

# Alkylidene Mechanism for the Fischer-Tropsch Synthesis

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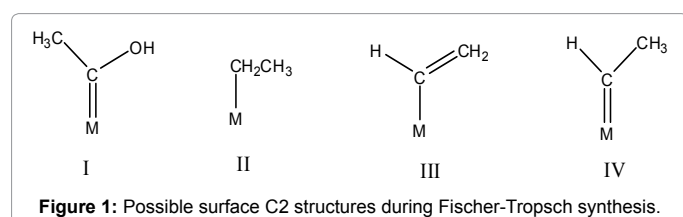
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The Fischer-Tropsch synthesis (FTS) has become an attractive industrial process to produce fuels and chemicals from coal, natural gas and biomass. It has also been invoked to explain the formation of abiogenic hydrocarbons in the Earth's crust, the formation of organic matters in the nebula, and the production of precursors of life-essential building blocks. The question of how the long chain hydrocarbons are formed from two simplest compounds CO and H<sub>2</sub> is of fundamental importance in chemistry and has challenged researchers for many years.

The key to understand the mechanism of the FT reaction is to know how the C-C bonds being formed from surface growing chains and the monomer. Even though the structures of growing chains and monomer are still not known, many possible structures have been proposed by analogy with organic compounds. The simplest surface growing chain is the surface C<sub>2</sub> species that is formed from monomers by C-C coupling promoted by metal catalyst. If we know how the C<sub>2</sub> species is formed, we will have a clear picture about the formation of longer chain hydrocarbons. Therefore, one of the most important tasks in studying mechanism for the FT reaction is to study C<sub>2</sub> surface species. There are at least four possible C<sub>2</sub> structures as shown in Figure 1, each of which corresponds to a different mechanism for the FT reaction: the structure I, the hydroxyl methylene mechanism proposed in 1951 by Storch and co-workers; the structure II, the alkyl mechanism proposed in 1980 by Brady and Pettic; the structure III, the alkenyl mechanism proposed in 1995 by Maitlis and co-workers; the structure IV is corresponding to the modified alkylidene mechanism proposed by us in 2011 [1,2].

## Formation of C<sub>2</sub> Species during Fischer-Tropsch Synthesis

FTS is considered to be a polymerization reaction. However, unlike normal polymerization reaction the "monomer" of the FT reaction is an "in-situ" produced surface C<sub>1</sub> species, and the identity of which is unknown. According to alkyl and alkenyl mechanisms, the "monomer" is M=CH<sub>2</sub>. The formations of C<sub>2</sub> species II and III can be represented in reactions 1 and 2 of Figure 2, respectively. While both reaction 1 and reaction 2 are reasonable the formation of IV from reaction 3 by assuming M=CH<sub>2</sub> as the "monomer" is awkward: it would require adding an H in one carbon and eliminating one from another. By assuming the M≡CH as the "monomer" of FTS, the formation of C<sub>2</sub> species though alkylidene mechanism is presented in reaction 4 where the coupling of two monomers followed by addition of 2 H gives the structure IV. The evidence that M≡CH could be the monomer during FTS is given by DFT calculations [3].

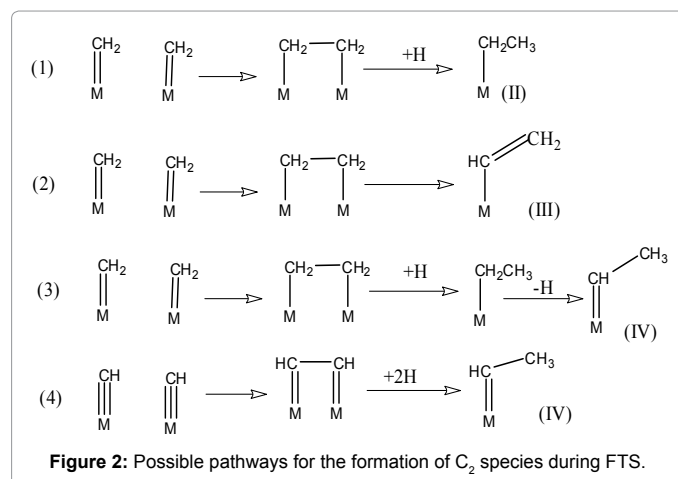


## Inverse Isotope Effect and Deuterium Enrichment during FTS

Our interests in studying mechanisms of catalytic reactions using isotopic tracer technique [4] led us to determine whether there is an inverse isotope effect and whether there exists the deuterium enrichment in hydrocarbons during FTS. We performed the H<sub>2</sub>/D<sub>2</sub> switch and competition experiments in cobalt and iron catalyzed FTS. We confirmed the early findings that there is an inverse isotope effect in the formation of hydrocarbons during FTS. We also found that during Co catalyzed FTS [1] there exists deuterium enrichments in hydrocarbons from C<sub>6</sub> to C<sub>24</sub>, and the deuterium enrichment is a function of carbon number as shown in A of Figure 3. The Fe catalyzed FTS also showed the deuterium enrichment in hydrocarbons as shown in B of Figure 3. These results indicate that the inverse isotope effect is originated from the C-C bond formation, and deuterium is enriched from every step of the propagations.

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To account for these results and the results accumulated over the years, we proposed an alkylidene mechanism for FTS as shown in Figure 4. According to this mechanism, the monomer in this polymerization reaction is the in-situ produced M≡CH, and coupling of two monomers generates the ethylidene. The propagation of ethylidene will generate

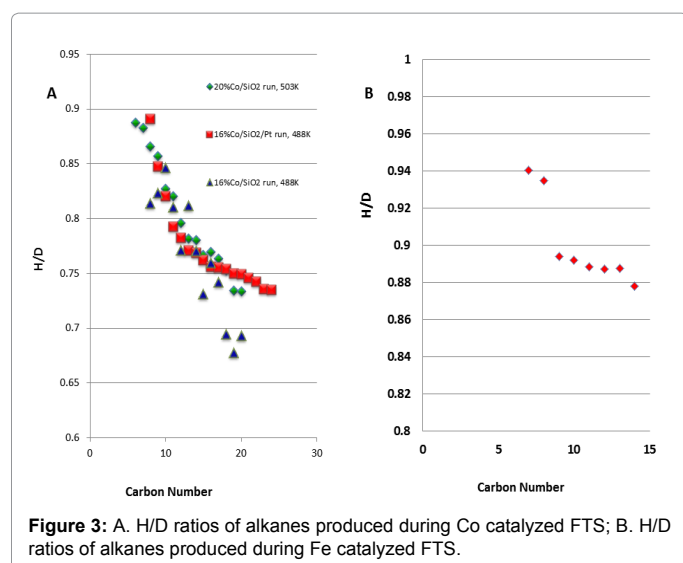


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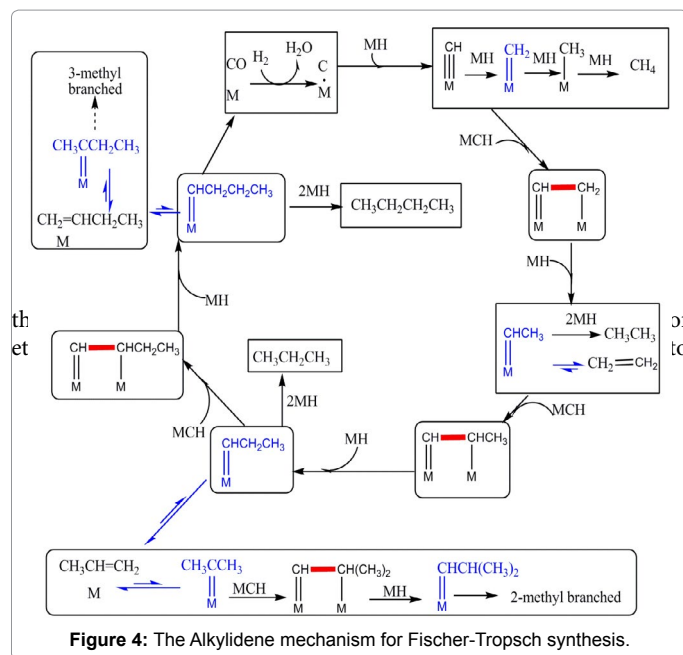
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reform ethylidene and continue to grow. Starting from the re-adsorbed propene, 2-alkylidene can be formed, the growth of which will result in the formation of methyl-branched hydrocarbons. The hydrogenation of the monomer  $M\equiv CH$  will produce methane.

To provide additional supports for the alkylidene mechanism, we conducted deuterated alcohol tracer experiments on cobalt catalyzed FTS [2,5]. We found that additions of ethanol- $d_6$  and 2-propanol- $d_8$  during the Co/SiO<sub>2</sub> catalyzed FT reactions did not produce detectable amount of deuterated isomer in any alkane while a constant number of deuterium atoms was incorporated into each alkane from C<sub>7</sub> to C<sub>14</sub> when FT reactions were conducted over a mixture of FT catalyst Co/SiO<sub>2</sub> and dehydration catalyst Al<sub>2</sub>O<sub>3</sub> and over Fe/Si/K catalyst. These results led us to conclude that the C<sub>2</sub> or C<sub>3</sub> species that initiates the chain growth in the FTS resembles ethene or propene, the possible structures of which are ethylidene and propylidene, respectively.

Another evidence to support the alkylidene mechanism is the formation of branched hydrocarbons. We found [6] that the branched hydrocarbons are monomethyl branched with little or no ethyl or dimethyl branched hydrocarbons. According to the alkylidene mechanism (Figure 4), the branched hydrocarbons are formed through the re-adsorption and re-growth of propene and other 1-alkenes, which will produce mainly the methyl branched hydrocarbons. The “kink” in C<sub>2</sub> in ASF product distribution plot can also be explained by the alkylidene mechanism: while the re-adsorption and re-growth of ethene will be re-adsorbed and re-grown will result in the significantly alter the ASF distribution the re-adsorption and re-growth of propene or other 1-alkenes will not.



#### Acknowledgement

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