TECHNICAL PROGRESS REPORT

**For Period Ending 3-31-05
(November 1, 2004 to March 31, 2005)**

Award Number DE-FC26-03NT41964

Sponsor: DOE Pittsburgh Energy Technology Center

**Design, Synthesis, and Mechanistic Evaluation of Iron-Based
Catalysis for Synthesis Gas Conversion to Fuels and Chemicals**

Akio Ishikawa, Manuel Ojeda, and Enrique Iglesia
Department of Chemical Engineering
University of California at Berkeley
Berkeley, CA 94720

DISCLAIMER:

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This project explores the extension of previously discovered Fe-based catalysts to hydrogen-poor synthesis gas streams derived from coal and biomass sources. These catalysts have previously shown unprecedented Fischer-Tropsch synthesis rate, selectivity with synthesis gas derived from methane. During the first reporting period, we certified a microreactor, installed required analytical equipment, and reproduced synthetic protocols and catalytic performance previously reported. During the second reporting period, we prepared several Fe-based compositions for Fischer-Tropsch synthesis and tested the effects of product recycle under both subcritical and supercritical conditions.

During this third reporting period, we have prepared a large number of Fe-based catalyst compositions using precipitation and impregnations methods with both supercritical and subcritical drying and with the systematic use of surface active agents to prevent pore collapse during drying steps required in synthetic protocols. These samples were characterized during this period using X-ray diffraction, surface area, and temperature-programmed reduction measurements. These studies have shown that these synthesis methods lead to even higher surface areas than in our previous studies and confirm the crystalline structures of these materials and their reactivity in both oxide-carbide interconversions and in Fischer-Tropsch synthesis catalysis. Fischer-Tropsch synthesis reaction rates and selectivities with low H_2/CO ratio feeds ($H_2/CO = 1$) were the highest reported in the literature at the low-temperature and relatively low pressure in our measurements. Current studies are exploring the optimization of the sequence of impregnation of Cu, K, and Ru promoters, of the activation and reaction conditions, and of the co-addition of light hydrocarbons to increase diffusion rates of primary olefin products so as to increase the selectivity to unsaturated products. Finally, we are also addressing the detailed kinetic response of optimized catalysts to reaction conditions (temperature, partial pressures of H_2 , CO , H_2O , CO_2 , olefins) in an effort to further increase rates and olefin and C_{5+} selectivities.

TABLE OF CONTENTS

TITLE PAGE	1
DISCLAIMER	2
ABSTRACT	3
TABLE OF CONTENTS	4
EXECUTIVE SUMMARY	5
OBJECTIVES AND SPECIFIC TASKS	6
TECHNICAL ACTIVITIES AND ACCOMPLISHMENTS	7
IMMEDIATE NEXT STEPS AND RESEARCH PLAN	9
APPENDIX A:	
1. EXPERIMENTAL DETAILS	10
2. RESULTS AND DISCUSSION	
2.1 <i>List of Prepared Catalysts, Preparation Method and BET Surface Area</i>	11
2.2 <i>Characterization of Iron Catalysts</i>	14
2.3 <i>Effect of Activation Condition on Fisher-Tropsch Synthesis Rate and Selectivity</i>	16
2.4 <i>Effect of Synthesis Gas Ratio ($H_2/CO = 1$ and $H_2/CO = 2$) on Fisher-Tropsch Synthesis Rate and Selectivity</i>	18
2.5 <i>Effect of Ru and Cu on Fisher-Tropsch Synthesis Rate and Selectivity Using Synthesis Gas ($H_2/CO = 1$)</i>	21
APPENDIX B:	
<i>Steady State FTS performance of Various Fe-Based catalysts Using Natural Gas-Driven Synthesis Gas ($H_2/CO = 1.7-2.0$)</i>	24

EXECUTIVE SUMMARY

This project exploits our recent discovery of catalyst compositions and synthesis and activation protocols that lead to iron-based catalysts with Fischer-Tropsch synthesis rates and selectivities similar to those on cobalt-based catalyst using stoichiometric H_2/CO streams at the low temperatures required to form olefins and large hydrocarbon chains with minimal selectivity to light products. These materials are being tested in this project for the conversion of substoichiometric synthesis gas streams to explore whether the unprecedented activities and selectivities achieved with synthesis gas compositions derived from natural gas can be extended to these more demanding synthesis gas ratios. Fe-based catalysts convert synthesis gas streams derived from coal and biomass, because they reject oxygen as CO_2 instead of water from CO-rich streams. Fe catalysts are much less active than Co-based catalysts, which reject oxygen as H_2O . Also, Fe-based catalysts are often less stable because phase transformations lead to structural disintegration. Higher Fischer-Tropsch synthesis (FTS) rates, lower CO_2 selectivity and greater structural stability remain critical hurdles to the conversion of H_2 -poor synthesis gas streams to high-value fuels and petrochemicals.

During the first reporting period, we certified a microreactor, installed required analytical equipment, and reproduced synthetic protocols and catalytic performance previously reported. During the second reporting period, we prepared several Fe-based compositions for Fischer-Tropsch synthesis and tested the effects of product recycle under both subcritical and supercritical conditions.

During this third reporting period, we have prepared a large number of Fe-based catalyst compositions using precipitation and impregnations methods with both supercritical and subcritical drying and with the systematic use of surface active agents to prevent pore collapse during drying steps required in synthetic protocols. These samples were characterized during this period using X-ray diffraction, surface area, and temperature-programmed reduction measurements. These studies have shown that these synthesis methods lead to even higher surface areas than in our previous studies and confirm the crystalline structures of these materials and their reactivity in both oxide-carbide interconversions and in Fischer-Tropsch synthesis catalysis. Fischer-Tropsch synthesis reaction rates and selectivities with low H_2/CO ratio feeds ($\text{H}_2/\text{CO} = 1$) were the highest reported in the literature at the low-temperature and relatively low pressure in our measurements. Current studies are exploring the optimization of the sequence of impregnation of Cu, K, and Ru promoters, of the activation and reaction conditions, and of the co-addition of light hydrocarbons to increase diffusion rates of primary olefin products so as to increase the selectivity to unsaturated products. Finally, we are also addressing the detailed kinetic response of optimized catalysts to reaction conditions (temperature, partial pressures of H_2 , CO, H_2O , CO_2 , olefins) in an effort to further increase rates and olefin and C_{5+} selectivities.

Design, Synthesis, and Mechanistic Evaluation of Iron-Based Catalysis for Synthesis Gas Conversion to Fuels and Chemicals

Description of Tasks

Task One (Years 1 and 2)

Extension of synthesis and activating protocols for Fe-based catalysts prepared by precipitation, treatment with surface-active agents, activation in synthesis gas, and promotion by Ru to materials suitable Fischer-Tropsch synthesis with coal- and biomass-derived synthesis gas

Task Two (Years 1 and 2)

Characterization of carbide-oxide phase transformations and their impact on catalyst mechanical integrity using electron microscopy and in situ X-ray absorption protocols

Task Three (Years 2 and 3)

Exploratory studies of the effects of CO₂ and light hydrocarbon recycle on the rate and selectivity of FTS reactions at low H₂/CO ratios on optimized Fe-based catalysts (developed in part (i))

(Tasks one and two were all of the first two years, task three started halfway through year two)

Objectives and Specific Tasks

Fe-based catalysts are typically preferred for converting coal or biomass derived synthesis gas streams with low H₂/CO ratios (H₂/CO = 0.7-1) because their significant water-gas shift activity ($\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2$) leads to rejection of excess carbon as CO₂. Fe-based catalysts typically show much lower catalytic activities than Co-based catalysts and lower mechanical stability, as a result of their tendency to interconvert between oxide and carbide phases as the redox properties change within catalytic reactors. Fe-based catalysts with higher Fischer-Tropsch synthesis (FTS) activity and greater structural integrity remain significant obstacles to their use in the synthesis of high-value fuels and petrochemicals.

Iron-based catalysts with FTS activities and selectivities similar to those on cobalt-based catalyst using stoichiometric H₂/CO streams derived from natural gas were recently reported by our research group. Novel synthesis methods based on supercritical and subcritical drying of powders after precipitation at a constant pH

led to significant improvements in the surface area of oxide precursors, while activation and promotion protocols led to active Fe carbide clusters with high surface areas and mechanical strength. These gave in turn unprecedented activity and C_5^+ selectivity during use with stoichiometric synthesis gas ($H_2/CO = 2$).

The principal objectives of this project are to:

1. optimize synthesis protocols to prepare Fe-based catalysts with FTS rates and hydrocarbon product distributions similar to those of Co-based materials using surface-active compounds and supercritical conditions and explore the use of Ru as activation promoter
2. evaluate the performance of prepared catalysts in synthesis gas streams derived from coal or biomass ($H_2/CO = 0.7-1.0$) and optimize activation protocols for high activity, selectivity and mechanical integrity
3. determine the effects of Ru loading and mode of addition on the concentration of active sites and on the intrinsic activity and selectivity of such active sites
4. establish the extent and dynamics of carbide-oxide transformations during reactions of synthesis gas mixtures with varying redox potential and their influence on the structural integrity and stability of Fe-based catalysts

Technical Activities and Accomplishments (FY 2005)

Two new post-doctoral fellows have arrived at Berkeley during this reporting period. Dr. Akio Ishikawa arrived at Berkeley on November 2004 and Dr. Manuel Ojeda on January 2005.

A beamtime request has been scheduled on May 2005 as part of an approved proposal at the Stanford Synchrotron Radiation Laboratory (SSRL) to carry out in-situ X-ray absorption spectroscopy (XAS) assessments of the structure and phase transformations of these materials during catalytic Fischer-Tropsch synthesis.

During this third reporting period, we have prepared and characterized a large number of Fe-based catalyst compositions and measured their Fischer-Tropsch synthesis reaction rates and selectivities. These studies have

- (1) established synthesis method of iron-based catalysts with higher surface area compared to the previous work.
- (2) determined the crystal structure of prepared catalysts.
- (3) shown that the activities of optimized Fe-based catalysts using synthesis gas with low H_2/CO ratios ($H_2/CO = 1$) are similar to those of catalysts using synthesis gas with $H_2/CO = 2$.
- (4) demonstrated the relative promoting effects of Cu and Ru as reduction enhancers and optimized the impregnation and drying protocols for greatest utilization of these reduction promoters
- (5) certified a second microreactor unit for more efficient testing of Fe-based Fischer-Tropsch synthesis catalysts.

Detailed results, findings and conclusions are included in the last part of this report as sections:

- 2.1 List of Prepared Catalysts, Preparation Method and BET Surface Area*
- 2.2 Characterization of Iron Catalysts*
- 2.3 Effect of Activation Condition on Fisher-Tropsch Synthesis Rate and Selectivity*
- 2.4 Effect of Synthesis Gas Ratio ($H_2/CO = 1$ and $H_2/CO = 2$) on Fisher-Tropsch Synthesis Rate and Selectivity*
- 2.5 Effect of Ru and Cu on Fisher-Tropsch Synthesis Rate and Selectivity Using Synthesis Gas ($H_2/CO = 1$)*

Immediate Next Steps and Research Plan are:

During the next reporting period, we will continue to explore the synthesis and activating protocols for Fe-based catalysts prepared by precipitation, treatment with surface-active agents, activation in synthesis gas, and promotion by Ru and Cu to materials suitable Fischer-Tropsch synthesis with coal- and biomass-derived synthesis gas and to examine the synthesis catalysis. We will also characterize their structure and surface properties by X-ray absorption and site titration methods before and after activation in synthesis gas at typical reaction condition. Specifically, we will characterize the extent of carbide-oxide phase transformations and their impact on catalyst mechanical integrity using electron detailed study of the effects of CO₂ recycle on selectivity and stability of these materials at low H₂ ratios on optimized Fe-based catalysts.

We will also extend the program into a limited exploratory study of the effects of additive concentrations and identity on rate and selectivity, as well as on the chemical and mechanical stability of these materials. This will prepare the project for year three, in which a chosen optimized composition and structure will be examined for longer terms and selectivity modified by recycling strategies in which CO₂ or light hydrocarbons are added to H₂-CO mixtures to test their impact on transport restrictions and morphological changes. During year two, these learnings will be assembled into an understanding model that will be used to suggest additional compositional, structural, or operational modifications best suited for the design and synthesis of materials with improved activity, selectivity and stability.

Detailed results, findings and conclusions

1. Experimental details

1.1 Synthesis of Precursors and Catalysts

Fe-Zn oxide precursors were prepared by co-precipitation from a mixed solution of Fe and Zn nitrates using ammonium carbonate. A solution containing $\text{Fe}(\text{NO}_3)_3$ (Aldrich, 98%, 3.0 M) and $\text{Zn}(\text{NO}_3)_2$ (Aldrich, 98+%, 1.4 M) at Zn/Fe atomic ratio of 0.1 was added into a large flask containing deionized water (ca. 100 mL) at 353 K at a rate of 120 mL/h using a liquid pump. A $(\text{NH}_4)_2\text{CO}_3$ (Aldrich, 99.9%, 1.0 M) solution was added separately into this flask at rate required to maintain the pH at constant value of 7.0 ± 0.1 , measured by pH meter (DENVER Ins., UB-10). The precipitated powder (30 g) were washed five times with isopropanol (ca 30 mL/g each time), dried in ambient air at 393 K overnight, and then treated in flowing dry air at 543 K for 4 h. Magnetic stirring was used during isopropanol washing in order to increase the rate at which liquid water within pores was replaced by the isopropanol. The K, Cu, and Ru promoters were added to these Fe-Zn oxide precursors by incipient wetness impregnation with aqueous solutions of K_2CO_3 (Aldrich, 99.99%), $\text{Cu}(\text{NO}_3)_2$ (Aldrich, 99.99%), or ruthenium (III) nitrosyl nitrate $[\text{Ru}(\text{NO})(\text{NO}_3)_x(\text{OH})_y \text{ (} x+y = 3 \text{)}]$ (Aldrich, dilute nitric acid solution, Ru 1.5%). These impregnated samples were then dried 393 K in ambient air. Finally, the samples were treated in flowing dry air at 543 K for 4 h. The resulting oxide precursors are denoted throughout as Fe-Zn-K₄, Fe-Zn-K₄-Ru₂, and Fe-Zn-K₆-Ru₃, respectively. The subscripts denote the atomic content of the corresponding promoter divided by the Fe atomic content and multiplied by 100. These catalysts were pressed into pellets, lightly crushed, and then sieved to retain the 100-180 mesh fraction for FTS reaction.

1.2 Fischer-Tropsch Synthesis Reaction and Product Selectivity

Fischer-Tropsch synthesis rates and selectivities were measured in a single-pass packed-bed reactor with plug-flow hydrodynamics. This reactor was held within a resistively-heated three-zone furnace. All lines after the reactor were kept at 433-553 K and a vessel placed immediately after the reactor was held at 408 K to collect liquid products.

Reactant and product streams were analyzed online using a gas chromatograph (Agilent Technologies, model 6890N). The analysis of N_2 , CO, CO_2 , and CH_4 was performed using a thermal conductivity detector and a Porapak Q packed-column (15.2 cm $\times$ 0.318 cm diameter). All hydrocarbons up to C_{15} were analyzed on-line using flame ionization detection and a cross-linked methyl silicone capillary column (HP-1, 50 m $\times$ 0.32 mm; 1.05 μm film).

Fe catalysts (100-180 μ , 0.4 g) were diluted with 11 g of quartz granules (100-180 μ) to avoid temperature gradients. Quartz was washed with concentrated nitric

acid and treated in air at 973 K before use. Catalysts were activated using flowing synthesis gas ($H_2/CO = 2$) at 0.1 MPa by increasing the temperature from 298 to 423 K at a rate of 10 K/min and from 423 to 543 K at 1 K/min. The catalysts were held at 543 K for 1 h. After activation, the temperature was decreased to 508 K, and the synthesis gas ($H_2/CO = 1$) pressure was gradually increased to 2.14 MPa. FTS reactions were carried out with the synthesis gas (Praxair; $H_2/CO/N_2$ mixture; (i) 0.62/0.31/0.07 [$H_2/CO = 2$], or (ii) 0.46/0.46/0.08 mol [$H_2/CO = 1$]) as reactant at 2.14 MPa gas pressure and 508 K.

1.3 Temperature-Programmed Reduction of Fe-Zn-K-Cu(Ru) Oxides in H_2

The reduction kinetics of promoted Fe-Zn oxide precursors were measured using temperature-programmed reaction (TPR) methods with H_2 as reactant. Samples (50 mg, 100-180 μ) were placed within a quartz cell (5 mm i.d.). These samples were heated in 20% H_2/Ar (80 mL/min) to 1173 K at 10 K/min. The rate and amount of H_2 consumption were measured by thermal conductivity analysis of inlet and outlet streams.

2. Results and Discussion

2.1 List of Prepared Catalysts, Preparation Method and BET Surface Area

The list of prepared catalysts, preparation methods, and BET surface areas are summarized in Table 1-1 and Table 1-2. The surface area measured by N_2 adsorption at 77 K were 251-291 m^2/g for oxyhydroxide precipitates obtained by drying in ambient air at 393 K. The surface area for Fe-Zn oxides decreased after drying in flowing air at 543 K for 4 h. The addition of K, Cu and Ru promoters to Fe-Zn oxides also decreased their surface area, apparently because of pore collapse caused by the removal of high surface tension intrapore liquids. The surface area for all Fe-Zn-K-Cu(Ru) catalysts were 2.5-3 times as high as those in the conventionally prepared Fe-Zn-K-Cu(Ru) (ca 60 m^2/g) via washing and drying processes involving pure water. In this study, Fe-Zn-K-Cu(Ru) catalysts were obtained high surface area compared to those for Fe-Zn-K-Cu(Ru) in the previous works (120 m^2/g).

Table1-1 List of Prepared Iron Catalyst, Preparation Method and BET Surface Area

Catalyst Code	Relative Composition (atom %)					Preparation Method	BET surface area
	Fe	Zn	K	Cu	Ru		m ² /g-cat
AK01-001 (FeZn hydroxide precipitate)	100	10	-	-	-	Co-precipitation, surface-active isopropanol replacement, followed by overnight drying in ambient air at 393 K	251
AK01-002 (FeZn oxide)	100	10	-	-	-	Drying of AK01-001 in flowing air at 623 K for 1h	198
AK01-003 (FeZnK ₄ Cu ₂)	100	10	4	2	-	K addition to AK01-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air. Cu was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	-
AK02-001 (FeZn hydroxide precipitate)	100	10	-	-	-	Co-precipitation, surface-active isopropanol replacement, followed by overnight drying in ambient air at 393 K	258
AK02-002 (FeZn oxide)	100	10	-	-	-	Drying of AK02-001 in flowing air at 543 K for 4h	198
AK02-003 (FeZnK ₄ Ru ₂)	100	10	4	-	2	K addition to AK02-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air. Ru was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	151
AK02-004 (FeZnK ₄ Ru)	100	10	4	-	1	K addition to AK02-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air. Ru was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	156
AK02-005 (FeZnK ₄ Ru ₄)	100	10	4	-	4	K addition to AK02-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air. Ru was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	123
AK02-006 (FeZnK ₄)	100	10	4	-	-	K addition to AK02-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air and 543 K drying in dring air for 4h.	178
AK02-007 (FeZnK ₆ Ru ₃)	100	10	6	-	3	K addition to AK02-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air. Ru was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	147

Table 1-2 List of Iron Catalyst Prepared, Preparation Method and BET Surface Area

AK03-001 (FeZn hydroxide precipitate)	100	10	-	-	-	Co-precipitaion, suface-active isopropanol replacement, followed by overnight drying in ambient air at 393 K	-
AK03-002 (FeZn)	100	10	-	-	-	Drying of AK03-001 in flowing air at 543 K for 4h	174
AK03-003 (FeZnK ₄ Ru)	100	10	4	-	1	K addition to AK03-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air. Ru was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	144
AK03-004 (FeZnK ₆ Cu ₃)	100	10	6	3	-	K addition to AK03-003 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air. Ru was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	141
AK04-001 (FeZn hydroxide precipitate)	100	10	-	-	-	Co-precipitaion, suface-active isopropanol replacement, followed by overnight drying in ambient air at 393 K	291
AK04-002 (FeZn oxide)	100	10	-	-	-	Drying of AK04-001 in flowing air at 543 K for 4h	154
AK05-001 (FeZn hydroxide precipitate)	100	10	-	-	-	Co-precipitaion, suface-active isopropanol replacement, followed by overnight drying in ambient air at 393 K	291
AK05-002 (FeZn oxide)	100	10	-	-	-	Drying of AK05-001 in flowing air at 543 K for 4h	237
AK05-003 (FeZnK ₅ Ru ₂)	100	10	5	-	2	Ru addition to AK05-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air and 543 K drying in dring air for 4h. K was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	179
AK05-004 (FeZnK ₆)	100	10	6	-	-	K addition to AK05-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air and 543 K drying in dring air for 4h.	-
AK05-005 (FeZnK ₆ Ru ₃)	100	10	6	-	3	Ru addition to AK05-002 first: incipient wetness impregnation (aqueous) by aqueous promoter additions followed by overnight drying 393 K in ambient air and 543 K drying in dring air for 4h. K was added in second step, followed by overnight drying at 393 K in ambient air and 543 K drying in dring air for 4h.	-

2.2 Characterization of Iron Catalysts

Fig. 1 XRD patterns for (a) Fe-Zn oxide, (b) Fe-Zn-K₆-Cu₃, (c) Fe-Zn-K₆-Ru₃, and (d) Fe-Zn-K₅-Ru₂.

Figure 1 shows X-ray diffraction (XRD) patterns for iron catalysts. All catalysts included two phases of Fe₂O₃ and FeOOH. The weak intensities of XRD patterns suggest that the crystallite sizes of catalysts are small and the samples include an amorphous phase. The crystallite sizes of Fe₂O₃ powders were determined by the Scherrer equation, using the (104) reflection ($2\theta = 33.4$ degree) of Fe₂O₃ for calculation. The crystallite size of catalysts increased with promoters addition. The crystallite size of Fe-Zn oxide was estimated to be ~ 6 nm. The crystallite size of Fe-Zn-K₆-Cu₃ and Fe-Zn-K₆-Ru₃ were estimated to be ~ 15 nm. Transmission electron microscopy (TEM) image and electron diffraction pattern are, however, needed to confirm these preliminary details.

Figure 2 shows oxygen removal rates for Fe-Zn-K₄, Fe-Zn-K₆-Cu₃ and Fe-Zn-K₅-Ru₃ oxides as a function of temperature during exposure to flowing H₂. For comparison, the oxygen removal rates for Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ in previous work are also shown in Figure 2. The amount of oxygen removed in each of the two major reduction peaks indicate that the reduction of Fe-Zn-K-Cu(Ru) follows the same sequential reduction steps observed for Fe₂O₃. Fe₂O₃ reduces to Fe₃O₄ and then to Fe in two steps with distinct kinetics. Fe-Zn-K₄, Fe-Zn-K₆-Cu₃ and Fe-Zn-K₅-Ru₃ oxides were prepared using a solvent replacement method. Fe-Zn-K₂, Fe-Zn-K₂-Cu₁, and Fe-Zn-K₂-Ru₁ in previous work were prepared with only pure water as a solvent. The different synthesis method results in the different surface area reported here for these catalysts. The surface area for catalysts obtained via a solvent replacement method are 2.5-3 times as high as those in previous work. The reduction of Fe-Zn-K₄ to Fe₃O₄ and Fe occurred at lower temperature compared to those of Fe-Zn-K₂. It appears that the high surface area and small crystallite size lead to reduction at lower temperature than on Fe-Zn-K₂. The addition of Cu and Ru to Fe-Zn-K oxides led to incipient reduction at lower temperature than on samples without Cu or Ru. The amount of oxygen removed during these incipient reduction processes increased with increasing amounts of Cu or Ru (Figure 2 (c) and (d), or (e) and (f)). These results reflect the formation of hydrogen dissociation sites by reduction of CuO to Cu metal or RuO to Ru metal at low temperatures. In particular, Ru promoted efficiently the reduction of Fe₂O₃ to Fe₃O₄ and Fe₃O₄ to Fe at the lowest temperature among all catalysts.

Fig. 2 Oxygen removal rates for Fe-Zn-K-Cu(Ru) oxides in H₂. (a) Fe-Zn-K₂^{ref}, (b) Fe-Zn-K₄, (c) Fe-Zn-K₂-Cu₁^{ref}, (d) Fe-Zn-K₆-Cu₃, (e) Fe-Zn-K₂-Ru₁^{ref}, and (f) Fe-Zn-K₅-Ru₂. Sample: 50 mg, 10 °C/min ramping rate; 20% H₂/Ar, 80 mL/min flow rate). ref: J. Catal. **2002**, 206, 202.

2.3 Effect of Activation Conditions on Fischer-Tropsch Synthesis Rates and Selectivities

During the activation process, Fe_2O_3 in catalysts reduces to Fe_3O_4 , Fe metal, and Fe_xC . The relative concentrations and rates of formation among those reduced Fe species depend on the composition of the synthesis gas and on the temperature used during the activation procedures and also during catalysis. It was expected that the different ratio of H_2 and CO in synthesis gases would lead to different catalytic activity and selectivity for the Fischer-Tropsch synthesis. Therefore, the effect of activation conditions on Fischer-Tropsch synthesis rate and selectivity using two synthesis gases with different H_2/CO ratio ($\text{H}_2/\text{CO} = 1$ and $\text{H}_2/\text{CO} = 2$) was investigated. In this section, catalysts were activated as follow. Catalysts were activated using flowing synthesis gas ($\text{H}_2/\text{CO} = 1$ or $\text{H}_2/\text{CO} = 2$) at 0.1 MPa by increasing the temperature from 298 to 423 K at a rate of 10 K/min and from 423 to 543 K at 1 K/min. The catalysts were held at 543 K for 1 h. After activation, the temperature was decreased to 508 K, and the synthesis gas ($\text{H}_2/\text{CO} = 1$) pressure was gradually increased to 2.14 MPa. FTS reactions were carried out with the synthesis gas with $\text{H}_2/\text{CO} = 1$ as reactant at 2.14 MPa gas pressure and 508 K.

Figure 3 shows the steady-state FTS rates on Fe-Zn-K₄-Ru₂ activated by synthesis gas streams with $\text{H}_2/\text{CO} = 1$ and $\text{H}_2/\text{CO} = 2$ at 543 K for 1 h. The steady-state FTS rates on Fe-Zn-K₄-Ru₂ activated by synthesis gas ($\text{H}_2/\text{CO} = 2$) were higher than those on the catalyst activated by synthesis gas ($\text{H}_2/\text{CO} = 1$). In this report hereafter, catalysts were activated by using $\text{H}_2/\text{CO} = 2$ at 543 K for 1 h. We will characterize their structure and investigate the effect of catalyst activation condition in detail during the next reporting period. Optimization of catalyst activation protocols is currently under investigation.

Fig. 3 Steady state formation rate on Fe-Zn-K₄-Ru₂ as a function of CO conversion (508 K and synthesis gas: 2.14 MPa, H₂/CO = 1).

Open mark: Catalyst was activated under synthesis gas (H₂/CO = 1).

Close mark: Catalyst was activated under synthesis gas (H₂/CO = 2).

2.4 Effect of Synthesis Gas Ratio ($H_2/CO = 1$ and $H_2/CO = 2$) on Fisher-Tropsch Synthesis Rate and Selectivity

The catalysts with high activities under synthesis gas streams with low H_2/CO ratios ($H_2/CO = 0.7-1$) are desired for FTS reaction from the view point of coal and biomass conversion to useful fuels and petrochemicals. Iron-based catalysts with FTS activities and selectivities similar to those on cobalt-based catalyst were recently reported by our research group at high H_2/CO ratios typical of synthesis gas streams derived from natural gas. Fe-based catalysts are useful for coal- and biomass-derived synthesis gas streams because oxygen rejection by excess CO reactants allows more efficient use of these CO-rich streams. As the next step, we measured, FTS rates and selectivities on those catalysts under synthesis gas stream with low H_2/CO ratios ($H_2/CO = 1$).

In FTS reaction, catalysts produce hydrocarbon via the following reactions:

where equation (4) is the water-gas shift reaction. The selectivities and steady-state FTS rates on Fe-Zn-K₆-Cu₃ as a function of CO conversion using two different composition of synthesis gas ($H_2/CO = 1$ and $H_2/CO = 2$) are shown in Figure 4. C_5^+ selectivity and CO_2 formation rate on Fe-Zn-K₆-Cu₃ under synthesis gas stream with $H_2/CO = 1$ were higher than those with $H_2/CO = 2$. On the other hand, CH_4 selectivity and hydrocarbon formation rate under synthesis gas stream with $H_2/CO = 1$ were lower than those with $H_2/CO = 2$. With $H_2/CO = 1$ ratio synthesis gas, H_2 partial pressures are lower than that with $H_2/CO = 2$ and this favors chain growth (eq. 2) and water-gas shift (eq. 4) reactions. The removal of chemisorbed oxygen atoms (O^*) formed in the CO dissociation steps required for monomer formation during FTS can occur via reactions of O^* with co-adsorbed hydrogen (H^*) or carbon monoxide (CO^*). These reactions lead to the formation of H_2O [equation (1)] and CO_2 [equation (2)], respectively, as the oxygen carriers. CO_2 and H_2O can also form via secondary reactions [equations (3) and (4)]. For synthesis gas streams with low H_2/CO ratios, the rate of water-gas shift reaction is an important factor because CO_2 formation via equation (4) leads to high H_2/CO ratios along the reactor bed and to lower olefin and C_5^+ selectivities. In order to increase hydrocarbon formation rate on iron-based catalysts, the control of oxygen removal via both primary removal and secondary oxygen removal pathways is essential in the design and use of Fe-based catalysts for FTS reactions. The evaluation of reaction pathways and the control of oxygen removal routes are currently under investigation. As a reference, steady-state FTS performance of Fe-Zn-K-Cu(Ru) prepared in this work using synthesis gases with $H_2/CO = 1$ and $H_2/CO = 2$ are summarized in Table 2.

Fig. 4 Steady state formation rate on Fe-Zn-K₆-Cu₃ as a function of CO conversion at 508 K and 2.14 MPa. Open mark; under synthesis gas (H₂/CO = 1), Close mark; under synthesis gas (H₂/CO = 2).

Table 2 Steady State FTS Performance of Fe-Zn-K-Cu(Ru) Using Synthesis Gas ($H_2/CO = 1$ or 2).

		Fe-Zn-K ₄	Fe-Zn-K ₄ -Ru ₁		Fe-Zn-K ₄ -Ru ₂		Fe-Zn-K ₅ -Ru ₂	Fe-Zn-K ₆ -Ru ₃	
Reactor Type		Fixed-bed	Fixed-bed		Fixed-bed		Fixed-bed	Fixed-bed	
Temperature	K	508	508		508		508	508	
Pressure	Mpa	2.14	2.14		2.14		2.14	2.14	
H ₂ /CO ratio		1	1	2	1	2	1	1	2
CO space velocity	NL/h.g-cat.	0.7	1.6	1.5	2.3	3.1	3.1	2.3	2.3
CO conversion	%	54.8	56.5	62.1	48.8	37.8	44.2	43.0	44.3
CO ₂ selectivity	%	37.2	39.7	31.1	42.7	32.4	39.2	40.2	31.0
CH ₄ selectivity	%	3.9	3.1	6.0	3.1	4.9	2.6	4.3	8.2
C ₅ ⁺ selectivity	%	84.3	85.1	77.2	82.3	75.6	84.3	81.3	73.2
1-C ₅ H ₁₀ /n-C ₅ H ₁₂ ratio		0.8	2.3	0.9	2.1	1.5	2.7	2.2	1.4
1-C ₁₀ H ₂₀ /n-C ₁₀ H ₂₂ ratio		0.04	0.8	0.1	0.6	0.4	1.6	0.8	0.4
CO rate	mol CO/h.g-cat.	0.02	0.04	0.04	0.05	0.05	0.06	0.05	0.05
CO reaction rate to HC	mol/h.g-at Fe	1.0	2.5	2.6	2.6	3.3	3.5	2.5	3.0
Hydrocarbon productivity	g/h.kg-cat.	158	387	403	400	497	524	368	438

CH₄ and C₅⁺ selectivities are reported on a CO₂-free basis.

2.5 Effect of Ru and Cu on Fischer-Tropsch Synthesis Rate and Selectivity Using Synthesis Gas ($H_2/CO = 1$)

Figure 5 shows steady-state FTS rates and selectivities on Fe-Zn-K₄, Fe-Zn-K₅-Ru₂, Fe-Zn-K₆-Cu₃ as a function of CO conversion at 508 K and 2.14 MPa. The CO₂ formation forward rates were calculated by the following equation (5).

$$r = r_f \left[1 - \frac{1}{K_{WGS}} \left(\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \right) \right] = r_f (1 - \eta) \quad (5)$$

where η is evaluated at the average partial pressures for each reactant and r is the measured rate of CO₂ formation. FTS rates were higher on the Ru-promoted sample (Fe-Zn-K₅-Ru₂) and on the Cu-promoted sample (Fe-Zn-K₆-Cu₃) than on unpromoted catalysts (Fe-Zn-K₄). Ru and Cu promoters appear to increase the number of active sites available on catalysts derived from Fe-Zn oxide precursors. It was also found that the slopes of the CO reaction rate and of the CO₂ forward rate-CO conversion curves are different on all three catalysts. These results suggest that the rates of secondary water-gas shift reactions were influenced by Ru and Cu promoters under $H_2/CO = 1$ synthesis gas, indicating that Ru and Cu promote the removal of O* by CO* to form CO₂ instead of using H* to remove oxygen as water. On the other hand, the nearly constant CO₂ rate on Fe-Zn-K₄ with increasing CO conversion suggests that K by itself does not introduce active sites for secondary water-gas shift reactions. Those results are different from the results under synthesis gas stream with $H_2/CO = 2$. Under $H_2/CO = 2$ synthesis gas, K increased the rate of the secondary CO₂-forming reactions involving a water co-reactant and Cu did not. In order to develop catalysts with high activities, the fundamental understanding of such differences is required and we will undertake a more detailed kinetic study of these effects during the next reporting period. The steady-state FTS performance of Fe-Zn-K-Cu(Ru) with different loadings of K, Ru and Cu using synthesis gases with $H_2/CO = 1$ are summarized in Table 3.

During the next reporting period, we will continue to explore the sequence and protocol for promoter introduction and the effects of activation procedures to further improve the reactivity and selectivity of these novel materials. We will select the most promising among these materials and carry out a detailed kinetic analysis with CO-rich synthesis gas compositions.

Fig 5. Steady-state FTS rate on iron based catalysts as a function of CO conversion (508 K, 2.14 MPa, H₂/CO = 1). (○): Fe-Zn-K₄, (□): Fe-Zn-K₅-Ru₂, (♦)Fe-Zn-K₆-Cu₃.

Table 3 Steady State Performance of Fe-Zn-K-Cu(Ru) with Different Loadings of K, Cu, and Ru ($H_2/CO = 1$, 508 K, 2.14 Ma, CO conversion 11-17%).

K/Fe atomic ratio (x100)	4	4	4	5	6	6
Ru/Fe atomic ratio (x100)	-	1	2	2	3	-
Cu/Fe atomic ratio (x100)	-	-	-	-	-	3
BET surface area ($m^2/g\text{-cat}$)	178	156	151	179	141	147
CO conversion rate (mol CO/h.g-at.Fe)	2.1	3.3	3.9	4.5	3.2	4.4
CO ₂ formation rate (mol CO/h.g-at.Fe)	0.6	1.0	1.4	1.5	1.0	1.2
Hydrocarbon formation rate (mol CO/h.g-at.Fe)	1.5	2.3	2.6	3.0	2.2	3.2
CO conversion (%)	16.5	12.7	15.0	16.8	11.8	16.7
CO ₂ selectivity (%)	28.1	29.6	34.7	33.8	31.5	28.3
CH ₄ selectivity (%)	4.3	3.4	2.9	2.9	4.5	2.8
C ₅ ⁺ selectivity (%)	82.3	81.8	81.8	83.0	80.0	85.7
C ₂ -C ₄ (%)	12.2	14.1	14.4	13.4	14.7	11.2
1-C ₅ H ₁₀ / <i>n</i> -C ₅ H ₁₂ ratio	2.3	2.7	2.5	2.7	2.5	2.8
1-C ₁₀ H ₂₀ / <i>n</i> -C ₁₀ H ₂₂ ratio	0.5	1.7	1.3	2.0	1.5	1.3
HC productivity (g/h.kg-cat)	231	357	394	445	324	481

CH₄ and C₅⁺ selectivities are reported on a CO₂-free basis.

Appendix B

Table 4 Steady State FTS Performance of Various Fe-Based Catalysts Using Natural Gas-Derived Synthesis Gas ($H_2/CO = 1.7$ -2.0).

		This work Fe-Zn-K ₅ -Ru ₂	This work Fe-Zn-K ₆ -Cu ₃	Previous work Fe-Zn-K ₄ -Cu ₂	Literature Fe-Si _{4.6} -K _{1.4}	Literature Fe-SiO ₂ -K _{5.9} -Cu _{4.4}
Reactor Type		Fixed-bed	Fixed-bed	Fixed-bed	Slurry	Spinning basket
Temperature	K	508	508	508	543	523
Pressure	Mpa	2.14	2.14	2.14	1.31	2.4
H ₂ /CO ratio		1	1	2	1.7	2
CO space velocity	NL/h.g-cat.	3.1	2.3	3.4	5.7	2.4
CO conversion	%	44.2	47.0	50.8	50	52.7
CO ₂ selectivity	%	39.2	38.4	31.7	40	42.3
CH ₄ selectivity	%	2.6	2.9	-	-	-
C ₅ ⁺ selectivity	%	84.3	85.4	-	-	-
1-C ₅ H ₁₀ /n-C ₅ H ₁₂ ratio		2.7	2.2	-	-	-
1-C ₁₀ H ₂₀ /n-C ₁₀ H ₂₂ ratio		1.6	0.5	-	-	-
CO rate	mol CO/h.g-cat.	0.06	0.05	0.08	0.12	0.05
CO reaction rate to HC	mol/h.g-at Fe	3.5	2.7	-	-	-
Hydrocarbon productivity	g/h.kg-cat.	524	415	765	1008	404

CH₄ and C₅⁺ selectivities are reported on a CO₂-free basis.

Literature: *Ind. Eng. Chem. Res.* **1999**, 38, 1277 and *Catal. Today* **1997**, 36, 335.