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**Isotopic Tracer Studies of Fischer-Tropsch Synthesis  
over Ru/TiO<sub>2</sub> Catalysts**

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by

Kamala Raghunathan Krishna

**ABSTRACT**

Fischer-Tropsch synthesis is a process in which CO and H<sub>2</sub> 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<sub>2</sub> catalysts. Experiments are conducted at a total pressure of 1 atmosphere, reaction temperatures of 453-498 K and D<sub>2</sub>/CO (or H<sub>2</sub>/CO) ratios of 2-5. Synthesis products are analyzed by gas chromatography or isotope-ratio gas chromatography-mass spectrometry.

Ru/TiO<sub>2</sub> 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  $^{12}\text{C}$ -labelled ethylene are added to  $^{13}\text{CO}/\text{H}_2$  synthesis gas, ethylene acts as the sole chain initiator. Ethylene-derived carbon also accounts for 45 % of the  $\text{C}_1$  monomer pool.

To

my parents,

my parents-in-law,

Ashok,

and

Ananth.

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### List of Symbols

ASF	Anderson-Schulz-Flory
$C_{\alpha}$	Carbodic carbon (ML)
$C_{\beta}$	Alkyl carbon chains (ML)
$C_{\beta}'$	Alkyl carbon chains that are precursors to the $C_{2+}$ hydrocarbon products (ML)
$C_{\beta}''$	Unreactive alkyl chains, of longer chain length than $C_{\beta}'$ (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 <sup>-1</sup> ) i.e., moles of CO converted per moles of surface-exposed metal atoms per sec
$N_{CO}^0$	Apparent turnover frequency of CO at $t_r = 0$ min
$N_C$	Turnover frequency of methane (s <sup>-1</sup> )
$N_{C_n}$	Turnover frequency of products of carbon chain length n (s <sup>-1</sup> )
n	Carbon number
$n_{av}$	Average carbon number of hydrocarbon products
$P_{CO}$	Partial pressure of CO
$t_r$	Time onstream after reaction startup
$\alpha$	ASF chain growth probability or chain growth parameter
$\theta$	Surface coverage
$\theta_{CO}$	CO coverage (ML)
$\theta_m$	Coverage by monomer building block
$\theta_1$	Coverage by methane precursor
$\theta_n$	Coverage by precursor to hydrocarbon products of chain length n
$\theta_\alpha$	Coverage by $C_\alpha + C_\beta'$ (ML)
$\theta_\beta''$	Coverage by $C_\beta''$ (ML)
$\tau$	Lifetime of surface alkyl chains
$\tau_m$	Lifetime of monomer pool

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