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NOTES

Carbon Number Distribution and the Chain-Growth Mechanism of Products in the Modified Fischer–Tropsch Synthesis on a Reduced Promoted Fused Magnetite Catalyst

The investigation of carbon number distribution of FT synthesis products through the use of the well-known Schulz–Flory equations in the chemistry of polymers is the subject of numerous publications (*1–3*) and is of interest in the study of the carbon chain-growth mechanism and the formation of synthesis products. To us, modified Fischer–Tropsch syntheses (CO + H_2 + substrate containing NH_2, OH, CHO, C=C, C≡C, and other groups) on iron catalysts are of particular interest in such studies. To date, only two works are dedicated to the carbon number distribution of separate components of the modified FT product (*1, 3*). In the former it has been shown that *n*-alkylamines isolated from the synthesis product of CO, H_2, and NH_3 obey the Schulz–Flory distribution; therein is suggested a mechanism of their formation. The latter discusses the effect of diethylamine on the distribution parameter α for hydrocarbons and alkanols.

The present work is dedicated to the study of carbon number distribution of a real polyfunctional product of ammonia-modified FT synthesis. It discusses the mechanism of formation of alkylamines in this synthesis and of the chain-growth process.

Syntheses of products from CO and H_2 (product I) and CO, H_2, and NH_3 (product II) were carried out in a continuous reactor (with a stationary layer of the catalyst) in a gas phase and under conditions ensuring the flow of reaction in the kinetic range: temperature 176°C, total pressure 12 MPa, space velocity of the synthesis gas (H_2/CO = 4) 10^3 h^{-1}, concentration of ammonia 12 vol%, CO conversion 10–11%. The catalyst was a fused iron which, on an unreduced basis, contained about 1% Al_2O_3, 1.5% BaO, and about 0.4% SiO_2. Prior to synthesis, the catalyst was reduced with hydrogen at 450°C (pressure 5 MPa and space velocity 2×10^4 h^{-1}) for 12 h (surface 13 ± 2 m^2/g, N_2, BET). The initial and unreacted synthesis gas was analyzed on a gas chromatograph LKhM-80-1 in a stainless-steel column (1 m × 3 mm) containing active carbon. A catharometer was used as detector.

The anhydrous (liquid at 20°C) part of the obtained product was investigated on a Micromat 412 HRGC in a quartz capillary column (25 m × 0.35 mm and statically coated with the liquid phase SE-30) using a flame ionization detector. The product components were identified on an LKB-2091 gas chromatograph/mass spectrometer using the aforementioned chromatographic columns.

The table lists the compositions of anhydrous parts of products I and II synthesized under similar conditions.

It is seen from Table 1 that product I is primarily a mixture of *n*-alkanols (a), *n*-alkanes (h), α-olefins (o), and methyl-*n*-alkylketones (k). The addition of ammonia to the initial mixture CO and H_2 (product II) is accompanied by the formation of *n*-alkylamines (am), and the yield of *n*-alkanols and methyl-*n*-alkylketones decreases from 50 to 6.5% and from 3.5 to 2%, respectively. Note that the total yield of *n*-alkanols and *n*-alkylamines in product II is almost equal to that of *n*-alkanols in product I. The yield of *n*-alkanes and α-olefins in product II somewhat increases.

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TABLE 1

Composition of Synthesis Products

Product	Composition (mass%)					
	n-Alkanols (a)	*n*-Alkanes (h)	α-Olefins (o)	Methyl-*n*-alkylketones (k)	*n*-alkylamines (am)	Unidentified components
I	50	26.5	9	3.5	—	11
II	6.5	32	11.5	2	37[a]	11

[a] Alkylamines contain 3.5 mass% of dialkylamines.

Earlier G. Henrici-Olive and S. Olive (*1*) proposed the Scheme 1 for the mechanism of formation of *n*-alkylamines in the ammonia-modified FT synthesis. In this scheme, ammonia competes with CO for occupying a catalyst–alkyl bond. This competition results in the decrease in intermediates ⧘—C(O)R and the yield of all components of the nonammonia part of the product; in this case the relative composition of this part must remain constant. Obviously, this scheme is inconsistent with the data listed in the table.

On the strength of the listed data, we propose two possible pathways of formation of *n*-alkylamines synthesized from CO, H_2, and NH_3 (see Scheme 2), where [OI] is an O-containing intermediate, which involves

(1) heterogeneously catalytic hydroamination of *n*-alkanols and methyl-*n*-alkylketones up to the corresponding alkylamines, according to Ref. (*8*);

(2) reaction of ammonia and hydrogen with the surface intermediate [OI] from which *n*-alkanols and methyl-*n*-alkylketones are obtained in the absence of NH_3.

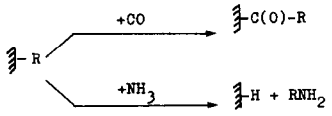
It seems to us that pathway (2) is more probable.

It is not yet fully known what causes the fraction of *n*-alkanes and α-olefins to increase in product II. But one thing is clear: nitriding of fused iron catalyst must be excluded from the causes responsible for such a change in the selectivity in modified FT synthesis, because nitriding is usually attended with a decrease in the yield of hydrocarbons (*9*).

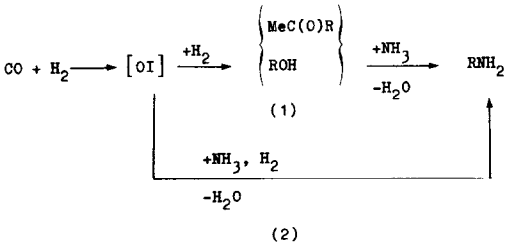
Figure 1 shows the results of processed data on the composition of product II in the Schulz equation coordinates. It is clear from the figure that the slopes of distribution lines for methyl-*n*-alkylketones, alkanols, olefins, and *n*-alkylamines are equal, and the distribution parameter computed from the slopes of these lines equal $\alpha_{tg} = 0.66 \pm 0.02$. At the same time, for *n*-alkanes $\alpha_{tg} = 0.73 \pm 0.02$. Similar results have been obtained by us for the product synthesized from CO and H_2.

The data on carbon number distribution of the components of product II permit us to assume that

(a) methyl-*n*-alkylketones, olefins, *n*-alkanols, and *n*-alkylamines are obtained from the common (for them) surface C_1 intermediate, as in Ref. (*10*);



SCHEME 1



SCHEME 2

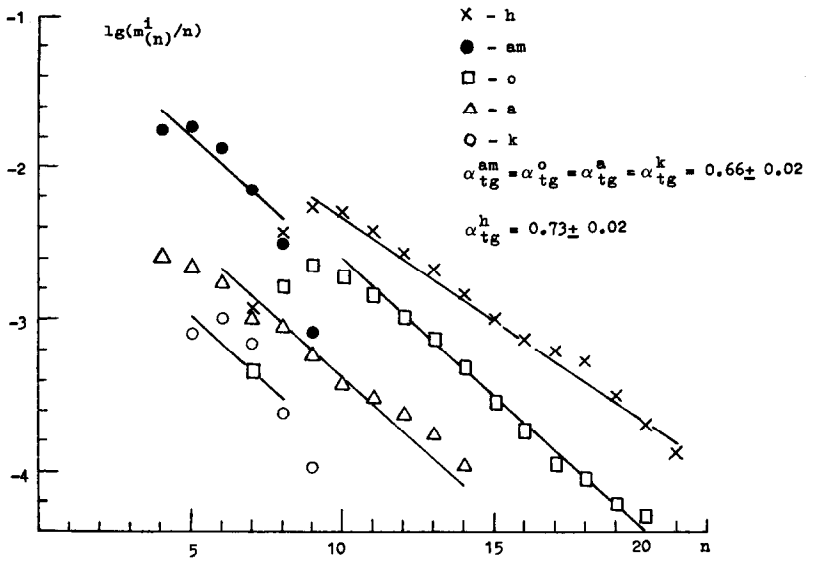


FIG. 1. Application of Schulz distribution for product II (according to the equation $\lg(m^i_{(n)}/n) = \lg(\ln^2\alpha) + n \cdot \lg \alpha$).

(b) *n*-alkanes are formed according to their reaction pathway (at least partially) which can be regarded as a pathway (i) via a C_1 intermediate of structure different from that in (a), or (ii) via the above-mentioned C_1 intermediate but on other active centers of the catalyst, or via (i) and (ii) simultaneously.

It must be noted that arguments in favor of the synthesis of *n*-alkanes via a pathway different from the pathways of synthesizing other components of the FT product are also found in Refs (*2*, *5*).

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REFERENCES

1. Henrici-Olive, G., and Olive, S., *J. Mol. Catal.* **4,** 379 (1978).
2. Huff, G. A., Jr., and Satterfield, C. N., *J. Catal.* **85,** 370 (1984).
3. Anderson, K. G., and Ekerdt, J. G., *J. Catal.* **95,** 602 (1985).
4. Bashkirov, A. N., Kagan, Yu. B., and Kliger, G. A., *Dokl. Akad. Nauk SSSR* **109,** 774 (1956).
5. Kryukov, Yu. B., Bashkirov, A. N., Simonyants, E. G., Liberov, L. G., Fridman, R. A., Smirnova, R. M., and Stepanova, N. D., *Kinet. Katal.* **10,** 135 (1969).
6. Loktev, S. M., *J. Mol. Catal.* **17,** 225 (1982).
7. Satterfield, C. N., Huff, G. A., and Summerhayes, R., *J. Catal.* **80,** 486 (1983).
8. Kliger, G. A., Glebov, L. S., Fridman, R. A., Bogolepova, E. I., and Bashkirov, A. N., *Kinet. Katal.* **19,** 619 (1978).
9. Anderson, R. B., *in* "Advances in Catalysis" (W. G. Frankenburg, E. K. Rideal, and W. I. Komarevsky, Eds.), Vol. 5, p. 355. Academic Press, New York, 1953.
10. Kaufmann, E., Schleyer, P., Gronert, S., Streiwieser, A., Jr., and Halpern, M., *J. Amer. Chem. Soc.* **109,** 2553 (1987).

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