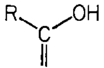
JOURNAL OF CATALYSIS 50, 176–180 (1977)

Mechanism of Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen

When a 1:1 mixture of hydrogen and carbon monoxide is passed over a suitable catalyst, Fischer–Tropsch synthesis (FTS) occurs:

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O.$$

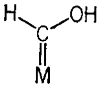
The special case of $n = 1$ is referred to as methanation. Many mechanistic schemes have been proposed for this synthesis (*1*) and the surface intermediate is currently thought to be of the type



chain growth occurring by elimination of water. Similar species are usually invoked in methanation (*1a*) although the involvement of dissociated carbon monoxide has recently been proposed (*2*).

In recent years much definitive information on the reactivity of simple gases with metal surfaces has been provided by photoelectron spectroscopy (*3*). The purpose of this note is to use some of this information to formulate what is thought to be a more realistic mechanism for Fischer–Tropsch synthesis. The proposed mechanism is not intended to apply at very high pressures (100–1000 atm), but is believed to reflect molecular events during synthesis at atmospheric pressure.

The interaction of methanol with nickel (*4*), palladium (*5*), and tungsten (*6*) has been studied at 295 K by ultraviolet photoelectron spectroscopy (ups). In each case the result, at a pressure of ~10^{-4} Pa, was the decomposition of methanol into an adsorbed monolayer of carbon monoxide. None of these studies has isolated any intermediate or precursor to chemisorbed carbon monoxide. Similarly Hall *et al.* (*7*) were unable to incorporate methanol into FTS products, observing instead its decomposition into carbon monoxide. We believe that these results cast serious doubts on the involvement of intermediates such as



which are closely related to methanol.

Both X-ray and ultraviolet photoelectron spectroscopy have shown that carbon monoxide can be dissociated on a number of metal surfaces (*8*). The resulting surface resembles a mixed monolayer of oxide and carbide, although this should not be interpreted as indicating the formation of *bulk* oxide or carbide. Subsequent heating causes recombination of carbon and oxygen, and desorption of carbon monoxide. The ease with which metals dissociate carbon monoxide can be related to the stability of the metal carbides (*3b*). Thus, tungsten and molybdenum dissociate CO below 170 K (*9, 10*). Metals with thermally unstable carbides, such as iron and nickel, dissociate CO between 300 and 420 K (*11, 12*), while adsorption on the platinum metals appears always to be predominantly molecular (*13*). We believe that these results suggest the involvement of CO dissociation in FTS, and the following are proposed to be the

ISSN 0021-9517

initial steps:

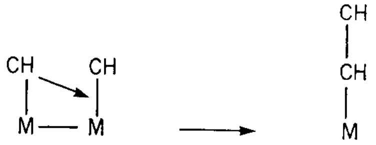
$$CO_{(g)} \rightarrow CO_{ads} \rightarrow C_{ads} + O_{ads}$$

$$H_{2(g)} \rightarrow H_{2_{ads}} \rightarrow 2H_{ads}$$

$$C_{ads} + H_{ads} \rightarrow CH_{ads};$$

$$O_{ads} + H_{ads} \rightarrow OH_{ads}.$$

All of these steps are believed to occur rapidly. Subsequent methanation results from the hydrogenation of CH_{ads} units, this being the rate-determining step. Formation of higher hydrocarbons involves addition of CH_{ads} units and hydrogenation. The addition probably occurs by a carbene-type CH insertion:



since this would lead to the predominance of straight-chain hydrocarbons which is usually observed. The detailed product distribution can still be analyzed within the scheme proposed by Anderson *et al.* (*14*), which is equally applicable to CH and oxygenated building blocks.

This mechanism is believed to provide, for the first time, an explanation of the relative activities of metals in FTS, which are governed by their effectiveness in carbon monoxide dissociation. On iron, and probably on cobalt, the complete adlayer is expected to be dissociated at synthesis temperature. The concentration of CH groups is therefore high and, in agreement with observation, formation of higher hydrocarbons is facilitated. On nickel, CO dissociation has a higher activation energy than on iron, desorption competing more effectively with dissociation. The concentration of –CH groups is thus likely to be low and hydrogenation (i.e., methanation) predominates. The extent of dissociative adsorption is least on the noble metals and activity, even in methanation, is very low. In the case of ruthenium only the close packed (0001) plane has been examined by photoelectron spectroscopy and a dissociated layer can be formed only by electron beam interaction (*15*). Ruthenium, which is an excellent methanation catalyst, may resemble nickel, where rough surfaces are more effective than close packed planes in CO dissociation (*16*).

Invoking carbon monoxide dissociation is open to the objection that tungsten and molybdenum, which dissociate CO more readily than either iron or nickel, are nevertheless poor FTS catalysts. It seems likely that on these metals the adsorbed carbon species is too stable to be easily hydrogenated.

The mechanism proposed here relies only on intermediates known to be stable in vacuum, the stability of CH groups on nickel having been demonstrated by Demuth and Eastman (*17*). The stability of intermediate surface species is thought to be a prerequisite in FTS, which unlike many catalytic reactions requires a high concentration of intermediates to facilitate chain growth. The involvement of CH rather than CH_2 entities is suggested for several reasons; various studies (reviewed in Ref. *1a*) have suggested that the surface stoichiometry is CH_2O, supporting the presence of CH and OH species. The involvement of CH_2 groups would also appear to be ruled out by the experiments of Blyholder and Emmett (*18*). They showed that ketene ($CH_2{=}CO$) fractured at the catalyst surface, yielding CH_2 and CO entities, but that the CH_2 species did not act as a chain-building unit in FTS.

The proposed mechanism is consistent both with the observed product distribution and reaction kinetics. Since the reaction can be viewed as a polymerization process, a wide range of molecular weights is expected and found. If the CH species is the chain-building unit it is also clear that primary and secondary carbon atoms will occur in the products, but that tertiary carbon atoms are, in accordance with experimental observation, forbidden. Again in agreement with observation, carbene insertion should favor straight chain over branched hydrocarbon synthesis.

The observed reaction kinetics are first order in hydrogen, as would be expected under any mechanism where hydrogenation is involved in the rate-determining stage. An explanation can also be offered for the negative pressure dependence in carbon monoxide which is noted on the more active metals (*1a*). On metals such as tungsten, where CO dissociation is facile, a weakly held pressure-dependent layer of molecular (α)-CO is observed, coexisting with the dissociated layer. On FTS active metals the existence of such a weakly held, molecular layer can also be expected, especially at high CO pressures. This will reduce access of hydrogen to the dissociated layer, resulting in a negative pressure dependence.

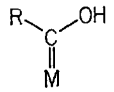
The proposed mechanism is thought to be compatible with the evidence from infrared spectroscopy. Thus Blyholder and Neff (*19*) were able to show the presence of C–H and O–H bonds at the surface of silica-supported iron, as would be expected from the ideas presented here. They presented no evidence to support carbon to oxygen bonding.

The mechanism suggests an alternative explanation of the role of sulfur as a poison in FTS. Rather than simply blocking sites for CO and H_2 adsorption, sulfur may act to suppress CO dissociation. Thus Kishi and Roberts (*11*) have shown that less than one-half of a monolayer of adsorbed sulfur suppresses CO dissociation on iron at 295 K, the adsorbed CO remaining molecular in nature. In this context it is interesting to note that sulfur is used commercially as a catalyst in the carbonylation of nickel, clearly a situation where it is necessary for CO to maintain its molecular identity.

The proposed mechanism is based mainly on experiments on clean metal surfaces generated under uhv conditions, and reactions carried out at pressures not exceeding $\sim 10^{-2}$ Pa. It is therefore open to attack on several grounds.

(i) Reaction may occur only at a very small number of active sites and may not involve stable, long-lived surface species. In general, this argument can be expected to have much force, but it seems inappropriate in the case of higher hydrocarbon synthesis. Here the close approach of suitable building units is required and this is possible only if the site density *and* the concentration of building blocks are high. FTS is therefore likely to be a particularly good case for argument of the sort employed here.

(ii) The stable surface species may change as the pressure is increased. This is probably the most difficult charge to answer. Under uhv conditions it is known that CH species are stable at a nickel surface at 295 K. Under a higher pressure of hydrogen it is possible that $CH_{2_{ads}}$ or even $CH_{3_{ads}}$ may be stabilized. We have given arguments above to indicate why the building unit is unlikely to be CH_2 or (CH_3) groups, and why we believe that intermediates of the type



are unstable. Also, at atmospheric pressure and synthesis temperature formation of methanol is thermodynamically forbidden. It is emphasized that different surface species may arise at much higher pressures ($>$100 atm), where alcohol synthesis becomes thermodynamically feasible. The Fischer–Tropsch process is, however, only successful in producing monohydric alcohols, which could result from direct ligand insertion of carbon monoxide.

(iii) Catalysis may occur in a weakly held "second adsorbed layer" rather than in the strongly held chemisorbed layer. The negative CO pressure dependency observed on FTS-active metals suggests, as noted above, that such a second layer inhibits rather than enhances activity.

(iv) The working catalyst surface may not resemble that inferred from the results of adsorption on a clean metal. This objection is believed to be at its least serious when applied to reactions carried out in hydrogen.

Lastly we consider the relationship between heterogeneous Fischer–Tropsch synthesis and homogeneous chemistry. Henrici-Olivé and Olivé (*20*) have recently proposed a mechanism for FTS based on steps known to occur in homogeneous catalysis. This approach may be misguided, as no exact homogeneous analogue of FTS is known. The nearest reaction scheme, described in a patent by Pruett and Walker (*21*), uses rhodium complexes under very high pressures (200–1000 atm) The prin-. cipal products of their synthesis are polyhydric alcohols containing two or three hydroxyl groups. Since the only alcohols efficiently produced even by high-pressure FTS are monohydric it seems likely that heterogeneous FTS and the homogeneous Pruett–Walker alcohol synthesis occur by different mechanisms. If, as suggested here, carbon monoxide dissociation is an important step in FTS it becomes clear that no homogeneous analog is expected since homogeneous CO dissociation is not known.

Note added in proof. K. J. Singh and H. Grenga (*J. Catal.* **47**, 328 (1977)) have recently shown that carbon monoxide is catalytically dissociated at steps near the low index poles of a ruthenium single crystal. This is in full support of the ideas presented above.

ACKNOWLEDGMENTS

The author is grateful for many stimulating discussions on this topic, in particular with Professor M. W. Roberts, Dr. J. R. H. Ross, and Dr. J. J. Rooney. He is also grateful to Dr. J. C. Fuggle, Professor D. Menzel, and Dr. M. A. Vannice for access to preprints and to I.C.I. Ltd. (Petrochemicals Division) for financial support.

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Received October 14, 1976; revised May 16, 1977