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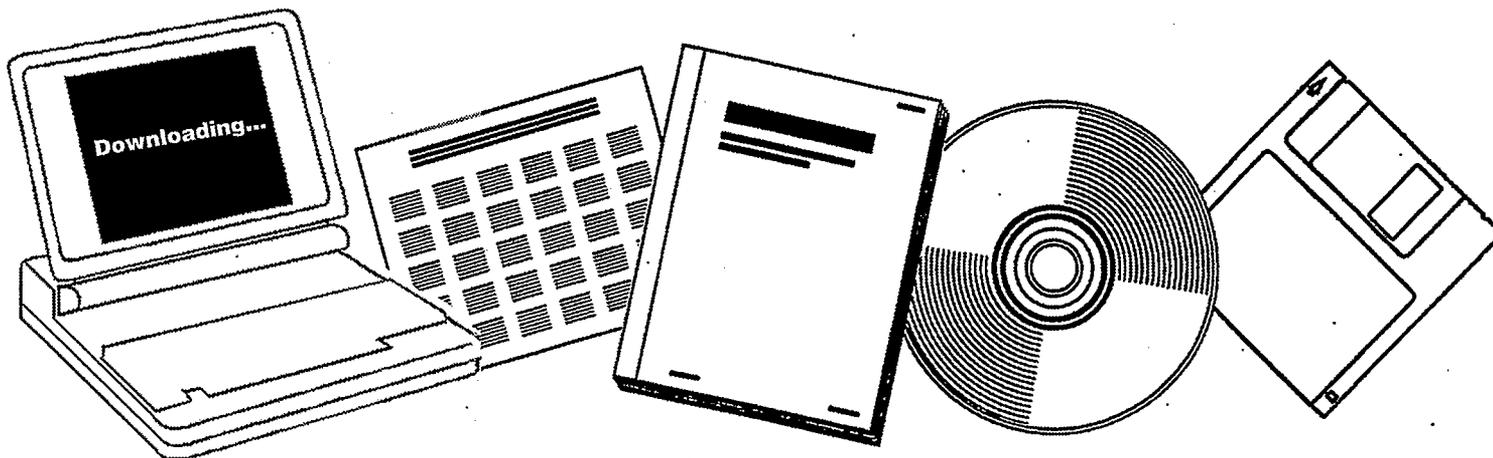
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MECHANISMS OF FISCHER-TROPSCH SYNTHESIS

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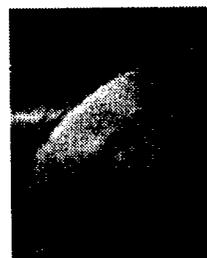
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Mechanisms of Fischer-Tropsch Synthesis

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Introduction

The past decade has seen an extensive effort devoted to elucidation of the fundamental processes occurring on a catalyst surface during Fischer-Tropsch synthesis. Evidence gained from these studies strongly suggests that the synthesis of hydrocarbons and C_2^+ oxygenated compounds is initiated by the dissociation of adsorbed CO to produce individual carbon atoms. Hydrocarbons are formed through hydrogenation of the nascent carbon and association of the resulting species. Aldehydes and alcohols are believed to be formed from acyl groups produced by CO insertion into growing alkyl chains. Much of the evidence supporting this view of Fischer-Tropsch synthesis has been presented in recently published reviews (1-8). As a consequence, the discussion presented here will be limited to an examination of hydrocarbon synthesis over ruthenium. The conclusions

drawn in this discussion are also applicable to other Group VIII metals.

Adsorption and Dissociation of Carbon Monoxide

Infrared studies (9) indicate that CO adsorbs on Ru in one of two principal forms: either as a linearly bound species attached to a single Ru atom or as a gem-diadsorbed species. Studies by Kellner and Bell (10) with Ru/Al₂O₃ catalysts suggest that the latter species predominate on small Ru clusters, or isolated Ru atoms and do not readily react with H₂ at the temperatures normally used for Fischer-Tropsch synthesis. Bridge-bonded CO has also been observed on Ru but this species is rarely observed in high concentration (9).

Under typical reaction conditions, the surface of a Ru catalyst will support close to a monolayer of adsorbed CO. The coverage by this species is relatively insensitive to reaction temperature, or to the partial pressures of H₂ and CO. Isotopic tracer studies by Cant and Bell (11) and Winslow and Bell (12) have shown that the exchange of gas phase CO with adsorbed CO is extremely rapid, and at temperatures above 473K is essentially at equilibrium.

The dissociation of CO to produce nascent carbon has been reported by a number of groups (12-17). The process requires temperatures in excess of 473K (14) and is characterized by an activation energy of approximately 43 kcal/mol (18). Recently, Wise and McCarty (19) have shown that the enthalpy of surface carbon formation on Ru is positive, relative to that of graphite. The insensitivity of the enthalpy of carbon deposition to the fractional coverage with carbon suggests that the formation of C-C bonds, and hence the formation of carbon islands and graphitic overlayers, does not occur readily. Such processes will take place, however, if carbon deposition occurs at elevated temperatures or the nascent carbon is allowed to age (8,17).

The reversibility of CO dissociation on Ru has also been investigated. Studies of isotopic scrambling of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ on Ru/Al₂O₃ catalysts carried out by McCarty and Wise (20) and by Bossi et al. (21) have shown extensive exchange of carbon and oxygen atoms strongly suggesting that CO dissociation is readily reversible. By contrast, the work of Bossi et al. (21), and more recently of Cant and Bell (11), with Ru/SiO₂ catalysts indicate that CO dissociation is virtually irreversible. A similar conclusion has been reached by Winslow and Bell (22) from studies with

Ru-black. It is believed that the high degree of isotopic scrambling observed with Ru/Al₂O₃ results not from the reversibility of CO dissociation, but rather from the formation and decomposition of formate structures on the Al₂O₃ support.

Adsorption of Hydrogen

In contrast to what is known about the concentration of adsorbed CO on the surface of ruthenium catalysts, little is yet known about the concentrations of adsorbed H₂. McKee (23) has observed that when H₂ and CO are coadsorbed on Ru-black at temperatures between 318 and 427K, more than two monolayer equivalents of H-atoms are taken up, together with nearly a monolayer of CO. Since the amount of H₂ adsorbed in the presence of CO was nearly twice that adsorbed in the absence of CO, McKee suggested that adsorbed CO strengthens the adsorption of H₂. The coexistence of high surface concentrations of H-atoms and CO on Ru-black has recently been confirmed by Winslow and Bell (22). It was observed that under reaction conditions (P = 1 atm, T = 443K, H₂/CO = 3) the catalyst contains about 0.8 of a monolayer of H atoms, together with an equivalent amount of CO. Since infrared spectra of adsorbed CO (10) indicate that CO is linearly adsorbed at on-top sites, it is presumed that the H-atoms

are located primarily in the three- and four-fold hollows between Ru-atoms. The exchange between adsorbed H-atoms and gaseous H_2 occurs very rapidly as demonstrated by experiments reported by Cant and Bell (11) which show near equilibrium H_2 - D_2 scrambling under conditions of hydrocarbon synthesis.

Reactions of Nascent Carbon

The nascent carbon atoms produced by CO dissociation are highly reactive. Methane and higher molecular weight hydrocarbons are formed upon interaction of nascent carbon with H_2 at temperatures as low as 275K (19). While the details of the hydrogenation process are not fully understood, it is believed that the first stages involve the formation of CH_x ($x=1-3$) groups by the stepwise addition of atomic hydrogen to single carbon atoms. The existence of such species as ligands in both mono- and polynuclear transition metal complexes is well established (24-26). Evidence for CH_2 groups produced via the decomposition of CH_2N_2 over Ru has recently been obtained by George et al. (27) using EELS, and Erley et al. (28) have observed the presence of CH_2 and CH_3 groups by EELS on an Fe surface following hydrogenation of CO. In situ detection of CH_2 and CH_3 groups on Ru has also been obtained by means of

reactive scavenging using low molecular weight alkenes (29-31). Thus, Ekerdt and Bell (29) and Tamaru et al. (30) have reported the formation of additional propylene when ethylene is added to the synthesis gas feed, and Baker and Bell (31) have reported the formation of cyclopropyl derivatives when cyclohexene or butenes are used as the scavenger.

Formation of Carbon-Carbon Bonds

The formation of C-C bonds via the insertion of a CH₂ group into the carbon-metal bond of an alkyl ligand has been demonstrated with a number of transition-metal complexes (24,26). In most cases, the mechanism of C-C bond formation was inferred from the products observed upon reaction of an alkyl-containing complex with a reagent such as CH₂Cl₂ or CH₂N₂. Direct evidence for reaction between an alkyl group and a methylene group coordinated to the same metal center has now been obtained in several instances. Hayes et al. (32) have reported that Cp₂W(CH₂)(CH₃)⁺ will rearrange to produce Cp₂W(H)(C₃H₄)⁺. Similar chemistry has been observed by Thorn and Tulip (33) working with the complex [P(CH₃)₃]₃BrIr(CH₃)(CH₂OCH₃) 1. As shown in Fig. 1, the reaction of 1 with a stoichiometric amount of HPF produces a "pyridine-trapped" methylene complex 2. Warming 2 results

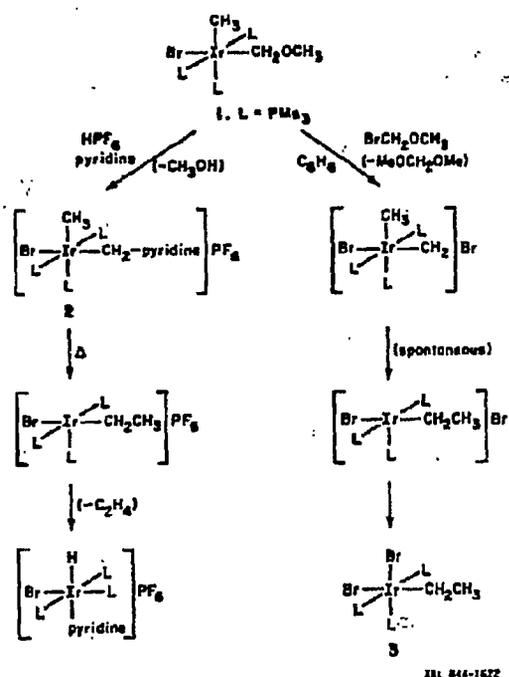


Fig. 1 Illustration of C-C bond formation via migration of an alkyl group to a methylene group. Taken from Thorn and Tulip (33).

in the displacement of the trapping pyridine and migration of the methyl group to the methylene group. The ethyl iridium complex thus formed is unstable and reacts rapidly to produce ethylene and a hydrido complex. A stable ethyl

complex is obtained, though, when 2 reacts in excess bromomethyl methyl ether. An illustration of multiple methylene insertion has been presented by Isobe et al. (34). They observed that pyrolysis of cis- $[\text{C}_5(\text{CH}_3)_5\text{Rh}]_2(\text{CH}_2)(\text{CH}_3)_2$ yields primarily methane (48%), ethylene (20%), ethane (2%), and propylene (30%); only traces of propane and C_4^+ hydrocarbons are formed.

Convincing evidence for the participation of CH_2 groups in the synthesis of hydrocarbons over supported Group VIII metals has been reported by Brady and Pettit (35). They observed that passage of a dilute stream of CH_2N_2 over nickel, palladium, iron, cobalt, ruthenium, and copper catalysts produced a mixture containing ethylene and nitrogen as the principal products. When hydrogen was mixed with the CH_2N_2 mixture, a noticeable change occurred in the product composition. With the exception of copper, each of the catalysts produced a mixture of hydrocarbons consisting mainly of normal alkanes and mono-olefins. The molecular weight distribution of these products is shown in Fig. 2. The similarity of these product distributions to those observed during Fischer-Tropsch synthesis is illustrated for the case of nickel. A strong similarity was also observed in the distribution of C_4 olefins and paraffins.

obtained via reaction of CH_2N_2 and H_2 , and CO and H_2 , over a cobalt catalyst.

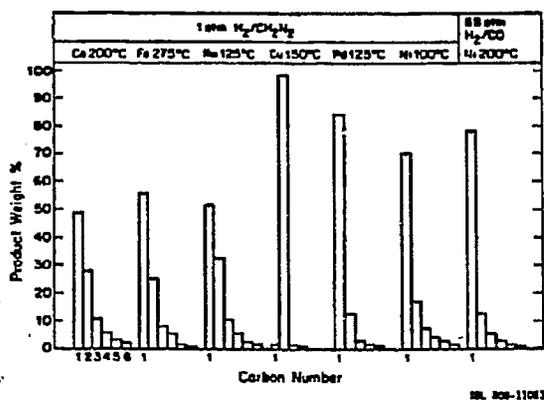


Fig. 2 Product distributions observed upon decomposition of CH_2N_2 over Group VIII metal catalysts in the presence of H_2 . Taken from Brady and Pettit (36).

In a subsequent study, Brady and Pettit (36) examined the effects of adding CH_2N_2 to a CO-H_2 mixture being passed over a cobalt catalyst. It was observed that upon addition of CH_2N_2 , the average molecular weight of the products increased, strongly suggesting that CH_2 groups released by CH_2N_2 decomposition contribute to chain propagation. To test this hypothesis, the experiments were repeated using

^{13}C -labeled CO and unlabeled CH_2N_2 . The distribution of isotopically labeled propylene observed at different levels of CH_2N_2 addition was consistent that predicted by the methylene insertion mechanism of chain growth, but could not be rationalized by either the enol-condensation or CO-insertion mechanisms proposed in earlier studies (1-8).

Structure and Reactivity of Carbonaceous Deposits

Considerable information concerning the kinetics of carbon formation and consumption and the existence of different modifications of carbon on Ru catalysts has been gained through the use of isotopic tracers (i.e., ^{13}C CO and C^{18}O). As noted earlier, work by Biloen et al. (16) and Cant and Bell (11) has shown that the dissociation of adsorbed CO appears to be irreversible under conditions of CO hydrogenation. The carbon thus formed exhibits a reactivity similar to that of carbon produced by CO disproportionation (12-17) with respect to the formation of methane and higher molecular weight hydrocarbons. Tamara and coworkers (30,37) have suggested that a part of the carbon inventory on the catalyst is in the form of hydrocarbon chains attached to the metal surface. It was proposed that these species can resupply the catalyst surface with single carbon atom units by scission of the C-C bonds in the chains.

More recently, Winslow and Bell (12,22) have shown that there can be two distinctly different forms of carbon on the surface of Ru/SiO₂ and Ru-black catalysts. The two forms, designated C_α and C_β, exhibit quite different kinetics of formation and consumption. As shown in Fig. 3, the surface coverage of C_α rapidly comes to a steady state value with time under reaction conditions. The steady-state rate of methane formation is found to be a linear function of C_α.

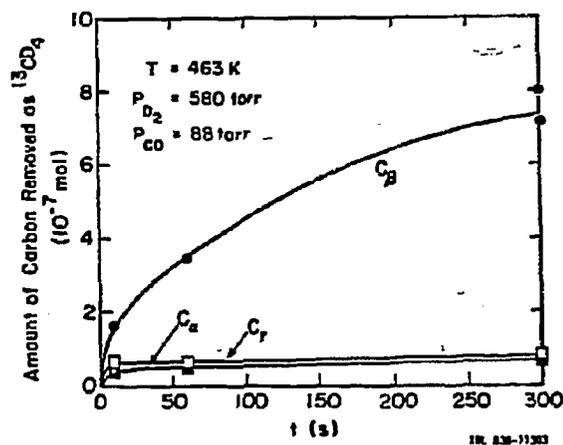


Fig. 3 Influence of reaction time on the distribution of carbon forms deposited on Ru/SiO₂ during CO hydrogenation. Taken from Winslow and Bell (12).

coverage. C_{β} is less reactive than C_{α} , and the surface inventory of C_{β} increases steadily with time. Studies carried out with Ru-black (22) indicate that the β -form of carbon contains some hydrogen and that the H/C ratio of the deposited C_{β} increases from 1.0 to 2.0 as the reaction proceeds. Since the adsorption of CO is not impeded to a large extent by the accumulation of C_{β} , it is concluded that only a small portion of the deposit is attached directly to the surface of Ru.

The characterization of C_{α} and C_{β} by solid-state NMR has been reported by Duncan et al. (38). Examples of the spectra obtained are given in Fig. 4 and the surface concentrations of different species are presented in Table 1. The spectrum of C_{β} is characterized by a narrow line centered at -20 ppm. Both the position of this feature and its broadening when the temperature of the sample is reduced suggest that it be assigned to alkyl-type structures attached to the Ru surface. By contrast to C_{β} , the spectrum of C_{α} is quite broad and spans the region from approximately -200 to -400 ppm. Peaks observed in this portion of the spectrum are best assigned to isolated carbon atoms bonded to several surface Ru atoms. The spectrum labeled unreactive carbon is observed after the reactive forms of carbon

have been removed from the catalyst surface by reaction with H_2 . The position and shape of this feature are in excellent agreement with those for graphite. It is interesting to note in Table 1 that the inventories of carbon in the different forms determined from ^{13}C NMR spectra and isotopic tracer studies are in very close agreement.

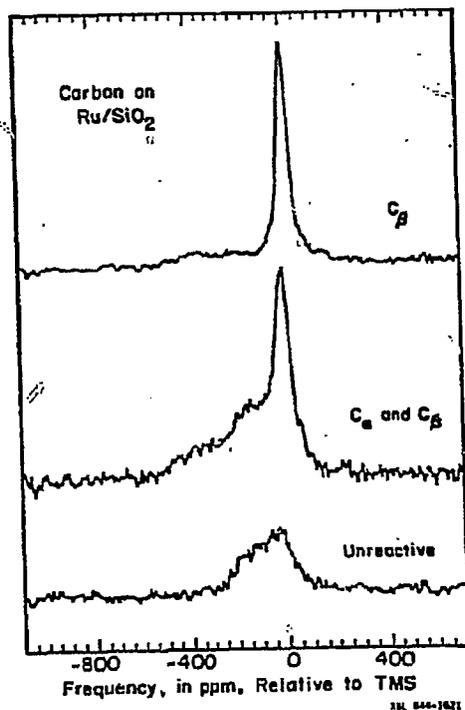


Fig. 4 ^{13}C NMR spectra of carbonaceous deposits formed on the surface of Ru/SiO_2 during CO hydrogenation. Taken from Duncan et al. (38).

Table 1 Distribution of Carbonaceous Species Deposited on Ru/SiO₂ during CO Hydrogenation

Sample	Carbon Type	Amount of Carbon	
		¹³ C-NMR	Isotopic Tracing
C _β	α	trace	0.002
	β	0.14	0.11
	graphite-like	0.06	b
C _α and C _β	α	0.07	0.06
	β	0.06	0.06
	graphite-like	0.07	b
Unreactive	graphite-like	0.05	b
CO _s	CO _s	0.22	0.27

^a Based on total Ru atoms

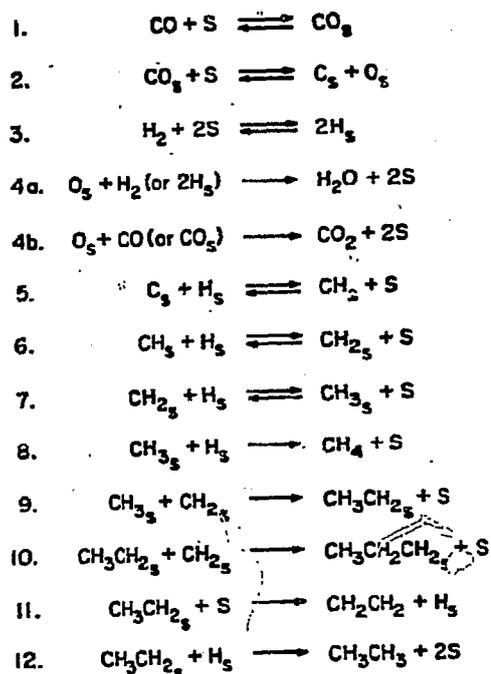
^b Not observable

Summary and Conclusions

A summary of the pathways linking CO and H₂ to various

surface species as well as the final products is given in Fig. 5. Both H_2 and CO in the gas phase are virtually in equilibrium with adsorbed H atoms and CO. The dissociation of CO is an activated process on Ru but is essentially irreversible. The carbon atoms released by CO dissociation react very rapidly via a reversible sequence of steps to form CH_x ($x=1-3$) groups. Carbon-carbon bonds appear to be formed via alkyl group migration to methylene groups and insertion of the latter species into the metal-carbon bond of the alkyl. Termination of chain growth can occur by β -hydrogen elimination to form 1-olefins or by reductive elimination to form normal paraffins. The extension of the proposed scheme to account for the formation of branched hydrocarbons and oxygenated products can readily be envisioned. Branching can result from isomerization of the growing chain. The insertion of CO into the metal-carbon bond of a surface alkyl group will produce an acyl group which is then a precursor to the formation of an aldehyde or alcohol. While the discussion presented here has been limited to Ru, the same chemistry is expected to occur on other Group VIII metals. Consistent with this, several recent studies of Fischer-Tropsch synthesis over Ni, Fe, and Co have proposed reaction mechanisms equivalent to that shown in Fig. 5. The observed differences in reaction

kinetics and product distribution are, therefore, very likely due to differences in the rate and equilibrium parameters associated with individual reaction steps.



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Fig. 5 Reaction mechanism for Fischer-Tropsch synthesis over Ru and other Group VIII metals.

Acknowledgment

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