

TECHNICAL PROGRESS REPORT

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

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ABSTRACT

This project explores the extension of previously discovered Fe-based catalysts with unprecedented Fischer-Tropsch synthesis rate, selectivity, and ability to convert hydrogen-poor synthesis gas streams typical of those produced from coal and biomass sources. Contract negotiations were completed on December 9, 2004. During the first reporting period, we certified a microreactor, installed required analytical equipment, and reproduced synthetic protocols and catalytic performance previously reported. During this second reporting period, we have prepared and tested several Fe-based compositions for Fischer-Tropsch synthesis and tested the effects of product recycle under both subcritical and supercritical conditions. These studies established modest improvements in rates and selectivities with light hydrocarbon recycle without any observed deleterious effects, opening up the opportunities for using of recycle strategies to control temperature profiles in fixed-bed Fe-based Fischer-Tropsch synthesis reactors without any detectable kinetic detriment. In a parallel study, we examined similar effects of recycle for cobalt-based catalysts; marked selectivity improvements were observed as a result of the removal of significant transport restrictions on these catalysts. Finally, we have re-examined some previously unanalyzed data dealing with the mechanism of the Fischer-Tropsch synthesis, specifically kinetic isotope effects on the rate and selectivity of chain growth reactions on Fe-based catalysts.

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EXECUTIVE SUMMARY

This project exploits our recent discovery of catalyst compositions and synthesis and activation protocols that lead to iron-based catalysts with FTS activities and selectivities similar to those on cobalt-based catalyst using stoichiometric H₂/CO streams, while retaining significant water-gas shift activities at the lower temperatures that favor the formation of high molecular weight hydrocarbons and minimize the undesired formation of light alkanes and alkenes. 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 syngas ratios.

Fe-based catalysts can be used to convert synthesis gas streams derived from coal and biomass, because their low H₂/CO ratios (H₂/CO=0.7-1) can be adjusted by rejecting the excess carbon as CO₂ via concurrent water-gas shift reactions (H₂O + CO → CO₂ + H₂O). In this manner, the stoichiometry required for the synthesis of hydrocarbons useful as fuels and chemicals can be achieved using H₂-poor synthesis gas streams. These Fe catalysts are typically much less active than Co-based catalysts, which do not possess water-gas shift activity at the temperatures at which they lead to significant hydrocarbon chain growth. In addition, Fe-based catalysts tend to exhibit lower stability as a result of phase transformations and mechanical disintegration, often as a result of their tendency to interconvert between oxide and carbide phases as the redox properties change within Fischer-Tropsch synthesis catalytic reactors. The development of Fe-based catalysts with higher Fischer-Tropsch synthesis (FTS) rates, lower CO₂ selectivity and greater mechanical stability remain the critical hurdles in our ability of convert hydrogen-poor synthesis gas streams, derived from coal and biomass, into high-value fuels and petrochemicals.

During this second reporting period, we have prepared and tested several Fe-based compositions for Fischer-Tropsch synthesis and tested the effects of product recycle under both sub-critical and supercritical conditions. These studies established modest improvements in rates and selectivities with light hydrocarbon recycle without any observed deleterious effects, opening up opportunities for the use of recycle strategies for temperature control in fixed-bed Fe-based Fischer-Tropsch synthesis reactors without any detectable kinetic detriment debits. In a parallel study, we also examined similar effects of recycle for cobalt-based catalysts; marked selectivity improvements were observed as a result of the removal of significant transport restrictions on these catalysts. Finally, we have re-examined some previously unanalyzed data dealing with the mechanism of the Fischer-Tropsch synthesis, specifically kinetic isotope effects on the rate and selectivity of chain growth reactions on Fe-based catalysts.

A post-doctoral fellow (Jian Xu) was required to leave Berkeley for personal and professional reasons and to return to his country of origin. A research visitor (Takashi Umeki) was incorporated into the Fischer-Tropsch synthesis activities to carry out the light hydrocarbon recycle and supercritical tests. The principal investigator undertook the task to analyze and report previously obtained data related to kinetic isotope effects and mechanism of Fe-based catalysts. Two new post-doctoral fellows have been contracted. Dr. A. Ishikawa will arrive in November 2004 and Dr. M. Ojeda on January 2005. Beamtime has been scheduled for fourth quarter 2004 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 the next reporting period, we will continue the synthesis of Fe-Zn-Ru-K catalysts and their testing at sub-stoichiometric H_2/CO ratios and characterized their structure and surface properties by X-ray absorption and site titration methods before and after activation in synthesis gas at typical reaction conditions. We will continue our analysis of the chain growth pathways and molecular weight and olefin selectivities as a function of reaction conditions and catalytic composition. We will also specifically address structural transformation and their implications for catalytic behavior and for mechanical stability.

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

The project consists of three specific tasks:

Task One

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

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

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 as part of Task 1)

This project explores the extension of previously discovered Fe-based catalysts with unprecedented Fischer-Tropsch synthesis rate, selectivity, and ability to convert hydrogen-poor synthesis gas streams typical of those produced from coal and biomass sources. Contract negotiations between the U.S. Department of Energy and the University of California were completed on December 9, 2003. During the first year, we have reconstructed and certified a decommissioned microreactor, ordered and installed a

budgeted gas chromatograph, developed and reviewed safe operating procedures and data analysis protocols and successfully reproduced previous synthetic protocols and catalytic performance of catalytic materials based on Fe-Zn-Cu-K and Fe-Zn-Ru-K oxide precursors synthesized using precipitation methods, drying using surface-active agents, and activated in synthesis gas within Fischer-Tropsch synthesis tubular reactors.

We have also started to study the behavior of these systems during operation in synthesis gas mixtures with varying H₂/CO ratios and explored the use of subcritical and supercritical phase hydrocarbons in the control of the rate and of the olefin and molecular weight selectivities on these materials. This task, originally set for year three was moved up because of some exciting results in a parallel program on cobalt-based materials and it was progressed well ahead of schedule. We have written a highly rated proposal for beamtime at the Stanford Synchrotron Research Laboratory for X-ray absorption experiments; this proposal was approved and beamtime will be allocated for late 2004 or early 2005 to carry out experiments required to establish the initial structure of these materials as well as their carbide-oxide structural transformations during Fischer-Tropsch synthesis catalysis under realistic conditions.

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 (H₂O + CO → CO₂ + H₂) 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 new activation and promotion protocols led to active Fe carbide clusters with high surface areas and

mechanical strength. These gave in turn unprecedented activity and C₅₊ selectivity during use with stoichiometric synthesis gas (H₂/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 Ru as activation promoter
2. evaluate the performance of prepared catalysts in synthesis gas streams derived from coal or biomass (H₂/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 (FY2004):

During this second reporting period, we have prepared and tested several Fe-based compositions for Fischer-Tropsch synthesis and tested the effects of product recycle under both subcritical and supercritical conditions. These studies established modest improvements in rates and selectivities with light hydrocarbon recycle without any observed deleterious effects, opening up opportunities for the use of recycle strategies for temperature control in fixed-bed Fe-based Fischer-Tropsch synthesis reactors without any detectable kinetic detriment debits. In a parallel study outside of this funded project, we also examined similar effects of recycle for cobalt-based catalysts; marked selectivity improvements were observed as a result of the removal of significant transport restrictions on these catalysts. Finally, we have re-examined some previously unanalyzed data dealing with the mechanism of the Fischer-Tropsch synthesis, specifically unusual kinetic isotope effects on the rate and selectivity of chain growth reactions on Fe-based catalysts.

A post-doctoral fellow (Jian Xu) was required to leave Berkeley for personal and professional reasons and to return to his country of origin. A research visitor (Takashi Umeki) was incorporated into the Fischer-Tropsch synthesis activities to carry out the light hydrocarbon recycle and supercritical tests. The principal investigator undertook the task to analyze and report previously obtained data related to kinetic isotope effects and mechanism of Fe-based catalysts.

Detailed results and findings and conclusions are included at the end of this report as appendices:

- A. Catalytic Evaluation and Characterization of Iron-Based Systems
- B. Effects of Recycle of Light Hydrocarbons and Synthesis and Testing of Fe-Zn-Ru-K Catalysts
- C. Fischer-Tropsch synthesis on Fe-based catalysts: Kinetic isotope effects and their mechanistic implications

Immediate Next Steps and Research Plan are:

Two new post-doctoral fellows have been contracted. Dr. A. Ishikawa will arrive in November 2004 and Dr. M. Ojeda on January 2005. Beamtime has been scheduled for fourth quarter 2004 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 the next reporting period, we will continue the synthesis of Fe-Zn-Ru-K catalysts and their testing at sub-stoichiometric H₂/CO ratios. 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 conditions. We will continue our analysis of the chain growth pathways and molecular weight and olefin selectivities as a function of reaction conditions and catalytic composition. We will specifically address structural transformation and their implications for catalytic behavior and for mechanical stability.

During year two, 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 to materials suitable Fischer-Tropsch synthesis with coal- and biomass-derived synthesis gas and to examine the structural evolution of these materials during synthesis and during Fischer-Tropsch synthesis catalysis. Specifically, we will characterize the extent of carbide-oxide phase transformations and their impact on catalyst mechanical integrity using electron microscopy and in situ X-ray absorption protocols. We will start in mid-period a detailed study of the effects of CO₂ recycle on selectivity and stability of these materials at low H₂ ratios on optimized Fe-based catalysts.

The program will be staffed by two full-time post-docs dedicated to synthesis and functional evaluation of the catalysts developed and to their characterization by titration and diffraction techniques; in addition, a post-doctoral fellow with specific expertise in X-ray absorption measurements will be assigned 50% for the critical X-ray characterization of these materials during synthesis and catalysis.

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.

Appendices

Appendix A: Catalytic Evaluation and Characterization of Iron-Based Systems

1. Summary of Iron Catalyst Prepared and Preparation Methods
2. BET surface area of prepared catalysts
3. Fixed bed tests

Summary of Iron Catalyst Prepared and Preparation Methods

(Also refer to lab notebook JX01), code example: JX01-006 (located at lab notebook JX01, page 6)

Catalyst code	Relative Composition (atom %)					Preparation Method
	Fe	Zn	K	Cu	Ru	
JX01-006 (FeZn)	100	10				Co-precipitation, surface-active isopropanol replacement, followed by overnight drying in ambient air at 393 K
JX01-007 (FeZn)	100	10	-	-	-	Drying of JX01-006 in flowing air at 623 K for 1 h
JX01-011	100	10	4	2	-	Following JX01-007, aqueous impregnation of K_2CO_3 followed by drying at 393 K overnight. $Cu(NO_3)_2$ was then added in the next step followed by overnight drying at 393 K. and 543 K drying in dry flowing air for 4 h
JX01-012 (FeZnK ₄ Cu ₂)	100	10	4	2	-	K addition to JX01-007 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 drying air for 4 h
JX01-015	100	10	-	-	-	JX01-006 dried in flowing air for 4 h at 543 K
JX01-016	100	10	-	-	-	JX01-015, impregnated by 0.86 ml 0.32 M K_2CO_3 , followed by drying at 393 K in ambient air overnight
JX01-017	100	10	4	2	-	JX01-015, aqueous impregnation of K_2CO_3 followed by drying at 393 K overnight. $Cu(NO_3)_2$ was then added in the next step followed by overnight drying at 393 K. and 543 K drying in dry flowing air for 4 h
JX01-019	100	10	-	-	-	Another preparation of FeZn precursor, Co-precipitation, surface-active isopropanol replacement, followed by overnight drying in ambient air at 393 K
JX01-020	100	10	4	2	-	JX01-019, impregnated in acetone by K_2CO_3 followed by drying at 393 K overnight. $Cu(NO_3)_2$ was then added in the next step with acetone followed by overnight drying at 393 K. and 543 K drying in dry flowing air for 4 h
JX01-022	100	10	4	2	-	Same as JX01-020, except impregnated in isopropanol alcohol

1. BET surface area of prepared catalysts

Catalyst	JX01-006 (FeZn)	JX01-019 (FeZn)	JX01-007 (FeZn)	JX01-019 (FeZnK ₄ Cu ₂)	JX01-020
BET surface area (m ² /g-cat)	258	273	101	273	169

3. Comparison of steady state FTS rates and selectivities

Fixed Bed Test Run CMRU1-003 of JX01-017 (FeZnK₄Cu₂)

Catalyst	JX01-017 (this work)		FeZnK ₄ Cu ₂ (previous work)		
Run number	CMRU1-003		11	12	13
Run conditions					
Temperature (K)	508	508	473	508	508
Pressure (MPa)	2.14	2.14	2.0	2.14	2.14
H ₂ /CO	2.0	2.0	2.0	2.0	2.0
CO space velocity (NL/h.g-cat)	3.4	13.9 ^b		13.6 ^b	3.4
Time on stream	40.5	62.9			
CO conversion (%)	31.6	8.61	18 ~ 21	13 ~ 16	50.8
CO ₂ selectivity (%)	25.1	15.9		20.5	31.7
CH ₄ selectivity (%) ^a	3.0	3.86	2.0	3.8	
C ₂ -C ₄ (%)	14.6	15.6	8.9		
C ₅₊ selectivity (%) ^a	82.3	80.5	89.1	80.8	
1-C ₅ H ₁₀ /n-C ₅ H ₁₂ ratio	2.2	2.4	2.1	2.7	
1-C ₁₀ H ₂₀ /n-C ₁₀ H ₂₀ ratio	1.3	2.0	1.6		
CO conversion rate (mol CO/h.g-at. Fe)	5.2	5.8		6.8	7.0

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

^b Calculated value from data

4. Fixed Bed Test Run (CMRU1-004) (FeZnK₄Cu₂)

Catalyst	JX01-017				
Run number	CMRU1-004				
Run conditions					
Temperature (K)	508	508	508	508	508
Pressure (MPa)	2.14	2.14	2.14	2.14	2.14
H ₂ /CO	1.0	1.0	1.0	1.0	1.0
CO space velocity (NL/h.g-cat)	3.4	13.9	20.6	7.0	
Time on stream (h)	20.8	54.9	70.7	82.8	105.9
CO conversion (%)	45.5	10.4	6.7	21.9	65.3
CO ₂ selectivity (%)	36.5	20.8	19.0	28.6	38.7
CH ₄ selectivity (%) ^a	2.1	2.2	2.8	2.3	2.2
C ₂ -C ₄ (%)	14.2	13.8	16.0	15.3	15.9
C ₅₊ selectivity (%) ^a	83.4	83.6	80.7	82.1	81.8
1-C ₅ H ₁₀ /n-C ₅ H ₁₂ ratio	3.4	3.2	3.2	3.4	3.5
1-C ₁₀ H ₂₀ /n-C ₁₀ H ₂₀ ratio	1.9	2.5	2.5	2.3	1.4

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

Appendix B. Effects of Recycle of Light Hydrocarbons and Synthesis and Testing of Fe-Zn-Ru-K Catalysts

1. Experimental details

Catalyst Synthesis and Characterization

Two Fe-Zn-Ru-K catalysts with different pellet size were prepared by coprecipitation of oxyhydroxides from a mixed solution of Fe and Zn nitrates using ammonium carbonate. A solution containing Fe(NO₃)₃ (Aldrich 98%, 3.0M) and Zn(NO₃)₂ (Aldrich, 98+%, 1.4M) at Zn/Fe atomic ratio of 0.1 was introduced into large flask containing deionized water (100cm³) at 353 K at a rate of 120 cm³h⁻¹ using a liquid pump. A (NH₄)₂CO₃ (Aldrich, 99.9%, 1M) 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 (Omega PHB-62). The precipitated powders (20 g) were washed five times with isopropanol (Fischer Chemical) five times (40 cm³/g each time), dried in ambient air at 393 K overnight, and then treated in flowing dry air at 523K for 1h. Magnetic stirring was used during alcohol washing in order to increase the rate at which liquid water within pores was

replaced by the alcohol. The K and Ru promoter were added to these Fe-Zn oxide precursors by incipient wetness impregnation with aqueous solutions of K_2CO_3 (Aldrich, 99.99%, 0.16M) and ruthenium(III) nitrosyl nitrate $[Ru(NO)(NO_3)_x(OH)_y]$ ($x+y = 3$) (Aldrich, dilute nitric acid solution, Ru 1.5%) at the concentrations required to obtain the desired K/Fe and Ru/Fe atomic ratios. (Ru/Fe = 0.02, K/Fe = 0.04) These impregnated samples were then dried at 373 K in ambient air. Lastly, the samples were treated in flowing dry air at 673 K for 4 h. The resulting oxide precursors are denoted as Fe-Zn-Ru2-K4. To make the catalyst particles of 0.14mm of average diameter and 2mm of average diameter, powder oxide was pressed and sieved. The surface area of catalyst measured by N_2 adsorption was $78 \text{ m}^2/\text{g-cat}$.

Fischer-Tropsch Synthesis Reaction and Product Selectivity

Fischer-Tropsch synthesis rates and selectivity were measured using an isothermal packed-bed reactor with plug-flow hydrodynamics. The catalyst bed temperature was kept within ± 0.5 K of the average bed temperature. All lines after the reactor outlet were kept above 453 K to prevent condensation. A 150 cm^3 trap after the reactor was held at 408 K to collect heavy hydrocarbons. Product and reactant analysis were carried out by gas chromatography (HP, model 5890 series II) using a ten-port sampling valve. The analysis of N_2 , CO, CO_2 , and CH_4 was performed using a thermal conductivity detector and a Porapak Q packed column ($15.2\text{cm} \times 0.318\text{cm}\phi$). All hydrocarbons up to C_{15} were analyzed using flame ionization detector and a cross-linked methyl silicone capillary column (HP-1, $50 \text{ m} \times 0.32 \text{ mm}$; $1.05 \mu\text{m}$ film)

Fe-Zn-Ru2-K4 catalysts were diluted with quartz (100 – 180 μm particles) using 0.4 g and 11 g, respectively. 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 rate of 10K/min and from 423 to 543 K at 1 K/min. The catalysts were held at 543 K for 1h. After activation, the temperature was decreased to 508 K, and the synthesis gas pressure was gradually increased to 2 MPa. FTS reactions were carried out at 508 K using synthesis gas (Praxair, 62% H_2 , 31% CO, 7% N_2 internal standard) at 2 MPa synthesis gas pressure. n-Pentane (T_c ; 470 K, P_c ; 3.37 MPa) was utilized as an additive representative of light hydrocarbon products. The standard reaction conditions were P (total) = $(2 + P_{n\text{-Pentane}})$ MPa, $P_{n\text{-Pentane}} = 0\text{-}3$ MPa. CO space velocities were 0.13 to 0.63 (mole CO/h-g-atom Fe) without n-pentane addition and 0.13 with n-pentane addition. n-Pentane was added to the synthesis gas reactant stream using an ISCO 440D Series high

pressure pump and all transfer lines were maintained above 473 K to prevent condensation.

2. Results

Table 1 shows CO conversion and product selectivity for Fischer-Tropsch synthesis on both catalyst sizes of Fe-Zn-Ru2-K4 with various CO space velocities. Large particle catalysts show lower CO conversion, higher CH₄ selectivity, and lower C₅₊ selectivity than small particles. This result indicates that reactions on large particles are limited by CO transport, which leads to low local CO concentrations and high local H₂/CO ratios. Lower CO space velocities lead to higher CH₄ and CO₂ selectivities and lower C₅₊ selectivity for both particle sizes. It is well known that FTS on Fe catalysts produce hydrogen from CO and water by water-gas shift reactions. High CO₂ selectivities at low space velocities lead to high H₂ concentration and thus to a decrease in the selectivity to higher hydrocarbons as a result of faster chain termination. The 1-olefin/n-paraffin ratios show almost the same value for both C₃ and C₈ products for all pellet size and space velocities.

Figure 1 shows CO conversion and product selectivities on Fe-Zn-Ru2-K4 catalysts with n-pentane addition. In this experiment, n-pentane partial pressures range from 0 to 3 MPa; thus, n-pentane remains subcritical throughout. CO conversions on large catalyst pellets increase with n-pentane partial pressure, but small catalyst pellets show almost constant CO conversion as n-pentane pressure is varied. This result shows that diffusivity of reactant CO increases with n-pentane addition because of the lower viscosity of intraparticle hydrocarbon liquids. CO₂ selectivity decreased with n-pentane partial pressure, apparently because of the higher diffusivity of H₂O within lighter intraparticle fluids, which leads, in turn, to lower water-gas shift reaction rates. The resulting lower H₂ prevalent pressures lead to an increase in C₅₊ selectivity and to a decrease in CH₄ selectivity with increasing n-pentane partial pressure. 1-Olefin/n-paraffin ratios slightly increased with n-pentane addition for both particle sizes.

In summary, n-pentane addition during Fischer-Tropsch reaction has been carried out on a co-precipitated Fe-Zn catalyst promoted by K and Ru. Water-gas shift activity is strongly suppressed by n-pentane addition. As a result, high C₅₊ selectivities are achieved because of the resulting lower pressured of H₂ along the reactor. FTS rates show that CO diffusion limits rates and selectivities, leading to lower rates and C₅₊

selectivities on larger particles and to stronger effects of n-pentane on such large particles, because of their effects on the average molecular weight and consequent viscosity of intraparticle liquids.

Table 1 CO conversion and product selectivity during FTS on Fe-Zn-Ru2-K4.

Reaction temperature = 508 K, synthesis gas pressure = 2 MPa, H₂/CO=2

Pellet Diameter (mm)	0.14				2			
1/SV(h·g-Fe/mole-CO)	7.9	4.0	2.6	1.6	7.9	4.0	2.6	1.6
CO conversion (%)	51.2	27.3	18.6	11.4	19.8	11.1	8.2	5.6
Carbon selectivity (%)								
CH ₄	5.5	5.3	5.2	4.9	8.4	8.2	7.6	7.1
CO ₂	39.3	33.9	30.7	26.5	33.3	30.3	27.4	24.8
C ₅₊	68.5	71.3	72.2	74.8	63.9	66.4	70.4	74.0
1-O/n-P ratio								
C ₃	3.0	3.0	3.0	3.0	3.0	3.0	3.1	3.1
C ₈	2.1	2.1	2.0	2.0	2.0	2.0	2.0	2.0

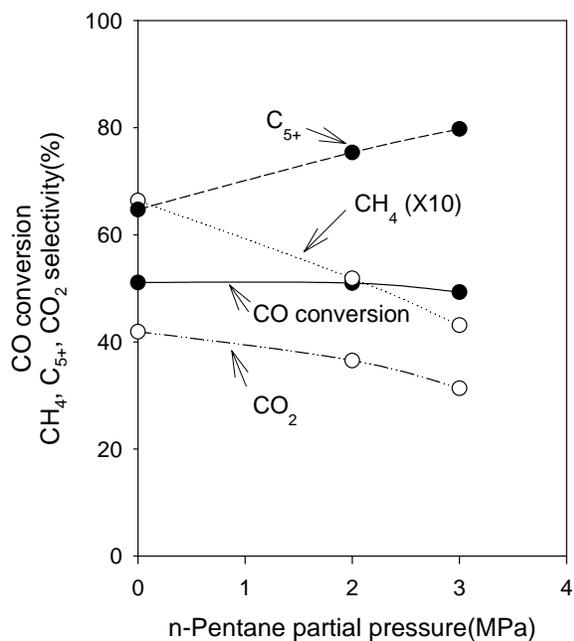


Fig. 1 (a)

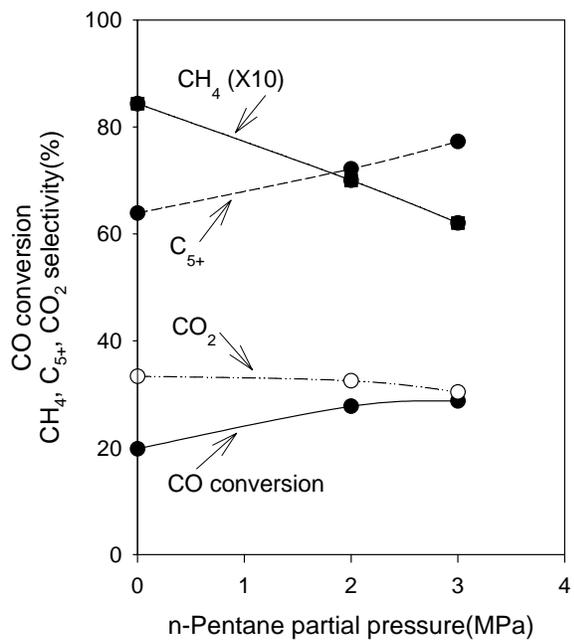


Fig.1 (b)

Figure 1. CO conversion, CH₄ and C₅₊ selectivities of on Fe-Zn-Ru2-K4 with n-Pentane.

508 K, synthesis gas pressure=2 MPa, H₂/CO=2

(a) d_p=0.14mm, (b) d_p=2 mm

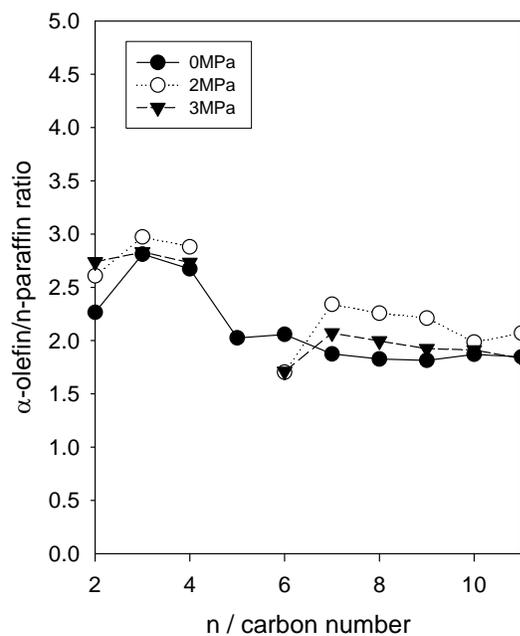


Fig. 2 (a)

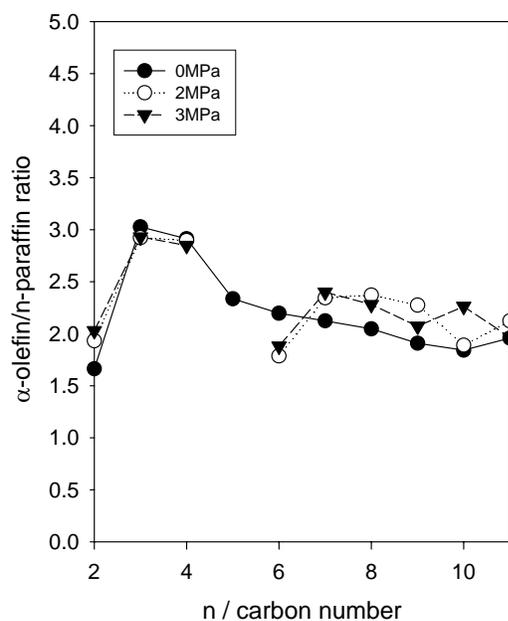


Fig. 2 (b)

Figure 2. Olefin/n-paraffin ratio as function of hydrocarbon chain size on Fe-Zn-Ru₂-K₄ catalyst with n-Pentane.

508 K, synthesis gas pressure=2 MPa, H₂/CO=2

(a) d_p=0.14 mm, (b) d_p=2 mm

Appendix C. Fischer-Tropsch synthesis on Fe-based catalysts: Kinetic isotope effects and their mechanistic implications

H₂/D₂ kinetic isotope effects (KIE) were investigated for the Fischer-Tropsch synthesis (FTS) on an Fe-based catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at various space velocities using a fixed-bed reactor at 235 °C and 21.4 atm and synthesis gas reactant mixtures with H₂/CO or D₂/CO ratios of 2:1. The unusual inverse kinetic isotope effects observed for hydrocarbon synthesis suggests that thermodynamic isotope effects leading to higher coverages of chemisorbed D than H dominate any effects of deuteration on the dynamics of elementary steps. This leads in turn to a lower olefin content and a lower CO₂ selectivity when D₂/CO mixtures are used instead of H₂/CO mixtures.

Figures 1-3 show CO conversion rates and hydrocarbon and CO₂ formation rates as a function of CO conversion on a Fe-Cu-Zn catalyst (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 235 °C and 21.4 atm. CO conversion and hydrocarbon synthesis rates were higher with D₂/CO than with H₂/CO reactant mixtures. In contrast, CO₂ formation rates were lower with D₂/CO than with H₂/CO, suggesting that oxygen rejection as water is faster with chemisorbed D-atoms than with H-atoms, either because of their higher reactivity or of their higher surface concentration during FTS reactions. It has been proposed that the formation of higher molecular weight hydrocarbons on Fe-based catalyst during FTS reactions is initiated by the addition of a methyl group to a methylene group and that further chain growth occurs by the reaction of methylene group with adsorbed alkyl groups. The alkyl groups then react to form olefins and paraffins via either hydrogen elimination or addition. Consistent with these views of CO hydrogenation, one would expect to observe a normal isotopic effect if D₂ were used instead of H₂. Instead, we find an inverse isotope effect, in which D₂-containing mixtures form hydrocarbons faster than H₂-containing feeds (Figure 2)

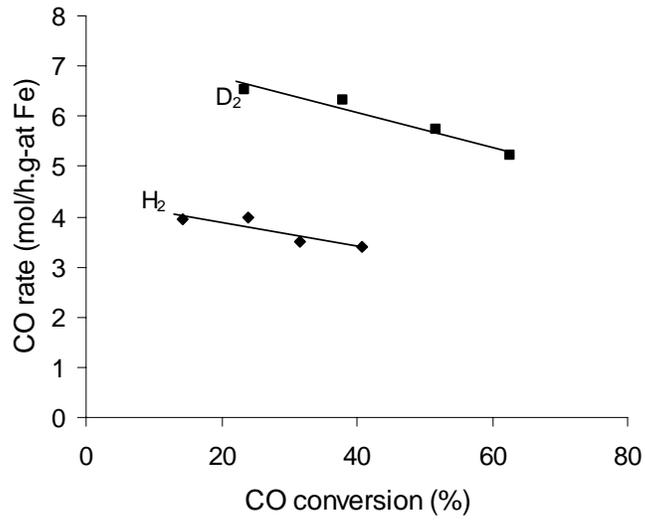


Figure 1. CO conversion rate as a function of CO conversion for H₂/CO or D₂/CO reactants (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 235 °C and 21.4 atm.

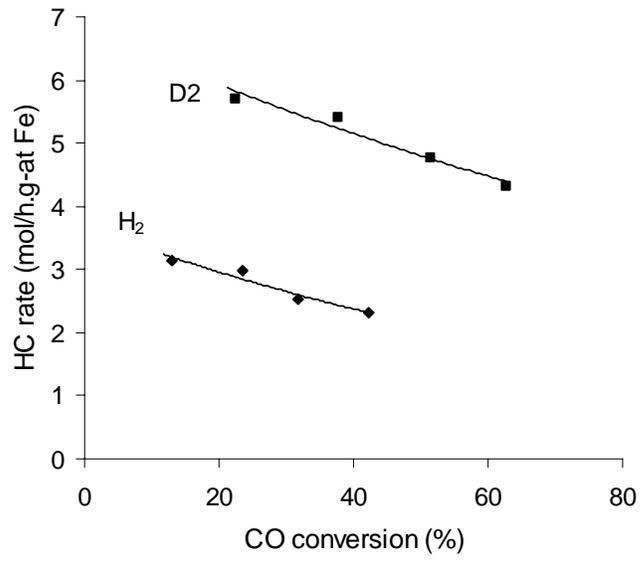


Figure 2. Hydrocarbon synthesis rate as a function of CO conversion for H₂/CO or D₂/CO reactants (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 235 °C and 21.4 atm.

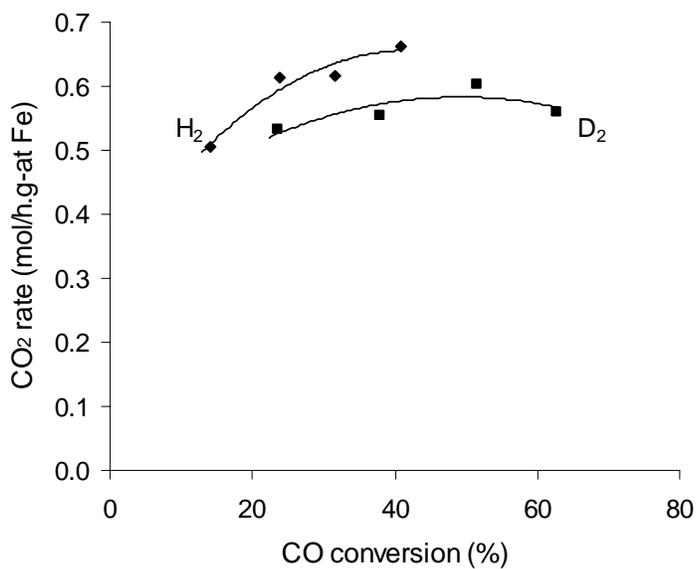


Figure 3. CO₂ synthesis rate as a function of CO conversion for H₂/CO or D₂/CO reactants (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 235 °C and 21.4 atm.

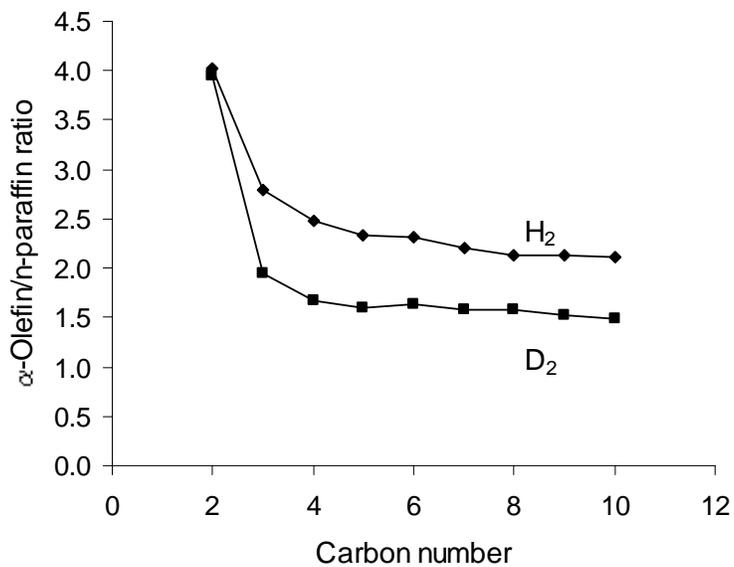


Figure 4. α -Olefin/n-paraffin ratio as a function of CO conversion for H₂/CO or D₂/CO reactants (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 235 °C and 21.4 atm.

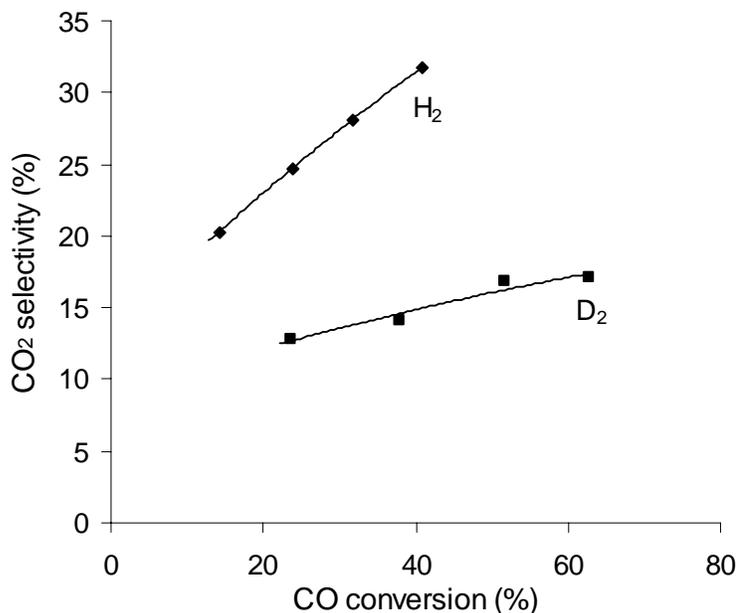


Figure 5. CO₂ selectivity as a function of CO conversion for H₂/CO or D₂/CO reactants (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 235 °C and 21.4 atm.

Previous studies have suggested that the overall isotopic effect for CO hydrogenation reflects a complex interplay of kinetic and thermodynamic isotope effects, with the former favoring reactions of H₂ and the latter favoring reactions of D₂. The inverse isotopic effects of our observations suggests a dominant role of thermodynamic isotope effects. The higher CO conversion and hydrocarbon formation rates observed for D₂/CO may reflect the stronger adsorption of D-atoms from D₂ compared with H-atoms from H₂ on Fe-based catalyst surfaces.

Figure 4 shows α -olefin/n-paraffin ratios as a function of carbon number for H₂/CO and D₂/CO reactant mixtures. Figure 5 shows CO₂ selectivities as a function of CO conversion for these two reactant mixtures. The increase in the concentration of D or H atoms on the catalyst surface would increase the probability of hydrogen addition of the adsorbed alkyl to form paraffins and decrease the probability of hydrogen elimination of adsorbed alkyls to form olefins. Any increase in chemisorbed H or D coverages would also decrease the formation of CO₂ via reactions of CO with chemisorbed O-atoms reaction by causing the removal of these O-atoms (formed in CO dissociation steps) to occur via reaction with adsorbed hydrogen instead of adsorbed CO. Hence, both lower α -olefin/n-paraffin ratios (Figure 4) and lower CO₂ selectivity (Figure 5) with D₂ are consistent with higher surface concentrations of hydrogen isotopes, which prevail when D₂ is used instead of H₂. The higher surface concentration of chemisorbed D atoms reflects its larger adsorption equilibrium coefficient. This result is in agreement with previous studies, which reported about 1.4 times more adsorption of D₂ than H₂ on Cu powder at 125 °C. Larger adsorption coefficients were also obtained for D₂ compared with H₂ on Ni during the hydrogenation of acetylene and of CO₂.

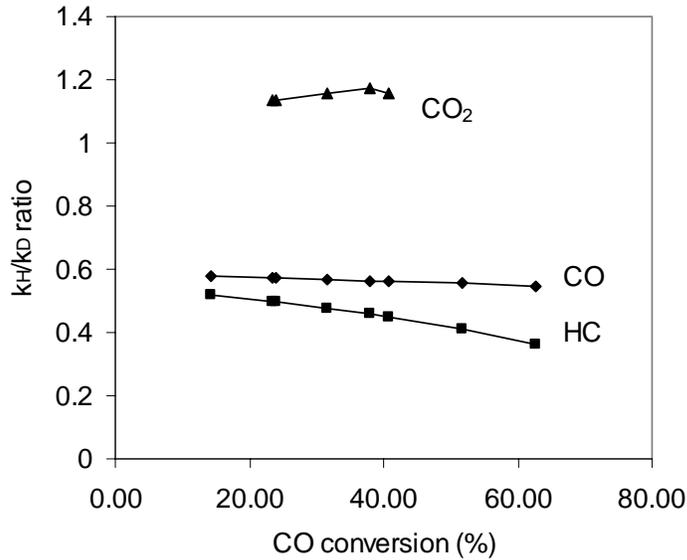


Figure 6. k_H/k_D ratio for CO conversion, hydrocarbon synthesis and CO₂ formation as a function of CO conversion for H₂/CO or D₂/CO reactants (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 235 °C and 21.4 atm.

A reaction rate expression proposed for FTS is

$$-r_{CO+H_2} = \frac{kP_{CO}P_{H_2}^2}{P_{CO}P_{H_2} + bP_{H_2O}}$$

where b is an adsorption parameter and k is a rate constant. Based on this rate expression, hydrocarbon formation rates ($-r_{CO+H_2}$) increase almost linearly with increasing H₂ at low conversions (when H₂O concentrations are low). Since FTS reactions proceed on the surface of the catalyst and surface hydrogen concentration is determined by hydrogen pressure, higher surface hydrogen concentration gave higher hydrocarbon formation rate. Therefore, CO conversion and hydrocarbon formation rates were higher with D₂ at same CO conversion, as shown in Figures 1 and 2.

The isotopic effect can be expressed by a ratio of k_H/k_D . k_H and k_D are rate constants for H₂/CO and D₂/CO mixtures, respectively. Since we did not have experimental values for both k_H and k_D at identical CO conversions and H₂ or D₂ concentrations, we estimated k_H values by fitting the curve of rate as a function of CO conversion for experimental values of k_D and also get a fitted value of k_D for each experimental value of k_H by a similar way.

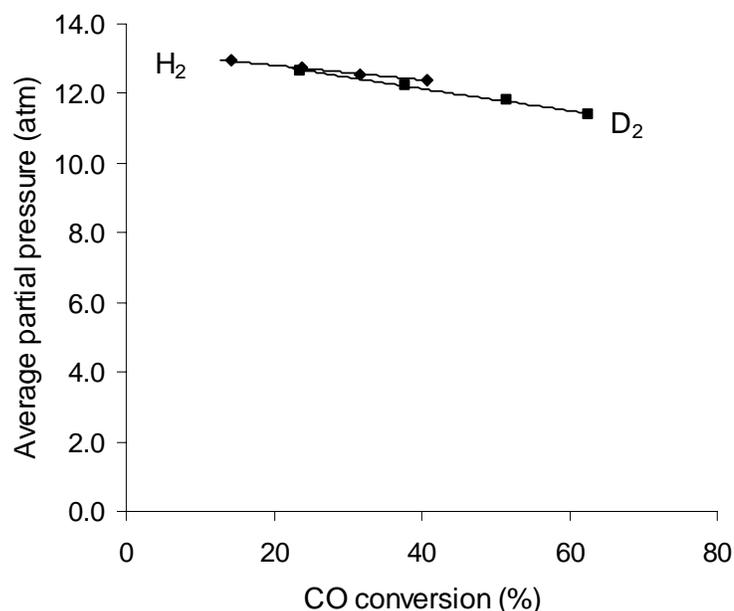


Figure 7. Average partial pressure of hydrogen as a function of CO conversion for H₂/CO or D₂/CO reactants (Zn/Fe=0.1, K/M=0.02, Cu/M=0.01) at 235 °C and 21.4 atm.

Figure 6 shows k_H/k_D ratios for CO conversion, hydrocarbon synthesis, and CO₂ formation as a function of the extent of CO conversion, which was varied by varying space velocity. The k_H/k_D ratio for hydrocarbon formation was about 0.5 and decreased slightly with increasing CO conversion level. The k_H/k_D ratio for CO₂ formation was greater than unity. The inverse isotopic effect observed for hydrocarbon synthesis ($k_H/k_D < 1$) and the normal isotopic effect for CO₂ formation ($k_H/k_D > 1$) are expected because higher surface coverages of hydrogen isotopes are prevalent when D₂ was used. It is not clear why the k_H/k_D ratio for hydrocarbon formation decreased slightly with increasing CO conversion. The reason might be that the partial pressure of hydrogen decreases with increasing CO conversion. Figure 7 shows the partial pressure of hydrogen as a function of CO conversion. It is seen that the partial pressures for both H₂ and D₂ decreased with increasing CO conversion. We speculate that surface hydrogen concentrations are more sensitive to the reduction of pressure in gas phase for H₂ than that for D₂ because the adsorption coefficient of D₂ is higher than that of H₂. Accordingly, hydrocarbon formation rate decreased faster with decreasing partial pressure for H₂ than for D₂, and consequently, the k_H/k_D ratio for hydrocarbon formation decreases with increasing CO conversion (Figure 6).

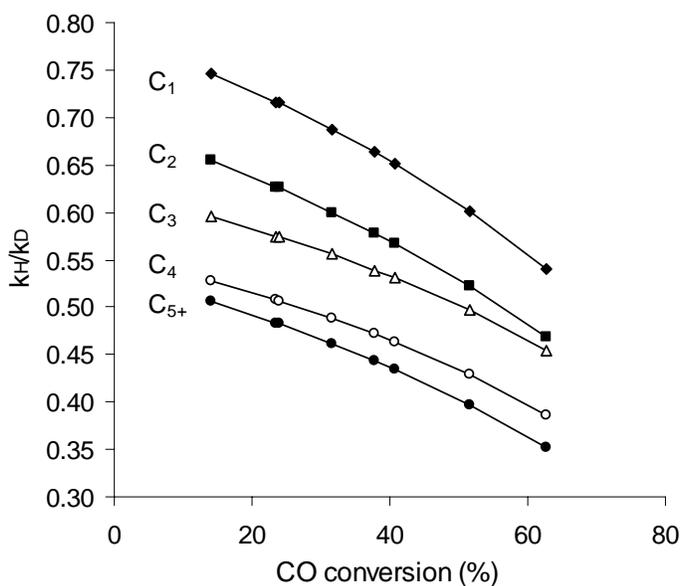


Figure 8. k_H/k_D ratios for C_1 - C_4 and C_{5+} as a function of CO conversion for H_2/CO or D_2/CO reactants ($Zn/Fe=0.1$, $K/M=0.02$, $Cu/M=0.01$) at $235\text{ }^\circ\text{C}$ and 21.4 atm .

Figure 8 shows k_H/k_D ratios for formation of C_1 - C_4 species and for C_{5+} formation as a function of CO conversion. Similarly, all ratios decreased with increasing CO conversion. It is also seen that at the same CO conversion, the k_H/k_D ratio systematically decreased with increasing carbon number, suggesting that the inverse isotopic effects are stronger larger hydrocarbons. Deuterium appears to favor the formation of hydrocarbon with higher molecular weight because the selectivity to C_{5+} was higher when D_2 was used (Fig. 1.20). Hence, k_H/k_D ratios decreased with carbon number.

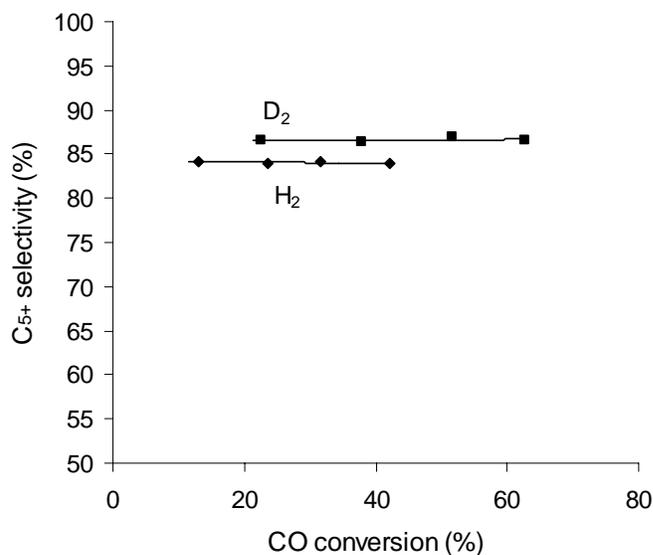


Figure 9. C_{5+} selectivity as a function of CO conversion for H_2/CO or D_2/CO reactants ($Zn/Fe=0.1$, $K/M=0.02$, $Cu/M=0.01$) at $235\text{ }^\circ\text{C}$ and 21.4 atm .

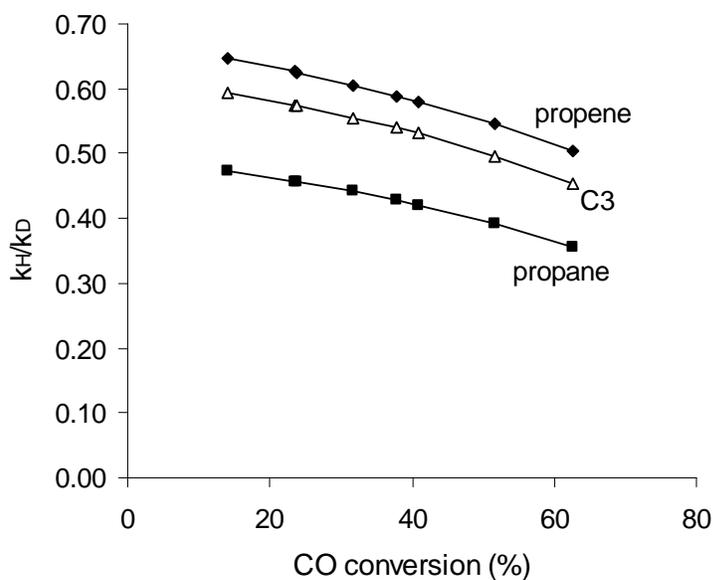


Figure 10. k_H/k_D ratios for propene, propane and total C_3 synthesis as a function of CO conversion for H_2/CO or D_2/CO reactants ($Zn/Fe=0.1$, $K/M=0.02$, $Cu/M=0.01$) at $235\text{ }^\circ\text{C}$ and 21.4 atm .

The isotopic effect for propene and propane formation is given in Figure 10. The k_H/k_D ratio for propene was higher than that for propane. Similar result was obtained for butene and butane (Figure 11), suggesting that the inverse isotope effects are more evident for paraffins than for olefins. This is because the probability of paraffin formation increased due to higher surface hydrogen concentration when D_2 was used.

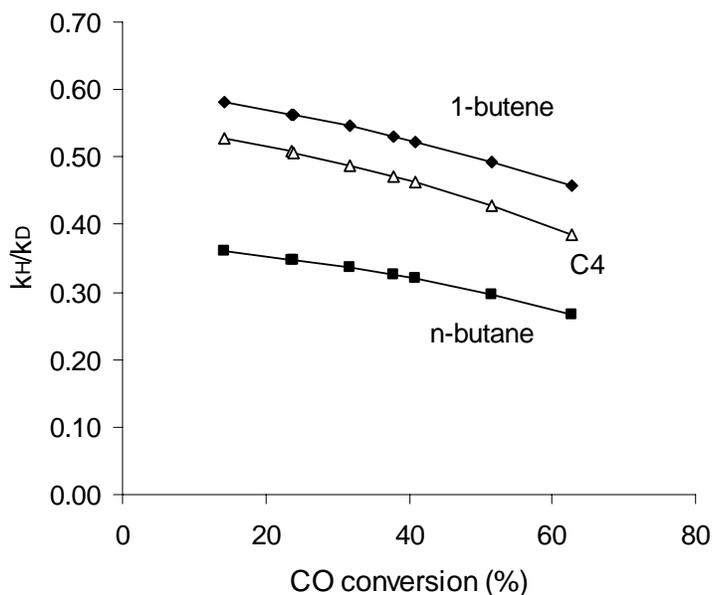


Figure 11. k_H/k_D ratios for 1-butene, n-butane and total C_4 synthesis as a function of CO conversion for H_2/CO or D_2/CO reactants ($Zn/Fe=0.1$, $K/M=0.02$, $Cu/M=0.01$) at $235\text{ }^\circ\text{C}$ and 21.4 atm .