THE MECHANISM OF COKE FORMATION

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The formation of a carbonaceous residue, coke, is a characteristic of all destructive processes, both thermal and catalytic.

For thermal processes the most generally acknowledged mechanism at the present time is the consecutive radical nature of coke formation according to the scheme: aliphatic hydrocarbon-polycyclics-resins-asphaltenes-coke. The isolation and identification of the intermediate products from the condensation reactions show a continuous increase in their molecular weight, degree of aromaticity and C:H ratio.

A similar situation is observed even in the cracking of the model hydrocarbon, methane. The production of the final condensation product, carbon black, is preceded by the formation of intermediate polycyclic hydrocarbons having a number of rings from three to seven, whose yields pass through a maximum.

According to [1] all types of carbon blacks contain 1-3% by weight of hydrogen, which corresponds to 12-36% atomic.

X-ray diffraction analysis of carbon blacks has shown that they consist of crystallites having dimensions which exceed the dimensions of the polycyclic hydrocarbon C_{26}H_{14} (ovalene) by only a factor of 2, and have a pseudo-graphite structure.

In reference [2] the successive nature of the condensation reactions in thermal processes is represented by a "chemical aggregation" scheme, by analogy with the physico-chemical aggregation scheme of P. A. Rebinder.

In the case of heterogeneous coking it is more complicated to prove "a drop-colloid" mechanism owing to the difficulty of isolating the intermediate products from the condensation reactions of resins and asphaltenes. This is explained by the adsorption properties of the catalysts, the high adsorption coefficients of condensation products possessing high molecular weights, the high degree of unsaturation and aromaticity, and also the formation of stable chemisorbed catalytic complexes between the condensation products and the active sites of the catalyst. Consequently, at the process temperature only the low molecular portion of the intermediate condensation products is desorbed with unconverted feedstock and low-molecular decomposition products, whereas the high molecular portion stays behind on the active sites, being converted into coke.

However, by operating with specially selected conditions which favor desorption e.g. at high temperatures, at low partial pressure of the hydrocarbons, or on low-active catalysts (in the chromatographic regime), one can succeed in finding beyond the reactor a considerable amount of intermediate products from the more advanced condensation stages. In the high-temperature decomposition of ethane, acetylene and alcohols on silica gel naphthalene, biphenyl, phenanthrene, anthracene, chrysene and other high molecular aromatic hydrocarbons have been identified in the resinous reaction products. From the curves given in [3] for product yields with extent of reaction, it is readily seen that the yield of resins passes through a maximum and that the resins are typical intermediate condensation products.

It is known that the concentration of intermediate condensation products on the surface of the catalyst can be artificially increased by increasing the pressure and lowering the cracking temperature. For example, the author of [4] used benzene to extract 27% hydrocarbons with the catalyst (zirconia/silica) in experiments on n-octene, carried out at 375°C and a pressure of 8 atm.

In [5] after the catalytic cracking of benzene and naphthalene under normal conditions, polycyclic hydrocarbons (chrysene, pyrene, fluorene, phenanthrene, anthracene), which may also be considered as intermediate condensation products, were found in the distillate.
The authors of [6] extracted the absorbed intermediate condensation products by vacuum desorption at high temperature. It was shown that coke contains a substantial amount of hydrogen (40-60% atomic). The hydrogen content of the coke depends mainly on the nature of catalyst, the temperature and the duration of the experiment.

In an X-ray diffraction study of the coke particles obtained from the catalytic cracking of various types of hydrocarbons the authors of [5] and [7] found a pseudographite structure, very similar to that observed in the production of carbon blacks and cookes by the thermal process.

The purpose of the experimental part of the present investigation* was to establish a link between the amount of reversibly adsorbed intermediate condensation products and the kinetics of coke formation on various types of catalyst.

Of the two methods mentioned above for removing intermediate condensation products reversibly adsorbed on coked catalysts, we used the desorption method as being the simpler although we established in preliminary experiments that extraction with hot benzene of finely crushed coked catalyst gives a larger quantity of intermediate condensation products, including products from more advanced condensation stages. To avoid the chemical conversion of the condensation products we restricted the period over which the coked catalyst was purged with inert gas to remove the hydrocarbons filling the pores of the catalyst and the spaces between the grains.

One liter of catalyst was used to obtain amounts of desorbed product measurable by normal methods, when carrying out the experiments. The temperature of the experiments was 460°C, the space velocity 1 h⁻¹. The reactor had a sectioned electrical heater. Immediately after cutting off the supply of feedstock the reactor was purged with natural gas (15 liters) for 4 min and then connected to a vacuum system (vacuum of the order of 5 mm Hg). The vacuum receiver was maintained at 20°C.

The results of the experiments are shown in the table and Fig. 1. From Fig. 1 it may be seen that for molybdenum and alumina-silica catalysts the amount of desorbed products is considerably reduced with an increase in duration of the experiment (by a factor of 3-4) while for aluminum oxide and silica gel it remains practically constant.

Fig. 2 shows the relationship between the rate of coke formation and the duration of the experiments for the same catalysts and a feedstock obtained in a reactor of the Grozny Petroleum Institute type†.

A comparison of the figures shows a parallelism between the curves representing the kinetics of coke formation and the corresponding curves for changes in the amount of intermediate condensation products with time.

The rate of coke formation on various types of catalyst and the amount of intermediate condensation products are compared in the table.

From these results it can be seen that the absolute amount of intermediate condensation products is higher on active catalysts possessing a stronger tendency towards coke formation. The calculated ratios of the rate of coke formation to the amount of intermediate condensation products for individual catalysts is practically constant over the course of the whole experiment. This ratio has the dimensions (mg · m⁻² · min⁻¹ / mg · m⁻³) = (1 · min⁻¹), similar to a reaction rate constant.

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† The work was carried out jointly with B. F. Morozov.