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**FTIR STUDY OF INTERACTION OF CROTYL  
ALCOHOL AND CROTONIC ACID WITH SURFACE  
OF SiO<sub>2</sub>, TiO<sub>2</sub> AND ZrO<sub>2</sub>**

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*Infrared studies of crotyl alcohol (2-butene-1-ol) and crotonic acid (2-butenic acid) adsorption were carried out on SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> supports. The results were used to analyze the surface intermediates of crotonaldehyde dehydrogenation to maleic anhydride. Crotyl alcohol was adsorbed mainly in the alkoxide form at room temperature on all the studied oxides. Crotonaldehyde and consequently also carboxylate were products of reaction between the crotyl alcohol and active sites of ZrO<sub>2</sub> surface at higher temperatures. During crotonic acid adsorption the undissociated acid molecules and the formation of hydrogen-bonded acid with surface hydroxyls were indicated for all the studied oxides. Crotonic acid was easily dissociated to form the surface carboxylate species on ZrO<sub>2</sub>. The presence of two different symmetric carboxylate species (maleate and crotonate) was shown from IR spectra following the crotonic acid adsorption. In contrast to the crotyl alcohol adsorption, the presence of surface asymmetric carboxylate species was not shown after adsorption of crotonic acid on ZrO<sub>2</sub>.*

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## Introduction

Pure silica ( $\text{SiO}_2$ ), titania ( $\text{TiO}_2$ ) and zirconia ( $\text{ZrO}_2$ ) have been extensively studied as catalysts or catalyst supports for heterogeneous catalytic reactions [1-3]. For example, titania is a well-known catalyst for photocatalytic reaction [4]. Titania is also often modified by addition of other metal oxides in order to obtain properties suitable for specific applications.  $\text{TiO}_2$  itself is recognized as an acidic oxide but becomes basic after reduction. As for  $\text{SiO}_2$ , its acidic and basic strength is small, however, this can be profitable for catalysis of many organic reactions [3]. Silica containing small quantities of titanium is used as catalyst for the selective epoxidation of alkenes by organic hydroperoxides [5].  $\text{ZrO}_2$  has both, weakly acidic and weakly basic properties, which can sometimes give interesting acid-base bifunctional catalysis. A  $\text{ZrO}_2$  catalyst is highly selective for the formation of 1-butene from *sec*-butanol and for isomerization of 1-butene [6].

Catalysts for industrial butane and 1-butene oxidation to maleic anhydride are usually based on vanadium and molybdenum oxides along with supporting  $\text{SiO}_2$ ,  $\text{TiO}_2$  or  $\text{P}_2\text{O}_5$ . Side reactions result in the formation of alcohols (e.g. crotyl alcohol), aldehydes (e.g. acrolein or crotonaldehyde) and ketones (e.g. 2-butanone) [7,8]. The oxidation of crotonaldehyde by oxygen on vanadium oxide catalysts leads with high selectivity and yield to a useful product — maleic anhydride.

In this work we use three different supports ( $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ ) for oxidative dehydrogenation of crotonaldehyde (CRA) to maleic anhydride (MA). The results of IR study of the adsorption forms of crotyl alcohol and crotonic acid on the surfaces of these supports are presented. These data can contribute to better explanation of the role of  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  in the oxidative dehydrogenation of crotonaldehyde to maleic anhydride over V/support catalyst.

## Experimental

Pure  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  were used for the measurements. The crystalline phase of the samples was confirmed by X-ray analysis and the IR spectra of crystals were measured by means of the KBr disc technique.

The pellets of the sample were formed by using of stainless steel press mould at a load  $10\text{-}20\text{ mg cm}^{-2}$  and were transferred to a stainless steel sample holder within the infrared cell. These samples were heated to 573 K and evacuated before adsorption. The spectra were obtained at room temperature on the FTIR spectrometer Nicolet Protege 460 with the resolution of  $2\text{ cm}^{-1}$  by collecting 256 scans. All the oxides were treated in crotyl alcohol and crotonic acid atmospheres at various temperatures (298-573 K). The reported spectra of adsorbed species were obtained by subtraction of the spectra measured before the adsorption (pure oxides) from those taken after adsorption. The IR spectra were deconvoluted into

Gaussian curves. Crotyl alcohol and crotonic acid were adsorbed at the pressure of 1 kPa. The crotonic acid vapor was obtained by sublimation at room temperature.

## Results and Discussion

### Crotyl Alcohol Adsorption on SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>

The experimentally obtained spectra of adsorbed crotyl alcohol are presented in Fig. 1. The room temperature adsorption (RT = 298 K) resulted in the formation of strong absorption bands in the wavenumber region 1500-1300 cm<sup>-1</sup> and of a strong band at 1675 cm<sup>-1</sup>. The intensity of the absorption bands at 1675, 1450, 1411, 1380, 1082 and 1002 cm<sup>-1</sup> decreased after evacuation at RT. As the positions of these bands are very close to those of gaseous crotyl alcohol [9], they can be associated with  $\nu_{C=C}$ ,  $\delta_{C-H}$ ,  $\nu_{C-O}$  in molecular form of crotyl alcohol. Table I presents characteristic IR absorption bands of crotyl alcohol corresponding to specific vibrations. The room temperature evacuation resulted in a large decrease in intensities of all observed absorption bands on SiO<sub>2</sub> and TiO<sub>2</sub> surfaces. Only bands at 1677, 1472, 1453 and 1381 cm<sup>-1</sup> (and 1360 cm<sup>-1</sup> for TiO<sub>2</sub>) remained in the obtained spectra (Fig. 1, spectra 2 of TiO<sub>2</sub>, SiO<sub>2</sub>). These bands can be assigned to  $\nu_{C=C}$ ,  $\delta_{C-H}$ ,  $\nu_{C-O}$  vibrations in the alkoxide.

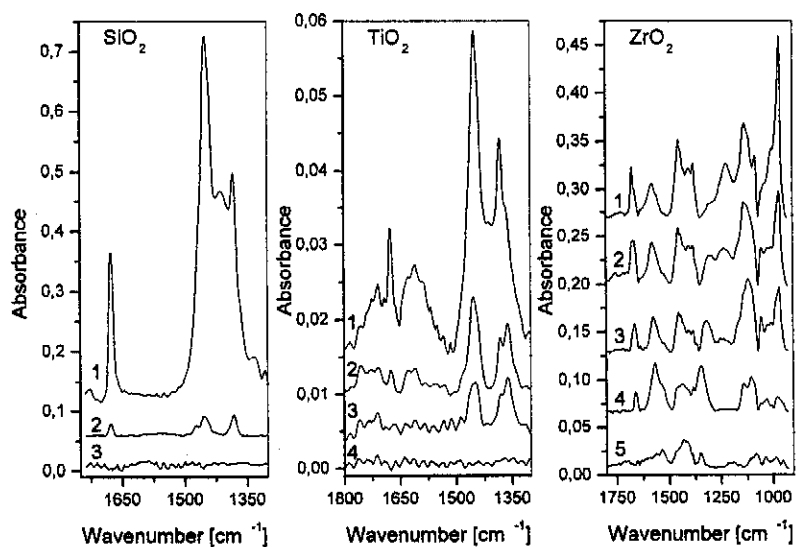


Fig. 1 IR spectra of crotyl alcohol adsorbed on SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> at room temperature-RT (1), evacuated at RT (2), evacuated at 373 K (3), evacuated at 473 K (4) and evacuated at 573 K (5)

Table I IR bands<sup>a</sup> of crotyl alcohol adsorbed on SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> at RT

Assignment of absorption bands	Gas	SiO <sub>2</sub>	TiO <sub>2</sub>	ZrO <sub>2</sub>
$\nu_{C=C}$	1678	1676	1675	1675
$\nu_{asCOO^-}$				1580 (1560)
$\delta(CH_3)$	1453	1450	1450	1451
$\nu_{sCOO^-}$				1440
$\nu(CH_2)$	1425	1411	1410	1402
$\delta_{C-H}$	1383	1380	1379	1380
$\delta(CH_3)$			1364	
$\delta(COH)$				1304
$\nu_{C-O}$	1186			1134
	1076			1082
	1007			1002
	970			966

<sup>a</sup> [cm<sup>-1</sup>]

The absorption bands at 1580 and 1560 cm<sup>-1</sup> (1587 cm<sup>-1</sup> for TiO<sub>2</sub>) observed for the ZrO<sub>2</sub> surface at 298-473 K can be attributed to  $\nu_{asCOO^-}$  vibrations in the asymmetric carboxylate structure (carbonyl-bound complex). In accordance with our previous results [10,11], the bands at 1662 and 1171 cm<sup>-1</sup> confirm the presence of coordinatively bonded crotonaldehyde. Increase of the temperature up to 473 K resulted in an appearance of the new bands at 1534 and 1345 cm<sup>-1</sup> which are typical of  $\nu_{C-O}$ ,  $\nu_{asCOO^-}$  and  $\nu_{sCOO^-}$  vibrations in bidentate carboxylates [12].

#### Crotonic Acid Adsorption on SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>

The contact of SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> samples with crotonic acid vapor caused formation of two strong absorption bands at 1705 and 1660 cm<sup>-1</sup> (Fig. 2, spectrum 1). New bands can also be observed in the lower wavenumber region, for example at 1449, 1425, 1380, 1313, 1293, 1222, 1102 and 968 cm<sup>-1</sup>. It can be concluded that the molecularly adsorbed crotonic acid was present on the surface. This conclusion is based on the good agreement between the bands at 1705, 1660 and 1222 cm<sup>-1</sup> and similar bands for gaseous crotonic acid as reported in Table II.

The band at 1521 cm<sup>-1</sup> in spectrum 1 (ZrO<sub>2</sub>) indicates that carboxylate ions were already present at RT. Increase of the interaction temperature up to 473 K

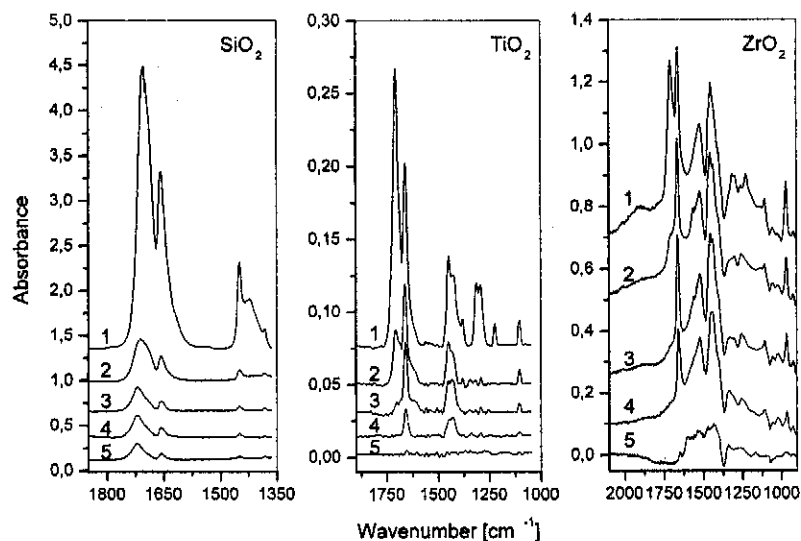


Fig. 2 IR spectra of crotonic acid adsorbed on  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  at room temperature-RT (1), evacuated at RT (2), evacuated at 373 K (3), evacuated at 473 K (4) and evacuated at 573 K (5)

Table II IR bands<sup>a</sup> of crotonic acid adsorbed on  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  at RT

Assignment of absorption bands	Gas <sup>b</sup>	$\text{SiO}_2$	$\text{TiO}_2$	$\text{ZrO}_2$
$\nu_{\text{C=O}}$	1770	1704 (1720)	1705	1707
	1760	1697		
	1718			
$\nu_{\text{C=C}}$	1665	1656	1659	1662
$\nu_{\text{asCOO}^-}$				1521
$\delta(\text{CH}_3)$	1453	1448	1447	1449
	1426	1421	1425	
$\delta_{\text{C-H}}$	1365	1381	1380	
$\delta(\text{COH})$	1311 (972)		1313	1312
$\delta(\text{COH}) + \nu_{\text{C-O}}$	1293		1293	1296
$\delta(\text{OH})$	1227		1222	1225
$\nu_{\text{C-O}}$	1411 (970)		1102	1103 (968)
$\tau(\text{CH}_3)$	1094			1054

<sup>a</sup> [ $\text{cm}^{-1}$ ], <sup>b</sup>Ref. [13]

resulted in an appearance of new bands at 1438 and 1340  $\text{cm}^{-1}$ , which are typical of  $\nu_{\text{sCOO}^-}$  in the carboxylate species on the surface. The intensity of the absorption bands due to H-bonded crotonic acid noticeably decreased with increasing temperature. The evacuation at 473 K resulted in a substantial decrease in the intensity of carboxylate ions bands (spectrum 5-  $\text{ZrO}_2$ ). Decrease in amount of these species was accompanied by increase in the water formation.

## Conclusion

Our FTIR studies of crotyl alcohol and crotonic acid adsorptions on  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  in the temperature range 298-573 K indicate formation of several surface complexes: crotyl alcohol and crotonic acid molecularly bonded due to hydrogen bonds with Brönsted acid sites of these oxides (physical adsorption), alkoxide, carbonyl-bound complex and carboxylates.

The molecularly bonded crotyl alcohol and crotonic acid do not participate in the reaction. They are very weakly bonded to the surface and can be easily removed by short application of vacuum at room temperature.

The alkoxide was observed at 298-373 K for all the oxides, it further converted to the carbonyl-bound complex (asymmetric carboxylate) and then subsequently to symmetric carboxylate ions. We believe that the carbonyl-bound species are most stable on  $\text{ZrO}_2$  (complex stability decreases as follows:  $\text{ZrO}_2 > \text{TiO}_2 > \text{SiO}_2$ ). Appearance of this complex on the surface of  $\text{ZrO}_2$  obviously initiated the formation of crotonaldehyde. The reaction of crotonaldehyde and the oxygen atom of the zirconia resulted in the formation of symmetric carboxylate ions (bidentate carboxylates) at higher temperature, which is in agreement with literature [10,11].

On the basis of obtained results and known properties reported in literature, the  $\text{ZrO}_2$  seems to be a best support for oxidative dehydrogenation of crotonaldehyde to maleic anhydride over V/support catalyst. The obtained spectra are valuable for further discussion of the adsorption of crotonaldehyde and its intermediates (furan, tetrahydrofuran and  $\gamma$ -butyrolactone) on oxide catalysts under oxidizing conditions which lead to maleic anhydride.

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