MECHANISM OF DEHYDROHYDROLYSIS OF CYCLOHEXYLAMINE

WITH WATER VAPOR ON A NICKEL-CHROMIUM CATALYST

V. Z. Fridman, A. A. Davydov, and

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E. D. Mikhal'chenko

The mechanism of the dehydrohydrolysis of cyclohexaylamine by water vapor on a nickel-chromium catalyst has been studied by IR spectroscopy of the adsorbed molecules and the response method. It has been shown that the reaction proceeds via the formation of a nickel oxide complex and its interaction with an adsorbed cyclohexylamine molecule.

Dehydrohydrolysis of cyclohexylamine (CHA) is used in the production of caprolactam from aniline [1]. However there is hardly any published data on its kinetics or mechanism.

$$\bigvee^{\mathrm{NH}_2} + \mathrm{H}_2 \mathrm{O} \longleftrightarrow^{\mathrm{O}} + \mathrm{NH}_3 + \mathrm{H}_2.$$
 (1)

It has been shown [2] that conversion of CHA on a Ni-Cr-catalyst proceeds directly to cyclohexanone (CHN) without the formation of molecular cyclohexylidenimine (CHDI) but the nature of the elementary stages has still to be clarified.

This present study is concerned with an investigation into the mechanism of the dehydrohydrolysis of CHA by water vapor on a Ni-Cr-catalyst using IR spectroscopy of the adsorbed molecules [3] and the response method.

EXPERIMENTAL

The catalysts used were Ni/Cr ones with compositions: 40% NiO:60\% Cr₂O₃ (catalyst A) and 20\% NiO:80\% Cr₂O₃ (catalyst B) prepared as in [5].

IR spectroscopy was used to investigate the catalysts, adsorption of CHA, water, and the conversion products [3, 5, 6]. Kinetic experiments were conducted on catalyst A in a flow type reactor with a fluidized catalyst layer [2] at 473 K.

RESULTS AND DISCUSSION

In studying reaction (I) on a Ni-Cr-catalyst one must take account of the fact that in the adsorbed state CHA is able to interact with a water molecule impinging from the gas phase (Rideal mechanism), molecularly adsorbed water, and also reactive oxygen-containing nickel complexes possibly formed as a result of mild oxidation of nickel by water vapor similar to that noted in [7, 8].

Information on the interaction between CHA and the surface was obtained by means of the response method using catalyst A, which was preliminarily reduced for 2 h in H_2 at 498 K. After reduction the water vapor was flushed from the catalyst for 3 h in He at 523 K. Then the conversion of CHA was studied in He at 473 K. The results, presented in Table 1, indicate that the main products of CHA conversion in He on the treated catalyst A are involatile compounds resulting from CHA condensation reactions [2]; cyclohexanone (CHN) is liberated in trace amounts (<1.0%). In the following cases the given sample was exposed to water vapor at 523 K for 1 h and then molecularly adsorbed water vapor was flushed from the catalyst for 3 h at 523 K in He. After this treatment it can be assumed [7] that only the reactive oxygen-containing centers remain on the surface. Subsequent CHA conversion in

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| Treatment conditions | 15 min | | | 30 min | | |
|--|--------|------|-------------------|--------|------|-----------------|
| | CHA | CHN | Σ [*] HB | СНА | CHN | Σ _{HB} |
| Reduced 2 h in H ₂ at 225°C, flushed 3 h in He at 250°C | 38,4 | 0,9 | 59,6 | 40,7 | 0,8 | 57,3 |
| Reduced 2 h in H ₂ at 225°C, exposed 1 h to water vapor at 250°C, flushed 3 h in He at 250°C | 44.2 | 15,4 | 39,4 | 42,1 | 13.4 | 44,6 |
| Treatment conditions | 43 min | | | 60 min | | |
| | CHA | CHN | Σ _{HB} | CHA | CHN | Σ _{HB} |
| Reduced 2 h in H ₂ at 225°C, flushed 3 h in He at 250°C | 39.6 | 0,6 | 59,1 | 42,3 | 0,7 | 56,2 |
| Reduced 2 h in H ₂ at 225°C, exposed 1 h to water vapor at 250°C, flushed 3 h in | 42,3 | 10,4 | 46,9 | 40,6 | 9,8 | 48. 7 |

TABLE 1. Effect of Preliminary Treatment of Ni-Cr-catalyst on the Composition (mass %) of Conversion Products of CHA in an Atmosphere of He at 200°C, $P_{CHA}^0 = 8.3$ kPa

 $*\Sigma_{\rm HB}$ - total high-boiling point products.

an atmosphere of He (Table 1) is accompanied by a sharp increase in the CHN concentration (up to 15%), but the amount decreases uniformly with the working life of the catalyst. The results allow us to rule out a Rideal mechanism and any interaction between adsorbed CHA and molecularly adsorbed water since CHN is formed in the absence of H_2O in the gas phase or in the molecularly adsorbed form. We can assume that water forms an oxygen-containing compound (center) on the surface of the catalyst, which reacts with CHA to form CHN. The fact that the CHN yield decreases with the working life of the catalyst indicates that in the absence of water these centers gradually break up.

Adsorption of CHA on the Ni-Cr-catalysts was studied by IR spectroscopy.

Adsorption of CHA at 293 K at its saturated vapor pressure on sample A reduced in H_2 resulted in the appearance in the spectrum of intensive absorption bands (AB) at 1455, 1590, 2870, and 2945 cm⁻¹ (Fig. 1, spectrum 3) and weak AB at 920, 1060, 1260, and 1380 cm⁻¹ in the same positions as the corresponding AB in the spectrum of CHA on its own (see Fig. 1, spectrum 2). The observed AB can be assigned to all types of vibrations characteristic of a CHA molecule (δNH_2 , δCH_2 and νCH_2) and point to adsorption of undissociated CHA. The AB at 1620 cm⁻¹ (δNH_2), observed in the spectrum of CHA on its own, is displaced to 1590 cm⁻¹ in the spectrum of adsorbed CHA. This suggests that one of the possible forms of the adsorbed CHA probably interacts with the surface by means of its NH_2 group. The AB at 1100 and 890 cm^{-1} (pCH₂) are also displaced to 1060 and 920 cm⁻¹ respectively, due to the participation of these groups of the molecule in the formation of the adsorption complex. As has been noted elsewhere [5], on reduction in H_2 of a Ni/Cr sample A at 523 K the catalyst surface consists of quite coarse crystals of metallic nickel and only insignificant amounts of chromium cations with reduced effective charge, from which it follows that for CHA to be adsorbed on this catalyst there must be at least two adsorption centers, and the spectrum recorded by us is apparently a combined one. As it is not possible to investigate CHA absorption on pure metallic nickel due to its low adsorption capacity, in order to estimate the interaction of CHA with each of the adsorption centers we must use data obtained from adsorption of NH3, when the spectral characteristics of coordinated ammonia on Cr- and Ni-containing systems are known to differ significantly and interaction via an NH2 group and NH3 should be similar.

Adsorption of ammonia (5 mm Hg) at 293 K on reduced sample B results in the appearance in the spectrum of AB at 1200 and 1620 cm⁻¹ (see Fig. 1, spectrum 6) caused by δ_s and δ_{as} of coordinately linked ammonia [6, 9], most likely on chromium ions [6]. In the case of the reduced sample it is not possible to obtain clear δ_s absorption of ammonia coordinated



Fig. 1. IR spectra for adsorbed CHA and NH_3 on Ni-Cr-catalyst A reduced at 523 K in H_2 (100 mm Hg): 1) background; 2) CHA spectrum; 3) adsorption of CHA 3 mm Hg at 298 K; 4) ditto at 573 K; 5) desorption at 298 K; 6) adsorption of NH_3 at 298 K.

by nickel (AB \sim 1100 cm⁻¹ for Ni²⁺ and even lower for reduced nickel [6]), the reason being either the superposition of AB in this region or the weak electron-acceptor properties of metallic nickel, which rule out adsorption of ammonia, and by analogy, of an amine on its surface by means of donor-acceptor bonds. Adsorption of ammonia on metals is known generally to proceed dissociatively with the formation of NH₂ groups, which are detected in the spectral region 1500-1560 cm⁻¹ [10].

Clearly when CHA is adsorbed by its NH_2 group the adsorption center must possess electron-acceptor properties. We will assume that on a Ni-Cr-catalyst CHA can be adsorbed in two ways: on chromium cations where the interaction will occur via the NH_2 group, and on Ni where adsorption will be due to interaction of a C-H bond of the cyclohexane ring with Ni. As CHA adsorption in this case should be similar to cyclohexane adsorption [11], we will assume that CHA is also adsorbed by the plane of the cyclohexane ring.

It should be noted that CHA is adsorbed in its molecular from right up to 493 K. A qualitative change in the spectra occurs at 573 K (see Fig. 1, spectrum 4). Analysis of this spectrum and the way it changes during desorption indicate that several adsorbed forms are present, one of which is characterized by an AB in the region ~ 1660 cm⁻¹ (see Fig. 1, spectrum 4). During the nondestructive adsorption of aldehydes and ketones [6, 12, 13] an AB is always observed in this region. In view of the above results on the nature of CHA conversion on the catalyst under investigation we can assume that this AB belongs to the vC=O in cyclohexanone. Other assumptions are also possible. After heating at 573 K there are AB at 1550 and 1590 cm⁻¹ as well as the one at 1660 cm⁻¹ (see Fig. 1, spectrum 4). According to [14] both these bands could be linked to imine type compounds, since it was shown earlier that during CHA conversion in helium, condensation products containing imino groups were formed. Also, the product formed is quite easily eliminated from the surface (there is virtually complete desorption at 293 K (see Fig. 1, spectrum 5). At the same time the AB at 1550 cm⁻¹ remains, confirming that the pair of AB at 1550 and 1660 cm⁻¹ do not result from the formation of a surface imine but characterize different substances. In our opinion the AB at 1420-1430 and 1550 cm⁻¹ could be caused by the formation of surface compounds containing a carboxylic group R-COO⁻ and the observed AB are characterized by v_s and v_{as} of the COO⁻ group respectively [6]. It would follow that the AB at 1660 cm⁻¹ could belong to vC=0 in cyclohexanone adsorbed on the catalyst. Our attention is drawn to the fact that the



Fig. 2. Variations in IR spectrum of oxide Ni-Cr-catalyst, reduced in H₂ at 523 K with subsequent evacuation at 523 K (1): 2) adsorption on (1) of CO, 15 mm Hg, at 298 K; 3) interaction with H₂O at 523 K (1 h); 4) adsorption on (3) of CO, 15 mm Hg, at 298 K (30 min); 5) adsorption on (3) of CO, 15 mm Hg, at 298 K (1 h).

Fig. 3. IR spectra of CHA (0.1 mm Hg) adsorbed on a Ni-Cr-catalyst oxidized by H_2O at 523 K for 30 min and reduced in H_2 at 523 K: 1) initial sample; 2) CHA adsorption at 298 K; 3) subsequent heating at 523 K for 10 min; 4) ditto at 573 K.

AB at 1660 cm⁻¹ is not very strong and there is no band at 1700 cm⁻¹ characteristic of the ν C=O in cyclohexanone in the gas phase. These results agree with the data in the table showing that on the reduced Ni-Cr-catalyst only a small amount of cyclohexanone (<1.0%) is formed in the absence of water.

Interaction of the reduced catalyst A with H_2O (5 mm Hg) at 523 K for 30 min with subsequent desorption of H₂O at 523 K increases the degree of surface hdyroxylation, which shows up by increased absorption in the region $3000-3700 \text{ cm}^{-1}$. Analysis of the spectrum in the carbonyl absorption region enables the characteristic changes in the state of nickel to be recorded in full (Fig. 2, spectrum 4) after interaction with water in comparison to a sample that has not been so treated (Fig. 2, spectrum 2). These changes are even more marked on increasing the contact time with water to 1 h (Fig. 2, spectrum 5): some of the nickel in the significant fraction of metallic clusters that are conserved is oxidized. This is supported by the conservation in the spectrum of AB in the 1900-2000 cm^{-1} region after adsorption of CO without any increase in the concentration of $Cr^{2+}-CO$ complexes (the formation of metallic clusters of nickel occurs on chromium ions) [5]. At the same time AB are detected at ~2030 (strong), 2080 (weak), and possibly 2130 cm⁻¹ (see Fig. 2, spectra 4, 5), indicating the presence of oxidized nickel in samples treated with water [5]. Increasing the contact time with CO results in an increase in intensity of these maxima indicating that the AB result from reduction in CO of other more highly oxidized states of nickel cations (most likely Ni⁺ and possibly even Ni²⁺); when CO is adsorbed on a surface oxidized by H_2O an AB at 2180 cm⁻¹ is observed in the spectrum immediately after the gas is admitted, which disappears as the contact time lengthens. In this process a maximum is detected at 2170 cm^{-1} characteristic of the Cr^{2+} -CO complex in which the chromium ion remains reduced. It is possible that the disappearance of the AB at 2180 cm⁻¹ is linked to reduction of Ni²⁺ cations involved in the formation of Ni²⁺-CO complexes (vCO 2180 cm⁻¹), resulting in the formation of a structure with an appreciable electron density at the nickel, i.e., a state close to that of metallic nickel formed on an oxidized sample at ~20°C, but differing from it slightly.

In our view the most valid explanation of these effects is as follows: a section of the surface of metallic nickel clusters (possibly the edges of the clusters) formed during reduction in H₂ at 523 K is completely oxidized by water to Ni²⁺ (the AB at \sim 2180 cm⁻¹ is analogous to the AB observed for the Ni/NiO system) and then these ions are reduced in CO (2020, 2080, and 2130 cm⁻¹) to a state corresponding to the Ni/Ni^{§+} system.

The interaction of CHA with this sample at low concentrations is accompanied by the formation of a complex analogous to that described above (Fig. 3, spectrum 2), which breaks up at higher temperatures to give carbosilicates (AB at 1560 cm⁻¹) and CHN. Evidence for the presence of the latter is given by AB at 1660 and 1700 cm⁻¹ (Fig. 3, spectrum 4) characteristic of the C=O bond in the adsorbed (1660 cm⁻¹) and free (1700 cm⁻¹) states of CHN [6]. It should be noted that where the Ni-Cr-catalyst is not reduced (see Fig. 1) as on the sample oxidized by water (Fig. 3, spectrum 4), significantly larger amounts of CHN appear to be formed. These results are in agreement with the kinetic data presented in the table where the amount of CHN increased by \sim 15 times on the hydrated sample. Our attention is drawn to the fact that at 293 K CHA adsorption is completely suppressed following CO adsorption and there are no AB in the spectrum for CO complexes either with nickel (Ni-CO, Ni⁶⁺-CO, Ni⁺-CO) or with chromium (Cr²⁺-CO).

From analysis of these results for the dehydrohydrolysis of CHA by water vapor on a Ni-Cr-catalyst the following mechanism can be proposed. The surface of the reduced Ni-Cr-catalyst consists mainly of clusters of metallic nickel [5] stabilized close to and/or on chromium cations and only a very small amount of chromium cations with reduced effective charge. When the catalyst surface interacts with water, reaction occurs according to scheme (1) with the formation of a complex center consisting of a nickel cluster with one (or several) oxygen-containing centers

○ Ni ● 0

During this chromium cations are not oxidized by the water. Adsorption of CHA occurs on both chromium cations and on the nickel clusters. Adsorption on the chromium can be represented as follows:



This form of CHA is quite stable and in our opinion is not involved in further conversions. This assumption is based on the fact that during conversion of CHA on pure chromium oxide no CHN is formed even at T > 498 K, and also on the fact that there is no reactive weakly bound oxygen in the vicinity of this complex analogous to that found in the case of nickel.

Employing the competing reaction method for adsorbed CO and CHA it was established that during CHA adsorption all the forms of nickel (Ni⁰, Ni¹⁺, and Ni^{δ +}) were involved in the formation of complexes with CHA.



Subsequent conversion of CHA results in rupture of the C-N and C-H bonds at the α -carbon atom and formation of adsorbed CHN with the evolution of NH₃ into the gas phase. Even if the NH₃ is adsorbed on vacant chromium cations this does not affect the catalytic act itself:

(2)

$$(4)$$

The final stage in the reaction is desorption of CHN from the catalyst surface. During this the metallic nickel cluster becomes vacant.

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