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On the Contributions of Feed Components to Hydrotreatment Catalyst Coking

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Abstract—The coking ability of some hydrocarbons (benzene, *n*-heptane, styrene, methylnaphthalene, durene, and phenanthrene) and heterocyclic compounds (thiophene and indole) under the conditions of hydrotreatment of feed is estimated for an Al–Co–Mo catalyst. The method of isotopic labels is used to determine the contributions of the components of binary mixtures to the formation of coke on the catalyst surface. These contributions do not coincide with the values of coking ability found for individual compounds.

INTRODUCTION

Coking abilities of separate components of the reaction medium and their contributions to catalyst coking are very important for understanding the mechanism of formation, structure, and properties of coke.

Obviously, the contribution of a component to the formation of coke may not correspond to its fraction in the reaction medium. One of the most probable reasons for that can be the process of concentrating and further compacting the components that have higher adsorption ability on the catalyst surface. Therefore, it would be incorrect to determine the main “monomers of coke” using individual substances as starting materials and compare the amounts of coke formed from them. A more exact determination of contributions from the separate components of the reaction mixture to coke formation is possible when the radioactive ^{14}C label is used. This method was used when studying coke formation in alcohol decomposition on a dehydrogenation catalyst [1], alkylation and metathesis of alkylbenzenes on zeolites [2, 3], and in transformations of binary benzene–methylbenzene mixtures on γ-Al_2O_3 [4], which is a traditional support for the hydrotreatment catalysts. Vetlugina et al. [4] estimated the contributions of toluene and xylene relative to the contribution of benzene labeled with ^{14}C to the formation of coke at different acidities of Al_2O_3 and different temperatures. It was shown that, when these parameters are varied, the series of coking abilities of the cited hydrocarbons (xylene > toluene > benzene) does not change. The temperature and acidity may change the effect of the methyl group, whereas the series does not change qualitatively. Thus, the structure of the initial compound plays the determining role.

Catalyst coking studies under the condition of oil refining become more difficult because of the complex composition of oil fractions. The starting materials subjected to hydrotreatment and hydrocracking has the most complex composition. In addition to various hydrocarbons, it contains heterocompounds. Problems concerning the coking of catalysts for hydrotreatment and hydrocracking of oil raw materials, specifically coking abilities of separate components are poorly studied [5], although this process is very important for deep refining of oil and manufacture of environmentally clean fuel.

In this work, we used the method of isotopic labeling to determine the contributions of some model compounds (benzene, *n*-heptane, styrene, methylnaphthalene, durene, and phenanthrene, thiophene, and indole) the coking of an Al–Co–Mo catalyst.

EXPERIMENTAL

Catalyst coking was carried out on a commercial catalyst sample. Individual compounds and their binary mixtures with labeled benzene were used as starting materials. The choice of benzene as a standard for comparison was due to its highest stability, isotopic equality of carbon atoms, and equal probabilities of their participation in coke formation. The process was carried out in a laboratory flow-type reactor at 420 and 500°C, a hydrogen pressure of 0.5–5.0 MPa, and a space velocity of feed of 2 h^{-1}. The duration of feed supply lasted for 1 h in each case. The catalyst composition was analyzed by chromatography. After a run, the reactor was cooled in a flow of nitrogen. The catalyst was discharged and evacuated in a dryer at 100°C and 1–2 torr for 2 h. The amount of coke was estimated by burning. The standard deviation was 0.1–0.3% depending on the amount of coke.

The radioactivity of the initial benzene-^{14}C and coke from the binary mixtures was determined according to the procedure described in [6]. Benzene and spend catalyst loadings were placed into a special setup for the burning of radioactive substances. Carbon dioxide evolved during a run was absorbed by a NaOH solution. Then, $BaCl_2$ was precipitated by a solution of $CaCO_3$ and the specific radioactivity was determined (in pulse min^{-1} (mg $BaCO_3)^{-1}$) using an end-window counter and a scaling unit. Deviations in the average values obtained in parallel measurements were at most 5%. When burning coke obtained in the runs with a mixture containing thiophene, traps with water to consume SO_2 were placed before traps with alkali. All these procedures were described in detail in [5].

Using binary mixtures of benzene-^{14}C with some compounds, we estimated the contribution of these compounds to adsorption on the catalyst surface at 200°C, the maximal temperature at which no product formation was observed. When preparing the samples to the determination of the specific radioactivity of the adsorption layer, we also used the same procedures as in the case of coke.

The contributions of the components of binary mixtures were calculated from the values of the specific radioactivity of the initial sample and coke (or mixtures adsorbed on the catalyst). For instance, if the specific radioactivity of coke was half the radioactivity of the initial radioactivity of benzene and the ratio of the components in the initial mixture was 1 : 1 (based on carbon), then the contribution of benzene and the second component were the same. If the radioactivities decreased by a factor of 3, then the contribution of the second component was taken equal to 2. In general, a decrease in the radioactivity by a factor of *n* means that the contribution of the second component is *n* - 1. The value of the contribution is equal to the ratio of carbon atoms in coke coming from the components of the initial binary mixture.

RESULTS AND DISCUSSION

Data on catalyst coking by individual compounds, their coking ability relative to benzene, and the compositions of liquid catalysts are shown in Table 1. We failed to determine the degrees of catalyst coking by individual compounds with high melting points (indole, 2-methylnaphtalene, durene, and phenanthrene) because of the problems related to carrying out the experiments in the flow-type reactor.

The coking ability of compounds is stipulated by several factors, including first of all the adsorption ability of initial components and the products of their primary transformations, as well as their susceptibilities to polymerization and polycondensation. Taking into account the acidic nature of the Al–Co–Mo catalyst, we assumed that the adsorption ability of the reactant depends mainly on its acidity. Note that coke can be considered as a polycyclic condensed system. Therefore, it is clear why benzene has the lowest coking ability of aromatic compounds. A higher coking ability of *n*-heptane is due to the presence of ~70% toluene (Table 1) in the products of its transformation under given conditions.

A higher adsorption ability of sulfur-containing compounds compared to hydrocarbons [7] can be one of the reasons for the maximal coking ability of thiophene. It is also necessary to take into account that the possible direction of its hydrogenolysis is the cleavage of the C–S bond at the first stage of the process and the formation of butadiene [8]. In our experiments, we did not find butadiene in the products of thiophene transformation, but it cannot be excluded that the unsaturated C_4 structure completely transforms into coke because of the high susceptibility to polymerization and polycondensation.

Table 2 shows the radioactivity of coke formed from the binary mixtures with benzene-^{14}C and data on the contributions of separate components to coke formation.

The values of relative coking abilities calculated from the degree of catalyst coking by individual compounds (Table 1) differ substantially from the values of the contributions of components to coking estimated using an isotopic label (Table 2). The difference is especially pronounced in the case of thiophene. The relative coking abilities of almost all compounds except for *n*-hexane found in the experiments with individual components is lower than in the mixtures with benzene-^{14}C. It is likely that the second components of binary mixtures and the products of their transformations under

Table 1. Concentration of coke in the catalyst coked by individual hydrocarbons, relative coking abilities of these compounds, and the composition of catalyzates (500°C)

Compound	Coke, wt %	Relative coking ability	Catalyzate composition, %										
			benzene	toluene	heptane	ethylbenzene	styrene	xylenes + polymethylbenzenes	thiophene	naphthalene	1-methyldihydronaphthalene	1-methylnaphthalene	others
Benzene	1.2	1.0	99.5	0.2	–	–	–	–	–	–	–	–	0.3
n-Heptane	8.9	7.5	3.8	19.7	70.0	–	–	–	–	–	–	–	6.5
1-Methylnaphthalene	12.8	11	1.8	1.3	–	–	–	13.0	–	17.5	20.0	42.5	3.9
Styrene	16.8	14	2.2	23.0	5.0	50.0	17.3	2.1	–	–	–	–	0.4
Thiophene	20.3	17	2.6	1.4	–	–	–	–	91.0	–	–	–	5.0

the conditions of competitive adsorption are concentrated on the catalyst surface and displace benzene.

n-Heptane has a lower adsorption ability [7] and, therefore its coking ability in the mixture with benzene is lower than in the case of catalyst coking by an individual compound.

A considerable difference in the contributions of 1- and 2-methylnaphthalenes to coke formation is notable. This can be explained as follows. If the process of coking is reduced to the formation of hexagonal condensed systems, then some steric hindrances to the formation of macromolecules of 1-methylnaphthalene should occur because the most probable direction of polymerization is the formation of bonds at position 1. There are no such hindrances in the case of 2-methylnaphthalene, and this provides an opportunity for a continuous growth of polycyclic condensed structures. We assume that coke formed from 1-methylnaphthalene has a more island-like nature. The correctness of this assumption was confirmed by the study of the composition and properties of coke formed from methylnaphthalenes [9]. Growing of benzene into methylnaphthalene coke in the case of 1-methylnaphthalene occurs more readily and this is why its contribution is more pronounced. We can explain a smaller contribution from 1-methylnaphthalene compared to durene in a similar way.

Note that the coking ability of thiophene compared to indole is very high. The adsorption ability of N-containing compounds is higher than that of S-containing compounds [7, 10, 11]. Therefore, the reason for the strong difference in the coking ability of these heterocompounds is somewhere in the mechanism of coke formation and the nature of intermediate products of heterocompound hydrogenolysis. According to published data [12, 13], the cleavage of the C–N bond in a heterocycle occurs after its saturation, whereas the removal of sulfur from thiophene can occur without preliminary hydrogenation of the cycle. The energies of C–S and C–N bonds are 272 and 305 kJ/mol, respectively [11], and these values agree with the above conclusions regarding the difference in the sequences of the steps of N- and S-containing compound hydrogenolysis. Thiophene is less capable of coke formation than some intermediate products of its hydrogenolysis, which largely lead to coke. An opposite rule is expected in the case of indole, which is more capable of coke formation than the products of its transformation.

To obtain additional information on the role of initial compounds in coking, let us consider the relative contributions of some compounds to adsorption from binary mixtures. According to this characteristics, the compounds are arranged into the following series: styrene (345) > indol (110) > 1-methylnaphthalene (93) > thiophene (45) > *n*-heptane (0.5). As can be seen, this series differs substantially from the series for the relative contributions to coke formation (Table 2). The contributions of styrene, indole, and methylnaphthalene to adsorption are much higher than their contributions to coking. For thiophene and *n*-heptane, we observed opposite trends. To explain these effects it is necessary to take into account the nature of transformations of any specific compound under the conditions of catalyst coking.

The lower contribution of styrene, 1-methylnaphthalene, and indole to coking points to the fact that, under the conditions of coking, they transform to products that are less capable of coke formation and that desorb more readily than initial compounds. These are hydrogenation products. Specifically, the amounts of ethylbenzene, toluene, and heptanes in liquid catalyzate isolated after styrene conversion were 50, 23, and 5%, respectively. In the liquid catalyzate after 1-methylnaphthalene conversion, we found 20% 1-methyl dihydronaphthalene and 13% alkylbenzenes (Table 2). Thus, the more hydrogenation products, the stronger the difference between the relative contributions to coke formation and adsorption: for styrene (57 and 345) these values are much higher than for 1-methylnaphthalene (22 and 93).

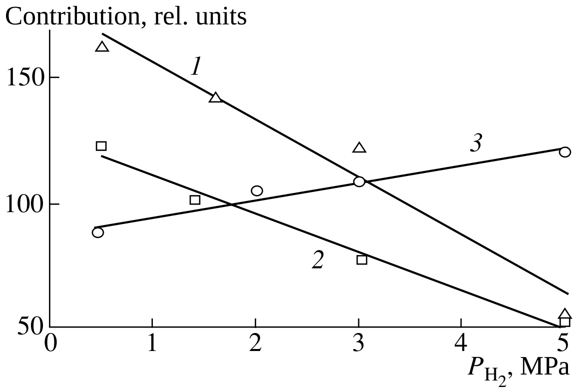
In the liquid products of *n*-heptane transformation, the concentration of toluene is ~70%, which is more capable of coke formation than the initial compound. This explains a higher contribution of *n*-heptane to coke formation than to adsorption. This explanation is also applicable to thiophene. As mentioned above, the absence of butadiene from the catalyzate in the case of thiophene can be due to the complete transfer of unsaturated C_4 fragment formed by the cleavage of the C–S bond to coke.

We assume that, according to the available classification of the mechanisms of catalyst coking [14], the formation of coke from styrene, 1-methylnaphthalene, and indole occurs in parallel with the main reaction, whereas the consecutive scheme works in the case of thiophene and *n*-heptane. We cannot exclude the formation of coke from the products of styrene, 1-methylnaphthalene, and indole transformation or from initial thiophene and *n*-heptane.

It is interesting to determine how the process conditions affect the contributions of feed components to catalyst coking.

Table 2. Relative contributions of different components of mixtures with benzene-^{14}C to the formation of coke (500°C)

Component	Coke radioactivity, pulse min^{-1} $(mg\ BaCO_3)^{-1}$	Relative contribution to coking
Benzene	1500	1.0
n-Heptane	300	4.0
1-Methylnaphthalene	65.0	22
Durene	44.0	33
Indole	31.0	47
Styrene	26.0	57
Phenanthrene	16.5	90
2-Methylnaphthalene	16.0	93
Thiophene	3.3	450



Relative contributions of (*1*) styrene; (*2*) 1-methylnaphthalene, and (*3*) thiophene to the formation of coke vs. hydrogen pressure (420°C).

A change in the process conditions affects the selectivities of the transformations of feed components in different ways and their conversions. Moreover, conversion affects the concentration of the initial compound, which may have different coking ability compared to the products of its primary transformations. Therefore, we may expect changes in the contributions of feed components to coke formation. To elucidate the nature and degree of these changes, we compared the contributions of aromatic hydrocarbons (styrene and 1-methylnaphthalene) and thiophene to coke formation at different temperatures and pressures. The results are summarized in the figure.

First of all, we should note that with a decrease in the process temperature from 500 to 420°C, the contribution of styrene to 1-methylnaphthalene substantially increases and the contribution of thiophene decreases (Table 2 and the figure). This is probably associated with a decrease in the conversion of cited compounds and the corresponding increase in the role of styrene and 1-methylnaphthalene, which are more cable of coke formation than the products of their hydrogenation, and thiophene, which is less capable of coke formation than the products formed via C–S bond scission.

A change in pressure (see the figure) also differently affects the contributions from these compounds. An increase in the intensity of hydrogenation with an increase in pressure and an increase in the product (ethylbenzene and dihydronaphthalene) yield result in a decrease in the contribution of styrene and 1-methylnaphthalene to coke formation. An increase in contribution from thiophene with an increase in pressure is probably due to the intensification of C–S bond hydrogenolysis and an increase in the yield of coke-forming structures.

When the hydrogen pressure is close to that used in the hydrotreatment of real crude oil, the role of the S-containing component in the catalyst coking becomes more important. This result agrees with data obtained in [15], according to which the desulfurization activity of the catalyst in the process of black oil hydrotreatment correlates with the amount of coke formed. The determining role of C–S bond scission products in catalyst coking is also supported by the distribution of coke over the catalyst bed. As it was shown in [16–18], in the hydrotreatment of real feed, the amount of coke at the reactor outlet is much higher than at the inlet, which is stipulated by an increase in the concentration of the hydrogenolysis products of the S-containing component in the reaction mixture as this mixture moves through the catalyst bed.

An important role of the hydrogenolysis of the S-containing component to catalyst coking should be taken into account in the optimization of the hydrodesulfurization process. Moreover, because the contribution of S-containing compounds to catalyst deactivation is high, the requirement of the low concentration of sulfur in petrochemicals is necessary to protect catalysts used for further treatment of feed. This requirement is in line with environmental safety suggestions.

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