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IR SPECTROSCOPIC STUDIES OF ADIPONITRILE AND AMMONIA ADSORPTION OVER Ti-Sb-O CATALYST

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The adsorption of adiponitrile (ADN), NH_3 and ADN+NH_3 and NH_3+O_2 mixtures over Ti-Sb-O catalyst has been studied. In the presence of NH_3 ADN is polymerized over the catalyst. NH_3 contribution to the polymerization process is suggested to consist in the formation of surface NH_x^- structures.

На Ti-Sb-O катализаторе изучена адсорбция адипонитрила (АДН), NH_3 и смесей АДН и NH_3, NH_3 и O_2. Показано, что в присутствии NH_3 происходит полимеризация АДН на поверхности катализатора. Предполагается, что влияние NH_3 на полимеризацию заключается в образовании поверхностных структур типа NH_x^-

It has been shown previously [1] that the ammoxidation of cyclohexane to ADN is limited by the product desorption from the catalyst. Hence it was of interest to examine the adsorption forms of ADN and the reasons for its strong bonding with the surface.

ADN adsorption was studied on a 30 mol% Sb_2O_5-70 mol% TiO_2 (S_{BET} = 18 m^2/g) catalyst. A 40-60 mg/cm^2 thick sample was subjected to oxygen-vacuum treatment at 773 K for 2 h and cooled down to room temperature in oxygen (oxidized sample). A reduced sample was obtained through NH_3 treatment (20 Torr NH_3, 773 K, 20 min). Spectra were recorded at room temperature on a UR-20 spectrometer with gas phase compensation.

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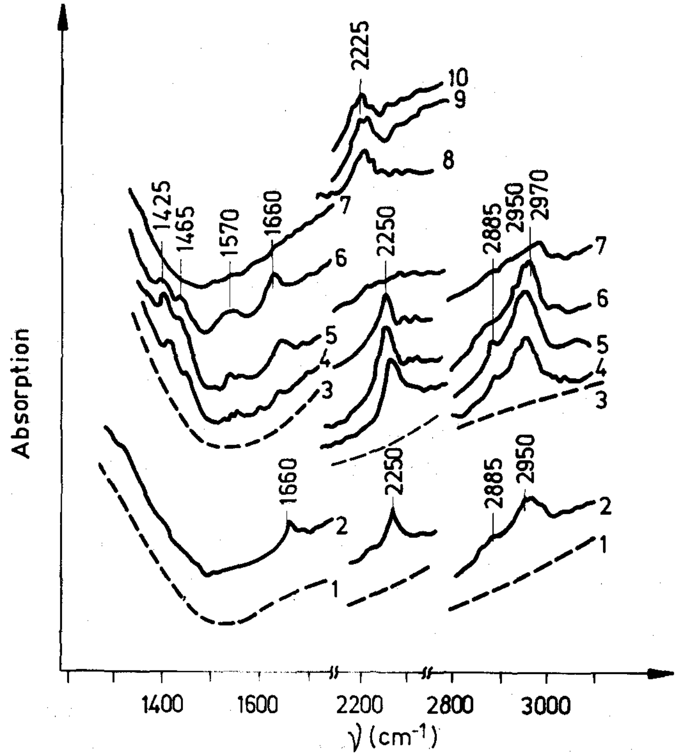

Fig. 1. IR spectra of ADN adsorbed on reduced and oxidized samples

1- reduced sample; 2- ADN adsorption on reduced surface at 298 K; 3- oxidized sample; 4- ADN adsorption on oxidized sample at 298 K; 5- ADN adsorption after 14 h; 6- desorption at 373 K, 1 h; 7- desorption at 473 K, 1 h; 8- ADN and NH_3 (60 Torr) adsorption at 473 K with subsequent desorption at 573 K, 1 h; 9- heating in 60 Torr C_6H_{12}, 120 Torr NH_3, 150 Torr O_2 at 573 K, 30 min; 10- subsequent desorption at 673 K, 1 h

ADN adsorption at room temperature over both oxidized and reduced samples (Fig. 1) is accompanied by the appearance of all the bands that are typical for liquid ADN [2]. The small shift towards lower frequencies $\nu(C \equiv N)$ (5 cm^{-1}) and the low desorption temperature (373-473 K) of this complex characterized by the above bands indicate that ADN is most probably bonded to the surface by a hydrogen bond. Besides the bands of the hydrogen-bonded ADN, adsorption on the oxidized sample provides a group of bands at 1400-1600 cm^{-1} and a band at 1660 cm^{-1} (Fig. 1.4). The intensity of these bands rises with time and increases after evacuation at 373 K (Fig. 1.5-6). Apparently, this is associated with the conversion of H-bonded ADN to more strongly bonded complexes. All of these bands are removed by evacuation at 473 K (Fig. 1.7).

In accordance with the literature data [3,4], the bands at 1570 and 1465 cm^{-1} can be ascribed to ν_{as} and ν_s of the R-C(O)NH group formed upon nitrile group oxidation by the oxide oxygen. This is confirmed by the absence of such bands on the reduced sample (Fig. 1.2).

The position of the band at 1660 cm^{-1} is close to ν(=N) This suggests that ADN can be adsorbed with the dissociation of the C ≡ N bond. ADN adsorption at 373, 473 and 573 K does not lead to the formation of any other surface ADN structures.

Thus the ADN adsorption at 293-573 K over oxidized and reduced catalysts is not accompanied by the formation of strong-bonded compounds with preservation of the nitrile bond that are stable at desorption temperatures above 473 K.

Studies of ADN adsorption under close-to-the reaction conditions (120 Torr NH_3, 150 Torr O_2, 573 K) indicate that in this case there appears a band at 2200-2230 cm^{-1} that cannot be removed by one-hour evacuation at 673 K.

A similar band at 2225 cm^{-1} unremovable during desorption at 673 K was also observed when the ammoxidation of cyclohexane was carried out under static conditions in the IR cuvette (60 Torr C_6H_{12}, 120 Torr NH_3, 150 Torr O_2, 573 K) Fig. 1.9-10). The formation of a strongly bonded surface ADN compound under the above reaction conditions agrees well with the experimental data obtained in the pulse microreactor [1].

According to literature data [3,4], the ν(C ≡ N) bands shifted towards lower frequencies are ascribed to ν(C ≡ N) in polymer compounds. We attribute the band at 2200-2230 cm^{-1} to

ν(C≡N) in the polymer. This is confirmed by the high desorption temperature of these surface compounds. Thus the most probable reason for the formation of a strongly bonded ADN compound is ADN polymerization under the reaction conditions.

It has been shown that for ADN polymerization the presence of O_2 in the gas phase is not necessary. In the presence of NH_3, starting from 473 K, the spectra exhibit the band of polymer compounds (Fig. 1.8).

It is of interest to note that the NH_3 contribution is not restricted to simple reduction of the catalyst surface, since upon ADN adsorption at 473-573 K on the reduced sample (120 Torr NH_3, 473 K, 30 min) we have not observed any appearance of bands of polymeric compounds. Thus for ADN polymerization the presence of adsorbed NH_3 complexes is needed. Hence it was of interest to study NH_3 adsorption.

The spectrum of NH_3 adsorbed on the oxidized smaple is illustrated in Fig. 2/4-6. The analysis of NH_3 adsorption and desorption IR spectra and also the comparison of these spectra with the literature data [5] permits to ascribe the broad band at 1400-1460 cm^{-1} to δ NH_4^+.

A weak band at 1605 cm^{-1} completely vanishing after desorption at 373 K, can be attributed to δ_{as} of either weakly coordinated or H-bonded NH_3 [5]. The position of the bands in the region of stretching vibrations confirms the above assignment of adsorbed NH_3 forms.

On NH_3 adsorption-desorption on the oxidized sample, the position of the bands belonging to free hydroxy groups at 3645 cm^{-1} remains practically unchanged and it eliminates their participation in the formation of adsorbed NH_3 complexes.

When NH_3 is adsorbed on the reduced sample no adsorption of NH_4^+ groups is practically observed (Fig. 2/1-3). Heating of both oxidized and reduced samples in ammonia up to 673 K does not lead to the formation of noticeable amounts of any other surface NH_3 compounds.

We have established that the NH_3 and O_2 adsorption provides new weak bands at 1500-1550 cm^{-1} that are typical for the

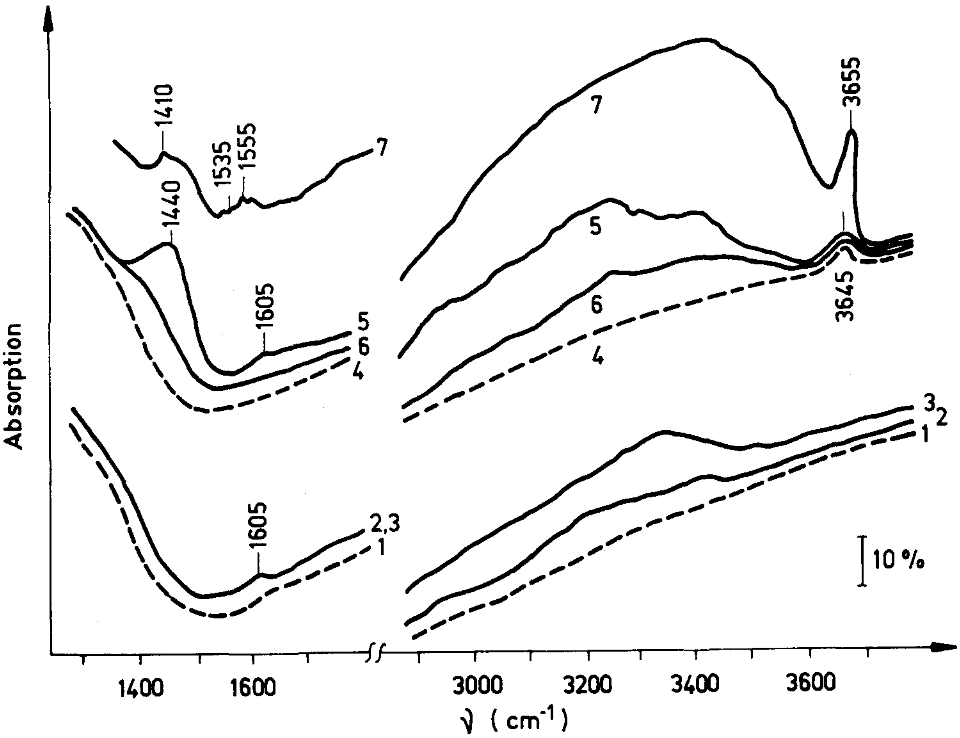

Fig. 2. IR spectra of NH_3 adsorbed on reduced and oxidized samples
1- reduced sample; 2- adsorption of 15 Torr NH_3 at 298 K; 3- heating in NH_3 up to 673 K; 4- oxidized sample; 5- adsorption of 15 Torr NH_3 at 298 K; 6- desorption at 373 K, 30 min; 7- adsorption of 120 Torr NH_3, 150 Torr O_2 at 673 K, 30 min; 7- with subsequent desorption at 373 K, 1 h

dissociative NH_3 forms [5] (Fig. 2/7).

We suggest that the contribution of NH_3 to polymerization consists in the formation of NH_x^- structures. Upon NH_3 adsorption over the 30% Sb_2O_5·70% TiO_2, the concentration of these structure is low and, apparently they are not observed owing to insufficient sensitivity of the method. On the centers of these type the proton can be detached. In accordance with Ref. [3], acetonitrile polymerization on ZnO can be caused by proton abstraction to form a sufficient amount of $(CH_2CN)^-$ structures. In the case of adiponitrile, the mobile protons in the α-position with respect to the nitrile groups on the NH_x^- centers can be removed and the structures formed can be polymerized [2].

Thus the reason for strong ADN bonding to the surface is, apparently, ADN polymerization in the presence of NH_3. The NH_3 contribution seems to consist in the formation of NH_x^- structures whereon proton abstraction takes place, leading to the polymerization of the structures formed.

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