LBL—31822

DE92 017085

Isotopic Tracer Studies of Fischer-Tropsch Synthesis over Ru/TiO_2 Catalysts

Kamala Raghunathan Krishna
Ph. D. Thesis

Department of Chemical Engineering
University of California

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

January 1992

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

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ABSTRACT

Fischer-Tropsch synthesis is a process in which CO and H_2 react to give predominantly liquid hydrocarbons. The reaction can be considered a special type of polymerization in which the monomer is produced *in situ*, and chain growth occurs by a sequence of independently repeated additions of the monomer to the growing chain. An investigation has been conducted to study the CO hydrogenation reaction in order to better understand catalyst deactivation and the elementary surface processes involved in chain growth.

Isotopic tracers are used in conjunction with transient-response techniques in this study of Fischer-Tropsch synthesis over Ru/TiO_2 catalysts. Experiments are conducted at a total pressure of 1 atmosphere, reaction temperatures of 453-498 K and D_2/CO (or H_2/CO) ratios of 2-5. Synthesis products are analyzed by gas chromatography or isotope-ratio gas chromatography-mass spectrometry.

Ru/TiO_2 catalysts deactivate with no change of product selectivity and the rate of deactivation correlates with initial

catalyst activity. Deactivation occurs at an initial rapid rate, followed by a slower activity loss. Deactivation is accompanied by a loss in CO uptake and the accumulation of various types of carbonaceous species. The long-term loss of activity is attributed to the buildup of long chain hydrocarbon product species.

Rate constants for chain initiation, propagation and termination are evaluated under steady-state reaction conditions by using transients in isotopic composition. The activation energy for chain termination is much higher than that for propagation, accounting for the observed decrease in the chain growth parameter with increasing temperature. Coverages by reaction intermediates are also estimated. The dominant reactive surface species are monomeric building units, which occupy 0.2-0.6 ML. Alkyl species that are the direct hydrocarbon product precursors occupy < 0.2 ML. Adsorbed CO covers 0.7 ML.

When small amounts of ^{12}C-labelled ethylene are added to $^{13}CO/H_2$ synthesis gas, ethylene acts as the sole chain initiator. Ethylene-derived carbon also accounts for 45 % of the C_1 monomer pool.

To

my parents,

my parents-in-law,

Ashok,

and

Ananth.

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ASF	Anderson-Schulz-Flory
C_α	Carbidic carbon (ML)
C_β	Alkyl carbon chains (ML)
C_β'	Alkyl carbon chains that are precursors to the C_{2+} hydrocarbon products (ML)
C_β''	Unreactive alkyl chains, of longer chain length than C_β' (ML)
F_1	Fraction of labelled carbon in the surface precursor to methane
F_m	Fraction of labelled carbon in the monomer pool
F_n	Fraction of labelled carbon in the pool of carbon chain length n
K	Equilibrium constant for CO adsorption
k	Rate parameter
k_i	Initiation rate constant (s^{-1})
k_p	Intrinsic Rate constant for propagation (s^{-1})
k_p'	Apparent rate constant for propagation (s^{-1})
k_t	Rate constant for termination (s^{-1})
k_1	Rate constant
k_2	Rate constant
k_3	Rate constant
ML	Monolayer, unit of coverage based on hydrogen chemisorption to estimate the number of surface exposed

	Ru atoms
N_{CO}	Turnover frequency of CO (s^{-1}) i.e., moles of CO converted per moles of surface-exposed metal atoms per sec
N_{CO}^{o}	Apparent turnover frequency of CO at t_r = 0 min
N_{C_1}	Turnover frequency of methane (s^{-1})
N_{C_n}	Turnover frequency of products of carbon chain length n (s^{-1})
n	Carbon number
n_{av}	Average carbon number of hydrocarbon products
P_{CO}	Partial pressure of CO
t_r	Time onstream after reaction startup
α	ASF chain growth probability or chain growth parameter
θ	Surface coverage
θ_{CO}	CO coverage (ML)
θ_m	Coverage by monomer building block
θ_1	Coverage by methane precursor
θ_n	Coverage by precursor to hydrocarbon products of chain length n
θ_α	Coverage by $C_\alpha + C_\beta'$ (ML)
θ_β''	Coverage by C_β'' (ML)
τ	Lifetime of surface alkyl chains
τ_m	Lifetime of monomer pool

Acknowledgements

I would like to thank Dr. Bell for his guidance, interest and constant encouragement throughout the course of my research. I would also like to thank Dr. Theodorou and Dr. Stacy for serving on my dissertation committee.

I am grateful to the members of the Bell group, past and present, for making my stay at Berkeley enjoyable and also for helping me through many crises! A special thanks to Phil, Reha, Rebecca, Gina, Judith, Grant, Rich, Bill, Rick, Mike, Catherine, Narcis, Debbie, Alon, Mark, Larry, Steve, Greg, Kevin, Janet, Ken, Marjorie, Karen, Dean, Bob, Rusty, Nick, Isao, Hiroshi, Takashi, Randy, Craig and Ed.

I would like to thank Wai Ming (Henry) Chan for writing and modifying my GC-MS software and for helping me troubleshoot my electronic equipment woes. Nancy Monroe provided drafting expertise that I am grateful for. Kay and Ferne have helped me with advice and encouragement.

Finally, I am deeply indebted to my parents for their support and encouragement throughout my academic career. My parents-in law have also been a source of strength. Ashok has been a pillar of strength and coped magnificently on the home front. I owe an extra special thank you to Ashok and my son Ananth, who actively kept my spirits up at every stage, and endured my long work hours without (too much) protest.