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INFRARED SPECTROSCOPIC STUDIES OF SURFACE PROPERTIES OF TIN-MOLYBDENUM OXIDE CATALYST

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According to studies of Brönsted and Lewis acid centers of a Sn/Mo catalyst, the Brösted centers are supposed to be protons acting as cations compensating the charge of surface anions.

Обсуждена природа бренстедовских и льюисовских кислотных центров оловомолибденового окисного катализатора. Предположено, что бренстедовскими кислотными центрами являются протоны, выступающие в качестве катионов, компенсирующих заряд анионов поверхности.

The aim of the present work was the infrared spectroscopic study of surface properties of solid solutions of molybdenum in tin dioxide.

Sn/Mo (99 : 1, 95 : 5, and 90 : 10) and Ti/Mo (90 : 10) catalysts were prepared as in Ref. /1/, and according to X-ray phase analysis, they were solid substitution solutions of molybdenum in SnO_2 and TiO_2. Their treatment involved multiple heating in O_2 and vacuum with final desorption of O_2 at 300 K.

The infrared spectrum of an oxidized sample of the Sn/Mo (90 : 10) catalyst exhibits an intense absorption band at 1010 cm^{-1} (Fig. 1, spectrum 1) which can be due to the stretching vibrations (ν) of $Mo^{6+} = 0$ bonds taking into account the presence of short bonds for the MoO_3 and Mo-containing catalysts /2/ in this spectral region. The displacement of the 1010 cm^{-1} band associated with electron donor properties of the ligand (the spectrum exhibits a band at 960 cm^{-1} (spectrum 2) for adsorbed NH_3, at 990 cm^{-1} for water and at 980 cm^{-1} for acetone) and its restoration after desorption of these molecules indicates that this frequency belongs to $\nu Mo^{6+} = 0$ bonds on the surface (in the near-surface region). Studies of the spectrum of fundamental vibrations of the catalyst indicated the absence of bands in the region of 1000 cm^{-1}, i.e. their absence in the catalyst bulk. This also confirms the interpretation suggested. Actually, for the reduced catalyst the band intensity

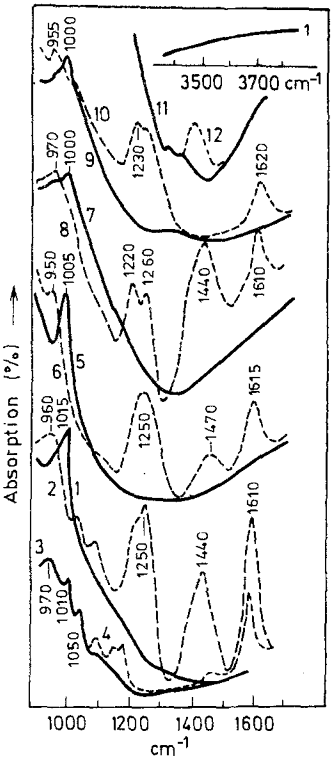

Fig. 1. Variations in the IR spectra of catalysts (heavy line) after adsorption of ammonium at 300 K (broken line 1, 4, 6, 8, 10). 1 – Sn/Mo (90 : 10), treatment at 773 K; 3 – Sn/Mo (90 : 10), reduction in H_2 at 600 K; 5 – Sn/Mo (95 : 5), treatment at 773 K; 7 – Ti(Mo) (90 : 10), treatment at 773 K; 9 – Sn/Mo (99 : 1), treatment at 773 K; 11 – MoO_3 – treatment at 673 K

at 1010 cm^{-1} (spectrum 3) significantly decreases. The appearance of a band at 970 cm^{-1} can be ascribed to the formation of $Mo^{5+} = 0$ bonds /3/. Reoxidation of the catalyst restores the initial intensity of the 1010 cm^{-1} band. The presence of the weak band at 1010 cm^{-1} for the reduced sample (spectrum 3) and the lack of displacement of this maximum after adsorption (e.g. of ammonium, Spectrum 4) is evidence for the presence of a definite number of $Mo^{6+} = 0$ bonds in the near-surface layer as well.

$Mo^{6+} = 0$ band for the 95 : 5 and 99 : 1 samples is at 1005 cm^{-1} (Spectrum 5) and 1000 cm^{-1} (Spectrum 9), respectively, thus indicating various degrees of support influence on the "excess" molybdenum ions.

Hence, the surface of the Sn/Mo oxide catalyst, which (according to X-ray phase analysis) is a solid solution, involves a molybdenum compound containing short Mo = 0 bonds. This is in agreement with XPS data on the molybdenum-rich surface of these catalysts /4/.

Studies of acidic properties of the Sn/Mo (90 : 10) catalyst according to the infrared spectra of adsorbed NH_3 /5/ indicated the presence of Lewis centers (coordinatively bound NH_3 is characterized by $\delta_S NH_3$ at ~ 1250 cm^{-1} and $\delta_{as} NH_3$ at 1610 cm^{-1}) and of Brönsted centers. The presence of the latter is evidenced by NH_4^+ ion formation (δNH_4^+ at ~ 1440 cm^{-1}) (Fig. 1, Spectrum 2). It has been shown previously /5/ that the symmetric deformation vibration of coordinated NH_3 ($\delta_S NH_3$) (i.e. the vibration which is the most sensitive to the electron-acceptor ability of the cation /6/) in the $Sn^{4+} \leftarrow NH_3$ complex is observed in the region of 1230–1250 cm^{-1}, i.e. close to $\delta_S NH_3$ of NH_3 coordinated to Mo ions /7/. Therefore, for the Sn/Mo catalyst the nature of the ammonium-coordinating center can hardly be judged. Studies of a Ti–Mo catalyst whose composition and structural properties are similar to the Sn/Mo system, except that the Ti^{4+} ions are weaker electron acceptors compared with Sn^{4+} (a.b. $\delta_S NH_3$ for the $Ti^{4+} \leftarrow NH_3$ at 1220 cm^{-1}), indicate that besides ammonium coordination by Ti^{4+} ions (1220 cm^{-1} Fig. 1, Spectrum 8) a band at 1260 cm^{-1} is observed, which can characterize $\delta_S NH_3$ in the $Mo^{6+} \leftarrow NH_3$ complex. The spectral analysis of NH_3 adsorbed on the Sn/Mo catalyst with a lower molybdenum content (Spectrum 10) also reveals a complicated band in the region of 1200–1260 cm^{-1} and the existence of at least two bands in this region with two maxima at 1230 and 1260 cm^{-1}, which can be due to δ_S in the $Sn^{4+} \leftarrow NH_3$ and $Mo^{6+} \leftarrow NH_3$ complexes, respectively.

Hence, surfaces of the systems examined contain both Mo^{6+} and $Sn^{4+}(Ti^{4+})$ ions capable of coordinating NH_3.

It has been assumed previously /5/ that the Brönsted acidity of Sn/Mo catalysts is determined by the presence of Mo ions and, to our mind, is attributed to excess molybdenum on the catalyst surface rather than to its presence in the solid solution. Actually, the decrease in the Mo concentration on the surface observed with decreasing its content in the catalyst /4/ reduces the concentration of Brönsted centers (intensity decrease of δNH_4^+ at 1440 cm^{-1} and the change in its position, Spectrum 6). For the (99 : 1) sample the band associated with the NH_4^+ ion is not observed at all (Spectrum 10). The latter cannot be attributed to the low sensitivity of the technique, since for MoO_3 ($S = 3.8$ m^2/g) the band does appear (Spectrum 12). The following tendency in the displacement of δNH_4^+ should be noted: for MoO_3 it is observed at 1420 cm^{-1}, whereas for the (90 : 10) and (95 : 5) samples it is recorded at 1440 and 1470 cm^{-1}, respectively. In the same order does the thermal stability of the NH_4^+ complex decrease. On MoO_3 it is decomposed by desorption at 600 K, whereas on Sn/Mo systems the NH_4^+ complex decomposes at 500 and 400 K, respectively. These data provide evidence for the decrease of proton acidity in this series.

Now let us analyze the Brönsted centers of the catalysts studied. It is customary to assume that they are either hydroxy groups possessing sufficiently mobile protons, or coordinated water or H_3O^+ type ions. All these compounds or fragments have sufficiently distinct spectral characteristics, e.g. in the νOH region. But for our catalysts, after dehydration at temperatures above 673 K (with the developed surface > 100 m^2/g), we have not revealed any distinct band in this region (Fig. 1, Spectrum 1) despite the presence of a sufficiently great number of mobile protons in such a sample (indirect evidence for their quantity is the intensity of δNH_4^+ appearing in the spectra after NH_3 adsorption). These experimental data can indicate the type of binding of these mobile protons, which inhibits νOH in the spectra as local MeO–H vibrations. We believe this is not improbable for systems with highly charged cations, where a mobile proton can act as a cation compensating the charges of several surface anions simultaneously. Thus "multi-centered" proton stabilization can lead to the significant band broadening for νOH (with displacement to lower frequencies) and as a result to the absence of distinct νOH absorption in the spectra. This phenomenon can be of general character and is, apparently, characteristic for catalysts with high-valent (+5, +6) ions. The absence of a distinct νOH band in the presence of Brönsted centers has been revealed for catalysts containing V^{5+} and Sb^{5+} ions.

It was of interest to determine the relative strength of Brönsted centers for the Sn/Mo catalyst, usually estimated according to the frequency displacement of νOH of surface hydroxy groups in their interaction with various bases. But for our systems this method cannot be applied due to the absence of a distinct band of the surface hydroxy groups. We have determined the relative proton mobility from the rate of proton transfer to weak bases. According to Ref. /8/, the strongest (in Brönsted sense) acid centers of HY zeolite can donate their proton to a weak base (such as propylene) to form a carbonium ion, whereas with ethylene, which is a weaker base than propylene, only hydrogen-bonded complexes were formed /8/. As was reported previously /8/ for the Sn/Mo (90 : 10) catalyst, proton transfer to molecules to form unsaturated compounds of C_3H_7–O–| and C_2H_5–O–| type, is observed for both propylene and ethylene. The formation of these compounds is evidenced by the appearance of δ and νCH only in the saturated compounds and of νC–O in the region of 1100 cm^{-1} (Fig. 2, Spectra 1 and 2). As is seen, spectra 1 and 2 are similar. The spectrum of adsorbed C_3H_6 was interpreted in detail elsewhere /9/. The results indicate that the Brönsted centers of the catalyst studied possess more mobile protons than does HY zeolite. The reduction of Sn/Mo

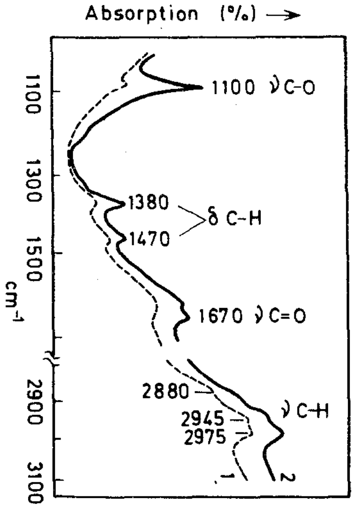

Fig. 2. IR spectra of ethylene (1) and propylene (2) adsorbed on Sn/Mo (90 : 10) catalyst

(90 : 10) catalyst at 600 K in H_2 and subsequent evacuation at 773 K lead to the disappearance of Brönsted centers (the spectra after NH_3 adsorption exhibit no δNH_4^+ band, Fig. 1, Spectrum 4). For this catalyst the appearance of $\delta_S NH_3$ of coordinated ammonium in the lower-frequency region (1190–1230 cm^{-1}, Spectrum 4) and the absence of absorption at 1260 cm^{-1}, characteristic for the $Mo^{6+} \leftarrow NH_3$ complex, after NH_3 adsorption indicate the reduction of molybdenum ions and confirm the assignment of Brönsted centers as high-valent molybdenum ions. These results are in good agreement with XPS data on the appearance of Mo^{4+} ions after similar reduction, whereas tin ions change the valence state insignificantly /4/. Taking into account the above data, the band at ~ 1200 cm^{-1} (Spectrum 4) can be attributed to $\delta_S NH_3$ of the Mo^{4+}-coordinated ammonia.

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