conductivity detector. Light hydrocarbon (C<sub>1</sub>-C<sub>9</sub>) was analyzed by using a GS-GASPRO capillary column with flame ionization detector. A capillary column (OV-1) with an FID was used for the analysis of the liquid compounds. The n-hexadecane was used as the internal standard for liquid products. The chain growth probability of the products was defined by the Anderson-Schulz-Flory plot, in which the carbon number extended from C<sub>9</sub>-C<sub>20</sub> [9-11].

## RESULTS AND DISCUSSION

### 1. Physicochemical Properties of Catalysts

The physicochemical properties of the catalysts are summarized in Table 1. The porous structure of the support could control the sizes of the supported cobalt particles. As expected, the BET surface area, pore volume, and average pore size of two catalysts (20% Co/SiO<sub>2</sub> in alumina support and 20% Co/Si-MMS in silica support) with high surface area supports were higher than those of the corresponding 20% Co/Al<sub>2</sub>O<sub>3</sub> and 20% Co/SiO<sub>2</sub>. In particular, the 20% Co/TiO<sub>2</sub> catalyst with the titanium support was found to have the lowest pore volume and surface out of the catalysts used. TPR is carried out to determine find out the reduction behavior of the cobalt oxide, and it is shown in Fig. 2. Reduction degree calculated by O<sub>2</sub> titration was in the following order: 20% Co/SiO<sub>2</sub>>20% Co/TiO<sub>2</sub>>

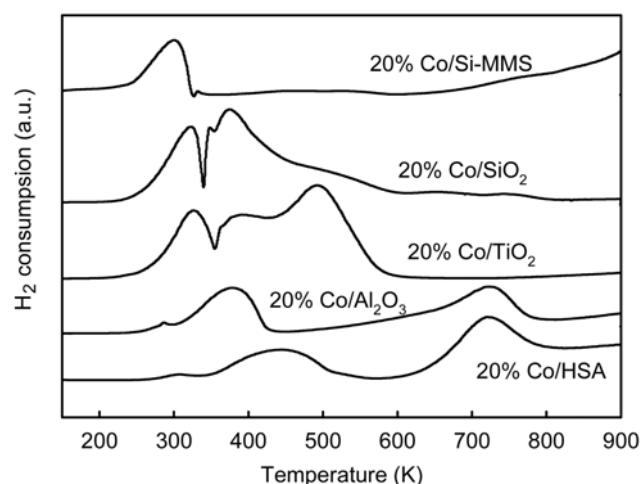


Fig. 2. Temperature programmed reduction profiles of cobalt supported catalysts.

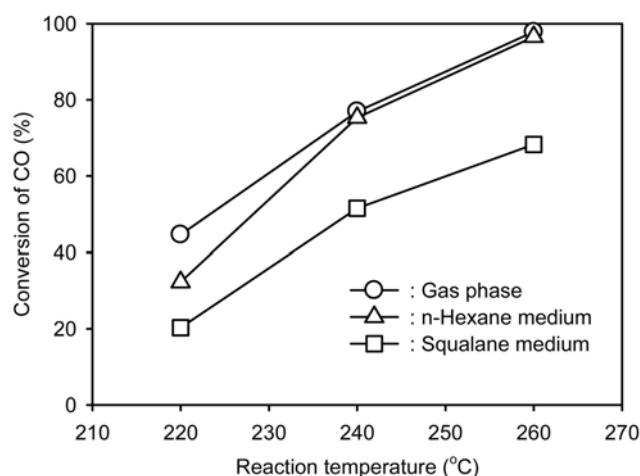


Fig. 3. Effect of reaction temperature on CO conversion in gas phase, n-hexane medium and squalane medium over 20% Co/SiO<sub>2</sub> catalyst (temperature: 260 °C, pressure in gas phase and squalane medium: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas (H<sub>2</sub>/CO) ratio=2/1, n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane or squalane)=1 cc/min).

20% Co/Al<sub>2</sub>O<sub>3</sub>>20% Co/HAS>20% Co/Si-MMS. The variety in the characteristics of the five different cobalt-based catalytic sys-

Table 1. Physical properties of the cobalt-based catalysts

	Catalysts				
	20% Co/HAS	20% Co/Al <sub>2</sub> O <sub>3</sub>	20% Co/TiO <sub>2</sub>	20% Co/SiO <sub>2</sub>	20% Co/Si-MMS
BET area (m <sup>2</sup> /g)	272.8	152.8	48.2	232.2	696.1
Pore volume (cm <sup>3</sup> /g)	0.63	0.33	0.16	0.84	0.60
Average pore size (nm)	9.29	8.83	13.12	14.48	3.46
Metal dispersion (%)	5.86	6.52	1.62	4.05	18.04
Crystal size (nm)	17.00	15.27	61.37	23.68	5.32
Reduction degree (%) <sup>a</sup>	55.80	69.13	77.51	99.90	30.12

<sup>a</sup>The degree of reduction (%) was determined by the following equation; [the amount of O<sub>2</sub> consumption (mmol O<sub>2</sub>; 3Co+2O<sub>2</sub>→Co<sub>3</sub>O<sub>4</sub>)]/[the theoretical amount of H<sub>2</sub> consumption with the assumption of fully reduced cobalt oxides (mmol H<sub>2</sub>; Co<sub>3</sub>O<sub>4</sub>+4H<sub>2</sub>→3Co+4H<sub>2</sub>O)]

tems enables a comparison of the influence of the catalyst surface characteristics on both the activity and selectivity of FTS under the reaction media applied.

## 2. Effect of Reaction Temperature and Reaction Phase on FTS over 20% Co/SiO<sub>2</sub> Catalyst

Under the reaction conditions used in this work, CO conversion decreased with time on stream at the initial stage, and then remained almost constant at the steady state as well as CH<sub>4</sub> selectivity. To compare the effect of reaction temperature and reaction phase over 20% Co/SiO<sub>2</sub>, reaction performance as a function of time-on-stream at constant temperature was carried out and each value maintained a steady state after about 40 hrs.

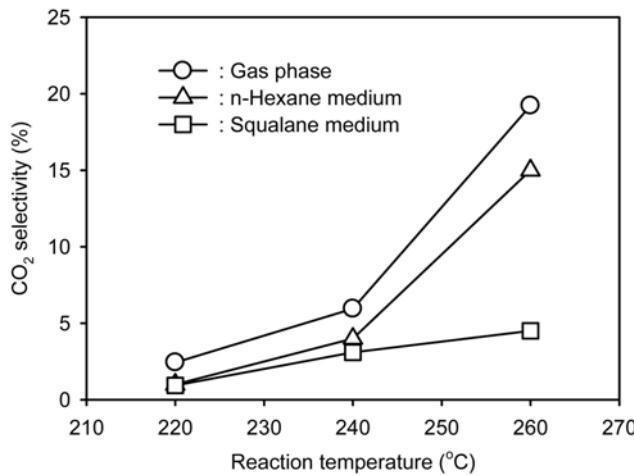


Fig. 4. Effect of reaction temperature on CO<sub>2</sub> selectivity in gas phase, n-hexane medium and squalane medium over 20% Co/SiO<sub>2</sub> catalyst (temperature: 260 °C, pressure in gas phase and squalane medium: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas (H<sub>2</sub>/CO) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane or squalane)=1 cc/min).

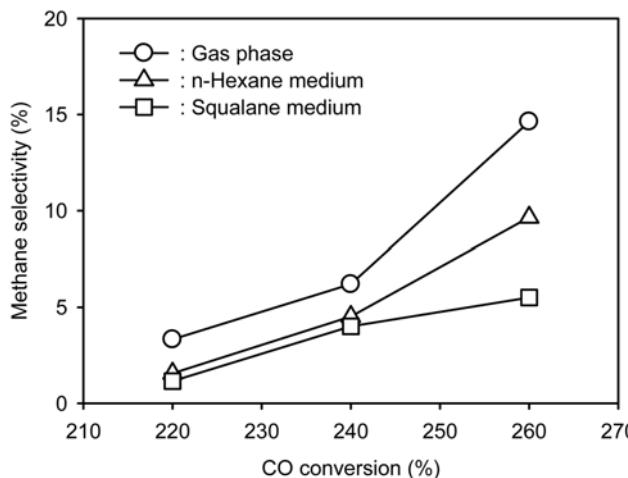


Fig. 5. Effect of reaction temperature on methane selectivity in gas phase, n-hexane medium and squalane medium over 20% Co/SiO<sub>2</sub> catalyst (temperature: 260 °C, pressure in gas phase and squalane medium: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas (H<sub>2</sub>/CO) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane or squalane)=1 cc/min).

Figs. 3-7 show the comparison of reaction performances of FTS in the gas phase only and with the media of n-hexane and squalane over 20% Co/SiO<sub>2</sub> catalyst. As shown in Fig. 3, CO conversion and selectivity of CO<sub>2</sub> and CH<sub>4</sub> increased in all reaction phases with the increasing reaction temperature, whereas the selectivity of C<sub>5+</sub> and olefin (Figs. 6 and 7) decreased. Here, olefin selectivity is calculated by C<sub>2</sub>-C<sub>4</sub> composition. Steady-state CO conversion over 240 °C was shown a similar trend under both gas phase only and n-hexane medium by high temperature owing to the hexane medium being changed into supercritical phase over 240 °C with the addition of n-hexane. However, a considerably higher CO conversion at 220 °C was shown in the gas phase only.

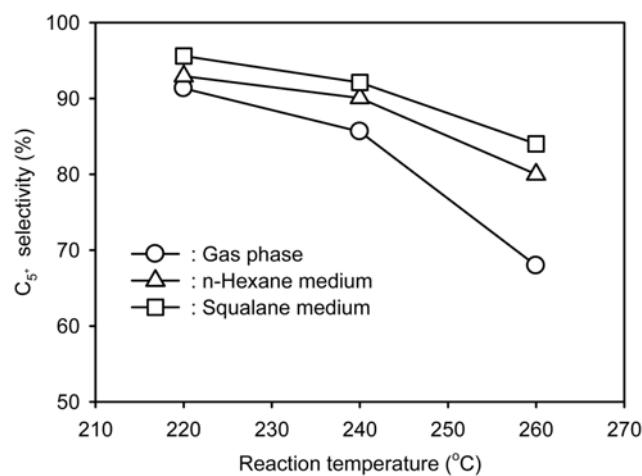


Fig. 6. Effect of reaction temperature on C<sub>5+</sub> selectivity in gas phase, n-hexane medium and squalane medium over 20% Co/SiO<sub>2</sub> catalyst (temperature: 260 °C, pressure in gas phase and squalane medium: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas (H<sub>2</sub>/CO) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane or squalane)=1 cc/min).

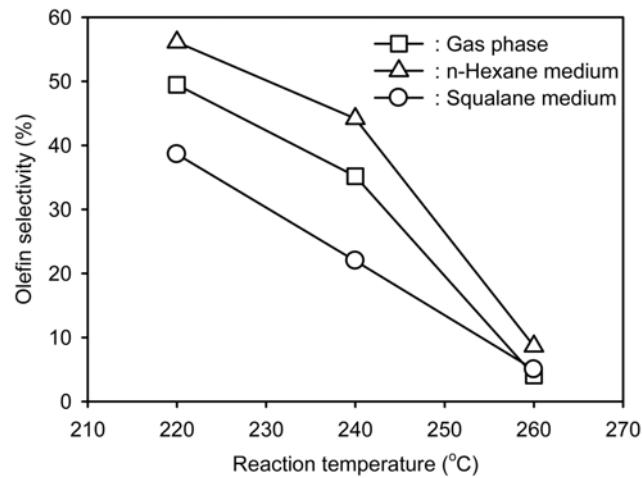


Fig. 7. Effect of reaction temperature on olefin selectivity in gas phase, n-hexane medium and squalane medium over 20% Co/SiO<sub>2</sub> catalyst (temperature: 260 °C, pressure in gas phase and squalane medium: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas (H<sub>2</sub>/CO) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane or squalane)=1 cc/min).

These results are reasonable because higher temperatures favor not only the conversion of CO but also the formation of  $\text{CH}_4$ . Carbon dioxide is mostly produced by the water gas shift reaction from the primary by-product, water. The higher the CO conversion, the more water formation. This enhances the process of the water-gas shift reaction [11,12].

In terms of the effect of the reaction phase, higher CO conversion was obtained in gas phase only reaction, whereas the olefin selectivity is higher in n-hexane medium than in gas phase and squalane medium. In addition, the undesired production of  $\text{CH}_4$  and  $\text{CO}_2$  was relatively reduced in solvent addition compared to the gas phase FTS. This result indicates that operating an FTS reaction in solvent media offers a better opportunity to minimize the selectivity of the most undesired product in the hydrocarbon products spectrum (i.e., methane), even at high CO conversion. One contributing factor involves enhanced local heat dissipation in solvent addition, such as improved heat transfer due to heat capacity and thermal conductivity [10,11]. Comparing based on olefin selectivity, a significantly higher level of olefin selectivity was observed in n-hexane addition than in the gas phase in  $\text{C}_2\text{-C}_4$  hydrocarbon portion. This phenomenon suggests that the olefins, the primary products of the FT reaction, can be effectively extracted and transported out of the catalyst particles in the fixed bed by the solvent fluid before they are read-sorbed and hydrogenated to the paraffins.

**Table 2. Catalytic performance of the cobalt-base catalysts under gas phase, n-hexane medium, and squalane medium FTS (temperature: 260 °C, pressure in gas phase and squalane medium: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas ( $\text{H}_2/\text{CO}$ ) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane or squalane)=1 cc/min)**

(a) Gas phase

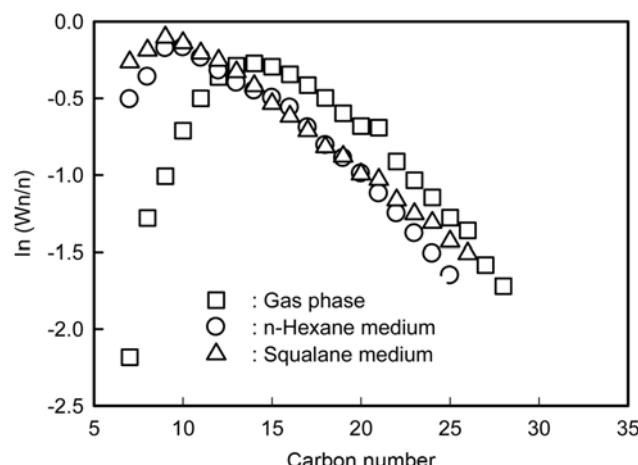
Catalyst (20 wt%)	Conv. of CO (%)	Conv. to $\text{CO}_2$ (%)	Selectivity (%)			Olefin sel. (%)
			$\text{C}_1$	$\text{C}_{2-4}$	$\text{C}_{5+}$	
20% Co/HAS	79.49	8.81	12.55	7.11	80.34	28.75
20% Co/ $\text{Al}_2\text{O}_3$	82.62	12.43	14.62	10.59	74.78	18.65
20% Co/ $\text{TiO}_2$	63.93	3.22	13.09	9.11	77.79	17.56
20% Co/ $\text{SiO}_2$	97.20	19.22	15.90	16.12	67.96	16.61
20% Co/Si-MMS	81.18	13.49	16.78	13.32	70.89	10.45

(b) n-Hexane medium

Catalyst (20 wt%)	Conv. of CO (%)	Conv. to $\text{CO}_2$ (%)	Selectivity (%)			Olefin sel. (%)
			$\text{C}_1$	$\text{C}_{2-4}$	$\text{C}_{5+}$	
20% Co/HAS	76.84	4.15	9.01	2.35	88.64	33.77
20% Co/ $\text{Al}_2\text{O}_3$	83.99	5.35	8.70	2.41	88.88	24.44
20% Co/ $\text{TiO}_2$	59.33	2.12	9.09	7.11	83.80	21.32
20% Co/ $\text{SiO}_2$	96.57	15.30	13.62	6.36	80.00	20.89
20% Co/Si-MMS	80.78	8.69	12.86	6.16	80.97	22.96

(c) Squalane medium

Catalyst (20 wt%)	Conv. of CO (%)	Conv. to $\text{CO}_2$ (%)	Selectivity (%)			Olefin sel. (%)
			$\text{C}_1$	$\text{C}_{2-4}$	$\text{C}_{5+}$	
20% Co/HAS	38.95	0.92	3.12	1.59	95.23	17.48
20% Co/ $\text{Al}_2\text{O}_3$	40.12	0.79	3.72	1.86	95.73	24.11
20% Co/ $\text{TiO}_2$	33.66	0.21	3.57	2.33	94.10	15.69
20% Co/ $\text{SiO}_2$	61.51	2.86	4.27	2.53	93.10	21.97
20% Co/Si-MMS	39.20	0.67	4.61	2.02	93.37	20.01



**Fig. 8. Effect of reaction phase on the carbon number distribution over 20% Co/ $\text{SiO}_2$  catalyst (temperature: 260 °C, pressure in gas phase and squalane medium: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas ( $\text{H}_2/\text{CO}$ ) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane or squalane)=1 cc/min).**

Fig. 8 shows the carbon number distribution of the products on gas phase only reaction and reaction medium as adding of solvents

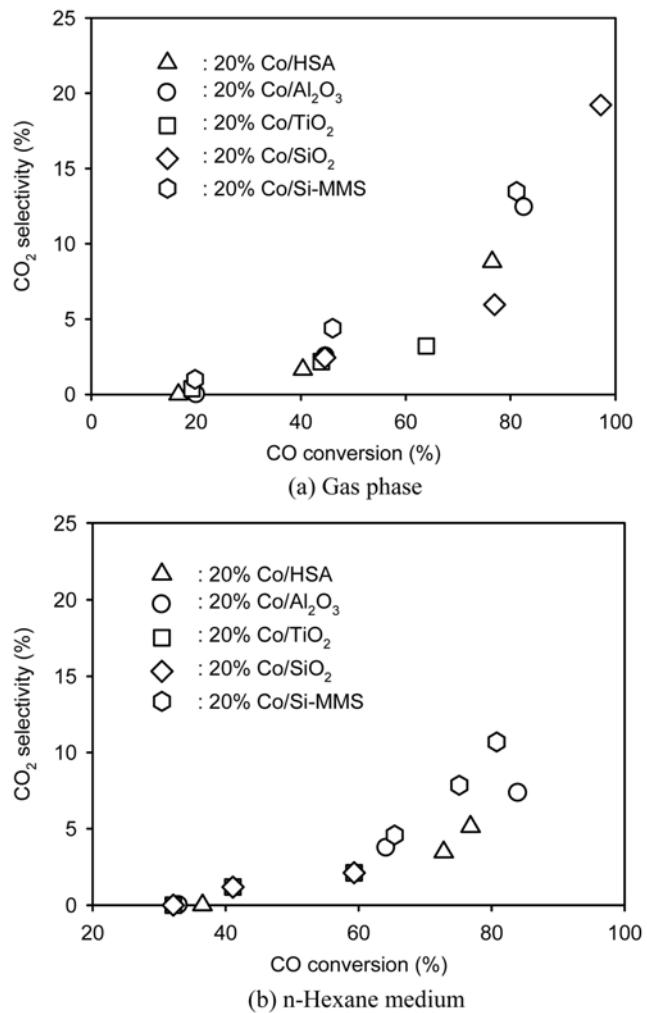
over 20% Co/SiO<sub>2</sub> catalyst. It can be seen that the  $\alpha$ -value was in the following order: squalane medium (0.89)>gas phase only (0.79)>n-hexane medium (0.72). In the gas-phase only, the carbon number distribution extended to more than 30, while on the other hand, the product distribution in the media of squalane and n-hexane was limited within the carbon number of 25. This should be considered the effect of the in situ extraction of the products, occurring with the addition of solvents, particularly with the formation of near and supercritical-phase by adding n-hexane.

### 3. Effect of the Type of Catalyst

To compare reaction performance by type of catalyst, five different supported catalysts were tested in the same 20% Co content. Table 2(a)-(c) shows the comparison of reaction performances of the types of catalysts in gas phase only (Table 2(a)), n-hexane medium (Table 2(b)) and squalane medium (Table 2(c)) at a constant reaction temperature of 260 °C. To determine the influence of the type of catalyst, CO conversion proceeded in the following order irrespective of solvent addition (Table 2): 20% Co/SiO<sub>2</sub>>20% Co/Al<sub>2</sub>O<sub>3</sub>>20% Co/HAS>20% Co/Si-MMS>20% Co/TiO<sub>2</sub>. The undesired production of CH<sub>4</sub> and CO<sub>2</sub> was relatively reduced in alumina support compared to the silica-supported catalyst, whereas the selectivity of C<sub>5+</sub> and olefin was increased. 20% Co/SiO<sub>2</sub> was shown in high CO conversion owing to its high reduction degree. Even though 20% Co/TiO<sub>2</sub> using TiO<sub>2</sub> support had a high reduction degree, low CO conversion is due to both low surface area and low metal dispersion.

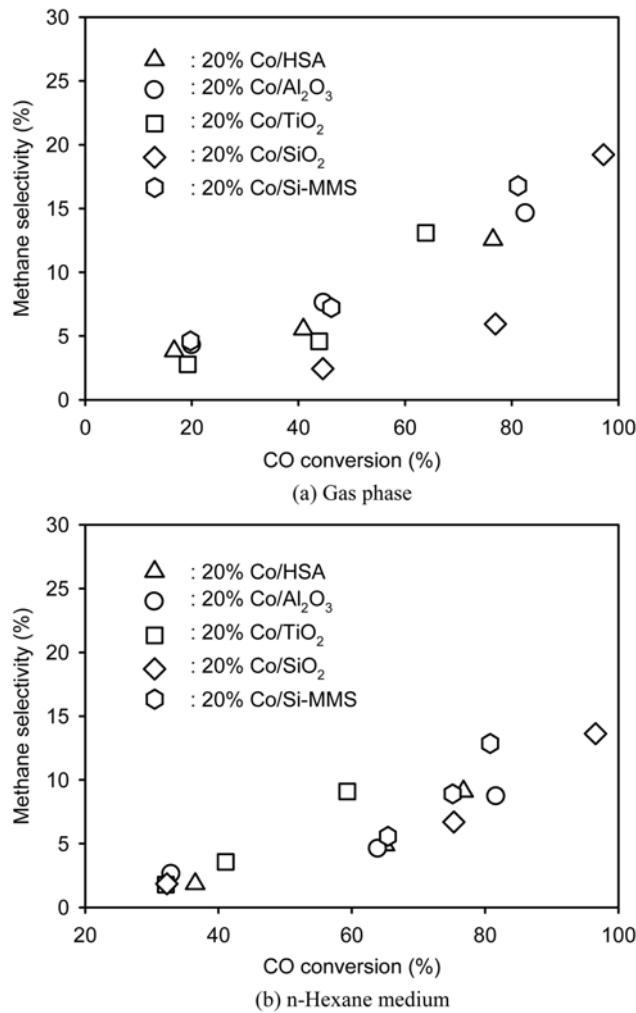
In influence of solvent addition, it can be seen that CO conversion and the selectivity of CO<sub>2</sub> and C<sub>1</sub> on the reaction phase in the same catalyst were in the following order: gas phase only>n-hexane medium>squalane medium. On the other hand, selectivity of C<sub>5+</sub> was in the following order: squalane medium>n-hexane medium>gas phase only. As shown in these results, CO conversion in the squalane medium is the lowest value, whereas CO conversion in the gas and n-hexane medium is similar except for 20% Co/TiO<sub>2</sub>. CO conversion in titanium support catalysts (20% Co/TiO<sub>2</sub>) is lower than in other catalysts, even though olefin selectivity is almost similar. Although the mass transfer rate in the n-hexane addition reaction is lower than in the gas-phase only, the olefin content in the hydrocarbons produced in the n-hexane medium was much higher than that in the gas-phase and squalane medium. This means that a fine balance between the rates of product desorption from the catalyst surface and its transfer from the catalyst pores is a characteristic feature for the effective overall transfer of the products in the n-hexane addition reaction. The olefins, therefore, were quickly extracted and transported out of the catalyst particles by the supercritical fluid before it was readsorbed and hydrogenated. On the other hand, the primary products in the gas phase only reaction, particularly those of high molecular weight, hardly desorbed to the gas phase only flow medium at all and for this reason had to be subjected to hydrogenation, resulting in their low olefin content. In the liquid-phase reaction, the low olefin content was mainly due to the slow diffusion of these olefins inside the catalyst pores, filled with liquid reaction medium, and enhanced the possibility of successive hydrogenation, even if these primary olefins desorbed quickly enough from the catalyst surface [5].

Comparing the selectivity of CO<sub>2</sub> and CH<sub>4</sub> by catalyst type, plots of CO<sub>2</sub> and CH<sub>4</sub> selectivity versus CO conversion are shown in Figs.



**Fig. 9. Effect of catalyst type on the plot of CO<sub>2</sub> selectivity versus CO conversion (a) gas phase, (b) n-hexane medium (temperature: 260 °C, pressure in gas phase: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas (H<sub>2</sub>/CO) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane)=1 cc/min).**

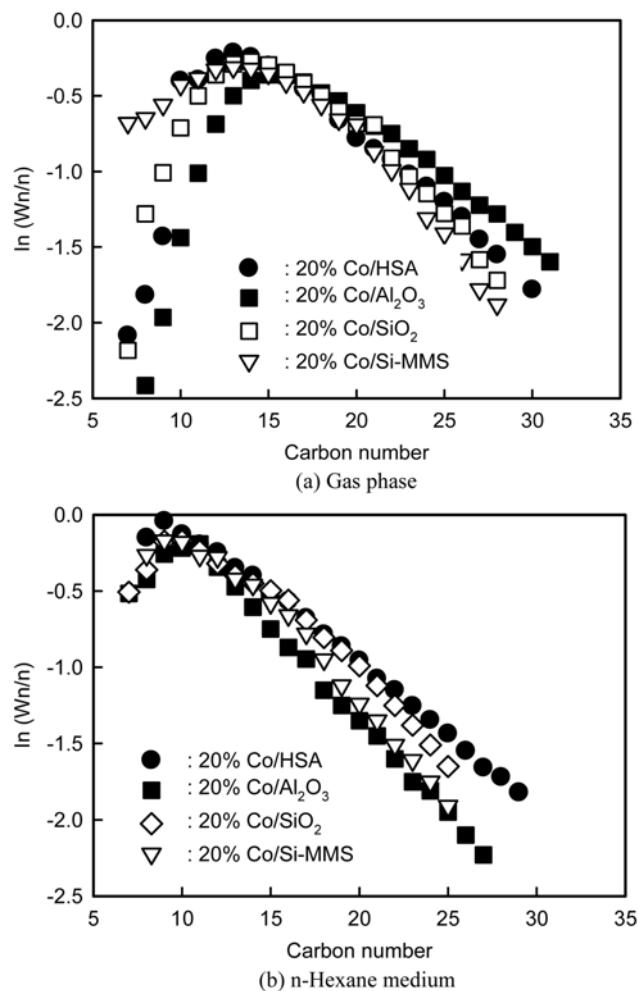
9 and 10. Fig. 9(a) and (b) shows the effect of catalyst support on CO<sub>2</sub> selectivity under gas phase and n-hexane medium. The x-axis is shown in the CO conversion instead of reaction temperature, owing to different CO conversions at the same reaction temperature. Increasing CO conversion, CO<sub>2</sub> selectivity was increased regardless of catalyst support and reaction phase. Similar CO<sub>2</sub> selectivity was obtained on the same CO conversion under different phase. However, CO<sub>2</sub> selectivity in gas phase was higher than that of the n-hexane medium. CH<sub>4</sub> selectivity has a similar tendency with CO conversion (Fig. 10(a) and (b)). It should also be noted that the methane and CO<sub>2</sub> selectivity are only higher in the gas phase than in the n-hexane medium. The interesting results shown in Fig. 10 indicate that operating FTS reaction in n-hexane media offers a better opportunity to minimize the selectivity of the most undesired product in the hydrocarbon products spectrum (i.e., methane) even at high CO conversion. In general, high temperature is favorable for the formation of methane. Therefore, the low methane selectivity in the n-hexane media should be attributed to the more effective



**Fig. 10.** Effect of catalyst type on the plot of  $\text{CH}_4$  selectivity versus CO conversion (a) gas phase, (b) n-hexane medium (temperature: 260 °C, pressure in gas phase: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas ( $\text{H}_2/\text{CO}$ ) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane)=1 cc/min).

removal of reaction heat from the catalyst surface than in the gas phase fixed bed. It has been found that solvent can also extract water in the n-hexane and squalane medium. Thus, the lower carbon dioxide selectivity in these media might be due to the quick removal of water from the catalyst bed, which suppresses the occurrence of the water gas shift reaction [11,12].

The selectivity of the products in the different catalyst supports under gas phase only and n-hexane medium FTS is shown in Fig. 11. In general, the change of the distribution of the products regardless of reaction phase applied was not obvious with the change of the operating conditions (time-on-stream, temperature, etc). The highest selectivities of hydrocarbons were at  $\text{C}_{12}$  for the 20% Co/HAS catalyst,  $\text{C}_{15}$  for the 20% Co/SiO<sub>2</sub> and 20% Co/Si-MMS, and  $\text{C}_{17}$  for the 20% Co/Al<sub>2</sub>O<sub>3</sub> catalyst. The hydrocarbons produced in the 20% Co/Catalap B were relatively richer in the heavy fractions. Table 3 shows the  $\alpha$ -value of the cobalt-base catalysts under reaction phases at 260 °C. It can be seen in the results of Table 3 that  $\alpha$ -value in the same catalyst was in the following order: squalane me-



**Fig. 11.** Effect of catalyst type on the carbon number distribution (a) gas phase, (b) n-hexane medium (temperature: 260 °C, pressure in gas phase: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas ( $\text{H}_2/\text{CO}$ ) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane)=1 cc/min).

**Table 3.**  $\alpha$ -Value of the cobalt-base catalysts under both gas phase and n-hexane medium FTS (temperature: 260 °C, pressure in gas phase: 2.0 MPa, syngas flow rate: 50 sccm/g, syngas ( $\text{H}_2/\text{CO}$ ) ratio=2/1, pressure in n-hexane medium: 5.5 MPa, solvent flow rate (n-hexane)=1 cc/min)

Catalyst (20 wt%)	Gas phase	n-Hexane medium	Squalane medium
20% Co/HAS	0.84	0.79	0.93
20% Co/Al <sub>2</sub> O <sub>3</sub>	0.75	0.78	0.91
20% Co/TiO <sub>2</sub>	0.87	0.92	0.90
20% Co/SiO <sub>2</sub>	0.79	0.72	0.89
20% Co/Si-MMS	0.79	0.76	0.91

dium>gas phase only>n-hexane medium.

## CONCLUSIONS

To gain a deeper insight into the effect of the type of support on the reaction performance on the conventional gas-phase in a Fisher-

Tropsch synthesis, the effects of catalyst supports and reaction medium (n-hexane and squalane) on the reaction behavior were mainly studied. Catalytic support used was two types of alumina (high surface alumina and commercial Catapal B) and silica ( $\text{SiO}_2$  and silica-based mesoporous molecular sieve) and  $\text{TiO}_2$ . On the effect of reaction performance on reaction medium, higher CO conversion was obtained in gas phase reaction, whereas the olefin selectivity is higher in n-hexane medium than gas phase and squalane medium. In addition, the undesired production of  $\text{CH}_4$  and  $\text{CO}_2$  was relatively reduced in n-hexane and squalane medium, compared to the gas phase FTS. Low methane selectivity was obtained in the n-hexane medium due to the effective removal of the heat from the catalyst bed by the addition of n-hexane. The olefin content of the products in the n-hexane medium was obviously higher than that in the gas phase only in fixed bed but was slightly lower than those in the squalane medium. This result suggests that the primary 1-olefins can be effectively extracted and transported by the solvent media out of the catalyst particles in the fixed bed before they are readSORBED and hydrogenated to the paraffins.

The reaction performances were also compared according to reaction temperature and the type of catalyst. CO conversion increased with increasing reaction temperature. The effect of the type of catalyst on CO conversion was as follows: 20% Co/ $\text{SiO}_2$  > 20% Co/ $\text{Al}_2\text{O}_3$  > 20% Co/HAS > 20% Co/MMS > 20% Co/ $\text{TiO}_2$ . The  $\text{C}_{5+}$  content

of products, however, was little affected by catalyst supports.

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