Kinetics and Mechanism of the Heterogeneous Catalytic Hydrogenolysis of Chlorobenzenes and Chlorocyclohexanes¹

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Abstract—The catalytic hydrogenolysis of hexachlorobenzene and hexachlorocyclohexanes (isomer mixture) on a nickel–chromia catalyst and hexachlorobenzene hydrogenolysis intermediates (1,2,4,5-tetrachlorobenzene, 1,2-trichlorobenzene, 1,2-dichlorobenzene, and chlorobenzene) are studied. The hydrogenation of an aromatic ring does not occur in the presence of chemisorbed chlorine atoms on the catalyst surface. A reaction mechanism for chlorobenzene hydrogenation was proposed taking into account experimental evidence that, in the presence of chemisorbed chlorine on the catalyst surface, hydrogen in a dissociated state is firmly bound to the surface. It is found that the desorption of the resulting hydrogen chloride is the slowest step in chlorobenzene hydrogenolysis. The hydrogenolysis of hexachlorocyclohexanes occurs via a dehydrochlorination stage with the formation of trichlorobenzenes, which are subsequently converted into chlorobenzene and benzene.

INTRODUCTION

The reactions of substituted benzenes with hydrogen can occur via the following two pathways: (a) hydrogen addition to the double bonds of a benzene ring with the formation of a hexane ring (hydrogenation) and (b) the abstraction of a substituent from the benzene ring followed by hydrogen atom addition (hydrogenolysis).

Many papers were devoted to the catalytic hydrogenation of benzene [1, 2], but the catalytic hydrogenolysis of halogenated benzenes is poorly studied as is evident from review [3].

The catalytic hydrogenolysis of chlorinated benzenes was primarily studied on metals supported on γ-Al₂O₃ or on sulfided nickel–molybdenum or cobalt–molybdenum samples supported on γ-Al₂O₃ [4–6]. Zanaveskin et al. [3], who summarized published kinetic data, concluded that the hydrogenolysis of chlorinated benzenes occurs via the Langmuir–Hinshelwood mechanism. In this case, hydrogen and chlorobenzenes are adsorbed on the active sites of the same type. Moreau et al. [5, 6] suggested that hydrogenolysis occurs via the two-site adsorption of a molecule with the rupture of a C–X bond, where X is a halogen atom.

Therefore, the hydrogenolysis of chlorinated benzenes on a catalyst whose surface has two types of active sites, which chemisorb hydrogen and chlorinated benzene, respectively, is of interest. We chose the nickel–chromia catalyst, which consists of nickel and chromium oxide [7]. It was found [8] that hydrogen is dissociatively adsorbed on nickel. Halogen-atom transit from one molecule to another (transhalogenation) readily takes place on chromium oxide [9]. Taking into account the existence of two different active sites on the given catalyst, it was of interest to study the mechanism of hydrogenolysis on this catalyst and to compare experimental and published data.

EXPERIMENTAL

Hexachlorobenzene and the following polychlorobenzene isomers that are intermediates in the hydrogenolysis of hexachlorobenzene were used as test materials in the reaction of catalytic hydrogenolysis: 1,2,4,5-tetrachlorobenzene (1,2,4,5-tetraCB), 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2-dichlorobenzene (1,2-DCB), and chlorobenzene (CB). Hexachlorocyclohexanes were studied as an isomer mixture with the following composition (wt %): α-hexachlorocyclohexane, 68; β-hexachlorocyclohexane, 6; γ-hexachlorocyclohexane, 12; δ-hexachlorocyclohexane, 7; ε-hexachlorocyclohexane, 5; and the balance heptachlorocyclohexane.

Experiments were performed on a nickel–chromia catalyst, which was prepared from nickel and chromium nitrate solutions according to a published procedure [7]. The chemical composition of the catalyst was as follows (wt %): nickel metal, 59.3; chromium oxide, 34.2; and a graphite binder, 6.5. The specific surface area of the catalyst before and after operation was equal to 80 ± 2 m²/g. Before the experiments, the catalyst was heated in a hydrogen flow at 623 K for 10 h. According to data published in [7], the catalyst composition after this treatment corresponds to nickel supported on chromium oxide. Thereafter, the test catalyst sample (volume of 2 ml, particle size of 0.2–0.5 mm, and Sₚ =...
Kinetic experiments were performed in a glass gradientless reactor designed by Korneichuk [10], and experiments on the simultaneous hydrogenation of chlorobenzene and benzene were performed in a glass flow reactor (with an inner diameter of 5 mm) with the same catalyst sample. The experiments were performed at 400–600 K; the contact time varied from 1 to 10 s.

The reaction mixture was prepared by saturating a hydrogen or helium–hydrogen mixture with vapors of organochlorine compounds, which were placed in an evaporator at a certain temperature. The kinetic experiments were performed at hydrogen concentrations of $0.005–0.04 \text{ mol/l}$ and organochlorine compound concentrations of $1 \times 10^{-5}–1.5 \times 10^{-3} \text{ mol/l}$. Because of the low partial pressure of hexachlorobenzene vapor, the experiments with this compound were performed in the concentration range $1.0 \times 10^{-5}–7.6 \times 10^{-7} \text{ mol/l}$.

The rates of reactions as functions of reactant concentrations were studied by maintaining a constant concentration of one of the reactants (hydrogen or an organochlorine compound). Note that, in the course of the hydrogenolysis of chlorobenzenes and chlorocyclohexanes, the catalyst operation was stable for more than 100 h without detectable changes in the activity. The initial substances and organic products were analyzed by chromatography using a flame-ionization detector. Samples for analyses were taken directly from gas flows at the inlet and outlet of the reactor using the same sampling valve, which was kept at 473 K.

RESULTS AND DISCUSSION

Benzene and chlorobenzenes with fewer chlorine atoms than in the parent compound were the chlorobenzene hydrogenolysis products. The products of aromatic ring hydrogenation (cyclohexene, cyclohexadiene, and cyclohexane) were not formed. Similar data (the absence of cyclohexene in the hydrogenolysis of chlorobenzenes on nickel and palladium catalysts) have been published [11, 12]. Cyclohexane was detected in the products of hydrogenolysis on platinum catalysts [13, 14].

In the simultaneous hydrogenation of chlorobenzene and benzene, the amount of the latter increases with temperature (Fig. 1, curve 1) and the amount of chlorobenzene decreases to zero (curve 2). The calculated material balance with respect to carbon demonstrates that the amount of benzene at the reactor outlet increased and the concentration of chlorobenzene decreased by the same value (benzene was not hydrogenated). If the chlorobenzene supply to the reactor was stopped, cyclohexene and cyclohexane appeared in the reaction products after some time (~1 h). The activity of the catalyst in benzene hydrogenation was completely restored by heating at 573 K in a hydrogen flow. The recovery of the catalyst activity was judged from the termination of hydrogen chloride release from the surface.

These data indicate that the hydrogenation of an aromatic ring does not take place in the presence of chemisorbed chlorine atoms or hydrogen chloride on the surface of a nickel–chromia catalyst.

Figure 2 demonstrates the rate of benzene hydrogenation as a function of benzene concentration in hydrogen and the effect of hydrogen concentration on the rate of this reaction.

Cyclohexene and cyclohexane were the products of benzene hydrogenation, and cyclohexadiene was not detected. The reaction orders with respect to benzene and hydrogen are 0.6 and 0.4, respectively; these values are consistent with published data [15, 16] obtained on nickel-containing catalysts. The absence of maxima on the rate-vs-concentration curves may indicate that benzene and hydrogen are adsorbed on different catalyst sites [17]. In the test nickel–chromium catalyst, metallic nickel and chromium oxide can be assumed to be these two types of sites.

Gaidai et al. [18] found that the hydrogenation of benzene on a Pt/Al$_2$O$_3$ catalyst is performed by weakly bound molecular hydrogen, whereas isotope exchange takes place through firmly bound atomic hydrogen. Taking into account these data and our experimental