Reactions of CH$_x$Cl$_{4-x}$ with Hydrogen: Relation to the Fischer–Tropsch Synthesis of Hydrocarbons

W. A. A. VAN BARNEVELD AND V. PONEC

Gorlaeus Laboratories, State University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Reactions of chlorinated methane molecules have been followed in mixtures with H$_2$ alone, or with H$_2$ and CO, on metals with varying activities and selectivities in the Fischer–Tropsch synthesis (Ni, Co, Cu, Fe, Rh, Pd) and on some alloys (Ni–Cu; Ni–Pd). It appeared that metals active in the Fischer–Tropsch synthesis produce higher hydrocarbons both in the absence and presence of CO. This confirms the idea that oxygen-free intermediates (–CH$_y$–) lead to the formation of hydrocarbon chains; the surface concentration of these species appears to be essential for the selectivity.

INTRODUCTION

It is now generally accepted that Fischer–Tropsch synthesis of hydrocarbons is a gradual growth of hydrocarbon chains, by addition (insertion) of monomeric units, and not a block-like polymerization of partially hydrogenated carbon, a reaction on which Fischer and Tropsch speculated in the early days of their studies. The very strong indication for a stepwise polymerization is the product distribution. It follows usually very closely the Flory–Schulz–Anderson equation derived for a stepwise polymerization (*1–8*).

While the overall character of the Fischer–Tropsch "surface-localized" polymerization could be considered as having been well established when the work for this paper started, the question as to *which monomeric units lead to polymerization* was still vividly discussed, and to a less extent discussion is still going on. The monomeric units suggested in the literature were: (i) oxygenated intermediates, like metal-bound hydroxycarbenes (*4, 9–12*); (ii) oxygen-free intermediates, generated by CO dissociation (*2*) or by dissociation of hydroxycarbenes (*13*); (iii) CO molecules, undergoing an insertion (alkyl-shift) which is followed by hydrogenolysis of the C–O bond (*14*). In the meantime, the mechanism

involving oxygen-free intermediates, generated by CO dissociation, has received very strong experimental support from the results of Biloen *et al.* (*2, 15*) and Brady and Pettit (*16, 17*). Nevertheless, it is hoped that readers of this Journal will be interested also in additional support of this mechanism, as obtained by the present study. The paper is intended to complete the information which has been mentioned earlier in a very fragmentary way (*3, 18*). Finally, results on the CH$_x$Cl$_{4-x}$/H$_2$ reaction should be of interest, as such, for those who are interested in C$_1$-chemistry in general.

EXPERIMENTAL

The metal catalysts used have been prepared by conventional methods. Ni, Fe, Cu, Co, and Ni–Cu alloys were prepared by precipitation and decomposition of carbonates followed by reduction (670 K, 2 h) in hydrogen (*19, 20*). Palladium has been prepared by reduction of chloride solution by hydrazine chloride (Kulifay (*21*)); Ni–Pd alloy was prepared by decomposition of a mixture of nitrates in a fast N$_2$ stream and by reduction of the products of decomposition at 655 K (15 h). X-Ray diffraction (as well as the catalytic data themselves) revealed that some alloying, although not perfect, was achieved. Rh was prepared by re-
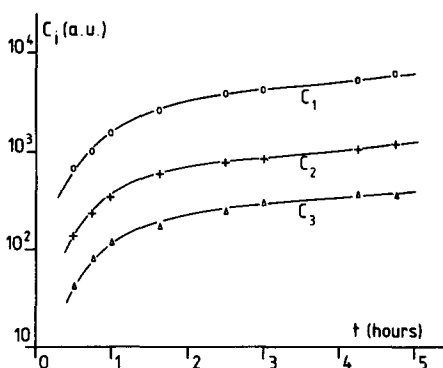
382

FIG. 1. Conversion of CHCl$_3$ into C$_i$ hydrocarbon (logarithm of the concentration in arbitrary units) at 483 K, as a function of time, with a Ni catalyst.

duction with H$_2$ at 665 K (2 h) of powdered RhCl$_3$. After the preparation described, catalysts have been placed in the catalytic reactor and rereduced *in situ* at 655–665 K, for at least 15 h. Chemical composition was also checked after the reactions with CH$_x$Cl$_{4-x}$ compounds, by using X-ray diffraction.

Only those experiments in which a long-term poisoning has been checked have been carried out in a conventional open flow apparatus. All other experiments discussed below have been made in a small, all-glass, static apparatus, where gases were circulated through the reactor. A magnetically agitated propeller has been used to move the gases. Reactions were studied in a standard way, at 110 kPa total pressure. When CO/H$_2$ mixture was used, the ratio was 4/7. Most of the reactions were performed in such a way that 0.55 kPa of CH$_x$Cl$_{4-x}$ was added into pure hydrogen (110 kPa). Alternatively, this amount was mixed with a CO/ H$_2$ mixture, or added to this mixture under a running reaction.

Analysis has been performed by GLC. Peak heights were converted, by using experimentally determined calibration factors, into values proportional to the molar concentrations, C$_i$'s (i = number of carbon atoms in the molecules) and the selectivity, S_{2+}, for the formation of higher hydrocarbons has been evaluated according to the

expression:

$$S_{2+} = \frac{2C_2 + 3C_3 + \ldots}{C_1 + 2C_2 + 3C_3 + \ldots}$$

RESULTS

No attempt has been made to analyze quantitatively components in the gas phase other than hydrocarbons and their chlorinated derivatives. However, a simple check revealed that HCl was indeed formed while, on the other hand, no indication was observed of the presence of Cl$_2$ in the gas phase.

A molecule of CH$_x$Cl$_{4-x}$ (with x = 1–3) can be adsorbed with dissociation in two ways: (a) by a fission of the C–Cl bond or (b) by splitting off of hydrogen. As the hydrocarbon/D$_2$ exchange of CH$_4$ or C$_2$H$_6$ shows, the second case (b) cannot be discarded. However, the first adsorption is clearly favored thermodynamically. For example, in CH$_3$Cl, the bond strength of the C–H bond is 422 kJ/mol (*22*), and that of the C–Cl bond 351 kJ/mol (*23*). Both adsorption modes would lead to similar products in the next reaction steps. However, as we shall see below, the experimental data themselves bring support for the view that the thermodynamically favored mode is indeed formed, either solely or as a strong prevailing contribution.

Typical data on the CH$_x$Cl$_{4-x}$ (x = 1–3) reactions are represented by Figs. 1 and 2.
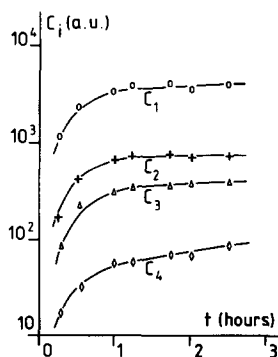

FIG. 2. Conversion of CH$_2$Cl$_2$ into C$_i$ hydrocarbon (logarithm of the concentration in arbitrary units) at 483 K, as a function of time, with a Co catalyst.

TABLE 1

A Comparison of Behavior of Various CH_xCl_{4-x} Compounds[a] in Mixtures with Hydrogen

Catalyst	Compound	S_{2+}	C_2H_4/C_2H_6
Ni	CH_3Cl	0	—
	CH_2Cl_2	0.07	0
	$CHCl_3$	0.37	0
Co	CH_3Cl	0	—
	CH_2Cl_2	0.47	1.2
	$CHCl_3$	0.68	1.6

[a] Standard mixtures with H_2 at 483 K, after 1 h of reaction time.

The reactions ran up to high conversions of the CH_xCl_{4-x} added. Figure 1 shows the time course of the reaction of $CHCl_3/H_2$ on Ni, at 483 K and standard conditions. Figure 2 shows the same, but for CH_2Cl_2/H_2 on cobalt. A comparison of the three compounds studied can be seen in Table 1.

As can be seen from Table 1, CH_3Cl neither dimerizes or polymerizes, but already CH_2Cl_2 does. One would expect that if the adsorption accompanied by C–H bond fission were extensive, these two compounds should not differ that much. Copper catalysts convert a small part of CH_2Cl_2 into CH_4; a reaction of CH_3Cl into CH_4 has been observed with Ni and Co. We see all these facts as additional support for the conclusion that the prevailing adsorption mode arises from C–Cl bond fission.

Also $NiCl_2$ has been tested as a catalyst. The reason was that possibly Ni^{n+}-ions and not Ni^0-metal atoms could have been the catalysts of hydrocarbon chain growth. However, $NiCl_2$ appeared to be completely inactive with CH_2Cl_2, under standard conditions. When the temperature was raised to about 575 K, the catalyst became active, but it was under conditions when, as a parallel study by DTA/GTA showed, the reduction of $NiCl_2$ had already started (ca. 547 K).

Evidently, according to these data, under standard conditions Ni metal is not converted into bulk chloride, in compliance with the fact that also by X-ray diffraction no chloride was observed after the contact of Ni with CH_xCl_{4-x}/H_2 mixtures. One might argue that Ni^{n+}-ions are necessary for the polymerization step, but $NiCl_2$ is inactive because some Ni metal is needed to supply hydrogen atoms, required for the reactive desorption of hydrocarbons. However, one might expect that a mixture of Ni metal and $NiCl_2$ would be the optimal catalyst, but this has been not observed. Also, when HCl was injected into the various reaction mixtures it had no effect on the reactions running.

Co, Cu, and Ni–Cu alloys are much more susceptible to poisoning than Ni, in particular, when CH_xCl_{4-x} is being administered continuously, in the experiments in the flow apparatus. After these experiments in the flow apparatus, formation of cobalt chlorides and oxychlorides has been seen by X-ray diffusion. Poisoned Co catalyst regained almost the original activity after 15 h reduction at 645 K.

The results obtained with various metals and alloys are summarized in Table 2.

It is interesting to notice the very low selectivity of Ni–Cu and Ni–Pd alloys, as compared with Ni. Also Rh shows, in the first place, a surprisingly low selectivity with CH_xCl_{4-x}/H_2 mixtures. In contrast to

TABLE 2

Selectivity (S_{2+}) in the Reaction of CH_xCl_{4-x}/H_2 Mixtures[a] and of CO/H_2

Catalyst	CO/H_2	CH_2Cl_2/H_2	$CHCl_3/H_2$
Ni	0.35	0.07	0.3
Ni–Cu (10% Cu)	0.08[b]	0.01[b]	—
Ni–Pd (50% Pd)	0.05	0.00	—
Co	0.52	0.47	0.68
Fe	0.85	0.21	0.04
Pd	0.00	0.00	0.00
Rh	0.45	0.00	0.01
Rh[c]		0.01	0.04

[a] Standard conditions, 483 K.
[b] At 573 K.
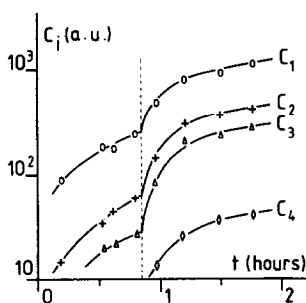[c] At 20 times usual concentration of CH_xCl_{4-x}.

FIG. 3. Conversion of CO into C_i hydrocarbon (logarithm of the concentration in arbitrary units) at 473 K, as a function of time with a Co catalyst. After 50 min a standard amount of CH_2Cl_2 has been added.

this, the selectivity with CO/H_2 mixtures is rather high.

It was attractive to check whether iron is also able to "polymerize" CH_y species, in particular when it is converted (as under the industrial conditions) into a mixture of Fe metal carbides and possibly oxides. An iron catalyst has been treated by 110 kPa CO at 493 K during 1 h. Then the gas phase was evacuated, and reactions with the standard mixtures were followed. The activity was lower than that of fresh Fe but higher hydrocarbons were again formed from CH_xCl_{4-x}/H_2 mixtures, although pure H_2 did not release any higher hydrocarbons from the CO-pretreated iron.

We have also checked in various ways that CH_xCl_{4-x} can intervene in hydrocarbon formation from H_2/CO mixtures. This is demonstrated, for instance, by data shown in Fig. 3, for cobalt. In these experiments, after, e.g., 50 min of reaction of a CO/H_2 mixture, a standard amount of CH_2Cl_2 has been injected into the reacting mixture. This resulted in an enhanced formation of all hydrocarbons. Results of similar character have been obtained when the reaction products and the rate of their formation are compared for CO/H_2 mixtures with or without a standard admixture of CH_xCl_{4-x}. The results of such an experiment is shown in Fig. 4, for Ni.

Experiments without isotopic labelling cannot reveal whether the polymerizations

of CH_y ex-CO and CH_y ex-CH_xCl_{4-x} are running in parallel (on different sites) or whether they are crosslinked. However, they show clearly that there is an additional polymerization due to oxygen-free units (ex CH_xCl_{4-x}) and that was also the main point of interest. Even in the presence of CO, a possible source of the frequently postulated oxygen-containing intermediates of polymerization steps, the polymerization of CH_y-units is visible.

DISCUSSION

The study reported by this paper has been very much inspired by the papers of Yamamoto (24) and of Young and Whitesides (25) who showed that alkyl ligands of Ni or Pt can be prolonged by one carbon by reacting the complex with CH_2Cl_2 in the solution. Also the paper by Anderson and McConkey (26) was of importance, since this paper showed that higher hydrocarbons can be formed from CH_2Cl_2 on Ti films. However, the latter authors concluded that in their case Ti was converted into Ti-chloride, which acted then as a Ziegler–Natta polymerization catalyst of the CH_2-units. At variance with Anderson
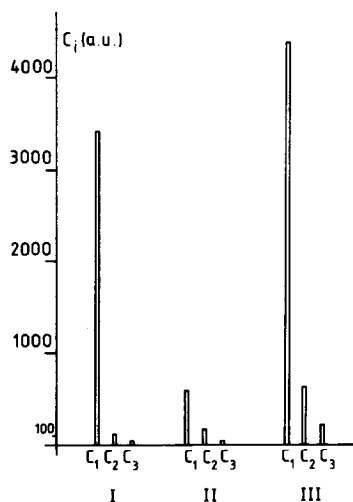

FIG. 4. Conversions in mixtures with hydrogen of (I) CH_2Cl_2, (II) CO, and (III) CO/CH_2Cl_2, after 1 h at 483 K, with an unsupported Ni catalyst. The concentration of products is plotted in arbitrary units. Enhancement of C_{2+} (in III) due to CH_2Cl_2 should be noticed.

and McConkey (26), we conclude that it is not the chlorides but the metallic part of the catalysts which is responsible for the hydrocarbon chain growth, so that the CH_xCl_{4-x}/H_2 reaction is analogous to the Fischer–Tropsch synthesis of hydrocarbons.

We believe that the main point from the results is sufficiently clear and supported by all data, namely that polymerization of oxygen-free units is possible under the conditions at which also Fischer–Tropsch synthesis can run and this polymerization is observable also in the presence of CO and concomitant with the chain growth of the normal Fischer–Tropsch synthesis.

There are also some minor points to which we would like to draw attention. First, it is demonstrated that the electronic structure of metal atoms is essential for their propensity of catalyzing the hydrocarbon chain growth. Palladium and copper are not very active in the Fischer–Tropsch synthesis and this is not just due to the fact that they do not dissociate CO. Even when the CH_y-units are supplied from CH_xCl_{4-x}, the chain growth rate is negligible.

Interesting is iron. It has been speculated (27) that iron has a particularly high tendency to form and to allow to react oxygenated intermediates, in particular when it is converted in part into carbides and oxides by the contact with the CO/H_2 mixture. While our results cannot lead to a conclusion regarding the oxygenated intermediates, they show nevertheless that a chain growth of hydrocarbons from oxygen free units is possible, also on spent catalyst.

Chain growth evidently needs a certain minimum concentration of the CH_y-units. This condition is most likely not fulfilled on Ni–Cu or Ni–Pd alloys, as well as on Rh. A substantial increase of the gas phase concentration of CH_xCl_{4-x} improves a little the selectivity S_{2+}, but the selectivity observed in CO/H_2 mixture is never approached by the CH_xCl_{4-x}/H_2 mixtures. The known high hydrogenation activity of Rh (12) is most probably the reason for that, although the

possibility that on Rh the oxygenated intermediates play an important role cannot yet be completely excluded.

A relation of a higher polymerization to a lower hydrogenation activity can be also seen from the comparison of Ni and Co. The ratio of S_{2+} selectivities for $CHCl_3$ and CH_2Cl_2 is 5.3 on Ni but only 1.4 on Co. This means that CH_1 has on Ni about four times higher probability than CH_2 to be inserted than to be hydrogenated. CH_2Cl_2 reacts faster than $CHCl_3$ on Ni, but much faster on Co. The total picture is as follows. The further from CH_3 the state is, the higher the chance to be polymerized, and this chance is for CH_2 lower on Ni (a better hydrogenation catalyst) than on Co.

REFERENCES

1. Vannice, M. A., in "Catalysis" (J. R. Anderson, M. Boudart, Eds.), Vol. 3, p. 139. Springer-Verlag, New York/Berlin, 1983.
2. Biloen, P., Sachtler, W. M. H., "Advances in Catalysis," Vol. 30, p. 165. Academic Press, New York, 1981.
3. Ponec, V., in "Catalysis," Specialist Periodic Reports (G. C. Bond and G. Webb, Eds.), Vol. 5, p. 48, Chemical Society, London, 1982.
4. Storch, H. H., Golumbic, N., and Anderson, R. B., "The Fischer–Tropsch and Related Syntheses." Wiley, New York, 1951.
5. Satterfield, C. N., and Huff, G. A., J. Catal. 73, 187 (1982).
6. Herington, E. F. G., Chem. Ind. (London) 347 (1946).
7. Schulz, G. V., Z. Phys. Chem. B 29, 299 (1935).
8. Flory, P. J., J. Amer. Chem. Soc. 58, 1877 (1936).
9. Kummer, J. T., DeWitt, T. W., and Emmett, P. H., J. Amer. Chem. Soc. 70, 3632 (1948).
10. Anderson, R. B., in "Catalysis" (P. H. Emmett, Ed.), Vol. 4, Reinhold, New York, 1956.
11. Kölbel, H. H., in "Chemische Technologie" (K. Winnacker and L. Küchler, Eds.), Band 3, p. 439. C. Hansen Verlag, Munich, 1959.
12. Bond, G. C., "Catalysis by Metals," p. 365. Academic Press, New York/London, 1962.
13. Eidus, Ya. T., Usp. Khim. 36, 824 (1967). (Engl. transl. p. 338).

14. Pichler, H., and Schulz, H., *Chem. Ing. Technol.* **42,** 1162 (1970).
15. Biloen, P., Helle, J. N., and Sachtler, W. M. H., *J. Catal.* **58,** 95 (1979).
16. Brady, R. C., and Pettit, R. J., *J. Amer. Chem. Soc.* **102,** 6181 (1980).
17. Brady, R. C., and Pettit, R. J., *J. Amer. Chem. Soc.* **103,** 1287 (1981).
18. Ponec, V., and van Barneveld, W. A. A., *Ind. Eng. Chem. Prod. Res. Dev.* **18,** 268 (1979).
19. Best, R. J., and Russell, W. W., *J. Amer. Chem. Soc.* **76,** 838 (1954).
20. Hall, W. K., and Alexander, L., *J. Phys. Chem.* **61,** 212 (1957).
21. Kulifay, S. M., *J. Amer. Chem. Soc.* **83,** 4916 (1961).
22. Cox, J. D., and Pilcher, G., "Thermochemistry of Organic and Organometallic Compounds." Academic Press, New York/London, 1970.
23. Furuyama, S., Golden, D. M., and Benson, S. W., *J. Amer. Chem. Soc.* **91,** 7564 (1969).
24. Yamamoto, T., *J. Chem. Soc. Chem. Commun.* 1003 (1978).
25. Young, C. B., and Whitesides, G. M., *J. Amer. Chem. Soc.* **100,** 5808 (1978).
26. Anderson, J. R., and McConkey, B. H., *Nature (London)* **216,** 681 (1967).
27. Frohning, C. D., Kölbel, H. H., Ralek, M., Rottig, W., Schnur, F., and Schulz, H., *in* "Chemierohstoffe aus Kohle." G. Thieme-Verlag, Stuttgart, 1977.