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Time resolved selectivity for unsteady regimes in catalytic petroleum chemistry

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ABSTRACT

Selectivity in petroleum chemistry generally means multi-compound product compositions, distributed over a wide range from, e.g. hydrocarbon gases up to vapors of high boiling substances – thus providing analytical problems. Temporal resolution is required for investigating unsteady regimes of reaction, as pertinent during self-organization of catalytic processes or phenomena of catalyst deactivation. It is also of interest in temperature programmed operation as for catalyst regeneration, pyrolysis of organic materials as oil shale and biomass or TPD of pollutants recovered on adsorbents. For temporal resolution instant ampoule sampling has been developed. Ampoule samples are taken from the (hot) gaseous product flow in pre-evacuated glass ampoules in less than 1 s and stored without compositional changes for later GC-analysis. High resolution gas chromatography has been developed, starting at −80 °C for the separation of light gases and ending at, e.g. 250 °C for separating high boiling compounds (e.g. vapors of hydrocarbons C20). In the article, initial selectivity changes in Fischer–Tropsch synthesis (referring to chain growth, chain branching and olefin reactions, as caused by self-organization of the FT-regime) and also thermal regeneration of a HZSM5 catalyst used for methanol conversion at low temperature (referring to reactivation by de-alkylation of bulky benzene derivates) are being presented.

1. Introduction

Analysis of the multi-compound composition of products in petroleum chemistry is a domain of gas chromatography. In order to cover the range of compounds from gases to vapors of high boiling liquids, a temperature program is used. For high resolution, thin film capillaries are chosen at low heating rate. Such chromatograms (e.g. of hydrocarbons C_1–C_{20}) need about 1 h to develop.

For investigating unsteady regimes of catalytic (or thermal) conversion, sufficient temporal resolution of product composition is required. For this purpose an *instant ampoule sampling* procedure has been developed with sampling duration less than 1 s [1–5]. The gas chromatograph has been adapted for ampoule-sample introduction. Also the reactor set up has been designed for time resolved measurements [4–7].

In heterogeneous catalysis, unsteady regimes of self-organization with re-structuring (re-assembling) of the catalyst occur in the initial time of a conversion. Changes of selectivity have been traced and related to elemental reactions and properties of the catalyst active sites. Specifically, Fischer–Tropsch synthesis on cobalt catalysts exhibits strong self-organization phenomena [6,8,9].

Relatively fast catalytic deactivation is observed during methanol conversion on zeolites in the MTO (Methanol-To-Olefins) process. The changes of selectivity refer to controlling spatial constraints of the zeolite and to the interplay of primary and secondary reactions within a complex mechanism [7,10].

Further applications also concern temperature programmed desorption- and reaction studies of, e.g. pyrolysis or hydrogenation.

Multi-compound product mixtures are of particular interest, having in mind the principle “the higher the complexity of product composition, the more information is offered – about mechanistic aspects and also the nature of catalyst active sites”.

2. Apparatus for studying unsteady regimes of heterogeneous catalysis

Specific requirements for investigating unsteady reactions must be acknowledged. Temporal resolution with ampoule sampling is ca. 0.1 s. This fits well with actual applications which need resolution in the range of minutes.

The sample size for a gas chromatogram – using flame ionization detection – is very low. This allows time-resolved – respectively temperature-resolved – selectivity studies even during TPD experiments, applying ampoule sampling and adapted GC-analysis to the TPD-effluent [7,10–12].

A sketch of the apparatus used for Fischer–Tropsch synthesis is shown in Fig. 1 [4–6]. Main features are the following.

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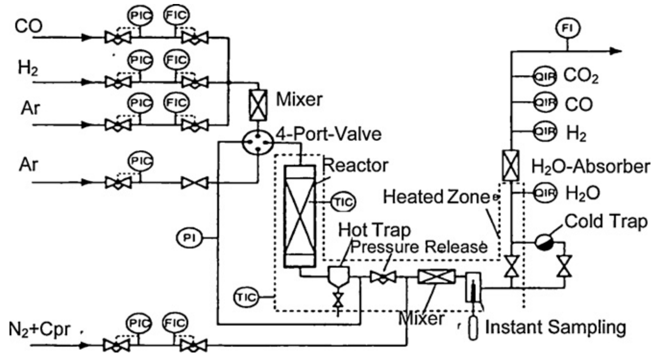


Fig. 1. Apparatus set up for temporal resolution in Fischer–Tropsch synthesis.

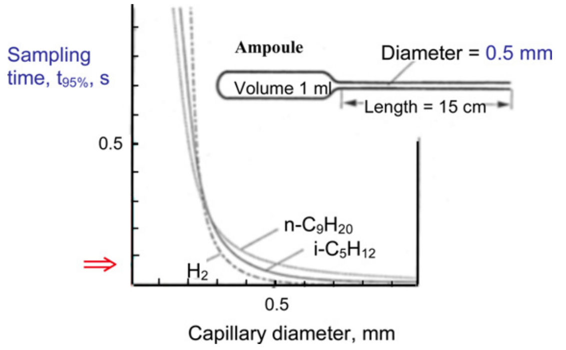


Fig. 3. Ampoule filling time (sampling duration) in dependence of capillary diameter for three compounds.

Ampoule samples are taken from the hot gaseous product flow behind the de-pressuring needle valve. These samples contain all gases and vapors representatively. Products being liquid at the temperature of the hot-trap are retained.

Yields of individual organic compounds are directly determined from the chromatogram by referring to the reference peak (e.g. cyclopropane) – the reference-mixture flow (argon + cyclopropane) having been admixed to the product flow behind the needle valve.

The pressure of reaction (e.g. 10 bar) is kept constant by adding a flow of argon (e.g. 10–20% of moles in relation to the H_2/CO synthesis gas) in a pressure controlled mode to the product flow after the hot trap.

In order to fix the zero time of reaction, the 4-port valve on top of the reactor is used. In the bypass mode (argon flow through the reactor and synthesis gas through the bypass) the conditions of reaction (temperature, pressure, flows of CO, H_2, Ar and reference gas) are precisely set. At zero time, the 4-port valve is switched and synthesis gas enters the reactor, whereas argon flows through the bypass (in the pressure controlled mode).

For avoiding reaction temperature changes caused by the enthalpy of reaction, the catalyst particles are applied highly diluted with fused silica particles (e.g. 1–10 volume-ratio).

On-line measurement of the exit gas flow and concentrations therein of CO, H_2, CO_2 and H_2O are performed for control and mass balance purposes.

The apparatus has been modified for individual applications, as for deactivation studies during methanol conversion on zeolites [7,10] or for temperature programmed desorption (respectively reaction) of used adsorbents, or deactivated catalysts [7,10–12].

3. Ampoule sampling

The sampling procedure is explained with the schematic drawing in Fig. 2. The product gas (at ca. 220 °C) flows through the sampling device. The capillary-end of the evacuated glass ampoule is inserted from below through the septum. At the moment of sampling, the tip of the capillary is broken by means of a fork from aside, and the ampoule is “immediately” filled with product (gases and vapors). The ampoule is then drawn down a few centimeters and sealed with a little hot flame. Most of the capillary length is thereby removed and the capillary volume closed by fusing the glass. The ampoule is stored without compositional changes for later GC-analysis.

The duration of sampling – of filling the ampoule – depends on the volume of the ampoule and the length and diameter of the capillary. Theoretical calculations of the ampoule filling time have been made for three gases (vapors) as shown in Fig. 3 [13]. For the chosen values (1 ml volume of ampoule, capillary length 15 cm) the 95%-filling time at a capillary diameter of 0.5 mm is less than 0.1 s for all the three molecules. Discrimination of sample composition due to the sampling procedure has not been noticed. For taking one sample shortly after the other (e.g. 1 s later) a multi-sampler with 10 ampoules in series has been designed and used for analyzing

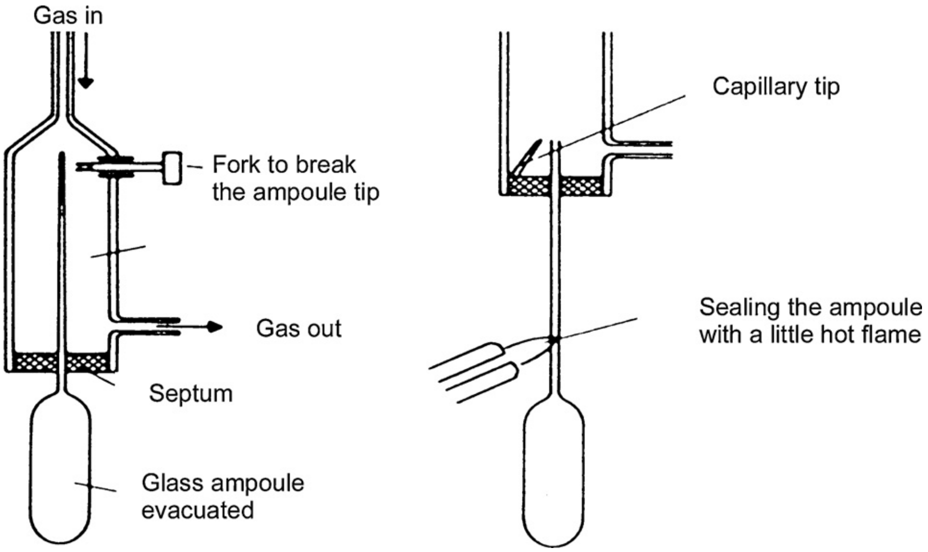


Fig. 2. Principle of instant ampoule sampling.

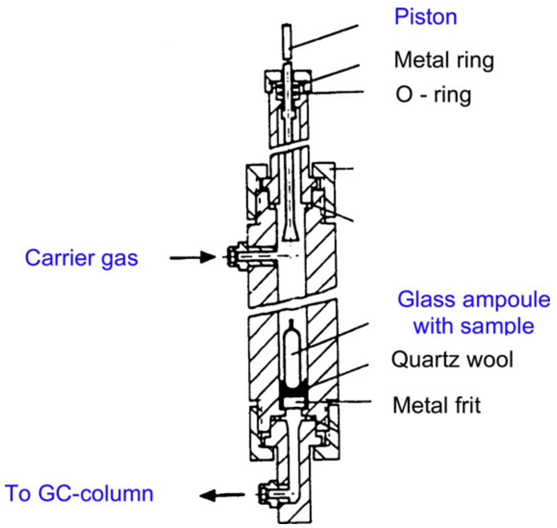


Fig. 4. Ampoule breaker used for introducing the sample into the gas chromatograph.

volatile organic compounds in diesel exhaust gas and studying TPD of aromatic compounds from diesel soot [11,13].

4. Adapted gas chromatograph and chromatograms

The gas chromatograph must be adapted for wide range product ampoule samples. The ampoule is put in the ampoule breaker (see Fig. 4). The breaker is heated to the temperature which had been used when sampling. To clean the breaker, nitrogen flows through the heated breaker. The flow is then switched to the gas chromatograph and the ampoule broken in parts with the piston. After some time when the compounds have entered the GC column, the carrier gas is switched to hydrogen for improved separation performance of the column.

With product compositions as in case of Fischer–Tropsch synthesis, the interest is in maximal peak resolution for all the many organic compounds, covering the range from light gases – beginning with methane – to vapors of high boiling compounds (e.g. C_{20}-hydrocarbons). The solution of the problem has been attained with cross-linked non-polar silicon in thin-film capillaries of e.g. 100 m length. In order to attain peak resolution of methane, ethane and ethene, the starting temperature must be low (e.g. −80 °C). Then the temperature is raised moderately up to e.g. 250 °C.

The chromatogram of a Fischer–Tropsch product ampoule-sample is shown as Fig. 5 [4–6]. It exhibits the features of FT-catalysis: Similar groups of compounds (mainly olefins and paraffins) at every carbon number, this resembling a polymerization process. The (almost) complete peak-resolution is used for studies of reaction mechanism and active site characterization. Of course – if with temporal resolution – this information, can be the key for elucidating Fischer–Tropsch synthesis self-organization.

By applying GC-pre-column hydrogenation, olefins and alcohols are converted to the respective paraffins. This is illustrated in Fig. 6 with the C_6/C_7-chromatogram section – hydrogenated and original. From these chromatograms, chain branching probability has been calculated as depending on chain length and reaction time (see below).

5. Olefins in Fischer–Tropsch synthesis

In Fischer–Tropsch synthesis, olefins and paraffins are the main products. However, mechanistically the role of olefins is complex.

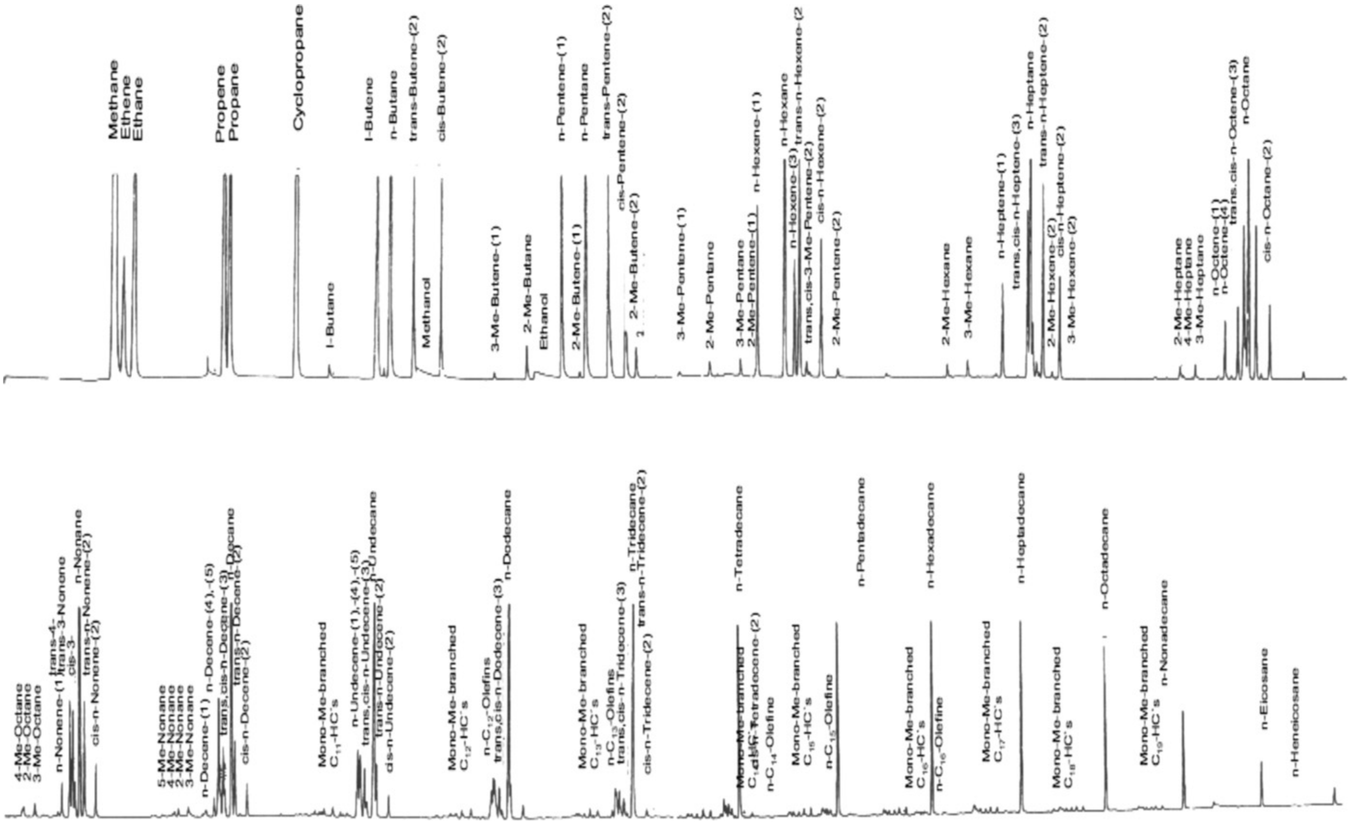


Fig. 5. Gas chromatogram of a Fischer–Tropsch product, FT-synthesis on cobalt, instant ampoule sample, GC-conditions: Capillary 100 m, di 0.25 mm, df 0.5 μm, methyl silicone cross-linked, Temperature: −80 to 275 °C, Carrier gas H_2, Introducing gas N_2, FID, Duration of chromatogram 75 min.

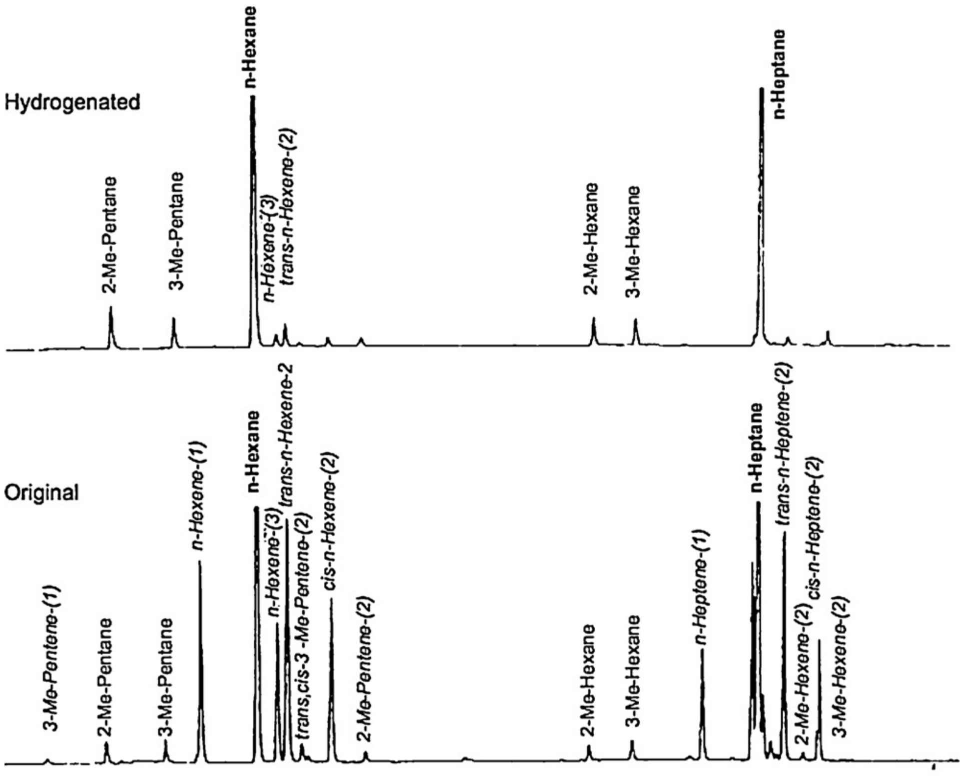


Fig. 6. Section C_6/C_7 of FT-product chromatograms, original (below) and pre-column hydrogenated (above). GC-conditions as in Fig. 5, pre-column hydrogenation at 250 °C on 0.35 wt% Pt on quartz particles dp = 0.2–0.25 mm.

The olefin content in product carbon number fractions is shown in Fig. 7 for two typical cases – synthesis on iron (left) and cobalt (right) as catalysts [6,14,15]. In Fig. 8 the content of olefins with terminal double bonds among the straight chain olefins is shown. The explanation of these results (as consistent with further work) is the following. The curves with iron reflect mainly primary selectivity – alpha-olefins are obtained (70–80%) together with 20–30% paraffins. With iron, increasing reaction time is concluded to favor re-adsorption of alpha-olefins on growth sites (because of increasing olefin residence time in the reactor, due to increasing amounts of retained hydrocarbon liquid on/in the catalyst particles, this causing a decline of olefin content with increasing carbon number). The (primary) olefin selectivity increases from ca. 60% in the beginning to ca. 75% at steady state, visualized as due to self-organization and catalyst re-assembling.

With cobalt, the role of olefins is more complex, because ample olefin hydrogenation and double bond shift proceed, this evidently

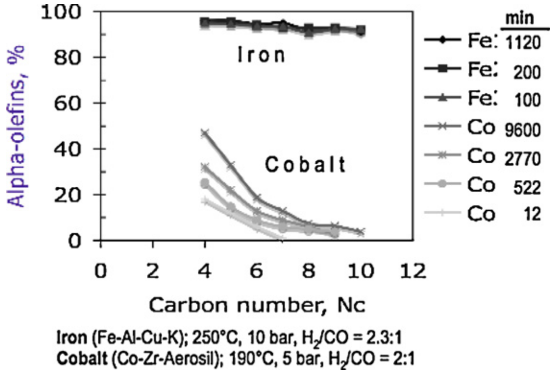


Fig. 8. Alpha olefins among n-olefins in FT-products, depending on carbon number, reaction time and catalyst (iron or cobalt).

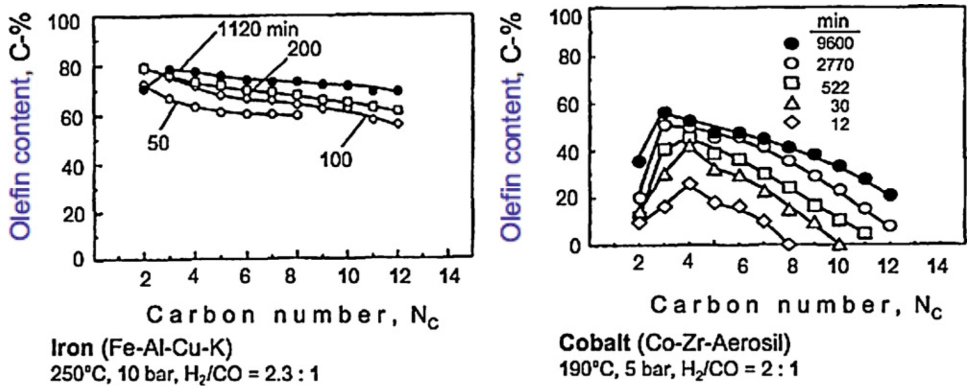
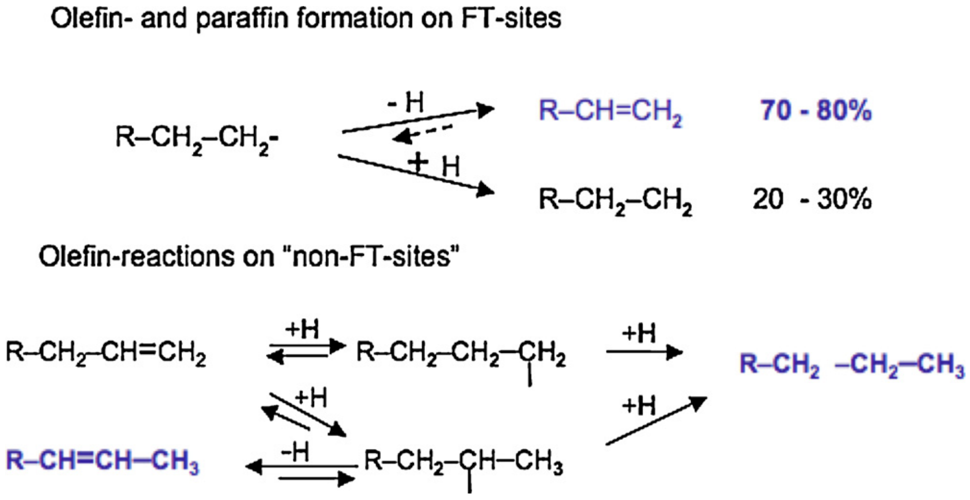
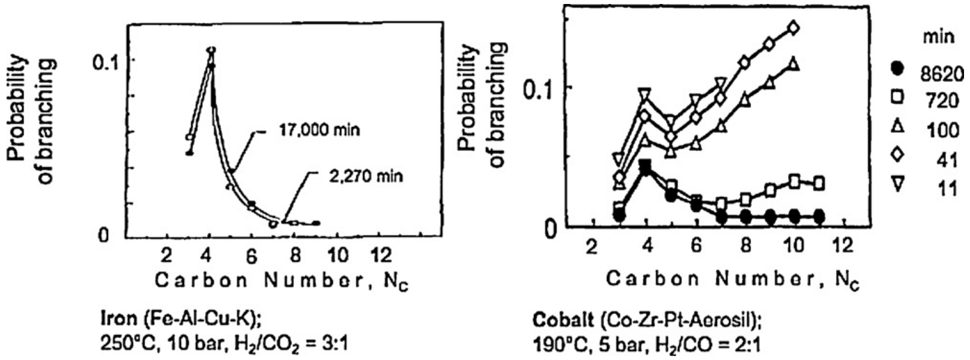


Fig. 7. Olefin content in carbon number fractions. Left: iron-, right: cobalt catalyst.


Olefin- and paraffin formation on FT-sites

Olefin-reactions on "non-FT-sites"

Fig. 9. Kinetic schemes of primary and secondary olefin- and paraffin formation (above primary reactions, below secondary reactions).



Iron (Fe-Al-Cu-K);
250°C, 10 bar, H_2/CO_2 = 3:1

Cobalt (Co-Zr-Pt-Aerosil);
190°C, 5 bar, H_2/CO = 2:1

Fig. 10. Chain branching with a cobalt- and an iron catalyst.

on hydrogenation catalyst sites, not active for chain growth. The curve shapes (Figs. 7 and 8) are well indicative for this conclusion. Specifically it is seen in Fig. 7 how the maximum of olefin content shifts with reaction time from carbon number 4 to carbon number 3, as explained by declining olefin isomerization (because at C_3 the two isomers are identical α-olefins and hydrogenation of α-olefins is generally much faster than hydrogenation of olefins with internal double bonds). During self-organization of cobalt catalysts, the extent of secondary olefin reactions declines distinctly (Fig. 8). In Fig. 9 kinetic schemes of primary and secondary olefin reactions are presented.

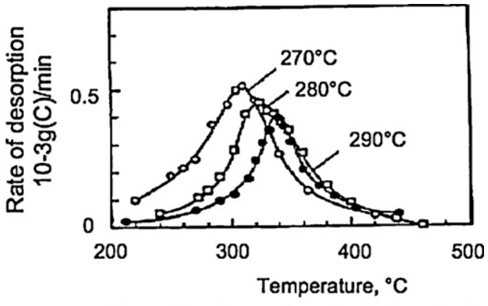
6. Chain branching in Fischer–Tropsch synthesis

Regarding chain branching, typical results are shown in Fig. 10. With cobalt, strong temporal changes are noticed, presumably due to with time increasing spatial constraints on the growth sites – as a branching-growth-step can thought to be more demanding in space comparing with linear growth, respectively, branching would be suppressed during self-organization. Also changes of shape of curves may be attributed to changes in spatial constraints on the site. Whereas at steady state a monotonous decline of branching probability from C_4 to higher carbon numbers is noticed, this turns to the opposite (increasing branching probability with increasing carbon number) in the beginning. This reflecting a change in mechanism has been explained as α-olefin re-adsorption being possible in the beginning of conversion with the second C-atom of the olefin on FT growth sites.

Remarkably, with iron as catalyst, the principle pattern of branching probability in dependence of carbon number is the same as with cobalt (Fig. 10), however, there is no change to be noticed during the initial time of conversion. It seems that the FT-growth sites of iron are merely of dynamic nature, when comparing with cobalt as FT-catalyst.

7. Further application of instant ampoule sampling

Ampoule sampling has been used in further applications: (1) Selectivity changes during methanol conversion on zeolites [7,10].



The retained organic matter is desorbed (decomposed) in the range 250 - 400 °C

Fig. 11. Thermal regeneration of zeolite H-ZSM-5 catalyst after deactivation in methanol conversion at low temperature (270, 280, 290 °C), [7,10,16]. At the indicated points, ampoule samples were taken from the effluent gas for detailed GC-analysis.

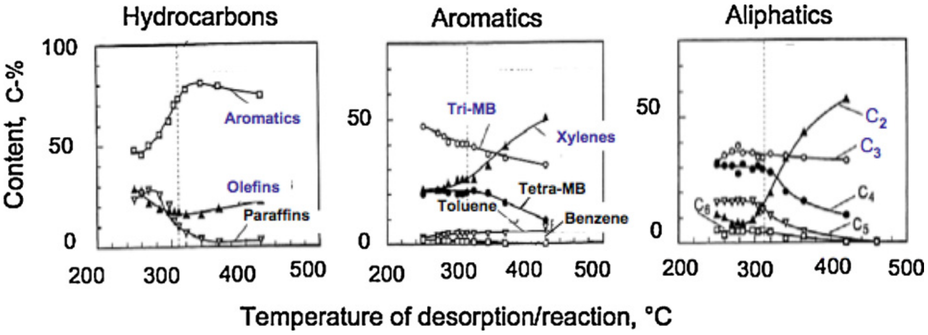


Fig. 12. Composition of the organic compounds in the TPD-effluent gas from thermal H-ZSM-5 regeneration [7,10,16]. Analysis of the ampoule samples by capillary GC-conditions as in Fig. 5. The many compounds in the chromatograms are grouped for classes and carbon number.

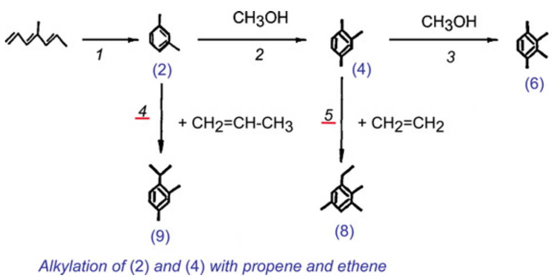


Fig. 13. Mechanism of HZSM5 deactivation in methanol conversion at low temperature (through retained compound formation by alkylation of benzene rings with olefins). At higher temperature, these reactions will become reversible (and no longer cause catalyst deactivation).

(2) Temperature programmed regeneration of zeolite HZSM-5, deactivated at low temperature methanol conversion [7,10]. (3) Temperature programmed pyrolysis of plastic materials and oil shale. (4) Temperature programmed desorption of aromatic hydrocarbons from diesel-soot, obtained with hexadecane as model fuel [11,12]. (5) Determination of volatile organic compounds in diesel engine exhaust gas [11,12]. (6) Catalytic cracking of model compounds [3]. (7) Industrial steam cracking of petroleum fractions [2].

8. HZSM5 catalyst deactivation and regeneration in methanol conversion

At low temperature (below 300 °C) methanol conversion on zeolite HZSM5, the catalyst deactivates fast under ample deposition of organic material (coke?) on/in the catalyst. At high temperature (above 400 °C), HZSM5 deactivation is slow and only small amounts of organic material are retained on the catalyst. This peculiar behavior of decreasing catalyst deactivation at increasing reaction temperature has been studied with TPD experiments and detailed analysis of the released compounds in the TPD-effluent, using the instant ampoule sampling technique. Fig. 11 shows the TPD curves for three catalysts having been used for methanol conversion at 270, 280 and 290 °C reaction temperature. The points on the curves indicate the taking of ampoule samples.

The composition of the samples – in dependence of their desorption-/formation-temperature as ordered for groups of hydrocarbons: aromatics, olefins and paraffins, is shown in Fig. 12, left. Composition of the aromatics (benzene, toluene, xylenes, tri-methyl-benzenes and tetra-methyl-benzenes) is shown in Fig. 12, middle and composition of the aliphatics (C_2–C_5) in Fig. 12, right.

The desorption temperature range 350–450 °C is of particular interest: The “desorbed” compounds are exclusively aromatics and olefins, indicating de-alkylation of ethene and propene from benzene rings.

It is concluded that low temperature HZSM5-deactivation during methanol conversion proceeds via ethylation and propylation of methylated benzene molecules, the obtained molecules being to big for diffusion in the ZSM5 pores. This alkylation with olefins becomes reversible at higher temperature. Correspondingly, deactivation is reversible at higher temperature. Isolation of the entrapped organic compounds from such catalysts were identified as preferentially 1-ethyl-,2,3,5-trimethyl-benzene and 1-isopropyl-,2,4-dimethyl-benzene. Thus the unique ZSM5 deactivation behavior in methanol conversion has been explained by reversible benzene alkylation/dealkylation with small olefins (see Fig. 13).

9. Concluding remarks

Instant ampoule sampling provides an interesting potential in catalytic (and thermal) petroleum chemistry and further fuel and bio-mass conversion processes. Some principle features of the method shall be underlined: (1) Temporal resolution of multi-compound selectivity is obtained by independent instant sampling and later GC-analysis. (2) Samples can be stored without changes in composition for long periods (years and longer). This is of interest also for reference- and calibration purposes. (3) The wide range chromatograms – covering gases and vapors at a time – provide enormous savings in labor and time and allow for much more precise analyses as compared with current conventional sampling and analysis. (4) Access to new areas of research can be imagined.

References

[1] H. Schulz, S. Nehren, Erdoel und Kohle-Erdgas-Petrochemie 39 (1984) 45.
[2] H. Schulz, W. Boehringer, C. Kohl, N. Rahman, A. Will, Kapillar-GC-Gesamtprobentechnik für Gas/Dampf-Vielstoffgemische, in: DGMK-Forschungsbericht 320, DGMK, Hamburg, 1984.
[3] H. Schulz, A. Geertsema, Erdoel und Kohle 30 (1977) 313.
[4] H. Schulz, E. van Steen, M. Cleays, Stud. Surf. Sci. Catal. 81 (1994) 455.
[5] H. Schulz, M. Claeys, Appl. Cat. A: Gen. 186 (1999) 71.
[6] H. Schulz, Zh. Nie, Stud. Surf. Sci. Catal. 130 (2000) 1145.
[7] H. Schulz, M. Wei, Mesopor. Micropor. Mater. 29 (1999) 205.
[8] H. Schulz, in: B.H. Davis, M.L. Occelli (Eds.), Advances in Fischer–Tropsch Synthesis, Catalysts, and Catalysis, CRC Press, 2010, p. 165.
[9] H. Schulz, Stud. Surf. Sci. Catal. 163 (2007) 177.
[10] H. Schulz, Catal. Today 154 (2010) 183.
[11] H. Schulz, G. Bandeira de Melo, Erdoel, Erdgas, Kohle 112 (1996) 163.
[12] H. Schulz, G. Bandeira de Melo, F. Ousmanov, Combustion and Flame 118 (1999) 179.
[13] H. Schulz, K. Beck, E. Erich, Stud. Surf. Sci. Catal. 36 (1998) 457.
[14] H. Schulz, G. Schaub, M. Claeys, Th. Riedel, Appl. Catal. A: Gen. 186 (1999) 215.
[15] H. Schulz, Zh. Nie, F. Ousmanov, Catal. Today 106 (2002) 351.
[16] H. Schulz, K. Lau, M. Claeys, Appl. Cat. A: Gen. 29 (1995) 132.