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Two Scenarios of Dechlorination of the Chlorinated Hydrocarbons over Nickel-Alumina Catalyst

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Abstract: Dechlorination processes attract great interest since they are involved in environmental protection and waste disposal technologies. In this paper, the process of gas-phase dechlorination of 1,2-dichloroethane, chloroform, and chlorobenzene over Ni/Al₂O₃ catalyst (90 wt% Ni) prepared by a coprecipitation technique was investigated. The reduction behavior of the oxide precursor NiO/Al₂O₃ was studied by thermogravimetric analysis in a hydrogen medium. A thermodynamic assessment of the conditions under which metallic nickel undergoes deactivation due to the formation of nickel chloride was performed. The dechlorination of chlorinated substrates was studied using a gravimetric flow-through system equipped with McBain balances in a wide range of temperatures (350–650 °C) and hydrogen concentrations (0–98 vol%). The impact of these parameters on selectivity towards the products of hydrodechlorination (C₂H₄, C₂H₆, and C₆H₆) and catalytic pyrolysis (carbon nanomaterial and CH₄) was explored. The relationship between the mechanisms of the catalytic hydrodechlorination and the carbide cycle was discussed, and the specific reaction conditions for the implementation of both scenarios were revealed. According to the electron microscopy data, the carbonaceous products deposited on nickel particles during catalytic pyrolysis are represented by nanofibers with a disordered structure formed due to the peculiarity of the process including the side carbon methanation reaction.

Keywords: hydrodechlorination; catalytic pyrolysis; carbon nanofibers; nickel catalyst; 1,2-dichloroethane; chloroform; chlorobenzene

1. Introduction

The organochlorine compounds and waste products, including chlorinated hydrocarbons (CIHCs), are known as harmful pollutants widely disseminated in the atmosphere, residual waters, and contaminated soils. The CIHCs are widely used in the manufacture of refrigerants, herbicides, dyes, wood protectors, plant growth regulators, dye carriers, pesticide intermediates, heat-transfer media, and dielectric fluids in transformers [1–4]. Most of them are typically hazardous to human health due to their carcinogenic, mutagenic, and teratogenic activities [5]. The accumulation of organochlorine waste during the production of some industrially important CIHCs (trichloroethylene, perchloroethylene,

chlorinated methanes, etc.) causes difficult ecological issues. For example, the commercialized process to produce a vinyl chloride monomer (VCM) is based on the pyrolysis of 1,2-dichloroethane (1,2-DCE) that gives a significant amount of waste containing nonconverted 1,2-DCE [6]. At the present time, 1,2-DCE has been found in ambient and residential air samples, as well as in the ground and drinking water [7].

There are a lot of different methods used for the abatement of the chlorinated organic compounds, such as high-temperature thermal incineration, catalytic combustion, electrochemical reduction, and radiolysis, thermal and catalytic hydrodechlorination, etc. Catalytic hydrodechlorination still attracts much interest due to the comparatively mild conditions of the process, absence of highly toxic by-products such as phosgene and dioxins, and the opportunity to adjust the selectivity towards the desired valuable products [8,9]. In addition, catalytic gas-phase hydrodechlorination can achieve complete dechlorination of the ClHCs and waste, which makes it possible to return the released olefins and HCl into the manufacturing cycle or utilize the obtained mixed hydrocarbons as a fuel [9].

The supported noble metals (Pt, Pd, Rh, and Ru) and their alloys are recognized as the most effective catalysts for the hydrodechlorination due to their high reactivity in the target reaction and very high resistance to the deactivation caused by the chlorination [2,3,8,10–16]. However, high prices and limited availability of the precious metals render their industrial applications unreasonable. Much attention is now being paid to more abundant and affordable metals such as Ni and Fe. The Ni-based catalysts supported on various substrates (metal oxides, carbon, graphene oxide, etc.) have been intensively studied in recent decades in the catalytic hydrodechlorination of various ClHCs [10,17–22]. One of the major problems in the practical implementation of the catalytic hydrodechlorination over supported Ni is catalyst deactivation. Two factors have been considered to be the main reasons for the catalyst deactivation; one is a coke deposition on the metal surface, and the other one is the chloride formation caused by the interaction between metal and HCl. The latter eventually leads to the transformation of the active metal into an inactive form of NiCl_2 [12,18]. With the purpose to enhance the catalytic performance and improve the catalyst's stability, Ni is often modified by such metals as Pd [14,23,24], Fe [25–27], Mo [10,11,28], Cu [29,30], and others.

On the other hand, Ni and Ni-based alloys are widely used as catalysts for the production of carbon nanomaterials (CNM). This approach is known as a catalytic chemical vapor deposition (CCVD) technique [31]. CCVD was demonstrated to be very effective for the purposeful catalytic pyrolysis of various chlorinated hydrocarbons and their multicomponent mixtures (waste) [32–38]. In addition, Ni was found to be the most productive and stable among the other metals of the iron subgroup (Fe, Co, and Ni), which are commonly used in the composition of catalysts for CCVD [32,33]. The catalytic pyrolysis of chlorinated organic substances occurs in accordance with the so-called “carbide cycle” mechanism that was earlier revealed for the decomposition of unsubstituted hydrocarbons [39]. The catalytic pyrolysis of ClHCs and their mixtures leads to the formation of a filamentous carbon material with unique structural features and high textural parameters [35,40]. Thus, the same Ni-based catalytic system can be active in the hydrodechlorination and catalytic pyrolysis processes, which are both of great interest in terms of further development of industrial dechlorination technologies.

The main objective of the present research was to study the relationship between two “adjacent” catalytic scenarios of the dechlorination process: hydrodechlorination (conversion into hydrocarbons) and pyrolysis (decomposition with the formation of carbon nanomaterial). Both techniques are quite powerful in providing exhaustive dechlorination of organochlorine waste with the formation of valuable secondary products. In addition, both reactions can be catalyzed by the same Ni-based catalyst supported on alumina. Three different substrates—1,2-dichloroethane (DCE), chloroform (CLF), and monochlorobenzene (CB)—were selected as chlorinated hydrocarbons since they are all the products of large-scale industry. The influence of the reaction conditions (temperature and H_2 concentration) on the selectivity of the coprecipitated $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst was thoroughly investigated for each type of the ClHCs. The obtained results permitted the definition of the principal parameters and specific conditions for the implementation of each reaction path.

2. Results

2.1. Reduction Behavior of the NiO/Al₂O₃ Precursor

The NiO/Al₂O₃ sample (an oxide form of the catalyst containing 90 wt% of Ni) was synthesized by the coprecipitation of nickel and aluminum nitrates. Before being used in the hydrodechlorination process, activation of the catalyst (conversion to the metallic state) was required. With the purpose of finding the optimal conditions for the NiO/Al₂O₃ activation, the oxide precursor was studied by thermogravimetry in a hydrogen flow. The obtained profiles of the thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) are shown in Figure 1a.

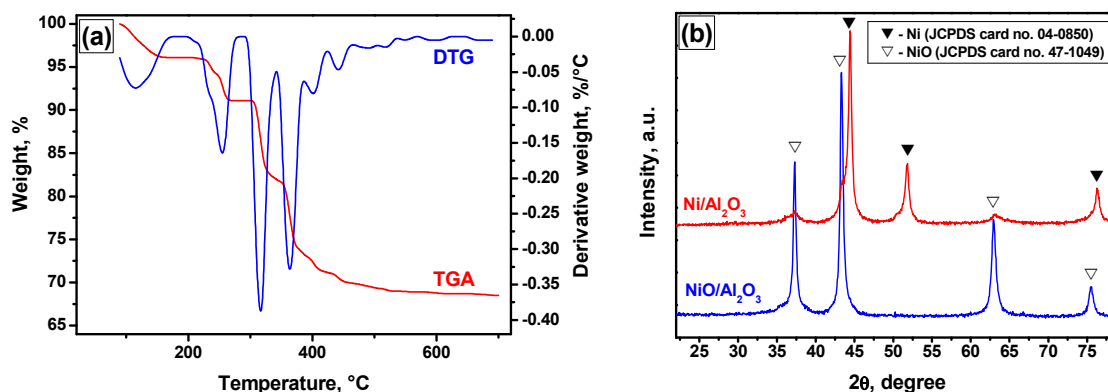


Figure 1. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) profiles for (a) the reduction of 90% NiO/Al₂O₃ precursor, (b) XRD patterns of the precursor and catalyst.

As follows from the TGA profile of the sample, the weight loss was represented by at least four peaks in the regions of 120, 255, 320, and 365 °C (Figure 1a). The first low-temperature effect (~120 °C) was probably caused by the loss of the chemisorbed moisture. The second peak at 255 °C may be associated with the reduction of highly dispersed nickel oxide particles about 5 nm in size [41]. The highest reduction rate of the sample was recorded at a temperature of 320 °C, which corresponded to a high specific surface area of bulk NiO (above 150 m²/g) [41–43]. The appearance of the next peak in the region of 365 °C was explained by the reduction of larger nickel oxide particles (about 40 nm) interacting with the surface of aluminum oxide [41]. A small peak of weight loss in the region of 400 °C was typical for larger nickel oxide particles on the surface of Al₂O₃ [42]. The reduction process was almost entirely completed at 500 °C, with the total weight loss of the sample of about 32%. The samples before and after the TGA procedure were characterized by an X-ray diffraction analysis. As follows from the profiles presented in Figure 1b, most of the NiO phase was transformed into the metallic nickel phase. Thereby, based on the data obtained, all the samples studied in the present work were activated by the treatment in a hydrogen flow at 500 °C for 30 min. The reduced catalyst comprised alumina (10 wt%) and nickel (90 wt%) in the form of highly dispersed metallic particles.

2.2. The Features of Nickel Chloride Interaction with Hydrogen

Hydrogen chloride resulted from the hydrodechlorination of chlorinated hydrocarbons interacting with the metallic nickel particles, thus leading to the formation of a nickel chloride phase, especially under the conditions of a lack of hydrogen. Such a phenomenon often serves as the main reason for the deactivation of the dechlorination catalysts. A layer of NiCl₂ formed on the metal surface blocked access of the gas-phase reagents to the catalyst's active sites responsible for the target reaction. The deactivation process of the nickel catalyst is sensitive to two main factors: temperature and hydrogen concentration (partial pressure) in the reaction mixture. The calculations were carried out in

order to define the conditions of nickel resistance towards the chlorination [32]. The reaction of nickel chloride with hydrogen can be represented by the following Equation:



The calculations were performed, taking into account the approximation that the isobaric–isothermal heat capacities of the substances (C_p°) do not change with the temperature. The estimation results are shown in Figure 2, where the temperature dependence of the equilibrium constant of reaction (1) is plotted.

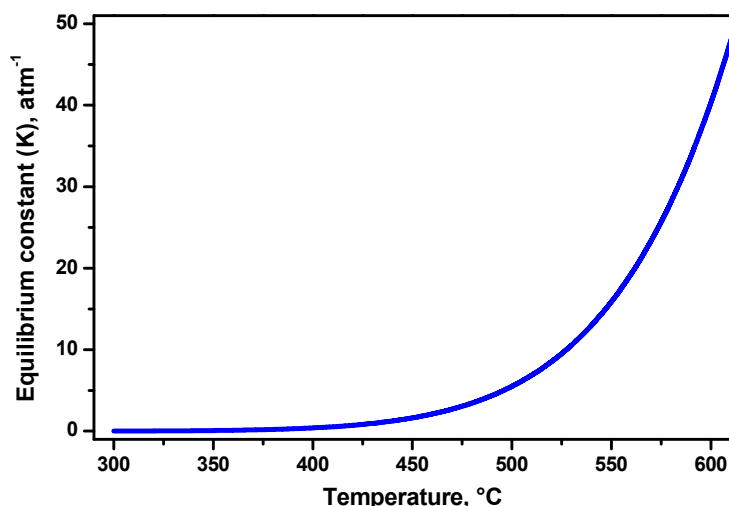


Figure 2. The temperature dependence of the equilibrium constant for the reaction (1) of hydrogen with nickel chloride. Thermodynamic calculations.

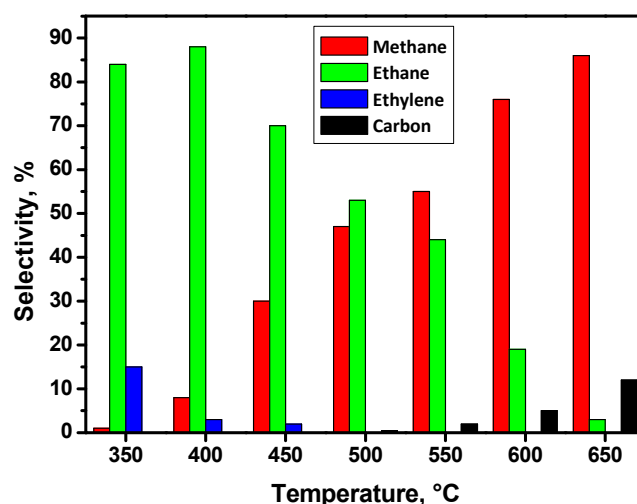
As follows from the presented data, the value of the equilibrium constant (K_p) exceeds 1 at temperatures above 450 °C. This means that nickel chloride should undergo a reduction with the formation of metal at such temperatures that consequently stabilizes the operation of the catalyst under the conditions of a lack of hydrogen. The obtained theoretical result was earlier confirmed experimentally in the study of the 1,2-DCE decomposition over Fe-, Co- and Ni-containing catalysts [32]. It is worth noting that, among the mentioned metals, Ni had the least tendency to chlorination, which made it possible to use the Ni-based catalysts in the dechlorination reactions in a wider temperature range. The process of nickel deactivation at temperatures below 450 °C can be suppressed by adding a significant excess of hydrogen to the reaction mixture, thus switching the process to the hydrodechlorination scenario.

2.3. (Hydro)Dechlorination of $\text{C}_2\text{H}_4\text{Cl}_2$

The process of 1,2-DCE hydrodechlorination over the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst was studied at the ratio $[\text{H}_2]:[\text{C}_2\text{H}_4\text{Cl}_2]$ of 10 in a temperature range from 350 to 650 °C. The experimental results on the 1,2-DCE conversion and process selectivity are summarized in Table 1. The diagram of the reaction products' distribution is presented in Figure 3. As seen, ethane and ethylene were the main products in a range of 350–400 °C, and the selectivity towards ethylene was sharply reduced with the reaction temperature increase. It was obvious that as the temperature increased, the rate of the reaction of ethylene hydrogenation with the formation of ethane sharply increased with a significant excess of hydrogen. The metallic surface of nickel was catalytically active in both reactions of the 1,2-DCE hydrodechlorination and the ethylene hydrogenation to form ethane [44,45].

Table 1. Catalytic properties of the Ni/Al₂O₃ catalyst in the hydrodechlorination of 1,2-DCE at different temperatures.

Temperature, °C	1,2-DCE Conversion, %	Selectivity, %		
		C	CH ₄	C ₂ H ₄ + C ₂ H ₆
400	98.0	0	8.1	91.9
500	99.6	0.5	47.3	52.2
600	99.4	5.0	76.1	18.9

**Figure 3.** The temperature dependence of selectivity towards the reaction products for the hydrodechlorination of 1,2-DCE over Ni/Al₂O₃ catalyst. Molar ratio [H₂]:[C₂H₄Cl₂] = 10:1; τ = 0.3 s.

It should be noted that with an increase in the reaction temperature, the selectivity for methane rose noticeably, from 1% at 350 °C to 86% at 650 °C (Figure 3). In this case, a significant accumulation of the carbon deposits on the catalyst was observed at a temperature of 550 °C. The selectivity towards carbon also increased with the temperature, reaching 11% at 650 °C. The formation of the structured carbon product is related to the process of 1,2-DCE decomposition in accordance with the “carbide cycle” mechanism, which underlies the functioning of catalysts for the CCVD-process [32,39,40,46].

The processing of 1,2-DCE with the preferential production of ethylene seems to be a very promising direction of its utilization since ethylene is a valuable feedstock for the synthesis of polymers. In a number of studies, Cu and Au were additionally introduced into the composition of the nickel–aluminum catalyst to improve its selectivity with respect to ethylene. In this work, the opportunity to enhance the yield of ethylene in the hydrodechlorination of 1,2-DCE at 350 °C and variable concentration of hydrogen in the reaction mixture (from 25 to 90 vol%) was studied. One can see from Figure 4 that, with a three-fold dilution of 1,2-DCE vapors with hydrogen, the ethylene selectivity of the catalyst reached the value of 96%. A further reduction of the hydrogen concentration in the mixture led to the deactivation of the catalyst due to the formation of bulk nickel chloride.

It should be noted that these results were obtained at a contact time (τ) of 0.4 s. It was found experimentally that this value was close to optimum: both the increase and reduction of the contact time resulted in a decrease in the ethylene yield. The value of 1,2-DCE conversion under these conditions was 90%. The obtained results are in good agreement with the literature data described for similar conditions [9].

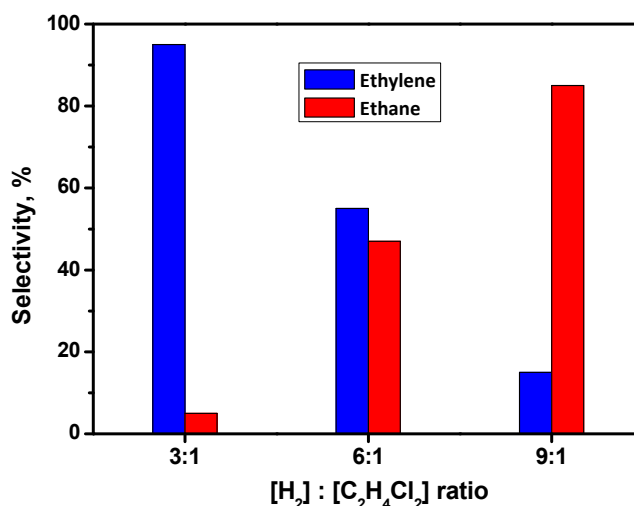


Figure 4. Effect of the hydrogen excess on the selectivity of Ni/Al₂O₃ catalyst towards ethylene and ethane. The hydrodechlorination of 1,2-DCE was performed at 350 °C and $\tau = 0.4$ s.

The dependence of the selectivity towards carbon and hydrocarbons on the hydrogen concentration in the H₂/C₂H₄Cl₂ reaction mixture is presented in Figure 5. The process was investigated at a temperature of 500 °C. It can be seen that, even in the absence of hydrogen in the reaction mixture, it was not possible to achieve 100% selectivity for carbon. The observed fact can be explained by the “intramolecular” excess of hydrogen within the molecule of C₂H₄Cl₂ ($\alpha = 2$): the released hydrogen partly participated in the reaction of carbon gasification with the formation of methane (methanation reaction). For hydrogen concentration in a range of 10–30 vol%, the existence of a transition region, where the contribution of both mechanisms was comparable, could be suggested. With an increase in the hydrogen content to 80 vol% and higher, the “carbide cycle” mechanism was suppressed, and the decomposition process of 1,2-DCE proceeded mainly with the formation of a mixture of hydrocarbons.

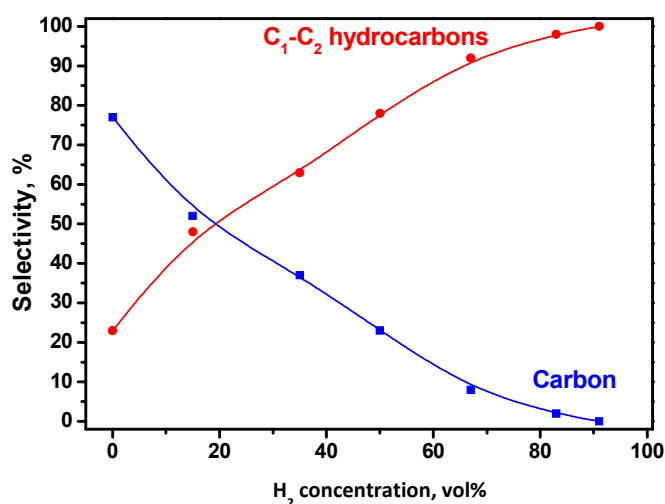


Figure 5. Effect of the hydrogen concentration in the H₂/C₂H₄Cl₂ reaction mixture on the selectivity of Ni/Al₂O₃ catalyst towards carbon and C₁-C₂ hydrocarbons. The reaction temperature is 500 °C.

2.4. Hydrodechlorination of CHCl₃

A good example to illustrate the relationship between the two scenarios was the process of CHCl₃ decomposition over Ni/Al₂O₃ catalyst at different hydrogen concentrations in the reaction mixture. As a result of the CLF processing, the two carbon-containing components only were found in the

reaction products, excluding trace amounts of CH_2Cl_2 and CH_3Cl : graphitic carbon and CH_4 . It should be noted that the conversion of CHCl_3 in all the cases was 98.2–98.4%.

The results of experiments on the CHCl_3 decomposition are shown in Figure 6. For 100% CHCl_3 , the value of $[\text{H}]:[\text{Cl}]$ atomic ratio (α) is 1:3, whereas for an equimolar mixture ($[\text{H}_2]:[\text{CHCl}_3] = 1:1$), the value of α is equal to 1 (3:3). As follows from Figure 6, when $\alpha \leq 2$, the selectivity for both carbon and methane was close to zero. This range of the α values corresponds to the area of the catalyst deactivation that occurs due to the nickel chlorination. Therefore, for the efficient decomposition of the chlorinated hydrocarbon over the Ni-containing catalyst, it is necessary to achieve the conditions when $\alpha \geq 2$. The obtained result is in complete agreement with the experimental data for the decomposition of $\text{C}_2\text{H}_4\text{Cl}_2$ in an argon atmosphere ($\alpha = 2$).

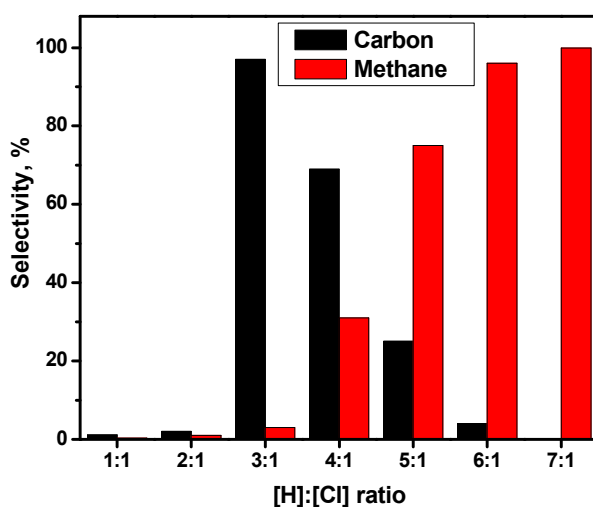


Figure 6. The dependence of the reaction selectivity upon the molar ratio $[\text{H}]:[\text{Cl}]$ (α) of the reaction mixture $[\text{CHCl}_3 + \text{H}_2]$ over $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst at 500 °C.

When the value of α was in a range of 2–3, the principal reaction product was the carbon nanomaterial, which indicated the predominance of the “carbide cycle” mechanism. With an increase in α to 5, a rapid transition from the “carbide cycle” mechanism to the hydrodechlorination region occurred, as evidenced by a sharp increase in the selectivity for methane. It can be seen that a further increase in the hydrogen concentration in the reaction mixture led to the complete termination of the carbon deposition process and the absolute dominance of the hydrodechlorination scenario. It should also be noted that the “carbide cycle” mechanism was limited by the regions of the catalyst deactivation and hydrodechlorination and was realized in a very narrow range of the hydrogen concentrations.

2.5. (Hydro)Dechlorination of $\text{C}_6\text{H}_5\text{Cl}$

This section presents the experimental results on the processing of chlorobenzene over the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst at temperatures of 350 and 500 °C and the variable content of hydrogen in the $\text{Ar}/\text{H}_2/\text{C}_6\text{H}_5\text{Cl}$ reaction mixture. The results are summarized in Table 2 and Figure 7.

Table 2. Catalytic properties of the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst in the hydrodechlorination of chlorobenzene (CB) at different temperatures and hydrogen concentrations.

Composition of the Reaction Mixture			Temperature, °C	CB Conversion, %	Selectivity, %		
Ar	H_2	$\text{C}_6\text{H}_5\text{Cl}$			C	CH_4	C_6H_6
8	1	1	500	96	88.5	8.5	3.0
8	1	1	350	88	0	traces	~100
-	9	1	350	100	0	0.2	99.8

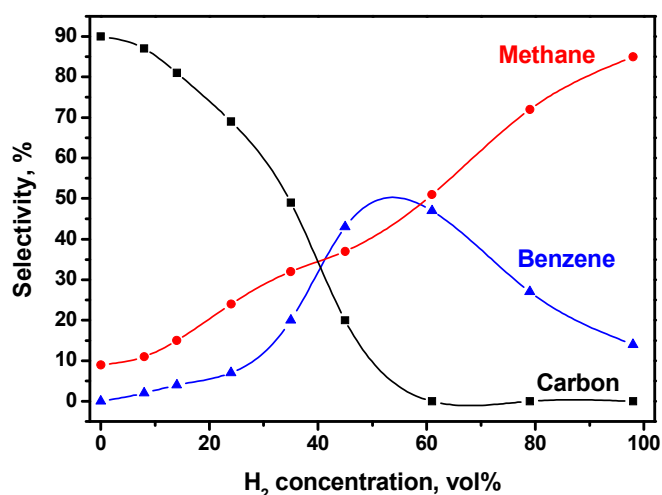


Figure 7. Effect of the hydrogen concentration in the $\text{H}_2/\text{C}_6\text{H}_5\text{Cl}$ reaction mixture on the selectivity towards carbon, benzene, and methane over $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst at 500 °C.

As follows from Table 2, at 500 °C and the equimolar ratio of $[\text{H}_2]:[\text{CB}] = 1$, the process of CB decomposition led to the formation of carbon as the main reaction product. Thus, under these conditions, the decomposition of chlorobenzene via the “carbide cycle” mechanism prevailed entirely. It was also seen that close to 100% benzene selectivity could be achieved at a temperature of 350 °C and the equimolar ratio of hydrogen and CB ($[\text{H}_2]:[\text{CB}] = 1$) in the diluted reaction mixture. In this case, the CB conversion was reduced to 88%. The complete replacement of argon with hydrogen in the reaction mixture ($[\text{H}_2]:[\text{CB}] = 9$) at 350 °C led to an increase in the CB conversion up to 100% with almost 100% yield of benzene (Table 2).

The dependence of the selectivity on the hydrogen concentration for the CB decomposition is demonstrated in Figure 7. The reaction was performed at a temperature of 500 °C. It is clearly seen that in the case of the CB decomposition without hydrogen addition, the carbon selectivity achieved 90%. The selectivity towards carbon demonstrated a sharp decrease with the rise of the hydrogen content in the reaction mixture. As in previous cases, the selectivity for methane tended to increase with the hydrogen concentration due to the intensification of the methanation reaction.

An interesting feature of the reaction was that the dependence of the selectivity for benzene on the hydrogen concentration passed through a maximum (Figure 7). Such behavior is typical for the intermediate products in the chain of successive transformations [47,48]. Apparently, the formation of benzene occurred at the first stage as a result of the CB hydrodechlorination. The further decomposition of benzene on nickel occurred with the formation of the carbon product.

2.6. Structure and Morphology of the Carbonaceous Deposits

The morphology and structure of the carbonaceous deposits resulted from the decomposition of the studied chlorinated hydrocarbons over $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst are illustrated by the selected scanning and transmission electron microscopy images presented in Figures 8–10.

As seen from Figure 8a,c and Figure 9a,b, the morphology of the produced carbon material was basically represented by rather long and entangled filaments. The diameter of the obtained carbon nanofibers (CNF) did not exceed the value of 1 μm ; it was to be determined by the size of the active nickel particles responsible for the growth of CNF at temperatures of 500–550 °C. One of these active Ni crystals is shown by the arrow in Figure 8b. It is obvious from the images presented in Figure 8b,d, and Figure 10a that such metallic particles were located on the top of grown carbon filaments. Therefore, in this case, the $\text{Ni}/\text{Al}_2\text{O}_3$ system behaved as a classical catalyst for the CCVD process, converting the chlorinated hydrocarbons into a nanostructured carbon material [33,34]. It should be noted that the growth of the irregularly packed disordered carbon nanofibers was caused by the presence of

chemisorbed chlorine species on the active metallic surfaces, thus bringing certain perturbations in a diffusion flux of carbon atoms inside the metal particle [40,49].

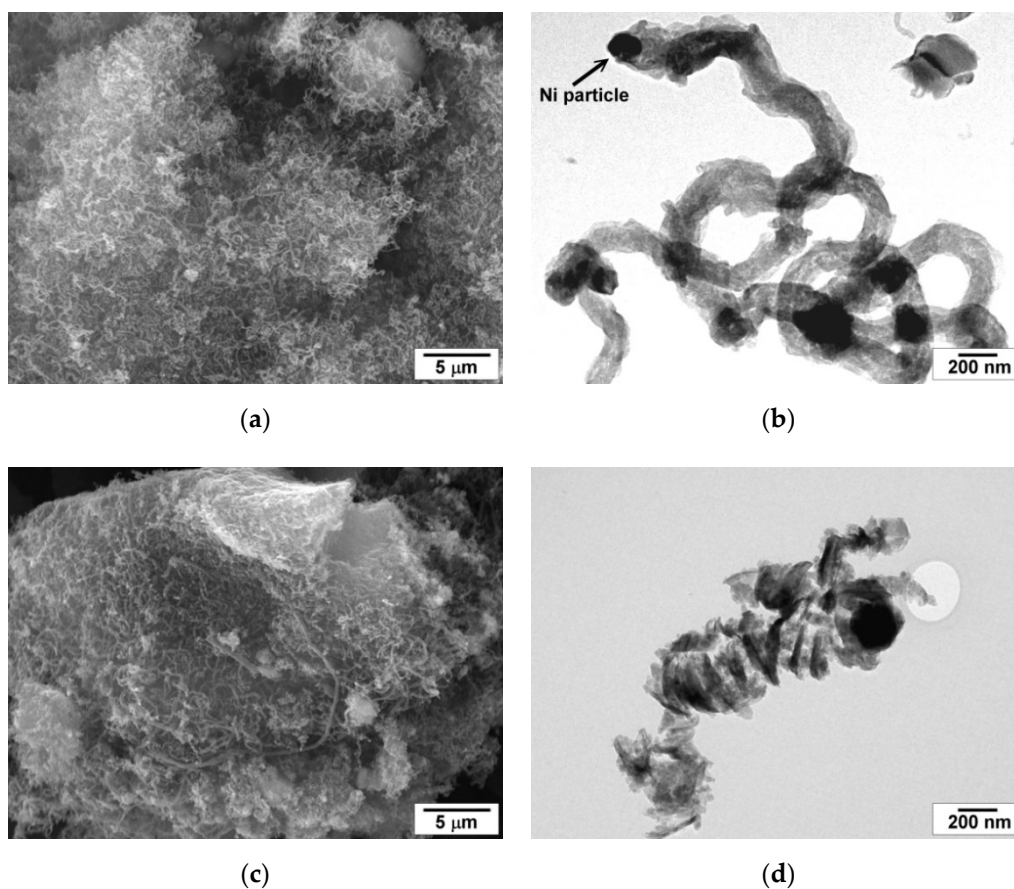


Figure 8. (a,b) SEM and (c,d) TEM images of the nanostructured carbon material produced via the processing of $C_2H_4Cl_2$ over Ni/Al_2O_3 at 550 °C: (a,c) without addition of H_2 ; (b,d) in the presence of H_2 (40 vol%).

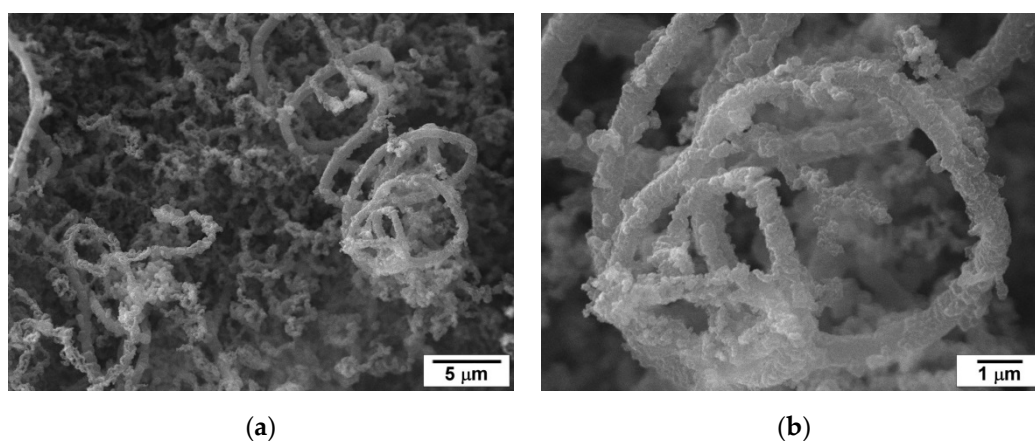


Figure 9. SEM images of the carbon nanofibers deposited over Ni/Al_2O_3 catalyst during the processing of $CHCl_3$ in the presence of H_2 (40 vol%) at 550 °C at different magnifications: (a) $\times 1000$ and (b) $\times 5000$.

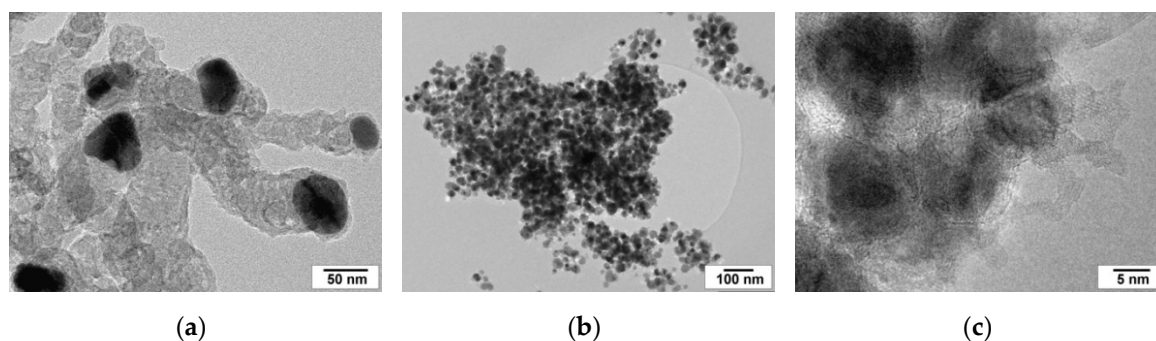


Figure 10. TEM images of the carbonaceous deposits produced over Ni/Al₂O₃ catalyst during the processing of C₆H₅Cl at 550 °C: (a) without addition of H₂; (b,c) in the presence of H₂ (50 vol%).

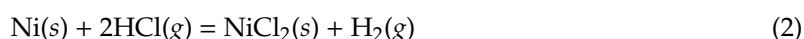
The impact of the hydrogen addition to the Ar/C₂H₄Cl₂ reaction mixture can be elucidated by the comparison of the TEM micrographs given in Figure 8b,d. The secondary structure of the carbon nanofibers formed in the presence of H₂ was seen to have the “segmental” character (Figure 8d). The body of the segmented carbon filament was built of alternating blocks of dense and loose graphitic matter [34,50]. At the same time, the addition of hydrogen excess into the Ar/C₆H₅Cl reaction mixture resulted in almost complete suppression of the CNF growth. Such impact is evidently demonstrated by the TEM images presented in Figure 10a,c.

3. Discussion

Let us take an example of 1,2-DCE and consider the principle reactions that may occur during the 1,2-DCE dechlorination on a nickel catalyst. So, depending on the process conditions (temperature and the [H₂]:[C₂H₄Cl₂] ratio in the reaction mixture), it is possible to implement one of three scenarios: (i) the nickel chloride formation; (ii) the hydrodechlorination; (ii) the catalytic pyrolysis with the formation of carbon nanomaterials.

3.1. Path (i) Catalyst Deactivation via the Formation of the Nickel Chloride

During the contact of the dispersed nickel with organochlorine compounds, catalyst deactivation may occur due to nickel chloride formation according to the following equation:



The thermodynamic possibility of this reaction is determined by the product of the reaction (Π):

$$\Pi = \frac{p(\text{H}_2)}{p^2(\text{HCl})} [\text{atm}^{-1}] \quad (3)$$

where $p(\text{H}_2)$ and $p(\text{HCl})$ are partial pressures of H₂ and HCl, respectively.

The reaction product Π has to be compared with the value of equilibrium constant (K_{eq}) that can be theoretically calculated at a certain temperature (Figure 2):

$$K_{\text{eq}} = \frac{\mathcal{P}(\text{H}_2)}{\mathcal{P}^2(\text{HCl})} = e^{-\Delta G^\circ_T / RT} [\text{atm}^{-1}] \quad (4)$$

where $\mathcal{P}(\text{H}_2)$ and $\mathcal{P}(\text{HCl})$ are partial equilibrium pressures of H₂ and HCl, respectively; ΔG°_T is the Gibbs energy change.

If the equilibrium is settled, the values of Π and K_{eq} are the same: $\Pi = K_{\text{eq}}$. The following inequality $\Pi < K_{\text{eq}}$ implies the tendency towards the formation of nickel chloride. The chlorination of nickel results in the decoration of the metallic surface, thus leading to the catalyst deactivation.

The addition of hydrogen in the reaction mixture enhances the value of Π to provide the condition $\Pi < K_{eq}$, when the formation of $NiCl_2$ would be suppressed.

3.2. Path (ii) Catalytic Hydrodechlorination

This regime is realized at temperatures below 400 °C and requires the presence of hydrogen in the reaction mixture. As was reported recently, the dechlorination reaction may occur by two different routes [51]. The first pathway is the classic hydrodechlorination leading to the formation of saturated hydrocarbons (ethane, in the case of 1,2-DCE). The second reaction pathway is known as a “hydrogen-assisted dechlorination” and predominantly leads to unsaturated hydrocarbons (ethylene). The existence of these two pathways for the hydrodechlorination reaction was earlier confirmed by the detailed kinetics investigations of the hydrogen-assisted dechlorination of 1,2-DCE catalyzed by Pd-Ag/SiO₂ sol-gel catalysts [13,52]. A set of different consecutive–parallel reactions was proposed a priori, and the experimental apparent reaction orders with respect to 1,2-DCE, H₂, C₂H₄, and HCl were fitted to different phenomenological models.

Flid et al. have suggested the mechanism of the 1,2-DCE hydrodechlorination over the supported Ni catalysts [9], where the first stage of the dechlorination is related to the replacement of C-Cl bonds by C-H ones with the formation of ethylene:



The occurrence of the reaction (5) implies the simultaneous cleavage of both C-Cl bonds as a result of C₂H₄Cl₂ molecule interaction with one H₂ molecule. The subsequent hydrogenation of ethylene to ethane is also possible and is catalyzed by the same metallic nickel species [47]:



Thereby, ethylene appears as an intermediate product during the 1,2-DCE processing by the hydrodechlorination mechanism. Consequently, there should be a set of optimal process parameters to achieve the maximum ethylene yield. Ethylene produced via the catalytic processing of the DCE-based waste can be used as a reagent, along with released HCl, in the industrial production of 1,2-DCE via the oxychlorination process [9].

3.3. Path (iii) Catalytic Pyrolysis via the “Carbide Cycle” Mechanism

While performing the decomposition process, the active metal particles of the catalyst produce the structured carbon fibers according to the “carbide cycle” mechanism proposed by Buyanov et al. [46]. The formed carbon product was found to have a very disordered structure and was named as a “feather-like” carbon due to its unique morphologic characteristics [33,34]. The gross-reaction for the catalytic pyrolysis of 1,2-DCE over Ni-catalyst can be written as follows:



According to the “carbide cycle” mechanism, the reaction (7) proceeds through the formation of unstable nickel carbide [Ni₃C] whose further decomposition ultimately results in the nucleation and growth of the graphitic filaments [46]:



It should be noted that the transformation of Ni to nickel carbide [Ni₃C] was experimentally observed during the hydrodechlorination of CHClF₂ and CCl₂F₂ [14,20,21,34]. It was established by Śrębowata et al. that the samples of Ni/C catalysts subjected to the hydrodechlorination of 1,2-DCE and CCl₂F₂ exhibited the presence of the hexagonal Ni₃C phase [21]. A similar observation was

reported by Morato et al. for the Ni-Al catalysts supported on the activated carbon and studied in the hydrodechlorination reaction of CHClF_2 and CCl_2F_2 in a temperature range of 250–290 °C [20].

As earlier reported by Kean and coworkers [34], the carbonaceous product deposited on the supported Ni catalysts as a result of the catalytic pyrolysis of chlorinated ethane at 400–800 °C is represented by the irregularly packed and fragmented filaments, bamboo-like and segmented fibers with a lot of defects. It was suggested that the formation of such disordered carbon fibers is to be driven by continuously changing conditions of the decomposition of chlorinated hydrocarbons upon the front side of the active Ni particles [40]. This causes the possible perturbations in the process of the carbon atom diffusion from front to rear side of the nickel particle, which ultimately gives rise to the formation of the disordered structure of the carbon deposits [49]. The reaction temperature has a very slight effect on the arrangement and structure of the produced nanofibers.

The addition of the hydrogen excess into the reaction mixture results in a few different effects on the structure of the produced CNF. First of all, this can switch the carbon deposition process into a regular cyclic regime, thus leading to the formation of so-called “segmented” carbon fibers [34], as shown in Figure 8d. The secondary structure of the segmented carbon fibers is assumed to be determined by the occurrence of regularly alternating “chlorination–dechlorination” reactions taking place on the active metallic surface [53].

The carbon nanofibers obtained as a product of chlorinated hydrocarbon utilization are characterized by a very loose and disordered structure consisting of the separate fragments of the graphitic phase. The addition of the hydrogen excess into the reaction mixture leads to an intensification of the methanation reaction (gasification of carbon) in accordance with the following equation:



The methanation reaction (9) is also catalyzed by metallic Ni, which is rather active in the creation of atomic hydrogen species via the dissociation of H_2 molecules. This phenomenon explains the appearance of CH_4 in the composition of the gas-phase products of the 1,2-DCE decomposition at 400 °C and above (Figures 3 and 5). The partial gasification of the deposited carbon was found to exert a significant effect on the structural and textural properties of the CNF material [54]. Due to a greater extent of disordering, the obtained carbon nanomaterials possess a rather high surface area and porosity (up to 400 m^2/g and 0.7 cm^3/g) [53]. Comparatively high textural parameters make this kind of filamentous carbon a very promising material for various areas of application, including hydrogen storage, lithium-ion batteries, concrete strengthening, modification of oils, etc. [55].

4. Materials and Methods

4.1. Preparation of Ni/Al₂O₃ Catalyst

The catalyst in the oxide form of NiO/Al₂O₃ (90 wt% Ni, 10 wt% γ -Al₂O₃, as calculated for the reduced state) was prepared by a coprecipitation technique. At the first stage, the mixed aqueous solution of the nitrate precursors, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Baltic Enterprise, Saint-Petersburg, Russia), was prepared. The coprecipitation procedure was carried out in a buffer solution ($\text{Na}_2\text{CO}_3 + \text{HCl}$) at a constant pH of 10. The 2M solution of KOH was used as a precipitating agent. The mixed solution of Ni, Al nitrates, and the precipitator were added dropwise with vigorous stirring into a buffer solution at 20 °C. The produced light-green colored sediment was settled, filtered out, and abundantly washed by distilled water. The produced sample was dried overnight and then calcined at 330 °C in air for 1 h.

4.2. Processing of DCE, CLF and CB on Ni/Al₂O₃ Catalyst

The processing of the chlorinated hydrocarbons in a gas-phase regime was studied using a flow gravimetric setup equipped with MacBain balances. The design of the reactor made it possible to follow the changes in catalyst weight during the experiment in real-time mode [32]. The loading of

the catalyst sample (in the oxide form of $\text{NiO}/\text{Al}_2\text{O}_3$) was 100 mg for all the experiments. Before each experiment, the catalyst sample was heated in an argon flow (20 L/h) up to 500 °C and then brought into contact with an H_2 flow (20 L/h) for 30 min. The completeness of the catalyst's reduction was controlled by the weight.

The chlorinated substrates used in the present study were $\text{C}_2\text{H}_4\text{Cl}_2$ (1,2-dichloroethane, DCE), CHCl_3 (chloroform, CLF), and $\text{C}_6\text{H}_5\text{Cl}$ (chlorobenzene, CB). The process temperature was varied within a range of 300–550 °C. All the catalytic studies were performed at atmospheric pressure (1 bar). The reaction gas feed was saturated with vapors of DCE (CLF or CB) via the bubbling of argon through a vessel filled with a liquid chlorinated hydrocarbon at 20 °C. Then, the reaction gas was mixed with a hydrogen flow and passed through a quartz reactor with the reduced catalyst sample. The hydrogen concentration in the reaction mixture was varied from 0 to 97 vol%. The composition of the gas-phase products was determined by a gas chromatography method using a "Tsvet-100" gas chromatograph (Russia). The components of the reaction mixture were divided using a column filled with a Porapak-Q adsorbent (Restek, Bellefonte, PA, USA). The calculations of the components' concentration from the chromatograms were performed in an automatic mode. The HCl vapors from the outlet gas mixture were trapped with a concentrated solution of caustic alkali. In order to calculate the chlorine balance, the concentration of the chlorine ions in the solution was measured via titration with AgNO_3 in a pH range of 6–8 in the presence of potassium chromate by Mohr's method.

After the experiment, the catalyst sample was cooled in an argon flow to room temperature. The mass of the produced carbonaceous product, if any, was measured by means of analytical balances (Sartorius, Moscow, Russia). The calculated values of the carbon yield were used to obtain the selectivity of the catalyst towards the carbon-containing products.

4.3. Characterization of Catalyst and Carbonaceous Products

An optimal temperature value for the reduction of $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst was determined by thermogravimetric analysis carried out in a hydrogen flow using a quartz reactor equipped with MacBain balances. The temperature was raised from 20 to 700 °C with a ramping rate of 5 °C/min. The specimen weight was 200 mg. The hydrogen was fed through the reactor at a rate of 20 L/h.

The X-ray diffraction (XRD) analysis was carried out using an X'TRA (Thermo ARL, Ecublens, Switzerland) diffractometer (Bragg–Brentano geometry, $\text{CuK}\alpha$ radiation, energy dispersed detector, step scan mode). Data were registered in a 2θ angle range from 5 to 80 with a 0.05 step. The accumulation time at each point was 5 s.

The textural characteristics of the catalyst and carbonaceous deposits were determined by a low-temperature nitrogen adsorption technique using an ASAP-2400 apparatus (Micromeritics, Norcross, GA, USA). Before the analysis, all the samples were calcined at 300 °C for 4 h at a pressure of $\sim 10^{-3}$ torr.

The structure and morphology of the carbon product were studied by scanning electron microscopy (SEM) on a JSM-6460 instrument (JEOL Ltd., Tokyo, Japan) at magnification factors from 8 to 300,000 $\times$. The detailed study of the produced carbon materials was carried out by means of a transmission electron microscopy (TEM) using a JEM-2010 (JEOL Ltd., Tokyo, Japan) microscope with a maximal resolution on a lattice of 0.14 nm and accelerating voltage of 200 kV. Before the examination, the samples were pretreated by an ultrasonic dispersion in ethanol with subsequent deposition of the resulting suspension on a copper grid covered with carbon.

5. Conclusions

Based on the obtained results, three main factors determining the scenario of the interaction of Ni-containing catalyst with chlorinated hydrocarbons can be suggested: (1) the process temperature; (2) the hydrogen concentration in the reaction mixture; (3) the intramolecular ratio $\alpha = [\text{H}]:[\text{Cl}]$ for the substrate molecule. It was shown that in the composition of the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst (90 wt%

Ni), the dispersed metallic nickel species are capable of carrying out the process of the gas-phase dechlorination (DCE, CLF, and CB) in two fundamentally different regimes:

1. Catalytic hydrodechlorination regime. It implies the replacement of C-Cl bonds with C-H or C-C bonds in the ClHC molecule. This route is characterized by a high selectivity for hydrocarbons (including olefins). It prevails in a region of low and moderate temperatures at a significant excess of hydrogen in the reaction mixture.
2. Catalytic pyrolysis regime. It proceeds via the “carbide cycle” mechanism. The complete destruction of all bonds in a ClHC molecule leads to the formation of nanostructured carbon as the main product. This route is effective at high temperatures (above 450 °C) without hydrogen addition (for ClHCs with an intramolecular ratio $[H]:[Cl] > 1$). The appearance of hydrogen in the reaction mixture (or reaction products) leads to partial gasification of the deposited carbon with the formation of methane.

The third scenario should also be mentioned when the catalyst interacts with the reaction mixture. This stoichiometric reaction of a noncatalytic nature results in nickel chloride formation. The conditions for this reaction are determined by the value of the reaction product $\Pi = p(H_2)/p^2(HCl)$. In the case when $\Pi < K_{eq}$, the process of nickel chlorination takes place (and vice versa). The value of the equilibrium constant K_{eq} at a given temperature T can be defined based on the thermodynamic calculation of the temperature dependence $K_{eq}(T)$. The bulk chlorination of nickel is undesirable since it leads to the blocking of the metal particles' surfaces and deactivation of the catalyst.

The contribution of each scenario in the dechlorination process ultimately determines the composition of the gas-phase reaction products and the rate of carbon accumulation. The notion of the reaction patterns and mechanistic aspects for the processing of ClHCs would allow adjusting the selectivity towards the desired products and define the optimal parameters for the processing of organochlorine waste of various compositions. The hydrodechlorination route can be recommended for the processing of the individual chlorinated hydrocarbons to produce corresponding saturated hydrocarbons and olefins. The regime of the catalytic pyrolysis is appropriate for the case of disposal of multicomponent waste consisting of mixed chlorinated hydrocarbons. As a result of the catalytic pyrolysis of waste, a filamentous carbon product with a developed surface area is formed. Such carbon material can be further used as an adsorbent, catalyst support, or component of the composite materials.

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