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**FTIR STUDY OF CROTYL ALCOHOL,  
CROTONALDEHYDE AND CROTONIC ACID  
ADSORPTION ON THE SURFACE  
OF THE V/Zr OXIDE CATALYST**

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*Infrared studies of crotyl alcohol (but-2-en-1-ol), crotonaldehyde (but-2-enal) and crotonic acid (but-2-enoic acid) adsorption were carried out on ZrO<sub>2</sub>-supported vanadium catalyst. The results were used to analyze the surface intermediates of crotonaldehyde dehydrogenation to maleic anhydride. Crotyl alcohol was adsorbed mainly in the alkoxide form, which is oxidized to crotonaldehyde and consecutively to crotonic acid. Final step in crotyl alcohol adsorption on V<sub>2</sub>O<sub>5</sub>-ZrO<sub>2</sub> catalyst is the conversion of carboxylate species into maleic anhydride. The reaction of adsorbed crotonaldehyde and the oxygen atom of the catalyst resulted in the formation of carboxylate at higher temperature. The presence of two different surface carboxylate species (maleate and crotonate) was shown from IR spectra following crotonic acid adsorption. As distinct from the crotyl alcohol adsorption, the presence of surface maleic anhydride after adsorption of crotonic acid and/or crotonaldehyde on V<sub>2</sub>O<sub>5</sub>-ZrO<sub>2</sub> catalyst was not shown.*

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## Introduction

$V_2O_5$  is frequently used in the catalysis due to its redox activity and surface acidity [1]. Zirconia ( $ZrO_2$ ) has been extensively studied as catalyst or catalyst support for heterogeneous catalytic reactions [2-5].  $ZrO_2$  has both weakly acidic and weakly basic properties, which sometimes results in interesting acid-base bifunctional catalysis. Catalysts for industrial butane and but-1-ene oxidation to maleic anhydride are usually based on vanadium and molybdenum oxide along with support ( $SiO_2$ ,  $TiO_2$ ,  $P_2O_5$ ). Side reactions result in the formation of alcohols (e.g., crotyl alcohol), aldehydes (e.g., acrolein, crotonaldehyde) and ketones (e.g., but-2-anone) [6,7]. The oxidation of crotonaldehyde by oxygen on vanadium oxide catalysts leads to a useful product – maleic anhydride, with high selectivity and yield.

We use  $V_2O_5$ - $ZrO_2$  catalyst for oxidative dehydrogenation of crotonaldehyde (CRA) to maleic anhydride (MA). In this work, we present results of IR study of the adsorption forms of crotyl alcohol, crotonaldehyde and crotonic acid on  $V_2O_5$ - $ZrO_2$  surface. These data can contribute to a better explanation of the mechanism of oxidative dehydrogenation of crotonaldehyde to maleic anhydride.

## Experimental

$V_2O_5$ - $ZrO_2$  catalyst with vanadium content 4.0 wt % was used for the measurements. The preparation of  $ZrO_2$  supported vanadium catalyst has already been reported [8].  $V_2O_5$ - $ZrO_2$  catalyst was prepared by impregnation method with an aqueous solution of ammonium vanadate. After impregnation, the sample was dried at 120 °C. Calcination at 180 °C and annealing in air at 300 °C gave the optimum catalyst. The crystalline phase of the sample was studied by X-ray analysis and the IR spectra of crystals were measured by means of the KBr disc technique.

The pellets of the sample (10-20 mg  $cm^{-2}$ ) were heated at 573 K and evacuated before adsorption. The spectra were obtained at room temperature with an FTIR spectrometer Nicolet Protege 460 at the resolution of 2  $cm^{-1}$  by collecting 256 scans. The  $V_2O_5$ - $ZrO_2$  catalyst was treated in crotyl alcohol, crotonaldehyde and crotonic acid atmosphere at various temperatures (298-573 K). The reported spectra of adsorbed species were obtained by subtraction of the spectra measured before adsorption (pure oxide) from those taken after adsorption. The IR spectra were deconvoluted into Gaussian curves. Crotyl alcohol, crotonaldehyde and crotonic acid were adsorbed at pressure of 100 Pa and 1 kPa, respectively. The vapor of crotonic acid was obtained by sublimation at room temperature.

## Results and Discussion

### General Observations

The experimentally obtained IR spectra of adsorbed crotyl alcohol, crotoaldehyde and crotonic acid presented in Figs 1-3 can be divided into two parts: (i) above  $2500\text{ cm}^{-1}$ ; (ii) below  $2000\text{ cm}^{-1}$ . In the hydrogen stretching region above  $2500\text{ cm}^{-1}$  there are absorption bands due to hydroxyl groups and bands of C–H vibrations. The second wavenumber region below  $2000\text{ cm}^{-1}$  is notable for the large number of infrared bands that are found there (C=C, C=O, C–O, C–C bond stretch and C–H bending vibrations). Hence, this region is often the most complex and confusing region to interpret.

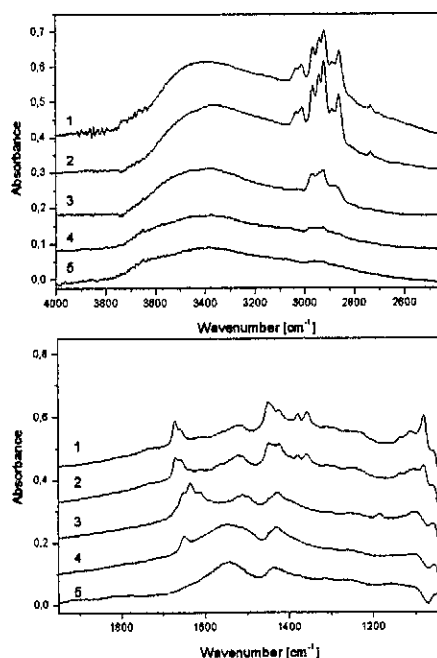


Fig.1 IR spectra of crotyl alcohol adsorbed on  $\text{V}_2\text{O}_5\text{-ZrO}_2$  at RT (1) and evacuated at RT (2), 373 K (3), 473 K (4) and 573 K (5)

All the spectra after adsorption showed a broad absorption band between  $3600$  and  $3200\text{ cm}^{-1}$ . This is caused by the interaction between the adsorbate and the hydroxyl groups on the surface of oxide. The shift of these hydroxyl bands depends on the adsorbate.

Stretching C–H vibrations of  $\text{CH}_3$  and  $\text{CH}_2$  groups are very similar for all the compounds studied. As the absorption bands in the wavenumber region above

2000  $\text{cm}^{-1}$  were badly resolved and not readable, only the second part involving absorption bands below 2000  $\text{cm}^{-1}$  was used for further analysis.

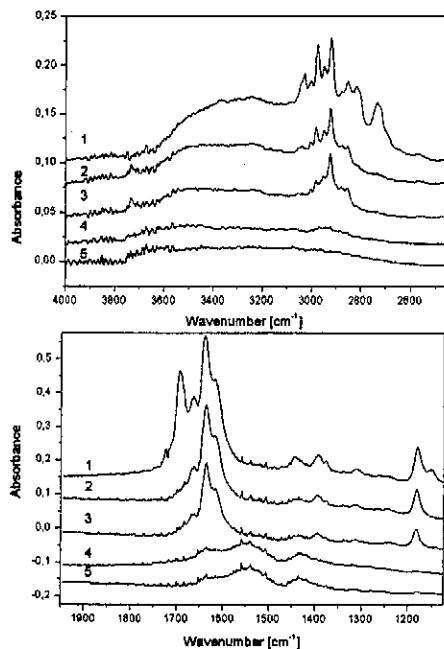


Fig. 2 IR spectra of crotonaldehyde adsorbed on  $\text{V}_2\text{O}_5\text{-ZrO}_2$  at RT (1) and evacuated at RT (2), 373 K (3), 473 K (4) and 573 K (5)

### Adsorption of Crotyl Alcohol

The adsorption of crotyl alcohol on the  $\text{V}_2\text{O}_5\text{-ZrO}_2$  sample leads to the appearance of the group of bands in the region of 1700-1000  $\text{cm}^{-1}$  (Fig. 1B, Table I): 1672, 1660, 1520, 1448, 1423, 1380, 1356 and 1079  $\text{cm}^{-1}$ . Absorption bands at 1672, 1448 and 1079  $\text{cm}^{-1}$ , which are very close to those of gaseous crotyl alcohol, can be associated with  $\nu_{\text{C-C}}$ ,  $\delta_{\text{CH}_3}$  and  $\nu_{\text{C-O}}$  in alkoxide [9]. Absorption bands at 1660, 1520, 1423, 1380 and 1356  $\text{cm}^{-1}$  shown in Fig. 1, spectra 1, 2 are typical of  $\nu_{\text{C=C}}$ ,  $\nu_{\text{asCOO}^-}$  and  $\nu_{\text{sCOO}^-}$  vibrations in the carboxylate structure I [6,9,10].

Heating of the adsorbed crotyl alcohol to 373 K and 473 K (after evacuation at RT) changes the spectra significantly (Fig. 1, spectra 3, 4). Increase of 1650, 1635, 1615, 1255 and 1185  $\text{cm}^{-1}$ . The 1635, 1255, 1185  $\text{cm}^{-1}$  bands disappeared after evacuation at 473 K, only the 1650 and 1430  $\text{cm}^{-1}$  bands remained and new broad bands at 1548 and 1436  $\text{cm}^{-1}$  appeared in the spectrum. The bands at 1635, 1255, 1185  $\text{cm}^{-1}$  are due to coordinatively bonded crotonaldehyde. The bands at

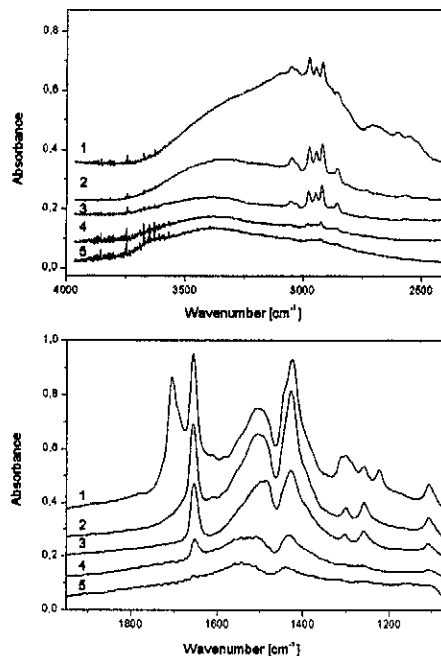


Fig. 3 IR spectra of crotonic acid adsorbed on  $V_2O_5$ - $ZrO_2$  at RT (1) and evacuated at RT (2), 373 K (3), 473 K (4) and 573 K (5)

1548 and  $1436\text{ cm}^{-1}$  corresponded to the asymmetric and symmetric vibration of carboxylate ions II [9,10]. Further evacuation of the sample at 573 K leads to the appearance of new low intensity bands in the region of  $1920\text{--}1770\text{ cm}^{-1}$ . In accordance with Refs [6,7], absorption bands at 1920, 1897, 1810,  $1776\text{ cm}^{-1}$  can be associated with  $\nu_{sC=O}$ ,  $\nu_{asC=O}$  vibrations in the molecule of maleic anhydride.

### Adsorption of Crotonaldehyde

After crotonaldehyde adsorption at RT on the  $V_2O_5$ - $ZrO_2$  catalyst, beside the bands of crotonaldehyde adsorbed physically ( $1725$ ,  $1694$  and  $1152\text{ cm}^{-1}$ ), which differ slightly from the spectrum of gaseous crotonaldehyde (Table 1) [11], the IR spectrum shows several new bands (Fig. 2B, spectrum 1). Evacuation at RT leads to the removal of physically adsorbed crotonaldehyde and the spectrum shows four intensive bands at  $1664$ ,  $1638$ ,  $1619$  and  $1180\text{ cm}^{-1}$ . These bands observed at  $298\text{--}373\text{ K}$  can be attributed to  $\nu_{C=O}$ ,  $\nu_{C=C}$  and  $\gamma_{CH_3}$  vibrations in the coordinatively bonded crotonaldehyde. Increase of the interaction temperature up to 573 K resulted in an appearance of bands above  $1600\text{ cm}^{-1}$  and at  $1550\text{--}1400\text{ cm}^{-1}$  (Fig. 1, spectra 3, 4, 5 and Fig. 2, spectra 2, 3, 4) that are typical of  $\nu_{C=C}$ ,  $\nu_{asCOO^-}$  and  $\nu_{sCOO^-}$  vibrations in the carboxylate structure [9,10].

Table I IR bands (in  $\text{cm}^{-1}$ ) and their assignment observed in crotyl alcohol, crotonaldehyde and crotonic acid adsorption on V-Zr oxide catalyst at room temperature

| Assign.                     | Crotyl Alcohol   |      | Crotonaldehyde   |      | Crotonic Acid    |      |
|-----------------------------|------------------|------|------------------|------|------------------|------|
|                             | gas <sup>a</sup> | V-Zr | gas <sup>a</sup> | V-Zr | gas <sup>a</sup> | V-Zr |
| $\nu_{\text{OH}}$           | 3660             |      |                  |      | 3590             |      |
|                             |                  | 3035 |                  | 3032 |                  | 3051 |
|                             |                  | 3010 |                  | 3003 |                  |      |
| $\nu_{\text{C-H}}$          | 2937             | 2965 | 2931             | 2976 | 2958             | 2975 |
|                             | 2877             | 2940 | 2800             | 2948 | 2931             | 2948 |
|                             | 2746             | 2923 |                  | 2921 |                  | 2920 |
|                             |                  | 2889 |                  | 2853 |                  | 2858 |
|                             |                  | 2861 |                  | 2818 |                  |      |
|                             |                  | 2736 |                  |      |                  |      |
| $\nu_{\text{C-H}}$<br>(CHO) |                  |      | 2722             | 2733 |                  |      |
|                             |                  |      |                  | 2722 |                  |      |
| $\nu_{\text{OH}}$<br>(COOH) |                  |      |                  |      | 2605             | 2712 |
|                             |                  |      |                  |      | 2566             | 2602 |
|                             |                  |      |                  |      |                  | 2555 |
| $\nu_{\text{C=O}}$          |                  |      | 1719             | 1725 | 1765             | 1705 |
|                             |                  |      |                  | 1694 | 1719             |      |
|                             |                  |      |                  | 1664 |                  |      |
| $\nu_{\text{C=C}}$          | 1676             | 1672 | 1652             | 1638 | 1663             | 1656 |
|                             |                  | 1660 |                  | 1619 |                  | 1612 |
|                             |                  | 1520 |                  |      |                  | 1510 |
| $\delta_{\text{CH}_3}$      | 1456             | 1448 | 1453             | 1442 | 1453             | 1440 |
|                             |                  | 1423 |                  | 1393 | 1423             | 1425 |
|                             |                  |      |                  | 1375 |                  |      |
|                             |                  |      |                  | 1311 |                  |      |
| $\delta_{\text{C-H}}$       | 1386             | 1380 |                  |      | 1360             |      |
|                             |                  | 1356 |                  |      | 1311             | 1310 |
|                             |                  |      |                  |      | 1294             | 1300 |
|                             |                  |      |                  |      |                  | 1258 |
| $\gamma_{\text{CH}_3}$      | 1188             | 1132 | 1145             | 1180 | 1151             | 1223 |
|                             |                  | 1110 | 1071             | 1152 | 1141             |      |
| $\nu_{\text{C-O}}$          | 1077             | 1079 |                  |      | 1092             | 1106 |
|                             | 1008             |      |                  |      |                  |      |
| $\nu_{\text{C=C}}$          | 965              |      | 971              |      | 972              |      |
|                             |                  |      | 935              |      |                  |      |

<sup>a</sup>this work

Table II Surface complexes observed in crotyl alcohol adsorption on  $V_2O_5$ - $ZrO_2$ 

| Position of a. b. in IR spectra, $cm^{-1}$ | Assignment of a. b.  | Observation temperature, K | Assignment of surface complexes      |
|--|--|----------------------------|--------------------------------------|
| 167214481423                               | $\nu_{C=C}$<br>$\delta_{CH_3}$<br>$\delta_{C-H}$                   | 298-373                    | alkoxide                             |
| 163516151255                               | $\nu_{C=O}$<br>$\nu_{C=C}$<br>$\delta_{C-H}$                       | 373                        | coordinatively bonded crotonaldehyde |
| 1660152013801356                           | $\nu_{C=C}$<br>$\nu_{asCOO^-}$<br>$\delta_{C-H}$<br>$\nu_{sCOO^-}$ | 298                        | carboxylate I (crotonate)            |
| 1650154813801436                           | $\nu_{C=C}$<br>$\nu_{asCOO^-}$<br>$\delta_{C-H}$<br>$\nu_{sCOO^-}$ | 473-573                    | carboxylate II (maleate)             |
| 1920189718101776                           | $\nu_{sC=O}$<br>$\nu_{asC=O}$                                      | 573                        | molecular form of maleic anhydride   |

a. b. - absorption bands

Table III Surface complexes observed in crotonaldehyde adsorption on  $V_2O_5$ - $ZrO_2$ 

| Position of a. b. in IR spectra, $cm^{-1}$ | Assignment of a. b.  | Observation temperature, K | Assignment of surface complexes      |
|--|--|----------------------------|--------------------------------------|
| 16941152                                   | $\nu_{C=O}$<br>$\gamma_{CH_3}$                                     | 298                        | molecular form of crotonaldehyde     |
| 1638161913931180                           | $\nu_{C=O}$<br>$\nu_{C=C}$<br>$\delta_{CH_3}$<br>$\gamma_{CH_3}$   | 298-373                    | coordinatively bonded crotonaldehyde |
| 1630154013801433                           | $\nu_{C=C}$<br>$\nu_{asCOO^-}$<br>$\delta_{C-H}$<br>$\nu_{sCOO^-}$ | 473-573                    | carboxylate II (maleate)             |

a. b. - absorption bands

### Adsorption of Crotonic Acid

The experimentally obtained IR spectra of crotonic acid adsorbed on  $V_2O_5$ - $ZrO_2$  catalyst are presented in Fig. 3. Adsorbed crotonic acid exhibits strong bands at 1705, 1656  $cm^{-1}$ , and in 1550-1400  $cm^{-1}$  region. The bands at 1705, 1310 and 1223  $cm^{-1}$  disappeared after evacuation at RT. Positions of these bands are very close to those of gaseous crotonic acid [12], they can be associated with  $\nu_{C=O}$ ,  $\delta_{C-H}$  and  $\gamma_{CH_3}$  in molecular form of crotonic acid. Absorption bands at 1656, 1425,

1300 and 1258  $\text{cm}^{-1}$  observable at RT were more clear after evacuation at the same temperature (Fig. 3, spectrum 3).

Positions of absorption bands at 1600-1400  $\text{cm}^{-1}$  observable at same temperature were closed to those of  $\nu_{\text{C}=\text{C}}$ ,  $\nu_{\text{asCOO}^-}$  and  $\nu_{\text{sCOO}^-}$  vibrations in the carboxylate structure (Table IV). The adsorption again exhibited similar results in which maleate (indicated by the bands around 1550 and 1440  $\text{cm}^{-1}$ ) was produced while the intensities of bands for crotonate (1515 and 1350  $\text{cm}^{-1}$ ) diminished. Increasing interaction temperature up to 573 K resulted in a substantial decrease in all the observed absorption bands (Fig. 3, spectrum 5).

Table IV Surface complexes observed in crotonic acid adsorption on  $\text{V}_2\text{O}_5\text{-ZrO}_2$

| Position of a. b. in IR spectra, $\text{cm}^{-1}$ | Assignment of a. b.   | Observation temperature, K | Assignment of surface complexes |
|---|---|----------------------------|---------------------------------|
| 170513101223                                      | $\nu_{\text{C}=\text{O}}$<br>$\delta_{\text{C-H}}$<br>$\gamma_{\text{CH}_3}$                          | 298                        | molecular form of crotonic acid |
| 1656151013791350                                  | $\nu_{\text{C}=\text{C}}$<br>$\nu_{\text{asCOO}^-}$<br>$\delta_{\text{C-H}}$<br>$\nu_{\text{sCOO}^-}$ | 298-473                    | carboxylate I (crotonate)       |
| 15491440  | $\nu_{\text{asCOO}^-}$<br>$\nu_{\text{sCOO}^-}$   | 298-573                    | carboxylate II (maleate)        |

a. b. - absorption bands

## Conclusion

On the basis the bands appearing in the spectra it can be concluded that crotyl alcohol undergoes various surface reactions at 298-573 K:

- chemisorption of crotyl alcohol resulted in the formation of crotonaldehyde,
- crotyl alcohol can be oxidized with the participation of surface oxygen resulting in surface carboxylate I (crotonate),
- conversion of carboxylate I (crotonate) to carboxylate structures II (maleate),
- transformation of maleate to maleic anhydride.

Appearance of carboxylate species II on the surface apparently initiated the formation of maleic anhydride. It is also worth mentioning that on vanadia-zirconia surfaces maleic anhydride was only detected after the adsorption of crotyl alcohol, but maleate species were formed in all cases. This behavior differs from that of vanadia, where maleic anhydride can also be detected after the adsorption of crotonaldehyde [13].



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