

Action of Water Vapor in the High-Temperature Hydrogenation of a Mixture of Coke-Plant Benzene and the Naphthalene Fraction of Coal Tar

Zh. K. Kairbekov^{a, b, *}, N. T. Smagulova^{a, b, **}, and A. S. Maloletnev^{c, ***}

^a*Al-Farabi Kazakh National University, Almaty, Kazakhstan*

^b*Research Institute of New Chemical Technologies and Materials, Almaty, Kazakhstan*

^c*Moscow Mining Institute, Moscow Institute of Steel and Alloys, Moscow, Russia*

**e-mail: zh_kairbekov@mail.ru*

***e-mail: nazym2011@inbox.ru*

****e-mail: anstanmal@mail.ru*

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Abstract—In the catalytic high-temperature hydrogenation (hydrodealkylation) of a mixture of raw coke-plant benzene and the 180–230°C naphthalene fraction of coal tar, water vapor (steam) acts in two ways: it blocks the smallest pores in the catalyst, from which the removal of products is difficult; and it facilitates their desorption from the large pores, thereby decreasing the likelihood of polymerization of the reactive products of intermediate hydrocracking and dealkylation. Steam is found to play a positive role in slowing the formation of high-molecular compounds, which are sources of coke deposits on the catalyst.

Keywords: coal tar, naphthalene fraction, raw benzene, high-temperature hydrogenation, hydrodealkylation, water vapor, steam, chemical analysis

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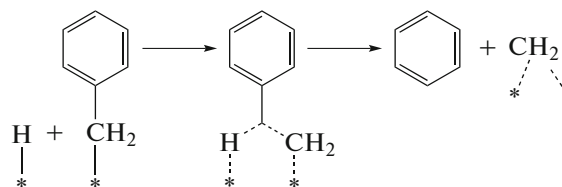
Coal tar and coking byproducts have been studied for a long time with a view to the removal of sulfur-bearing impurities, unsaturated hydrocarbons, and other compounds by hydrogenation and also the production of tetralin.

The products formed by hydrogenation of the naphthalene fractions of coke-plant tar at 540–560°C have a low content of saturated hydrocarbons (0.3–0.4%). That indicates the hydrocracking of saturated hydrocarbons at 540°C and above, suggesting the possibility of obtaining hydrogenates that consist almost entirely of aromatic hydrocarbons [1].

Dealkylation is the main reaction in the hydration of aromatic hydrocarbons at low hydrogen pressure above 500°C with catalytic and thermal processes. In the range 4–6 MPa, deep dealkylation of aromatic hydrocarbons is usually observed in the presence of catalysts containing Mo, Cr, and Co compounds on aluminum oxide, as established in [2, 3].

Phenolic hydrocarbons and naphthalene fractions of coal (coke-plant) tar should not be processed together, as shown in [4]. In high-temperature hydrogenation, benzene and naphthalene homologs undergo deep transformation, and the content of saturated hydrocarbons is 0.4–0.6% [4].

We do not adequately understand the catalytic high-temperature hydrogenation (hydrodealkylation) of aromatic hydrocarbons, individually or in mixtures. Radical and ionic reaction mechanisms have been considered in the literature. Data regarding the hydrodealkylation of toluene (580°C, 2.6–8.0 MPa; Cr₂O₃ + Al₂O₃) suggest the formation of a chemisorbed benzene radical at the surface of the catalyst. That radical reacts with chemisorbed hydrogen, splitting the methylene radical



This is analogous to the mechanism proposed for the reaction with hydrocarbon in [5]. The only difference is that the methylene radicals are hydrated predominantly with the formation of methane. By contrast, in the presence of water, hydration is accompanied by oxidation in CO and CO₂. The alkyl group may also undergo splitting as a result of the addition of a proton to the aromatic hydrocarbon, with the forma-