

## INTERACTION OF AMMONIA WITH THE SURFACE OF Cr-Mo AND Cr-Mo-Te OXIDE CATALYSTS

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The adsorption of  $\text{NH}_3$  on Cr-Mo and Cr-Mo-Te catalysts has been investigated by IR spectroscopy. It is shown that there are both electron acceptor and proton donor acid centers on the surface of these catalysts. The introduction of tellurium into a Cr-Mo catalyst decreases adsorption on the electron acceptor centers.

Методом ИК спектроскопии изучена адсорбция  $\text{NH}_3$  на окисных Cr-Mo и Cr-Mo-Te контактах. Показано, что на поверхности указанных катализаторов имеются как электронно-акцепторные, так и протонно-донорные кислотные центры. Введение теллура в Cr-Mo контакт понижает адсорбционную способность электроноакцепторных центров.

The investigation of surface acidic properties of oxide catalysts is of great interest since the acidity of catalysts influences their selectivity in the oxidation of olefins /1, 2/. The nature of acidic centers on  $\text{Cr}_2\text{O}_3$ , a catalyst of complete oxidation, was studied earlier /3/. The mixed Cr-Mo catalyst shows an ability for partial oxidation, but it has a low selectivity /4/. According to Refs /5, 6/, the introduction of tellurium into such catalysts increases the selectivity to partial oxidation.

The present study of  $\text{NH}_3$  interaction with Cr-Mo and Cr-Mo-Te catalysts was performed to elucidate the nature of acidic centers on their surfaces,

## EXPERIMENTAL

The Cr-Mo catalyst ( $S = 60 \text{ m}^2/\text{g}$ ) was prepared via  $\text{Cr}_2\text{O}_3$  impregnation with an aqueous solution of ammonium paramolybdate (1 mol  $\text{MoO}_3$  per 10 mol  $\text{Cr}_2\text{O}_3$ ) followed by calcination. According to Ref. (7), the catalyst prepared represents  $\text{Cr}_2\text{O}_3$  particles covered with  $\text{Cr}_2(\text{MoO}_4)_3$ . In addition, tellurium oxide (0.5 mol  $\text{TeO}_2$  per 10 mol  $\text{Cr}_2\text{O}_3$ ) was also introduced into the Cr-Mo-Te catalyst ( $S = 47 \text{ m}^2/\text{g}$ ). Sample preparation and the recording of spectra have been described /3/. The weight of the Cr-Mo and Cr-Mo-Te catalyst samples was 18 mg (surface  $1.1 \text{ m}^2$ ) and 21 mg (surface  $1.0 \text{ m}^2$ ), respectively. Before measurements, the samples were heated for 1 hr in  $\text{O}_2$  at  $450^\circ\text{C}$ , evacuated for 1 hr ( $10^{-2}$  Torr) at the same temperature and then heated in  $\text{O}_2$  again, after cooling to room temperature,  $\text{O}_2$  was pumped off.

## RESULTS AND DISCUSSION

The initial spectra of Cr-Mo and Cr-Mo-Te catalysts (Fig. 1-1) exhibit several bands in the range from  $900$  to  $1250 \text{ cm}^{-1}$ , which may be ascribed to surface oxygen vibrations /3/. The bands at  $945$ ,  $1050$ ,  $1075$ ,  $1100$ ,  $1150$  and  $1235 \text{ cm}^{-1}$  are present in the spectra of both samples. In addition the spectra of Cr-Mo and Cr-Mo-Te catalysts show bands at  $990$  and  $1005$ , and at  $985 \text{ cm}^{-1}$ , respectively. A band with a peak at  $1620 \text{ cm}^{-1}$  is detected in the spectra of both catalysts, which is apparently due to OH groups deformation of chemisorbed water /8/. The spectrum of the Cr-Mo catalyst also has a peak at  $3450 \text{ cm}^{-1}$ , corresponding to the stretching vibration of OH groups /8/. The spectra of the Cr-Mo-Te catalyst were recorded only up to  $3000 \text{ cm}^{-1}$ , owing to intensive absorption of the sample in the high frequency range.

Ammonia adsorption at  $20^\circ\text{C}$  on a Cr-Mo catalyst leads to the appearance of bands at  $1240$ ,  $1420$ ,  $1610 \text{ cm}^{-1}$  and a broad band with a peak near  $3260 \text{ cm}^{-1}$

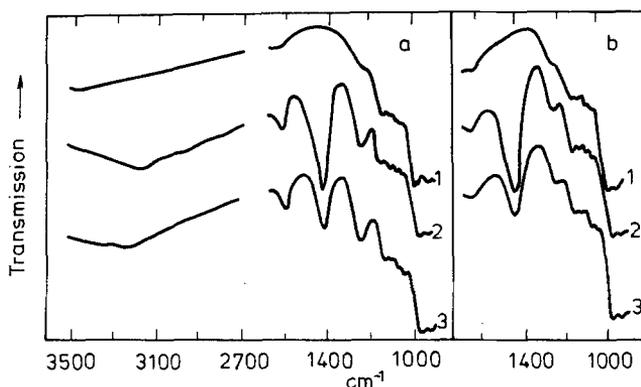


Fig. 1. Infrared spectra of Cr-Mo (a) and Cr-Mo-Te (b) catalysts before and after adsorption of  $\text{NH}_3$ . (1) original spectrum, (2) spectrum after  $\text{NH}_3$  adsorption at  $20^\circ\text{C}$ ; (3) spectrum 2 after evacuation at  $20^\circ\text{C}$

(Fig. 1-2a). Instead of two bands at  $990$  and  $1005\text{ cm}^{-1}$ , one band appears at  $985\text{ cm}^{-1}$ . Ammonia evacuation at  $20^\circ\text{C}$  decreases the intensity of the bands at  $1240$  and  $3260\text{ cm}^{-1}$  and produces a shoulder at  $3360\text{ cm}^{-1}$  on the  $3260\text{ cm}^{-1}$  band (Fig. 1-3a). After heating the sample to  $200^\circ\text{C}$ , the band at  $1420\text{ cm}^{-1}$  disappears and the intensity of the bands in the  $2800$ – $3500\text{ cm}^{-1}$  range decreases. The bands at  $1240$ ,  $1610$  and  $32\text{ cm}^{-1}$  disappear completely only above  $300^\circ\text{C}$ .

Ammonia adsorption at  $20^\circ\text{C}$  on the Cr-Mo-Te catalyst leads to the appearance of an intensive band at  $1420\text{ cm}^{-1}$ , and less intensive bands at  $1230$  and  $1615\text{ cm}^{-1}$  (Fig. 1-2b). No changes in the intensity and position of oxygen bands are observed. As a result of  $\text{NH}_3$  evacuation at  $20^\circ\text{C}$ , the intensity of the bands at  $1420$ ,  $1230$  and  $1615\text{ cm}^{-1}$  decreases (Fig. 1-3b), and upon heating the sample to  $200^\circ\text{C}$ , they disappear.

The data obtained may be interpreted as follows [3, 8]. The bands at  $1240$  and  $1610\text{ cm}^{-1}$  in the case of the Cr-Mo catalyst and those at  $1230$  and  $1615\text{ cm}^{-1}$  in the case of the Cr-Mo-Te sample are ascribed to the symmetric and asymmetric

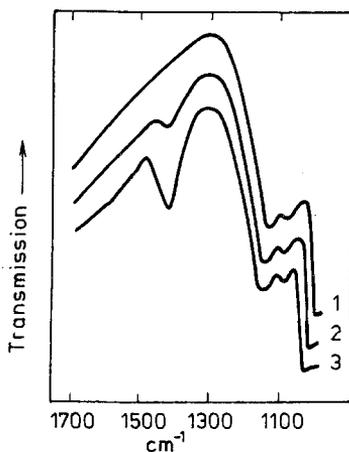


Fig. 2. Adsorption of  $\text{NH}_3$  on  $\text{MoO}_3$ . (1) original spectrum; (2) spectrum after  $\text{NH}_3$  adsorption at 20 °C; (3)  $\text{NH}_3$  adsorption after  $\text{H}_2\text{O}$  pre-adsorption

deformational vibrations of  $\text{NH}_3$  bound to Lewis acid centers. The assignment of the bands in the 1200–1300  $\text{cm}^{-1}$  region to  $\delta_s\text{NH}_3$  vibrations is confirmed by the fact that in this region as well as in the case of  $\text{Cr}_2\text{O}_3$  /3/ no new bands appear during  $\text{ND}_3$  adsorption on these catalysts. Hence these bands cannot be ascribed to the vibrations of nitrogen-oxygen bonds. The intensive band at 1420  $\text{cm}^{-1}$  is assigned to the  $\text{NH}_4^+$  vibration and the bands in the 2800–3500  $\text{cm}^{-1}$  range are attributed to stretching vibrations in adsorbed ammonia molecules and hydrogen-bonded OH groups.

Thus the introduction of  $\text{MoO}_3$  into  $\text{Cr}_2\text{O}_3$  results in the appearance of Brønsted centers on the surface of the mixed catalyst, not observed on  $\text{Cr}_2\text{O}_3$ . The  $\text{NH}_4^+$  band at 1425  $\text{cm}^{-1}$  is detected during the adsorption of  $\text{NH}_3$  on  $\text{MoO}_3^*$  (Fig. 2-2) after pretreatment of the sample by a standard method. The intensity of this band significantly increases after pre-adsorption of  $\text{H}_2\text{O}$  at 20 °C (Fig. 2-3). Apparently,

\* $\text{MoO}_3$  ( $S = 6.3 \text{ m}^2/\text{g}$ ) was prepared by decomposing ammonium paramolybdate.

the Brønsted centers on Cr-Mo catalysts as well as those on  $\text{MoO}_3$  are protonated hydroxy groups of chemisorbed water bonded to molybdenum atoms. It should be noted that in the case of  $\text{Cr}_2\text{O}_3$  the formation of  $\text{NH}_4^+$  cannot be detected even after  $\text{H}_2\text{O}$  pre-adsorption /9/.

Comparison of the intensities of the coordinated  $\text{NH}_3$  bands in the spectra of Cr-Mo and Cr-Mo-Te catalysts shows that the introduction of tellurium into the catalyst decreases the number of surface Lewis centers which can interact with  $\text{NH}_3$ . The optical densities of  $\delta_S\text{NH}_3$  bands in the spectra of Cr-Mo and Cr-Mo-Te catalysts per unit catalyst area are equal to 0.14 and 0.02  $\text{m}^{-2}$ , respectively. In this case the relative optical densities of  $\text{NH}_4^+$  bands differ insignificantly (0.36 and 0.30  $\text{m}^{-2}$ ).

The bands at 1005 and 990  $\text{cm}^{-1}$  in the Cr-Mo catalyst spectrum are shifted to 985  $\text{cm}^{-1}$  upon  $\text{NH}_3$  adsorption. A similar shift in the oxygen bands in the range of 980-1020  $\text{cm}^{-1}$  was previously observed for  $\text{Cr}_2\text{O}_3$  /3/ and explained by the increase of surface cation saturation. Upon introduction of tellurium into the Cr-Mo catalyst, in the range of 980-1020  $\text{cm}^{-1}$  the spectrum exhibits only a band at 985  $\text{cm}^{-1}$ . Comparing the above data, one can assume that the tellurium atoms in the Cr-Mo-Te catalyst, interacting with surface cations playing the role of Lewis centers, increase their saturation and block  $\text{NH}_3$  adsorption on these centers.

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