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The Formation of Hydrocarbons via the Reaction of HCN with H_2 on Iron Catalysts

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It is shown that HCN reacts with H_2 on a Fischer–Tropsch catalyst to form hydrocarbons. As can be concluded from the product spectrum and the olefin contents in the hydrocarbon fractions the mechanism of the HCN–H_2 reaction is that of the Fischer–Tropsch synthesis. These results strongly support a mechanism which includes the formation of higher hydrocarbons by the reaction of carbidic C species formed by the dissociation of the reactant gas.

INTRODUCTION

A number of recent investigations using modern surface analysis have shown that carbidic and graphitic carbon species can be detected on the surface of Fischer–Tropsch catalysts (*1*, *2*). Although these findings strongly support a carbide mechanism for Fischer–Tropsch syntheses, it could be objected that the composition of the surface is drastically changed during the transfer of the catalyst into an ultrahigh-vacuum chamber and that these carbon species are not the real intermediates of the Fischer–Tropsch reaction.

To support the carbide mechanism, additional evidence may be sought from experiments in which carbon monoxide is substituted by oxygen-free carbon species, since the presence of undissociated carbon monoxide plays an important role in earlier mechanistic models (*3*). Experiments of this kind were carried out by Brady and Pettit (*4*) who showed that CH_2N_2 reacts with hydrogen on Fischer–Tropsch catalysts to form higher hydrocarbons. Furthermore, van Barneveld and Ponec (*5*) investigated the reaction of chlorinated methanes with H_2 on Fischer–Tropsch catalysts. Although the presence of chlorine could induce severe changes in the structure of the catalytic surface, the authors were able to show that higher hydrocarbons were produced and that the selectivity for the formation of higher hydrocarbons depends on the number of hydrogen atoms x in the intermediate CH_x radicals. Results of experiments with H_2/C_2H_2-mixtures are also insufficient in that the product gas contains high amounts of C_2- and C_4-hydrocarbons, which are formed apart from the Fischer–Tropsch reaction (*6*). It is therefore of interest to carry out experiments with HCN, since this molecule is expected to decompose into CH and N upon adsorption, and it is the aim of this paper to show that carbidic surface species formed upon adsorption of HCN on Fe catalysts do indeed react with hydrogen to give typical Fischer–Tropsch products.

Due to their analogous electronic structures there are a number of similarities between CO, HCN, and the CN radical, respectively, and significant ones are listed in Table 1.

No experimental data exist about the dissociation of adsorbed CN species on Fe surfaces. Indirect evidence is given by the results of Bridge and Lambert (*7*) who showed that CN radicals are adsorbed dissociatively on Pt(110) and Pt(110) surfaces. On the other hand, Brodén *et al.* (*8*) showed that a borderline exists in the Periodic Table of the elements between molecular

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TABLE 1

Similarities between CO, HCN, and the CN Radical

	Interatomic distance (Å)	Dissociation energy (eV)
CO	r_{C-O} 1.13	$D(C-O)$ 11.11
CN	r_{C-N} 1.17	$D(C-N)$ 7.76
HCN	r_{HC-N} 1.16	$D(HC-N)$ 9.69
Standard enthalpy of methane formation (kJ mol^{-1})		
$HCN + \frac{3}{2} H_2 \rightarrow CH_4 + \frac{1}{2} N_2$		$\Delta H = -205.2$
$HCN + 3H_2 \rightarrow CH_4 + NH_3$		$\Delta H = -251.2$
$2CO + 2H_2 \rightarrow CH_4 + CO_2$		$\Delta H = -247.0$
$CO + 3H_2 \rightarrow CH_4 + H_2O$		$\Delta H = -205.9$

and dissociative adsorption of diatomic molecules. This borderline shifts with decreasing dissociation energy of the adsorbate to higher atomic numbers. Since the adsorption of CO on Fe has been shown to be dissociative and since the dissociation energies D(C–N) and D(HC–N) are lower than D(C–O), it can be concluded that HCN and CN dissociate on Fe surfaces.

EXPERIMENTAL

Experiments were carried out in a tubular flow reactor which contained 0.2 g of an iron catalyst. The catalyst was prepared by reducing a mixture of 86% carbonyl-iron (reduced pentacarbonyl iron), 9% $Al(OH)_3$, 4% Fe_2O_3, and 1% K with hydrogen at a temperature of 300°C. The reduction was extended over a period of 3 weeks to remove the carbon impurities from the catalyst which react with the hydrogen to form hydrocarbons.

The feed gas (8 l stp $H_2:HCN = 1:1$) was prepared by decomposing an aliquot of KCN with H_2SO_4 in a stainless-steel tank. After the decomposition the tank was filled with hydrogen to a pressure of 8 bar. During the experiments the tank and the lines were heated to 60°C to prevent the condensation of the HCN.

After the reduction the gas stream was switched from hydrogen to the H_2/HCN feed. The space velocity was 300 h^{-1}, the temperature of the reactor 300°C. Because of the limited feedstock the pressure decreased during the experiment as shown in Fig. 1. The product gas was passed through an $AgNO_3$ solution to remove the unreacted HCN. Samples were collected in appropriate gas flasks and analyzed by gas chromatography.

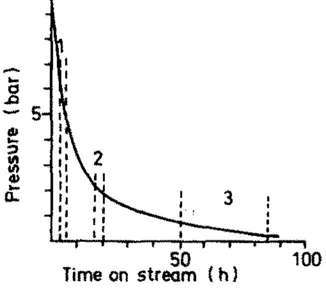


FIG. 1. Decrease of H_2/HCN feed gas pressure during the experiment.

RESULTS

The result of a typical experiment is given in Table 2. As can be seen from the corresponding Schulz–Flory–Anderson plot in Fig. 2 a typical Fischer–Tropsch product spectrum is obtained. It should be noted that despite the decreasing pressure

TABLE 2

Production of Hydrocarbons from H_2/HCN on a Supported Iron Fischer–Tropsch Catalyst

Sample No.[a]	1	2	3
Temperature (°C)	300	300	300
Pressure (bar)	6.6	3	2
Time on stream (h)	5	19	69
Hydrocarbons, $C_n + C_n^{2-}$ (vol%)			
C_1	5.2	9.6	6.4
C_2	0.42	1.37	1.47
C_3	0.08	0.35	0.47
C_4	0.02	0.08	0.13
Olefin content $\gamma_n = C_n^{2-}/(C_n + C_n^{2-})$			
γ_2	0.029	0.033	0.01
γ_3	0.072	0.152	0.077
γ_4	0.338	0.429	0.343

[a] See Fig. 1.

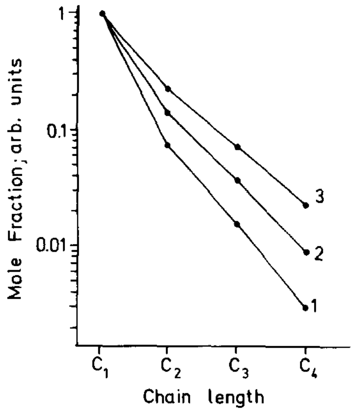


FIG. 2. Schulz–Flory–Anderson plot of the reaction products for different times on stream; (1) 5 h, (2) 19 h, and (3) 69 h.

the probability of chain growth α increases with time on stream. This effect has to be attributed to the normal induction period of the catalyst. No NH_3 could be detected in the outlet gas.

Additional evidence that the H_2/HCN reaction on Fe catalysts really is a complete analog of the Fischer–Tropsch synthesis comes from an analysis of the olefin content of the hydrocarbon fractions. To make this clear, we would like to demonstrate that a correlation exists between the olefin contents in the Fischer–Tropsch products. In Fig. 3 the olefin contents of the C_2 and the C_4 fractions [defined as the molar ratio $\gamma_n = C_n^{2-}/(C_n^{2-} + C_n)$] are plotted as a function of the olefin content of the C_3 fraction, γ_3. Although these data were taken from the results of a large number of different experiments and laboratories, it is obvious that the γ_2 and γ_4 values are grouped near to two curves. Since this correlation holds independently of the individual conditions

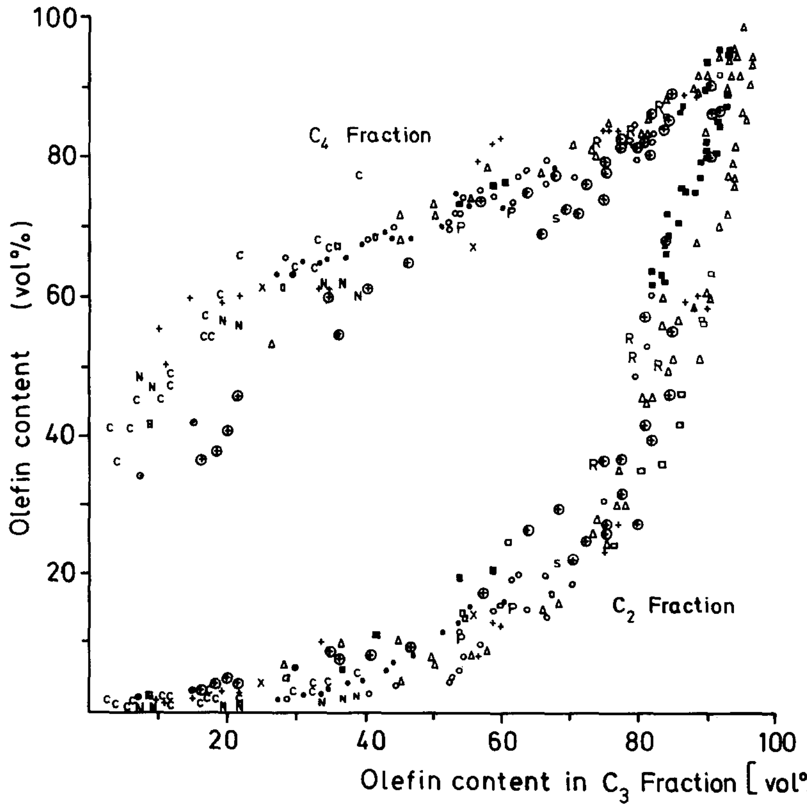
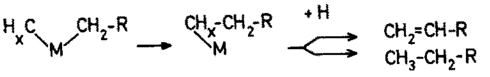


FIG. 3. Correlation between the olefin contents in the C_2, C_3, and C_4 fractions. ⊕, Schering report (*10*); ■, Fe-whisker catalyst; □, Fe-whisker catalyst + 1% K; ×, technical iron; +, variation of CO/H_2 ratio on whisker catalysts; R,P, whisker + 1% Ru or 1% Pt, respectively; ○, HCN + H_2 reaction; N, nickel catalyst; C, H_2 + CO_2 on Fe whisker.

it has to be concluded that the correlation is due to a characteristic step in the Fischer–Tropsch synthesis. The γ_2 and γ_4 values of the H_2/HCN experiments agree well with the bulk of the values in Fig. 3, indicating that the mechanism of this reaction is that of the Fischer–Tropsch synthesis.

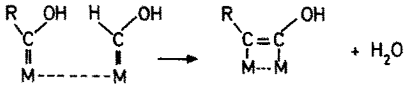
DISCUSSION

The results of our experiments can easily be explained in terms of a mechanism which involves the insertion of carbidic surface species (e.g., CH_x radicals) into a M—CH_2—M bond (*2*):



(1)

On the other hand, our results give rise to severe objections to any mechanism based on the condensation of oxygenated compounds, e.g.,



(2)

The analog of reaction (2) in the H_2/HCN system would be the condensation of adsorbed amines according to

(3)

Although NH_3 is stable under the prevailing conditions it could not be detected in the product gas.

Finally we should discuss mechanisms which are based on the chemistry of iron complexes (*9*). In these mechanisms chain growth is explained by the insertion of undissociated CO into the M—R bond of a $(CO)_xM$—R surface complex:

(4)

The analogous reaction in the H_2/HCN system would be the insertion of CN or HCN to form a $(CN)_xM$—(CN)—R complex. However, it seems quite improbable that this complex can be hydrogenated without formation of NH_3 and that the substitution of CO by CN should not alter the olefin–paraffin ratio of the reaction products (see Fig. 3).

TABLE 3

Formation of Nitrogen, as Derived from Data Obtained from Experimental Values and Stoichiometry

Reaction products (vol%); experimental values		Nitrogen formed according to $HCN + \frac{1}{2}H_2 \rightarrow -(CH_2)- + \frac{1}{2}N_2$
C_1	1.67	0.83
C_2	0.33	0.33
C_3	0.094	0.14
C_4	0.015	0.03
N_2	3.39	N_2 = 1.33

According to the stoichiometric equation

$$HCN + \tfrac{1}{2}H_2 \longrightarrow -CH_2- + \tfrac{1}{2}N_2 \qquad (5)$$

$\frac{1}{2}$ mol of nitrogen should be formed for each mole of carbon atoms in the product gas. A typical analysis of the product gas is given in Table 3.

As can be seen, the observed amount of hydrocarbons can account for 1.33 vol% of nitrogen, whereas 3.39 vol% have been found. Taking into account the production of nitrogen which arises from the formation of the C_4^+ hydrocarbons, the amount of nitrogen will not change appreciably. The difference is obviously due to the formation of carbon species and carbidic phases on the surface of the catalyst.

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