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RESIDENCE TIMES AND COVERAGE BY SURFACE INTERMEDIATES DURING THE FISCHER-TROPSCH SYNTHESIS

C.A. MIMS [1], J.J. KRAJEWSKI [2], K.D. ROSE [2] and M.T. MELCHIOR [2]

[1] *Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, M5S 1A4 Canada*

[2] *Exxon Research and Engineering Company, Corporate Research Laboratories, Rte 22E, Annandale NJ 08801, U.S.A.*

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Isotope tracing of alkene readsorption has been used to examine reversibility in the growth of higher hydrocarbons in the Fischer-Tropsch synthesis. Some reversibility is indicated, but the degree is insufficient to change previous conclusions from isotope transient studies; namely that the surface concentrations of the growing hydrocarbon oligomers during the reaction are very small.

1. Introduction

The growth of higher hydrocarbons is the central feature of Fischer-Tropsch catalysis. It has been known for decades that the product distribution arises from a relatively simple surface polymerization sequence. While many plausible reaction sequences have been proposed, the reaction pathway is still not well understood and the identities of the monomers and growing surface bound oligomers are unknown [1]. Early investigations of the reaction which relied on the interruption of the reaction indicated that the process of chain growth was slow and that the surface was covered by actively growing hydrocarbon chains [2]. Over the past ten years there has been a resurgence in the appreciation for the importance of mechanistic information gained at reaction steady state. A particularly valuable tool has been the use of isotopic transients [3]. This method allows one to probe the timing of the reaction mechanism without disturbing the often delicate balance of the reaction.

RAPID HYDROCARBON CHAIN GROWTH

Several studies of hydrocarbon growth rates using in-situ techniques have been reported over the past several years [3–10]. These studies have tended to indicate

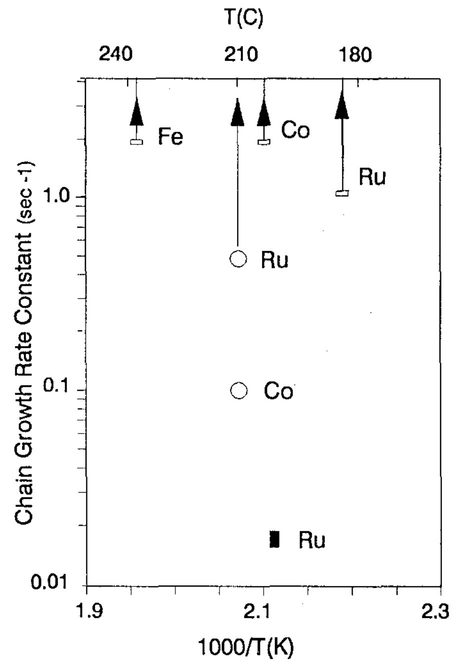

Fig. 1. Chain growth rate constants reported in the literature: arrows symbolize lower limits. Open boxes Fe, Co are from ref. [7]; Open box Ru from ref. [8]; Open circles are from ref. [6]; Closed square is from ref. [2].

that polymerization is rapid, although this conclusion has not been unanimous. We have reported detailed isotopic transient studies of higher hydrocarbon formation on several catalysts at one atmosphere and low conversion. On Fe and Co catalysts, the "new" isotope appears in unison in all carbon atoms in the higher hydrocarbons [8]. On Ru catalysts, this is true for all carbon atoms added after the C_2 stage [9]. The only plausible explanation for the data is that the time required for an individual monomer addition is very short compared to total residence time of the surface. Since the new isotope appears isotropically, we can only place a lower limit to the oligomer growth rate constant. Fig. 1 shows the limits obtained from our studies compared with others obtained at similar conditions.

Although these results prove that hydrocarbon chain growth is rapid, the surface concentrations of the growing oligomers is not constrained by these findings without further assumptions [8]. If the chain growth is irreversible, the coverage must consequently be small. On the basis of this assumption we estimated very small coverages (< 0.001) for the growing chains on our catalysts. However, if chain growth is reversible, and each chain polymerizes and depolymerizes many times during its stay on the surface, much higher coverages are consistent with the results. It has been noted [6] that the regular (Anderson-Schulz-Flory) product distributions are consistent with a simple polymerization

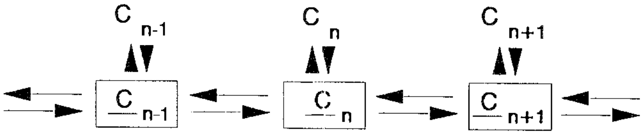

Fig. 2. Reversible polymerization scheme for higher hydrocarbons formation.

and are unlikely to result from a mechanism where chain growth is reversible. This, of course, is not a conclusive argument, and one can devise mechanisms with reversible chain growth which are consistent with such a product distribution [11]. Furthermore, evidence of depolymerization has been reported in some olefin readsorption experiments.

OLEFIN INCORPORATION AS A PROBE OF REVERSIBILITY

It is known from tracer studies that the alkene products can re-enter the reaction pathway [5,12]. Carbon atoms from these alkenes can enter the monomer pool. The alkenes can initiate new chains, presumably via the main mechanistic sequence as illustrated in fig. 2. Tamaru and co-workers reported [5] a binomial label distribution in small (C_3–C_5) hydrocarbons upon the addition of labelled hexene and other alkenes to unlabelled CO–H_2 over a Ru catalyst. This indicated that chain assembly and disassembly is very rapid compared to the gas residence time in their experiment. In this paper, we use the same technique to investigate the reversibility of hydrocarbon growth under the conditions of our isotope transient studies.

2. Experimental

The results discussed here were obtained on the ruthenium-alumina catalyst discussed in ref. [9]. The experiments were performed at one atmosphere and at low CO conversion. We added ^{12}C labelled olefins to H_2–^{13}CO mixtures. The detailed isotopic distribution in the products was determined by GCMS and NMR as in previous studies. Three alkenes were used; ethylene, 1-hexene, and 1-octene. The olefin was added in variable concentrations (up to 5 mole%) to the CO–H_2 mixture outside the reactor. A substantial fraction was hydrogenated: other studies show that this occurs near the top of the bed [12]. The low olefin concentrations were obtained by a capillary leak in the case of ethylene, and by saturation of the reactant gas stream for hexene and octene.

3. Results and discussion

The results show that the alkenes take part in at least three processes: they (1) initiate the growth of higher molecular weight hydrocarbons, (2) depolymerize to

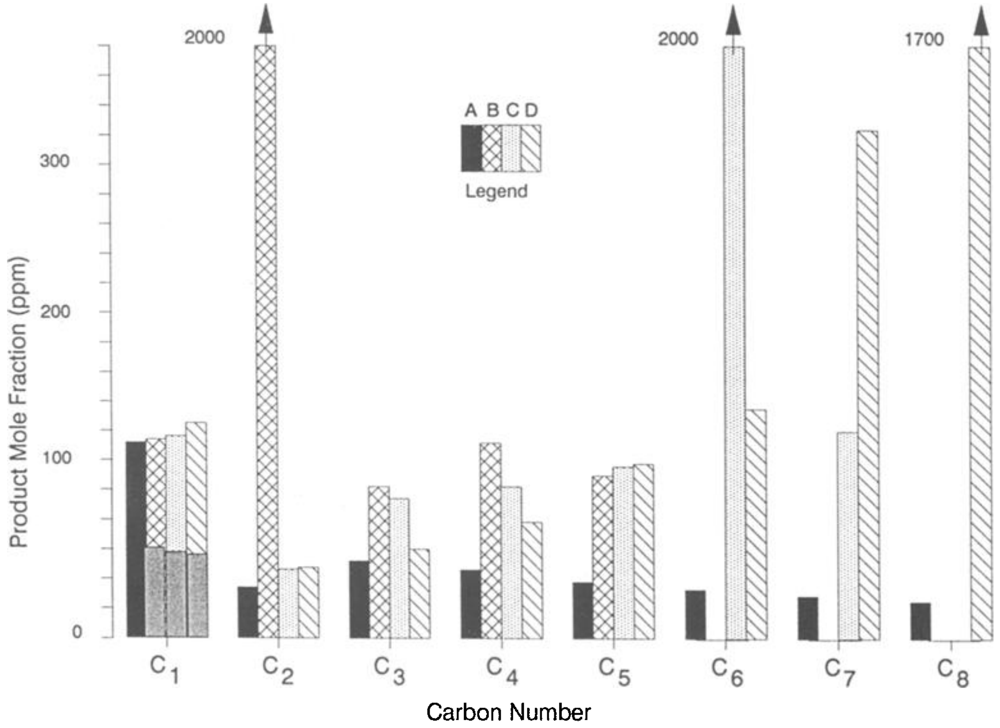

Fig. 3. Carbon number product concentrations at 205C on Ru/Al_2O_3, $^{13}CO/H_2/Ar = 1/2/1$, 1 atmosphere: Legend A = no added alkene, B = added ethylene, C = added 1-hexene, D = added 1-octene: the numbers atop the added peaks are the exit concentrations of the parent alkene; The shaded portion of the C_1 bars represent the amount of carbon derived from CO.

form lower molecular weight hydrocarbons, and (3) contribute to the monomer pool, likely as a result of (2). Fig. 3 shows that at our conditions, incorporation of the alkenes into the reaction is facile. With alkene mole fractions of less than 1%, the product distribution is substantially altered. The production rates of all hydrocarbon products are increased, except for methane. Fig. 3 shows sizeable increases in the production rates of all hydrocarbons except methane. The increase in rates are highest for carbon numbers adjacent to the added alkene and decrease for progressively higher and lower carbon numbers. The falloff is more rapid for products with smaller carbon numbers (depolymerization products) than for the larger ones. This is consistent with a depolymerization probability which is smaller than the polymerization probability.

The isotope distributions are not random, as illustrated in figs. 4 and 5. In fig. 4, the C_3 and C_4 products resulting from the addition of ethylene show evidence of a two-carbon initiator derived from ethylene at the alkyl end of the 1-alkene products. The remainder of the carbon atoms have approximately the same isotopic composition as the methane product. These results are consistent with

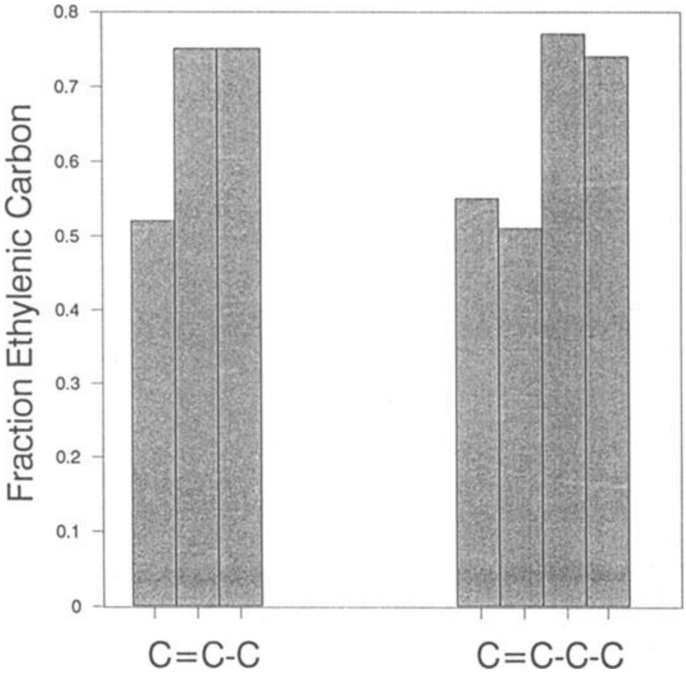

Fig. 4. Fraction ^{12}C at various positions in propene and butene from ethylene tracer experiment: conditions are as in fig. 3.

initiation from adsorbed ethylene of additional hydrocarbon chains and further growth from a common C_1 pool.

Fig. 5 shows that the isotopic distribution in the 1-butene products resulting

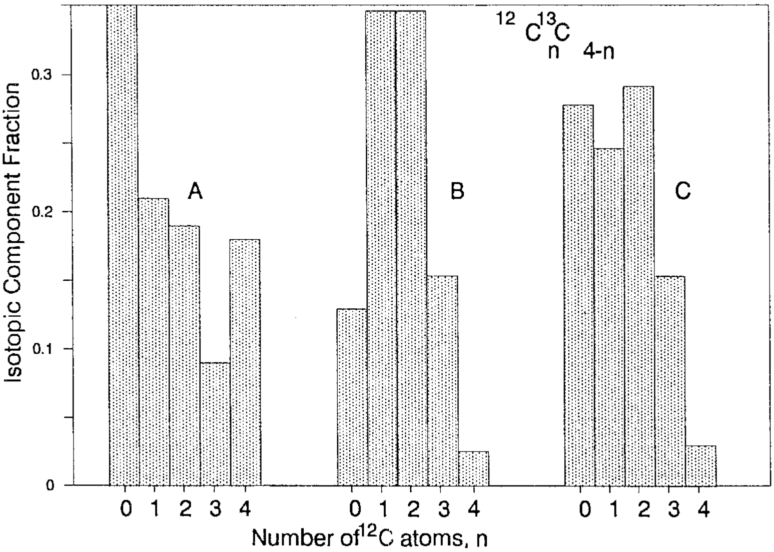

Fig. 5. Isotope distribution in butene from hexene tracer experiments: conditions as in fig. 3: A = experimental distribution; B, C = calculated distributions (see text).

from the addition of hexene is also not random. There is a substantial amount of the $^{12}C_4$ product expected from depolymerization of adsorbed hexene. Distributions which are expected for two simple reaction models are also depicted. Distribution B is a random (binomial) distribution, and distribution C would arise from a two component mixture consisting of a) $^{12}C_4$ depolymerized from $^{12}C_6$ and b) a component built randomly from a monomer bath with the isotopic composition of the methane product. Model C clearly provides a better fit than B, in that it predicts appreciable quantities of $^{12}C_4$. However, this distribution fails to reproduce other features, however. For instance, there is more $^{13}C_4$ (all carbon atoms from CO) than would be expected from a random assembly of a single C_1 species. This may indicate that the pathway for hydrocarbon growth from CO and that for depolymerization of adsorbed alkenes are not completely mixed as illustrated in fig. 2. Such a conclusion requires testing with a model which includes integral analysis of the catalyst bed.

A complete model capable of explaining all the results is beyond the scope of this paper. Preliminary simulations based on a model such as that in fig. 2 indicate that the polymerization rate constant for the adsorbed alkene is 4–5 times larger than the depolymerization rate constant. If we assume that this is representative of chain growth in the undisturbed reaction, it means that a growing chain takes 1 step back for every 4 or 5 steps forward. In this case, chain growth would not differ significantly from rigorous irreversibility. Therefore, the upper limits to the oligomer surface concentrations on this catalyst derived in ref. [8] need to be revised upward, but only by approximately 20%. The original conclusions stand, therefore; that 1) active carbon on the surface spends most of its time as precursors to growing oligomers and that 2) the surface concentrations of the growing oligomers are very small.

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