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Calcination Temperature Effect on Supported Ruthenium Catalysts for Fischer-Tropsch Synthesis Reaction

LI FAN*, Michiharu MIYAUCHI, and Kaoru FUJIMOTO

Dept. of Applied Chemistry, School of Engineering, The University of Tokyo,
Hongo 7-3-1, Bunkyo-ku, Tokyo 113

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Adjustment of air calcination temperature can significantly change the metal dispersion of Ru/Al₂O₃ catalyst and control the activity and selectivity of the Fischer-Tropsch synthesis. The reaction characteristics of the low-temperature-calcined catalysts were different from those of the high-temperature-calcined catalysts. The change in CO conversion by the catalysts calcined at different temperature took place in the range 200-250°C. *n*-Hexane in supercritical state was used to effectively extract high-molecular-weight products in the catalyst bed and reactor, to attain a complete distribution of the products. The chain-growth probability, as well as the olefin-to-paraffin ratio of the products was remarkably influenced by Ru dispersion. The water added to the synthesis gas promoted the chain-growth probability and enhanced the olefin contents in the products. The strength of the bond between adsorbed CO and surface Ru atoms was greatly controlled by calcination temperature. Oxygenates were formed on low-temperature-calcined catalyst but hydrocarbons were formed only on high-temperature-calcined catalyst in the ethylene-added Fischer-Tropsch reaction.

1. Introduction

In indirect conversion of fossil resources such as coal, natural gas or heavy oil into transportation fuels or chemicals, the Fischer-Tropsch (FT) synthesis that produces hydrocarbons *via* CO hydrogenation plays a key role. Ruthenium-based catalysts are known to be some of the most active FT catalysts, especially for production of long chain hydrocarbons from synthesis gas.

The effect of metal crystallite size (dispersion) in FT synthesis has been discussed in several previous studies for its great influence on the reactivity, selectivity and carbon chain-growth probability. Unfortunately, published results disagreed on the role and effect of the supported metal dispersion. There even exists an argument whether or not the FT reaction on supported Ru catalysts is structure-sensitive. Also the existence of interaction between metal and support in FT reaction is debated.

Dalla Betta *et al.* observed that methanation activity of Ru/Al₂O₃ catalysts increased with increasing dispersion. Later, they reported that hydrogenation of CO on Ru catalysts was a structure-insensitive reaction, and the initial rate of CO hydrogenation was independent of the

diameter of Ru crystallite (1.0-9.0 nm)^{1,2}. Recently, Iglesia *et al.* also reported that FT synthesis on Ru catalysts was a structure-insensitive reaction. They also reported that the specific FT catalytic activity on Ru catalysts was not influenced by the size of the metal crystallite or by the nature of the metal oxide support³⁻⁷, at least for Ru crystallites larger than about 1.6 nm. Kikuchi *et al.* reported that the specific rate of CO hydrogenation decreased by less than a factor of two when Al₂O₃ replaced TiO₂ as a support for Ru crystallites (7-19% Ru dispersion), while the chain-growth probability remained unchanged⁸. It was reported that the turnover frequency of CO hydrogenation was similar on Ru(001) and Ru(110) single crystals and it was close to that on supported Ru catalysts⁹. Moreover, it was reported that alloy effects were consistent with the structure-insensitive pathways that required small ensembles of Ru surface atoms^{10,11}.

In contrast, King observed that specific activities of supported Ru catalysts for methanation decreased from 0.16 to 0.01 s⁻¹ as Ru dispersion increased from nearly zero (Ru powder) to 64% (Ru/Al₂O₃)^{12,13}. Kellner and Bell reported King's similar observations of the relationship between dispersion and specific activity, as well as the existence of a support interaction with Ru

* To whom correspondence should be addressed.

metal^{14),15)}. However they claimed that neither the chain-growth probability nor the olefin-to-paraffin ratio was affected by Ru dispersion. In another study, the turnover rate were found to decrease markedly in the Ru dispersion range of 0 to 25%¹⁶⁾. Smith and Everson also reported a 10-fold decrease in turnover rate as the dispersion of 0.5% Ru/Al₂O₃ eggshell catalyst increased from 16 to 78%¹⁷⁾. In a study of support effects for Ru-based FT catalysts¹⁸⁾, similar conclusions were obtained. One of the present authors showed that supported Ru catalysts on a variety of carriers showed higher catalytic and higher chain-growth activities when they were calcined at higher temperatures^{19),20)}. Besides, Mieth and Schwarz prepared Ru/Al₂O₃ catalysts from various Ru-containing precursors and observed that for CO hydrogenation, turnover frequencies (TOFs) on larger Ru crystalline were higher²¹⁾.

It is considered that the contradictory observations observed in previous studies on the relationship between reaction performance (activity, selectivity, chain-growth probability) and catalyst structure (Ru particle size, support identity, metal-support interaction), should be due to low pressures and high temperatures that favored the methanation reaction in FT synthesis and that also favored extensive secondary reactions and deactivation. Moreover, high-molecular-weight hydrocarbons showed a tendency to remain inside the catalyst bed and catalyst pores, especially in the gas-phase reaction.

The objective of this study is to control Ru metal dispersion by altering the calcination temperature and to investigate the catalytic factors which affect activity, selectivity and chain-growth probability. Although the FT reaction was conducted in gas phase in the present study, supercritical phase hexane was employed after the reaction to extract the residual waxy hydrocarbons in the catalyst bed to evaluate the intrinsic capacity of the catalyst and to get an overall distribution of the products^{22)~24)}. We also reported here that added water and ethylene in the synthesis gas greatly affected the performance of FT reaction, in which alumina-supported ruthenium catalysts calcined at different temperatures were used.

2. Experimental

2.1. Catalyst Preparation

Alumina-supported Ru catalysts (Ru content: 2.0 wt%) were prepared by incipient wetness impregnation of γ -Al₂O₃ (Aerosil, C-type, 100 m²/g) with an aqueous solution of RuCl₃ (Koso Chemicals). In some reproducibility experiments, an-

other type of γ -Al₂O₃ (JRC-ALO-4, Catalysis Society of Japan, 200 m²/g) was used to eliminate the differentiation arising from other alumina supports. The impregnated samples were evacuated in a desiccator for 2 h and then dried by slow evaporation at room temperature. The catalyst precursors were dried at 120°C in air for 12 h and then calcined in air for 1 h at specified temperatures. Only ruthenium oxide was detected by XRD for ruthenium species on these catalyst precursors.

After sieving to the desired pellet sizes (60-80 mesh), all catalysts were reduced in flowing hydrogen at 150°C for 1 h, 300°C for 1 h, and 400°C for 2 h in series and then cooled to room temperature to be passivated with a diluted air stream. The catalysts were reduced *in situ* again at 400°C for 1 h before use. The catalysts at this stage were washed with hot water and the washing solution was analyzed by ion chromatography. Chlorine was neither detected by it nor by Energy Dispersive Spectroscopy (EDS) analysis. Induced Coupling Plasma (ICP) was employed to determine the Ru content in the catalyst after calcination. But it was found unchanged (1.99 wt%) for the 120°C-calcined catalyst; however, it was markedly decreased (1.95 wt%) for the 400°C-calcined catalyst, probably because of the sublimation of ruthenium oxide at higher temperatures of calcination. In order to prevent the formation of hot spots during the reaction, the catalyst was diluted to the same volume with quartz beads.

2.2. Reaction, Extraction and Analysis

The Fischer-Tropsch synthesis reaction was performed in a high pressure flow system with a fixed bed reactor in which gas phase, liquid phase, and supercritical phase reactions could all be performed. The details of the reaction apparatus and procedure have been reported elsewhere²²⁾. The catalyst was reduced in hydrogen at 400°C for 1 h, cooled to the reaction temperature and then exposed to the feed gas. All kinetic data were obtained after 4 h on stream to ensure steady-state conditions. In the reaction using the water-added synthesis gas, the water was injected quantitatively with a high-pressure microfeeder and mixed with the synthesis gas in a vaporizer which was set upstream of the catalyst bed. The stoichiometric ratio of the feed gas was maintained at H₂/CO=2.

The supercritical fluid (hexane at 45 atm and 240°C) was introduced into the reactor with a high pressure pump to extract the residual waxy products in the catalyst bed after the gas-phase FT reaction. The extracted products and supercritical fluid were collected in an ice trap downstream.

Gaseous compounds were analyzed with an on-

line gas chromatograph. CO, CH₄, and CO₂ were analyzed by using an activated charcoal column with a thermal conductivity detector. Light hydrocarbons were analyzed with a Porapak-Q column with a flame ionization detector. Effluent hydrocarbons were analyzed with Silicone SE-52 and Dexil-300 GC columns each equipped with a flame ionization detector. Some of the high molecular weight hydrocarbons were analyzed by high-temperature gel permeation chromatograph (Walters, 860/V2.2).

Serving as internal standard, 3% inert argon gas was included in the feed gas. The chain-growth probability (α value) of the product was defined by the Anderson-Schulz-Flory plot of the total products including those extracted.

2. 3. Catalyst Characterization

The ruthenium dispersion, defined as the fraction of metal atoms residing on the surface of supported metal crystallites, was determined by means of hydrogen chemisorption. Chemisorption was performed at room temperature by using a flow-through cell connected to a glass vacuum system. Passivated catalyst samples were first activated in flowing hydrogen *in situ* at 400°C for 1 h, then evacuated at 450°C for 2 h. Chemisorption of hydrogen or that of CO was determined as the difference between the first isotherm and the second isotherm, in which the second isotherm was measured following evacuation for 30 min at room temperature after the measurement of the first isotherm. The metal dispersion was calculated assuming that one hydrogen atom was chemisorbed on one surface ruthenium atom. The particle size of ruthenium metal was calculated from equation $D=11/(H/Ru)^{25}$, where D is the diameter in angstroms and H/Ru is the ratio of the number of hydrogen atoms adsorbed divided by the total number of Ru atoms in the catalyst.

Experiments on Temperature Programmed Reaction (TPR) of CO were conducted in hydrogen flow at the rate of 400°C/h after removing the physically adsorbed CO. Such products as CH₄, CO, CO₂ were analyzed by gas chromatograph equipped with a methanator and a flame ionization detector. Experiments on Temperature Programmed Desorption (TPD) was conducted similarly as those of TPR except for helium, carrier gas, and for the desorbed products, CO and CO₂. The desorbed products were analyzed by a thermal conductivity detector.

High-pressure infrared spectroscopy was recorded on JASCO A-3 infrared spectrometer with a home-made high-pressure IR cell.

X-Ray diffraction (XRD) measurements were performed with a Rigaku Rotaflex instrument

using Cu K α irradiation (40 kV, 100 mA). Scherrer equation was used to determine the average size of Ru particle. Transmission electronic microscopy (TEM) (JEOL, JEM-2010, 200 kV) was also used to observe the Ru particles.

3. Results and Discussion

3. 1. Reaction Characteristics of Ru/Al₂O₃ Calcined at Different Temperatures

3. 1. 1. Catalytic Activity

Catalytic activities of alumina-supported ruthenium catalysts calcined at 120, 200, 250, 300, and 400°C, respectively, are shown in Fig. 1. The reaction temperature was 240°C. Generally, the activity was enhanced with increasing calcination temperature but an activity gap appeared at 200°C and 250°C. To ensure reproducibility, another type of γ -Al₂O₃ (JRC-ALO-4, Catalysis Society of Japan) instead of aerosil alumina was used to prepare alumina-supported Ru catalyst. A gap in CO conversion was observed also at calcination temperature around 200-250°C, when the reaction temperature was either 240°C or 270°C, as shown in Fig. 2. It was referred that this kind of catalytic activity change was independent of the type of alumina support or of the reaction temperature, at least under the reaction conditions involved.

The results of hydrogen chemisorption, along with X-ray diffraction and transmission electronic microscopy data, are compared in Table 1. From the dispersion of Ru metal, it was found that the catalysts calcined at lower temperature had a larger dispersion. The turnover frequencies (TOFs) of various catalysts are also given in Fig. 1. The catalysts whose calcination temperature varied from 120 to 250°C exhibit similar, low TOF values. Catalysts calcined at 400°C showed remarkably large TOF values. But those calcined at lower temperature showed low TOF values even if high metal dispersions existed in these catalysts. However for the catalysts calcined at higher temperatures, the metal dispersions were low in spite of their high TOF values. It proved that Ru crystallite size remarkably influenced the intrinsic activity of FT reactions.

Another important fact for the catalysts calcined at different temperatures is the change in the chain-growth activity as shown in Fig. 3. The chain-growth probability of the catalyst calcined at 120°C or at 200°C was low and nearly the same (0.84 and 0.86). On the other hand, catalysts calcined at 250°C, 300°C or 400°C displayed another pattern of product distribution, that is, they included more high-molecular-weight products; also the chain-growth probabilities of

Ru/Al₂O₃ (Aerosil), 2 wt%, 21 atm, 240°C, H₂/CO=2/1, W/F=4 g·h/mol.

Fig. 1 The Relationship among CO Conversion, H₂ Uptake, Turnover Frequency, and Catalyst Calcination Temperature

Ru/Al₂O₃ (JRC-ALO-4), 2 wt%, 21 atm, H₂/CO=2/1, W/F=2 g·h/mol.

Fig. 2 The Relationship among CO Conversion and Catalyst Calcination Temperature

Table 1 Particle Size of Supported Ru Crystalline

Calcination temp. [°C]	120	200	250	300	400
H/Ru	0.24	0.22	0.16	0.14	0.04
D=11/(H/Ru) [Å]	46	50	68	79	275
XRD [Å]	nd ^{a)}	nd	nd	144	360
TEM [Å]	55	76	88	115	310

a) Not detected in XRD data.

these catalysts were higher (0.93-0.96). It should be noted that the products here included not only the effluent products but also the extracted products from inside the catalyst bed with a supercritical fluid. Chain-growth probability is greatly controlled by Ru crystallite size, as predicted by Nijs and Jacobs²⁶.

The same reaction condition as in Fig. 1.

Fig. 3 Hydrocarbon Product Distributions of Various Catalyst

The reason for the remarkable changes in activity and selectivity of the catalyst calcined between 200°C and 250°C is not clear, because the compromising effect of TOF change and dispersion variation derived from different calcination temperatures seem unable to elucidate all details clearly. Presumably, the Ru particles on the catalyst calcined at 200°C and 250°C in air had a special crystalline configuration to influence the CO adsorption state. It was estimated that Ru atoms on the crystalline faces were more active than those at the edges or corners^{14), 27-30)}. Similarly, it can be expected that high-temperature-calcined alumina-supported ruthenium possessed a different crystallographic plane, where the CO adsorbed could be decomposed more efficiently, leading to a high chain-growth probability and a gap in the relationship between CO conversion and catalyst calcination temperature. We also agreed that the SMSI effect did not appear to influence the catalytic rates here because of the exposure to the water produced in the FT synthesis⁷⁾.

Many of the contradicting reports on the effects of dispersion and supports may reflect the differences in operating conditions, that can alter the identity and structural requirements of the rate-limiting step. Previously reported effects on dispersion and supports on Ru catalysts were obtained under the conditions that favored the formation of light products.

3.1.2. Selectivity and Carbon-chain Growth Probability

Heavy hydrocarbon products often accumulate inside the catalyst pores in common gas-phase FT reactions, especially in heavy hydrocarbon synthesis. The present authors have developed a

Supercritical fluid: *n*-hexane, 240°C, 45 atm. Extraction time: 1 h.

Fig. 4 Comparison of Distribution of Effluent and Extracted Products

supercritical phase Fischer-Tropsch synthesis reaction to suppress deactivation of the catalyst^{(22)~(24)}. The quick mass transfer and heat transfer in the supercritical-phase FT reaction led to effective extraction of waxy products *in situ* and prevented secondary reactions of olefins. A satisfactory product distribution by gas-phase FT reaction could be attained if the residual waxy products inside the catalyst pores and the catalyst bed were extracted by supercritical fluid after gas-phase reaction. **Figure 4** shows the distribution of effluent and extracted products for the catalyst calcined at 120°C or at 400°C. It should be noted that extraction of the residual hydrocarbons was implemented after the reaction. Standard reaction time was 10 h. The amount of residual hydrocarbons per hour was determined by dividing the total extracted hydrocarbons by reaction time. It is astonishing that for the catalyst calcined at 400°C (**Table 2**), more than half of the total hydrocarbon products (carbon base) remained inside the catalyst bed instead of flowing out of the reactor. The total product distribution of the 400°C-calcined catalyst was a flat distribution and was likely to produce high-molecular-weight hydrocarbons, and as a result, the chain-growth probability was as high as 0.96; however the chain-growth probability of 120°C-calcined catalyst was lower (0.86) under the same conditions. Thus, it could be concluded that the carbon-chain growth

probability was higher on larger ruthenium particles.

Some investigators advocated that the chain-growth probability was independent of the Ru crystalline size in the supported Ru catalyst for FT synthesis^{(1)~(11)}. Based on the fact that so much waxy products remained inside the catalyst pores, the chain-growth probability should be calculated carefully in the gas-phase FT reaction especially for Ru catalysts that could produce much heavy hydrocarbons. Full "spectra" of total products are necessary to determine the intrinsic chain-growth probability. In fact, high-temperature gel permeation chromatography analysis showed that the average molecular weight (weight average) of the solid-state extracted hydrocarbons (prepared by evaporation of the extracted products and solvent in vacuum) formed on the 120°C-calcined catalyst was 570 while that on the 400°C-calcined catalyst was 1000.

Both 400°C-calcined and 120°C-calcined catalysts showed stable activity during 10 h of reaction. As mentioned above, all data were obtained after 4 h of reaction from the start to ensure a steady state. It was found that 120°C-calcined catalyst reached the steady state after 4 h, while the 400°C-calcined catalyst attained it after 3 h. Steady state requires the formation of waxy liquid inside the catalyst micropores and the equilibrium between desorption of hydrocarbons from the catalyst inner surface and diffusion of syngas as well as that of the hydrocarbons. As 400°C-calcined catalyst produced more waxy hydrocarbons, it could attain a steady state more rapidly.

Figure 5 indicates a difference in the olefin contents of the products of 120°C- and 400°C-calcined catalysts, in which more olefins were found in the 400°C-calcined catalyst. However, the difference was not changed by reaction period.

Olefins which are considered primary products in FT synthesis can be readsorbed onto the Ru sites to undergo such secondary reactions as hydrogenation to paraffin, chain propagation, isomerization, and others. The above difference in reaction performances of the catalysts calcined at different temperatures could be attributed to several reasons: at first, for the 120°C-calcined catalyst, Ru particles are small, so the adsorbed CO would be difficult to be decomposed, as will be explained below. Consequently, the active carbide produced from the decomposition of adsorbed CO was little and the adsorbed hydrogen concentration on the catalyst surface was relatively higher. Olefins could be hydrogenated more easily than would be involved in a chain-growth reaction. Secondly, it seems that small Ru par-

Fig. 5 Olefin Content in FT Reaction Product of 120°C- and 400°C-Calcined Catalysts

Table 2 Reaction Behavior of Catalyst Calcined at Different Temperatures

Calcination temp.	[°C]	120	400
CO conversion	[%]	55	40
Metal dispersion (H/Ru)		0.24	0.04
Turnover frequency	[s ⁻¹]	0.53	2.38
Chain-growth probability		0.84	0.96
Residual ratio ^{a)}		0.31	0.55
Propene/(Propane+Propene)		0.51	0.77
CO ₂ formation rate	[mmol/g·h]	0.26	0.05

a) The ratio of extracted hydrocarbons to total hydrocarbons. Reaction conditions: Ru/ γ -Al₂O₃, 2 wt%, Gas phase, 240°C, 21 atm, H₂/CO=2, W/F=4 g·h/mol, Particle size: 60-80 mesh.

ticles could enhance the decomposition of H₂O more effectively and lead to a high surface hydrogen concentration³¹⁾. Lastly, for the catalyst treated at 120°C, the primary olefins could be readsorbed more readily onto the surface-active Ru sites to undergo secondary hydrogenation while being transported inside the catalyst pellets, because of its high surface Ru site concentration²²⁾.

It is interesting to find that the rate of formation of carbon dioxide was also different for 120°C and 400°C calcined catalysts as shown in **Table 2**. The rate of CO₂ formation on 120°C-calcined catalyst was about five times higher than that on 400°C-calcined catalyst.

The slow rate of CO₂ formation on larger ruthenium particles in the FT synthesis indicated that the surface oxygen, product CO dissociation, reacted with surface hydrogen kinetically more rapidly than with the CO adsorbed on the surface. Another possibility for CO₂ formation is the water gas shift reaction on the surface by the FT by-product water and CO:

Surface species are indicated by s. The low possibility of this reaction occurring on 400°C-

calcined catalyst should be attributed to the low concentration of surface hydroxyl or to the low ability of water dissociation on large Ru particles.

Over highly dispersed Ru, some of the reasons for large quantities of CO₂ formed can be the rapid removal of surface oxygen by CO instead of by hydrogen and the occurrence of effective surface water gas shift reaction. In this case, it is suggested that highly dispersed ruthenium has effective sites to cleave H₂O³¹⁾.

3. 2. Effect of Calcination Temperature on Catalytic Features

3. 2. 1. Effect of Added Water

Water is a byproduct in the Fischer-Tropsch synthesis. Water was provided as a component in the feed gas to enhance the partial pressure of hydrogen by water gas shift reaction. In order to fix the partial pressure ratio of CO and H₂, nitrogen gas was used as the balancing gas to compensate the pressure change resulted from water gas. It was found that the rate of CO₂ formation increased tremendously in the water-added FT reaction. The main reason for this was the water gas shift reaction. **Figure 6** exhibits the relationship between the hydrocarbon yield of the FT reaction and the partial pressure of water of its feed gas. It was interesting to note that, for the catalyst calcined at 120°C, the hydrocarbon yield increased when the water gas partial pressure was increased, but when it became above 3.4 atm, the hydrocarbon yield was increased but only to some extent. As opposed to this, the hydrocarbon yield was decreased slightly when the water gas partial pressure increased for the catalyst calcined at 400°C.

The simulation model of FT reaction kinetics showed that both limited diffusion of CO and limited transportation olefin readsorption could affect the activity and selectivity of FT reaction process^{4), 7), 22)}. For the catalyst calcined at 120°C, which had higher Ru surface atom density, the limited diffusion behavior of reactant CO had greater impact on the activity and selectivity of FT reaction than the transportation of primary olefins. As the 120°C-calcined catalyst had a larger surface of Ru site because of its high Ru dispersion, the CO concentration inside the pellet dropped more sharply than that inside the 400°C-calcined catalyst pellet³²⁾. The CO diffusion restriction could be released and the intrapellet CO concentration could be enhanced when the water partial pressure was increased, because the dissolved water selectively increased the diffusivity of the diffusion-limited reactant CO, due to the affinity between them. It is referred that CO concentration inside 120°C-calcined catalyst increased more remarkably.

Ru/Al₂O₃ (Aerosil), 2 wt%, 21 atm, 240°C, H₂/CO=2/1, W/F=2 g·h/mol.

P_{CO}=5.1 atm, P_{H₂}=10.5 atm, P_{H₂O}+P_{N₂}=5.4 atm.

Fig. 6 Effect of Added Water in the Feed Gas: Water Partial Pressure vs. Hydrocarbon Yield

In contrast, the removal of the hydrocarbon products played a more obvious role than the arrival of reactant CO for the 400°C-calcined catalyst which had a lower surface Ru atom concentration. Increased water partial pressure had but slight influence on the transportation of primary olefins due to the weak affinity between water and hydrocarbons. The 400°C-calcined catalyst produced more high-molecular-weight and olefinic hydrocarbons in greater yields, as exhibited in Figs. 3-5. The CO in 400°C-calcined catalyst could not diffuse rapidly through the waxy membrane to reach the Ru surface^{(22), (23)}, for gas-phase FT reaction. Meanwhile olefins adsorbed more strongly than paraffins onto the Ru surface, to hinder the mass transfer efficiency^{(3), (4), (19)}. Consequently, the increased intrapellet CO concentration could not contribute effectively to hydrocarbon formation for 400°C-calcined catalyst.

Moreover, hydrocarbon distributions under various water partial pressures for 120°C or for 400°C calcined catalyst are shown in Fig. 7. On either of the two catalysts, the proportion of light hydrocarbons in the total product decreased and that of heavy hydrocarbons increased when the partial pressure of water increased, but methane formation was restrained especially by increasing the water vapor partial pressure. In general, the 400°C-calcined catalyst could produce more heavy hydrocarbons, in other words, exhibited higher chain-growth probability than the 120°C-calcined catalyst, even if water gas was added to the feed gas.

Several reasons for the above observations can be offered: when the partial pressure of water was increased on the inner surface of the catalyst pellet, water could suppress the desorption of hydrocarbon products and could inhibit secondary

The same reaction condition as in Fig. 6.

Fig. 7 Product Distribution of Water-added Fischer-Tropsch Reaction under Various Water Partial Pressures

hydrogenation of the olefins because of their low affinity to water, as Nijs and Jacobs had observed that water enhanced the readsorption of some light olefins on Ru catalysts⁽³³⁾. As a result, the residence time of the primary hydrocarbon products was extended and the chain-growth probability was enhanced due to the readsorption of the primary products. Another reason refers to the adsorption of water onto the metal surface sites that suppressed the adsorption of hydrogen onto it to decrease the possibility of carbon chain growth termination. Another possible reason is that water was capable of increasing the diffusivity of CO molecules inside catalyst pellets and the concentration of CO near the chain growth site was enhanced, relatively the partial pressure of hydrogen decreased. The hydrogen-lack circumstances were favorable to carbon chain propagation because it would make carbon chain termination probability decreased. We found that the olefin content in the water-cofed FT reaction products increased remarkably. This fact is interesting because the partial pressure of hydrogen was increased and it was higher in the water-fed FT reaction compared with the nonfed FT reaction because of the water gas shift reaction, even if the activity was slightly decreased when water was

Tabel 3 Effect of Ethylene Addition to Feed Gas

Calcination temp. [°C]		120		400	
C ₂ H ₄ feed	[mmol/g·h]	0	16.8	0	16.8
CH ₄ yield	[mmol/g·h]	1.48	0.71	0.41	0.32
C ₂ H ₆ yield	[mmol/g·h]	0.05	9.46	0.01	16.85
C ₂ H ₄ yield	[mmol/g·h]	0.02	3.09 ^{a)}	0.01	0.84 ^{a)}
C ₃ H ₈ yield	[mmol/g·h]	0.05	0.08	0.01	0.02
C ₃ H ₆ yield	[mmol/g·h]	0.15	0.27	0.03	0.05
C ₄ H ₁₀ yield	[mmol/g·h]	0.06	0.09	0.02	0.01
C ₄ H ₈ yield	[mmol/g·h]	0.11	0.17	0.02	0.01
<i>n</i> -C ₃ H ₇ OH	[mmol/g·h]	0	1.50	0	0.06
C ₂ H ₅ CHO	[mmol/g·h]	0	0.28	0	0.02

240°C, 21 bar, *W/F*=4.0 g·h/mol, CO/H₂=1/2.

a) Unreacted ethylene.

introduced into the feed gas.

3. 2. 2. Reactions of Added Ethylene

As compared in Table 3, ethylene was added to the feed gas as probe molecule to investigate its effects on catalyst reaction. With the 120°C-calcined catalyst, ethylene was formed from syngas at a rate of 0.02 mmol/g·h in the conventional FT reaction. It was calculated that 81.6% of the added ethylene reacted, of which, 56.2% was hydrogenated to ethane while 1.7% to propionaldehyde and 8.9% to propyl alcohol. The residual 14.8% was involved in the chain growth that resulted in increasing formation rates of C₃, C₄ but decreasing rate of methane formation.

With the 400°C-calcined catalyst, 95.0% of the added ethylene reacted; however nearly all of it was hydrogenated to ethane. Only 0.1% of the added ethylene was converted to propionaldehyde and 0.4% to propyl alcohol. The contribution of the added ethylene to chain growth was not obvious, since there was no change in the chain-growth probability. On either catalysts calcined at 120°C and 400°C, methane selectivity was suppressed by addition of ethylene, probably by the combination of added ethylene and carbene. Carbene was recognized as the precursor of methane.

As will be discussed in detail below, for 120°C-calcined catalyst, small Ru crystalline can not easily decompose the CO combination of the adsorbed CO. The hydroformylation reaction that occurred between nondissociative adsorbed CO and propyl species led to oxygenate formation. But for 400°C-calcined catalyst, CO adsorbed dissociatively onto large Ru crystallines to enhance the chain-growth probability, and the possibility of oxygenate formation was very low.

3. 3. Characteristics of Adsorbed Carbon Monoxide

3. 3. 1. IR Spectra of Adsorbed CO

High pressure IR was utilized to probe the reaction behavior of syngas and hydrocarbons on Ru catalysts. In Fig. 8 the IR spectra of adsorbed species reacting on the 120°C-calcined catalyst

at 240°C are shown. The large absorbance at 2064 cm⁻¹ and 2000 cm⁻¹ should be assigned to the adsorbed CO. Its strength did not change with ethylene introduction. The absorbance peaks at 2978, 2958, 2878, 1476, 1447 cm⁻¹ were attributed to the C-H bond, and the strengths of these bands increased when ethylene was introduced into syngas, indicating that the added ethylene adsorbed onto the Ru surface.

As shown in Fig. 8, on the 400°C-calcined catalyst, the absorbance at 2040 cm⁻¹, which represents the adsorbed CO on Ru, was very small. This evidence supports the fact that 400°C-calcined catalyst had a small metal surface and cleaved the CO bond more easily. Peaks at 2914 cm⁻¹ and 2846 cm⁻¹ represent the C-H stretch vibration. Strengths of these peaks were larger than those on the 120°C-calcined catalyst, for the adsorption of syngas only. This observation is in good accordance with the reaction performance that TOF of CO hydrogenation is higher on the higher-temperature-calcined catalyst. As similar to the case of 120°C-calcined catalyst, 1474 cm⁻¹ and 1441 cm⁻¹ which appeared after the introduction of ethylene should be considered as brought about by ethylene adsorption.

3. 3. 2. TPR and TPD of Adsorbed CO

In Fig. 9, the TPR profiles of the catalysts calcined at 120°C and 400°C are shown. For the 120°C-calcined catalyst, the main peak of methane formation is located at 160°C, but it is shifted to 240°C for the 400°C-calcined catalyst. It seemed that the combination between Ru atom and adsorbed CO was stronger when the catalyst was calcined at high temperature.

The TPD results shown in Fig. 10 characterize different desorption behavior of the catalysts calcined at different temperatures in air. The desorbed product was CO formed along with CO₂ via disproportionation reaction of the adsorbed CO. It is shown that, for the catalyst calcined at 120°C, the distribution of the CO₂ formed was extended to higher temperatures about to 380°C. A large amount of CO could be detected at low temperatures. On the other hand, for the catalyst calcined at 400°C, the main fraction of the CO₂ formed was shifted to lower temperatures and it could not be detected above 300°C. Meanwhile, the CO desorbed could not be detected at low temperatures and it was concentrated at above about 200°C.

Considering the route of CO₂ formation in TPD experiments, it seemed that on the 120°C-calcined catalyst, the adsorbed CO had a strong carbon-oxygen bond and thus a weak metal-carbon bond. Reversely, the adsorbed CO on the 400°C-calcined

Gas phase, 21 atm, flow rate: 40 ml/min, H₂/CO=2/1.

Fig. 8 Comparison of IR Spectra for 2 wt% Ru/Al₂O₃ Catalysts

catalyst had a tight metal-carbon combination and a loose carbon-oxygen bond.

Much work has been done in correlating the catalytic activity of the FT reaction with the characteristics of different crystallographic planes³⁴. Yokohama *et al.*³⁵ proved that CO molecule ad-

Fig. 9 Temperature Programmed Reaction (TPR) Profiles of Adsorbed CO on Ru/Al₂O₃ (Aerosil) Calcined at Different Temperature with 6.67 K/min

Fig. 10 Temperature Programmed Desorption (TPD) Spectra of Adsorbed CO on Ru/Al₂O₃ (Aerosil) Calcined at Different Temperature with 6.67 K/min

sorbed on the incomplete coordination sites of the metal surface, such as steps or kinks on crystalline planes, formed in a linear mode. But on the flat plane of a metal surface, one CO molecule was readily adsorbed by an assembly of Ru atoms, resulting in a bridge mode or other mode of combination between carbon and multiple metal atoms.

It is considered here that carbon monoxide adsorbed on a flat Ru plane exhibits a strong ruthenium-carbon combination and thus a weak carbon-oxygen bonding, similar to the behavior expected on Ru/Al₂O₃ calcined at 400°C. The present authors found that on the alumina-supported Ru catalyst calcined at 427°C, the bridge-type adsorbed CO was more active to hydrogenation than the linear-type adsorbed CO and it was the main source of hydrocarbons formed in the usual FT reaction temperature³⁶⁾. On the 400°C-calcined catalyst of large-size crystallites and flat Ru atom planes, more CO seems to be adsorbed in the bridge type, and the carbon atom was coordinated by more than one surface Ru atom. This strong metal-carbon combination structure weakened carbon-oxygen bond and it was readily to cleave because of the electron shift. On the other hand, for 120°C-calcined catalyst, in which there were more unperfected spots and incomplete coordination surroundings for constructing a linear-type CO adsorption structure, the carbon-oxygen bond was somewhat too strong to be cut off and it was not favorable for hydrogenation, as well as for carbon chain growth, as its reaction performance had indicated.

The TPD results are not contradictory to TPR profiles. The formation of methane from adsorbed CO consisted of two main steps: the cleavage of carbon-oxygen bond and hydrogenation of surface carbide. As shown, the main peak of methane for 400°C-calcined catalyst was at 240°C, which was higher than 160°C for 120°C-calcined catalyst. The difference could be attributed to the strong combination of metal-carbon bond on a large, flat Ru plane in the Ru crystalline. This type of carbide was difficult for complete hydrogenation to form methane³⁷⁾ but was resultantly favorable for carbon chain propagation to form partially hydrogenated species: -CH₂- or -CH₃-. This should be the reason that the carbon chain-growth probability was so high on the 400°C-calcined Ru catalyst.

4. Conclusions

Calcination temperature in the preparation of catalysts showed remarkable effects on the reaction characteristics by controlling such factors as metal dispersion and structural change.

1) The Fischer-Tropsch synthesis reaction on the alumina-supported ruthenium catalyst was structure-sensitive. The specific activity of large supported Ru crystalline was somewhat higher than that of smaller one. However, the apparent activity of the catalyst calcined at lower tem-

peratures was higher due to its high metal dispersion.

2) On the high-temperature-calcined catalysts, the carbon chain-growth probability was higher, and more waxy products remained inside the catalyst bed and reactor. Also, high-temperature-calcined catalysts were favorable for producing more olefins than low-temperature-calcined ones.

3) Addition of water to syngas enhanced the chain-growth probability as well as the olefin-to-paraffin ratio of the products. For the catalyst calcined at 120°C, the hydrocarbon yield increased as water gas partial pressure was increased, but the yield decreased slightly when water gas partial pressure was increased for the catalyst calcined at 400°C.

4) In the ethylene-added FT reaction, oxygenates formed markedly on the 120°C-calcined catalyst due to the hydroformylation reaction. But this reaction was not observed on 400°C-calcined catalyst.

5) For the adsorption of CO on the Ru site, the metal-carbon bond was stronger on the larger Ru crystalline while the carbon-oxygen bond became weaker, but on the smaller Ru crystalline, relatively weak metal-carbon combination as well as strong carbon-oxygen bond existed.

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References

- 1) Dalla-Betta, R. A., Piken, A. G., Shelef, M., *J. Catal.*, **35**, 54 (1974).
- 2) Dalla-Betta, R. A., Piken, A. G., Shelef, M., *J. Catal.*, **40**, 173 (1975).
- 3) Iglesia, E., Soled, S. L., Fiato, R. A., *J. Catal.*, **137**, 212 (1992).
- 4) Iglesia, E., Reyes, S. C., Madon, R. J., *J. Catal.*, **129**, 238 (1991).
- 5) Madon, R. J., Iglesia, E., *J. Catal.*, **139**, 576 (1993).
- 6) Iglesia, E., Soled, S. L., Fiato, R. A., Via, G. H., *J. Catal.*, **143**, 345 (1993).
- 7) Iglesia, E., Reyes, S. C., Madon, R. J., Soled, S. L., *Adv. Catal.*, **39**, 221 (1993).
- 8) Kikuchi, E., Matsumoto, M., Takahashi, T., Machino, A., Morita, Y., *Appl. Catal.*, **10**, 251 (1984).
- 9) Kelzenberg, J. C., King, T. S., *J. Catal.*, **126**, 421 (1990).
- 10) Datye, A. K., Schwank, J., *J. Catal.*, **93**, 256 (1985).
- 11) Peden, C. H. F., Goodman, D. W., *Ind. Eng. Chem. Fundam.*, **25**, 58 (1986).
- 12) King, D. L., *J. Catal.*, **51**, 386 (1978).
- 13) King, D. L., *J. Catal.*, **35**, 54 (1978).
- 14) Kellner, C. S., Bell, A. T., *J. Catal.*, **75**, 251 (1982).
- 15) Kellner, C. S., Bell, A. T., *J. Catal.*, **71**, 296 (1981).
- 16) van Hardeveld, R., Hartog, F., *Adv. Catal. Relat. Subjects*, **22**, 75 (1972).

- 17) Smith, K. J., Everson, R. C., *J. Catal.*, **99**, 349 (1986).
- 18) Stoop, F., Verbiest, A. M. G., Van der Wiele, K., *Appl. Catal.*, **25**, 51 (1986).
- 19) Fujimoto, K., Nobusawa, T., Fukushima, T., Tominaga, H., *Bull. Chem. Soc. Jpn.*, **58**, 3164 (1985).
- 20) Fukushima, T., Fujimoto, K., Tominaga, H., *Appl. Catal.*, **14**, 95 (1985).
- 21) Mieth, J. A., Schwarz, J. A., *J. Catal.*, **118**, 203 (1989).
- 22) Fan, L., Yokota, K., Fujimoto, K., *AIChE J.*, **38**, 1638 (1992).
- 23) Yokota, K., Fujimoto, K., *Ind. Eng. Chem. Res.*, **30**, 95 (1991).
- 24) Yokota, K., Hanakata, Y., Fujimoto, K., *Chem. Eng. Sci.*, **45**, 2743 (1990).
- 25) Anderson, J. R., "Structure of Metallic Catalysts," Academic Press, London (1975).
- 26) Nijs, H. H., Jacobs, P. A., *J. Catal.*, **65**, 328 (1980).
- 27) Poltorak, O. M., Boronin, V. S., *Russ. J. Phys. Chem.*, **40**, 1436 (1966).
- 28) Van Hardeveld, R., Hartog, F., *Surf. Sci.*, **15**, 189 (1969).
- 29) Van Hardeveld, R., Hartog, F., *Adv. Catal.*, **22**, 75 (1972).
- 30) Basset, J. M., Ugo, R., "Aspects of Homogeneous Catalysis," ed. by Ugo, R., Vol. 3, Reidel, Boston (1977).
- 31) Abrevaya, H., Cohn, M. J., Targos, W. M., Robota, H. J., *Catal. Lett.*, **7**, 183 (1990).
- 32) Fan, L., Yokota, K., Fujimoto, K., *Topics in Catalysis*, **2**, 267 (1995).
- 33) Nijs, H. H., Jacobs, P. A., *J. Catal.*, **66**, 401 (1980).
- 34) Vannice, M. A., "Catalysis, Science and Technology," eds. by Anderson, J. R., Boudart, M., Vol. 3, Springer-Verlag, Berlin (1982).
- 35) Yokohama, A., Komiyama, H., Inoue, H., Matsumoto, T., Kimura, H., *J. Catal.*, **68**, 355 (1981).
- 36) Fujimoto, K., Kameyama, M., Kunugi, T., *J. Catal.*, **61**, 7 (1980).
- 37) Poncet, V., van Barneveld, W. A., *Ind. Eng. Chem., Prod. Res. Dev.*, **18**, 268 (1979).

要 旨

担持ルテニウム触媒を用いる Fischer-Tropsch 合成： 触媒焼成温度の反応挙動への影響

範 立, 宮内 理治, 藤元 薫

東京大学工学部応用化学科, 113 東京都文京区本郷 7-3-1

アルミナに担持したルテニウム触媒の空気焼成温度が変わると、金属分散度など触媒物性が変化したので、担持ルテニウム触媒を用いた Fischer-Tropsch 合成の反応挙動も大きく変化した。この反応挙動は低温焼成触媒と高温焼成触媒の二つのパターンに分けられる。アルミナに担持したルテニウム触媒上の Fischer-Tropsch 合成反応は構造敏感反応であった。超臨界流体を用いて反応後の触媒層に残された高分子量炭化水素を抽出して分析したが、炭素連鎖成長確率とオレフィン/パラフィン

比は金属分散度に大きく依存することが分かった。合成ガスに水を添加すると、炭素連鎖成長確率とオレフィンの割合は増加した。一方、合成ガスにエチレンを添加すると、低温焼成の触媒ではアルコール、アルデヒドなど含酸素化合物の生成が見られ、高温焼成の触媒ではこのような含酸素化合物の生成はできなかった。吸着 CO とルテニウム表面の結合の強さがルテニウム粒子のサイズに制御され、反応成績に影響した。

Keywords

Fischer-Tropsch synthesis, Ruthenium catalyst, Catalyst structure, Calcination, Extraction