JOURNAL OF CATALYSIS **109**, 303–313 (1988)

Infrared Spectroscopic Investigation of the Adsorption States of 1-Butene, 1,3-Butadiene, Furan, 2,5*H*-Furanone, and Maleic Anhydride on Alumina-Supported V_2O_5–P_2O_5 Catalyst

I. Adsorption under Nonreactive Conditions

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Received August 30, 1985; revised July 20, 1987

Adsorption states of 1-butene, 1,3-butadiene, furan, maleic anhydride, and 2,5*H*-furanone on an alumina-supported V_2O_5–P_2O_5 catalyst were investigated by infrared spectroscopy. Measurements were carried out at temperatures between 373 and 423 K. Within this temperature range oxidation of the primarily formed adsorbates was mostly negligible. Maleic anhydride was also adsorbed up to 573 K. 1-Butene adsorbed at 373 K forms two different π complexes; the formation of carboxylates can be neglected. 1,3-Butadiene seems to be adsorbed in two different states on the catalyst at 423 K: both C=C double bonds form (a) a π complex with the surface and (b) a 1,4 addition complex via σ bonds. Furan adsorbs by forming an addition complex via the 2-position of the ring; this complex undergoes reaction at 403 K. 2,5*H*-Furanone forms another 2-furanone complex by abstraction of an allylic hydrogen, which then reacts to 4-oxo-2-butenoic acid under oxidative conditions. Maleic anhydride forms a maleate structure with the surface, but physisorbed maleic anhydride is also found even at elevated temperatures. © 1988 Academic Press, Inc.

INTRODUCTION

Catalysts for commercial 1-butene oxidation to maleic anhydride (MA) are usually based on vanadium, molybdenum, or tungsten oxide along with P_2O_5. In this multistep reaction many intermediates and side products are formed; selectivity usually amounts to 50 to 60 mol%. Intermediates of the reaction desorbed into the gas phase have been determined by several authors [e.g., (1–3)], but there is little information on the intermediates adsorbed on the catalyst surface. Increased knowledge about the interaction of the reactants with the catalytic surface may lead to a better understanding of the reaction mechanism and to the development of better catalysts.

1-Butene is oxidized to MA via 1,3-butadiene and furan (*1*–*5*). Other postulated intermediates are 2-butenaldehyde (*1*, *3*–*5*) and 2-butenoic acid and 2,5*H*-furanone (3,5); 2,5*H*-furanone, which was not found in the gas phase, is considered as a direct precursor of MA. Side reactions result in the formation of acids (e.g., acetic acid, acrylic acid), aldehydes (e.g., acrolein), and ketones (e.g., 2-butanone). 1-Butene also isomerizes to *cis*- or *trans*-2-butene already at low temperatures; rates of isomerization are higher than those of oxidation. It is assumed that both reactions take place via an intermediate π-allyl complex (*6*). Similarly, a π-allyl complex has been found by Dent and Kokes (*7*) by infrared spectroscopy; in the adsorption of propene and butene on zinc oxide the frequency of the C=C double bond was shifted by about 100 cm^{-1} to lower values. 1-Butene may also form π complexes upon adsorption on oxide surfaces; their infrared spectra have been characterized by Burfield (*8*). Förster and Seelemann (*9*) observed two different C=C bands for π complexes when adsorbing 1-butene on A-type zeolites depending on the site of adsorption. Following the ad-

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sorption of olefins, Gerei *et al.* (*10*) and Rozhkova *et al.* (*11, 12*) found carboxylates on catalysts that favored total oxidation and π complexes on catalysts that favored partial oxidation.

Intermediates of the oxidation of furan to MA have been studied by Jovel and Shimanskaya (*13*) and by Rivasseau *et al.* (*14*). Jovel and Shimanskaya adsorbed and oxidized furan on a V_2O_5/MgO catalyst. They assigned a certain group of bands to a succinate structure as an intermediate toward MA. Sathyanarayana and Patel (*15*) found similar bands for vanadyl maleate dihydrate, and a similar intermediate structure seems possible from the results given by Jovel and Shimanskaya. Rivasseau *et al.* (*14*) could not identify any adsorbate structures on molybdenum–titanium oxide from their IR spectra. From temperature-programmed desorption, however, a component of mass 82 was found, which they attributed to acetylene dialdehyde. Weiss (*16*) suggested an addition complex between the catalyst and the carbon atom next to the oxygen in the furan ring.

The absorption bands of 1-butene,1,3-butadiene, 2-butenaldehyde, 2-butenoic acid, furan, and MA, which may be adsorbates formed in butene oxidation, are listed in Table 1. It is obvious that difficulties may arise in assigning bands to a single compound. The situation may be even more complicated by band shift due to adsorption. 2-Butenaldehyde and 2-butenoic acid are especially difficult to distinguish from each other: their strongest bands, which result from the carbonyl group, are only about 10 cm^{-1} apart, and it is impossible to discriminate with certainty between the two compounds.

For multistep reactions the concurrent formation of many different surface compounds may occur, and their discrimination is usually not possible. In these circumstances it is necessary to restrict the investigation to selected steps of the reaction network.

The present study was aimed at obtaining more detailed information on the processes occurring on the surface of alumina-supported V_2O_5–P_2O_5. For this purpose the adsorption of 1-butene as the reactant and of MA as the desired product, as well as of several gas-phase intermediates of the oxidation reaction, i.e., 1,3-butadiene, furan, and 2,5*H*-furanone, was investigated. To untangle the complex reaction system, adsorption was first carried out under conditions where predominantly only adsorptive interaction occurred between adsorbate and catalyst, but no significant further oxidation of the primarily formed complexes took place. This is the subject of the present paper (Part I); surface adsorbates under reactive conditions will be dealt with in Part II (in preparation). For assigning the absorption bands to individual surface species, the process of adsorption, i.e., the development of surface structures with time, was also observed. Results of adsorption at higher temperatures leading to further oxidation of the adsorbates in the presence of oxygen or by the catalyst itself will be discussed in a subsequent paper.

EXPERIMENTAL

Infrared spectroscopy is a well-known tool for investigating adsorbate interaction with the catalyst under reaction conditions (*23, 24*). Sample thicknesses of 10 to 40 mg cm^{-2} usually enable good adsorbate spectra to be obtained over a wide wavenumber range (*25*). Obtaining adsorbate spectra in the presence of gaseous compounds requires compensation for the latter by passing the IR reference beam and the gas through a cell that has the same geometry as the one containing the catalyst specimen; in the present study this compensation was experimentally verified. Two infrared cells, as described by Gallei and Stolz (*26*), were incorporated into a Perkin–Elmer 580 A spectrometer. IR transmission values of catalyst plus adsorbate were registered at constant wavenumber intervals by means of a minicomputer. The adsorbate spectrum was then obtained

TABLE 1

Absorption Frequencies (cm^{-1}) of Main Reactants in the Oxidation of 1-Butene to Maleic Anhydride

Butadiene (*17*)	2-Butenaldehyde (*18*)	2-Butenoic acid (*19*)	Furan (*20*)	2,5*H*-Furanone (*21*)	Maleic anhydride (*22*)
			3167 w		3180 w
			3161 m		
			3140 w		
			3129 m		3123 w
				3100 w	
2980 s					
	2956 m				
		2940 m		2940 w	
2928 sh	2933 m				
	2892 m			2880 w	
2797 w	2793 s				
	2712 s				
		2650 w			
1821 s					1855 m
1767 w				1775 s	1780 s
				1745 s	
	1687 vs	1698 vs			
	1637 s	1655 s			
1592 vs				1605 m	1592 m
			1556 s		
1497 w			1491 s		
1437 w	1441 s	1446 s		1450 m	
		1420 m			
	1390 s				
1377 m	1374 s	1375 m	1384 s		
	1303 m	1310 s			
1292 w		1285 sh			
1280 vw			1267 w		1266 s
					1240 s
		1225 s			

Note. Very weak bands are not listed. Data given correspond to gaseous 1,3-butadiene, to solid maleic anhydride, and to the liquid state of all other compounds.

by dividing the transmission values of catalyst plus adsorbate by the respective values of the clean catalyst. One drawback of the method is that the adsorbate spectra are overlapped by spectral changes of the catalyst itself, resulting from its interaction with the adsorbate; this secondary effect cannot be eliminated.

To decide whether different bands were to be assigned to the same compound, their extinctions obtained at different times were compared with one another. If their ratio was constant at different times, the IR bands were considered to belong to the same compound. For adsorbate structure identification the IR bands were compared with the spectra of pure compounds similar to expected adsorbate structures.

The alumina-supported V_2O_5/P_2O_5 catalyst was prepared by impregnation after Kerr (*27*). V_2O_5 was dissolved in a solution of oxalic acid forming vanadium(IV) oxalate. Phosphoric acid was then added to the solution. The P/V atomic ratio was 1.2/1.

Solid γ-alumina (Alon C from Degussa) and the solution were mixed to obtain 10 wt% vanadium and phosphorus oxide on 90% alumina. The solution was evaporated and the residue was dried at 393 K and then held at 573 K for 2 days. The powder was pressed into 13-mm disks of about 26 mg. For IR measurements a disk was inserted in the cell and heated to 723 K *in situ* in air until a steady-state spectrum was obtained. The BET surface area after this pretreatment was 66 m^2/g. Nitrogen or air (for maleic anhydride) was used as carrier gas for the gaseous organic compounds to be adsorbed (the following concentrations were applied at total pressure of 1 bar: 0.8 vol% butene, 0.01 vol% MA, 0.01 vol% 2,5*H*-furanone, 0.4–2 vol% furan). At a chosen temperature the spectrum of the clean catalyst was registered. Then the adsorbate was added to the carrier gas. Gaseous compounds were fed via capillary flowmeters, while fluids were added by a saturator with reflux. Adsorbate formation lasted several hours; therefore, adsorbate spectra corresponding to different amounts adsorbed were registered as a function of time. The purity of the adsorbed compounds was 98% for 2,5*H*-furanone and better than 99% for 1-butene, 1,3-butadiene, furan, and maleic anhydride.

RESULTS AND DISCUSSION

General Observations

All adsorbate spectra showed negative bands at 3780–3790, 3730, and 3670 cm^{-1} and a broad absorption band between 3470 and 3540 cm^{-1}. The negative bands are at positions of catalyst hydroxyl bands; this is an indication of interaction between the adsorbate and the hydroxy groups on the surface. The broadband that results from bridged hydroxy groups originates from the shift in the unperturbed hydroxy groups of the catalyst with adsorption. The shift of the hydroxyl bands depends on the adsorbate. It cannot be decided whether additional hydroxy groups are formed during adsorption since the extinction coefficient of the hydroxy groups increases with the formation of bridged hydrogen bonds (*28*).

Adsorption of 1-Butene

The adsorbate spectrum of 1-butene (Fig. 1) shows the negative hydroxy bands and the broad, positive hydroxy band that were mentioned above. C–H bonds can be assigned to wavenumbers at 2980, 2930, and 2880 cm^{-1}, the intensity ratio of the bands at 2930 and 2880 cm^{-1} being about 1.5. According to Francis (*29*), this implies that the concentrations of CH_3 and CH_2 groups are nearly the same. Thus, it may be concluded that the ethyl group of 1-butene is preserved, and therefore only very little 2-butene formed by isomerization may be adsorbed on the catalyst. Olefinic C–H bands above 3000 cm^{-1} could not be detected.

Below 2000 cm^{-1} further bands were observed at 1680, 1625, 1595, 1465, 1385, and 1335 cm^{-1}. All bands are of similar intensity. The bands at 1465, 1385, and 1335 cm^{-1} can be assigned to deformations of hydrocarbons, while the other three bands (1680, 1625, 1595 cm^{-1}) are in a range where C=C as well as C=O bonds absorb. [Ketones absorb at 1680 cm^{-1}; Rozhkova *et al.* (*12*) found a band in this region when adsorbing methyl vinyl ketone and 1-butene on a silica-supported V_2O_5/P_2O_5 catalyst. They assigned this band to methyl vinyl ketone; however, another band arises in the same position when maleic anhydride and 1,3-butadiene are adsorbed; for maleic anhydride the formation of methyl vinyl ketone can be excluded.]

The band of gaseous 1-butene (1645 cm^{-1}) is most probably shifted to lower values due to adsorbate/catalyst interaction. This agrees with the observations of Förster and Seelemann (*9*) who found bands of 1-butene physisorbed on different Na–, Li–, and Ca–A zeolites in the region 1635 to 1627 cm^{-1}. π complexes of 1-butene with a solid surface were assigned by Burfield (*8*) to 1595 cm^{-1}. Hence, the bands observed at 1625 and 1595 cm^{-1} can cer-

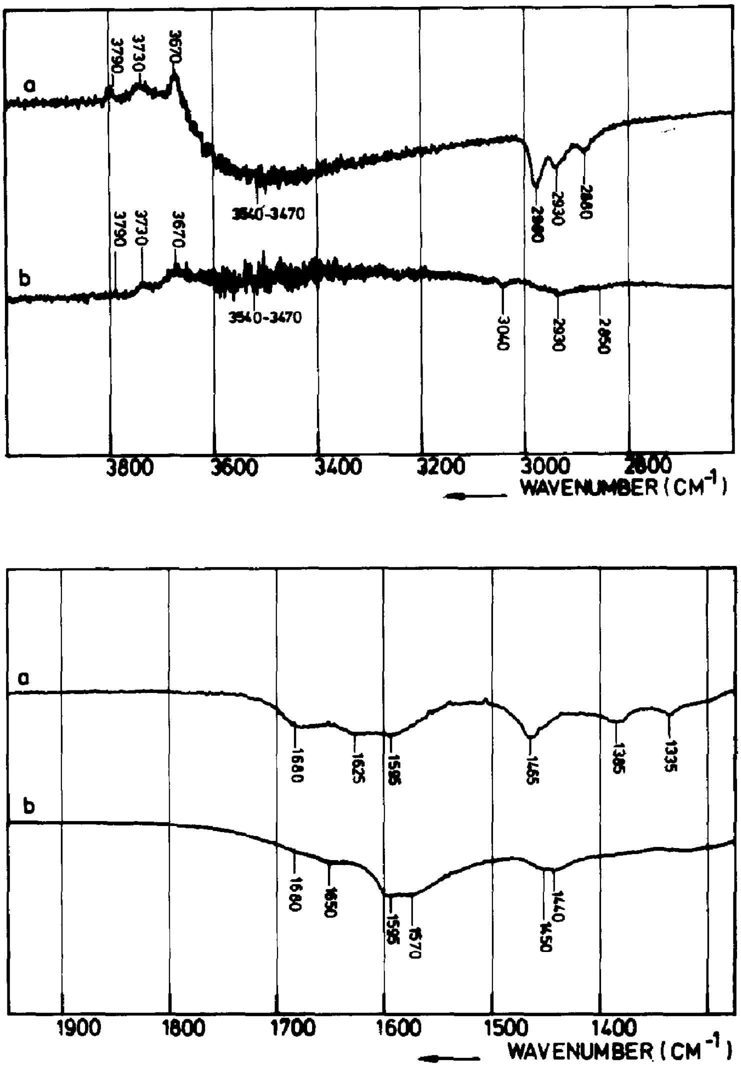

FIG. 1. Absorption spectra of 1-butene at 373 K (a) and 1,3-butadiene at 423 K (b).

tainly be attributed to these adsorbate structures.

Adsorption of 1,3-Butadiene

Similarly to 1-butene the adsorption of 1,3-butadiene at 423 K also leads to negative hydroxyl bands; a small absorption band occurs at 3540 cm^{-1}. Hydrocarbon bands are identified at 3040, 2930, and 2850 (sh) cm^{-1}. Below 2000 cm^{-1} there are absorption bands at 1680 (sh), 1650, 1595, 1570, 1450 (sh), and 1440 cm^{-1}. The spectrum is shown in Fig. 1.

Bands at 2930, 1595, 1570, and 1440 cm^{-1} agree with those of gas-phase butadiene. The 1650 cm^{-1} band indicates an isolated C=C double bond (e.g., 1645 cm^{-1} in 1-butene). The lack of a hydrocarbon band around 3080 cm^{-1} shows that the terminal olefinic CH_2 group disappears by adsorption. A possible structure for adsorbed 1,3-butadiene is therefore either a 1,4-addition complex on the catalyst (two σ bonds) or a

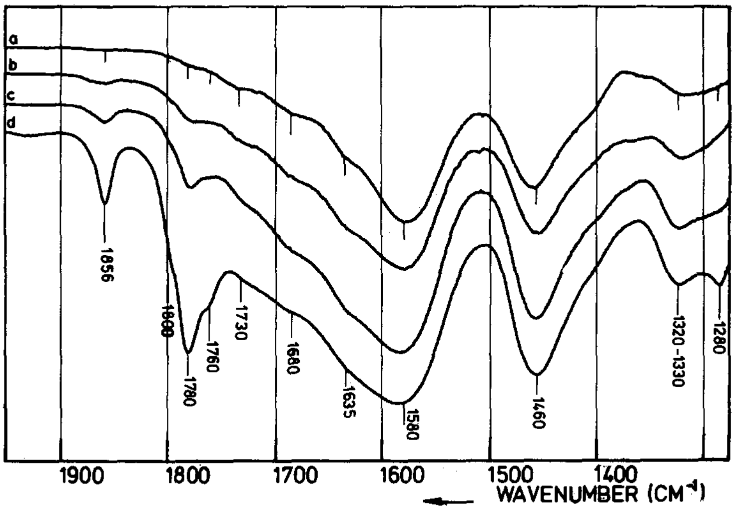

FIG. 2. Absorption spectra of maleic anhydride adsorbate at 573 K (a), 473 K (b), 423 K (c) and 373 K (d).

π complex of both C=C double bonds with the catalyst surface. The latter complex would have only very weak absorption in the 3080 cm^{-1} region.

The 1680 cm^{-1} absorption band cannot safely be assigned to a single adsorption structure as many compounds absorb in this region; however, since a weak double peak was observed the structure may be most probably assigned to 1,3-butadiene.

Adsorption of Maleic Anhydride

Maleic anhydride was adsorbed between 373 and 573 K. The adsorbate spectra in the range 1950 to 1275 cm^{-1} are shown in Fig. 2, and the wavenumber values of the absorption bands are listed in Table 2. At all temperatures negative and positive hydroxy bands were found. On the basis of the change of their extinction at different temperatures and adsorption times, the other bands can be divided in three groups: Group A bands [1856, 1800 (sh), 1780, 1760(sh), and 1280 cm^{-1}] change their extinction very much with temperature. Extinction of group B bands (1580, 1460, and 1320–1330 cm^{-1}) increases very slowly with adsorption time. Group C bands (1730, 1680, and 1635 cm^{-1}) develop very quickly after adsorption. Whether an absorption band belonging to group B exists around 1635 cm^{-1} is uncertain. Assignment of the hydrocarbon bands at 3120, 3080, 2970, and 2940 cm^{-1} is impossible because these bands are very weak and are detectable only at low temperatures.

Group A bands can easily be assigned to physisorbed maleic anhydride. The 1856 and 1780 cm^{-1} bands result from the symmetric and asymmetric anhydride vibrations, while the 1280 cm^{-1} band arises from the C–O–C bridge in the molecule. The values are in nearly the same positions as given by Ref. (*22*). The C=C band of maleic anhydride is of medium intensity and absorbs at 1590 to 1595 cm^{-1}. The observed 1580–1585 cm^{-1} band cannot be assigned to this vibration, since its intensity is independent of the other maleic anhydride bands as derived from their time dependence. Most probably the band of the C=C bond is covered by this band.

Group B bands at 1580 and 1460 cm^{-1} are very strong, while the 1320 cm^{-1} band is of medium intensity; whether the 1640 cm^{-1} band belongs to group B is uncertain. The 1580 cm^{-1} band is typical for a carboxylate structure. It corresponds to the asymmetric

TABLE 2

Wavenumbers (cm^{-1}) of Absorption Bands after Maleic Anhydride Adsorption at Different Temperatures

373 K	423 K	473 K	573 K	Assignment
3780	3780	3780	3780	OH groups
3730	3730	3730	3730	
3680	3680	3680	3680	
3500 vs,br	3480 vs,br	3450 vs,br	3450 w,br	Bridged OH groups
3120 vw	3120 vw			CH stretch
3080 vw				
2970 vw				
2940 vw				
1930 vw				Combination
1856 m	1856 w	1856 w		C=O asymmetric stretch
1780 s	1780 m	1780 w	1780 sh	C=O symmetric stretch
1760 sh	1760 vw			Combination
	1730 sh	1730 sh	1730 w	
1680 sh	1680 sh	1680 sh	1680 sh	
1640 sh	1640 sh	1635 sh	1635 w	C=O asymmetric stretch
1585 vs	1585 vs	1580 vs	1580 m	C=C, C=O symmetric stretch
1455 vs	1460 vs	1460 vs	1460 m	C—O asymmetric stretch
1400 sh	1400 sh	1400 sh		
			1360 vw	
1330 m	1320 m	1320 m	1325 w	C—O symmetric stretch
1280 m	1280 sh	1280 sh		

vibration of the carboxylate ion. The 1460 cm^{-1} band lies within the range 1390 to 1470 cm^{-1}, being characteristic for the symmetric vibration of carboxylates (*30*). Carboxylate structures that might be formed by adsorption of maleic anhydride are maleate, acid maleate, oxalate, and carbonate; however, oxalate and carbonate are unlikely to be present here as can be deduced by comparison with the absorption bands published for carbonates (*31*) and oxalates (*32, 33*). Sathyanarayana and Savant (*34*) reported infrared spectra of maleate hydrates and acid maleate hydrates of Ni, Co, Cu, and Zn; a comparison of the group B bands with these spectra indicates that maleate is the most likely structure for the maleic anhydride adsorption complex.

Group C bands at 1730, 1680, and 1635 cm^{-1} reach their final intensity immediately after the onset of adsorption. That additional bands of this adsorbate structure are covered by other compounds cannot be excluded. Structures of acid maleate and maleic acid that appear to be possible adsorbates could not be identified on the basis of these bands only. Also, no other assignment was possible.

Summarizing, it may be concluded that a physisorbed maleic anhydride and a maleate formed by chemical interaction exist on the catalyst surface. Moreover, there exist other complexes the structure of which could not be identified.

Adsorption of 2,5H-Furanone

The adsorption of 2,5*H*-furanone was carried out at 373 and 403 K. For both temperatures similar results were obtained. Obviously, the adsorbate underwent reaction on the catalyst even at 373 K. As several different adsorbate complexes were formed interpretation of the spectra was difficult. The adsorbate spectra obtained at 373 K after different adsorption times are shown in Fig. 3 (spectra a–e). In the beginning,

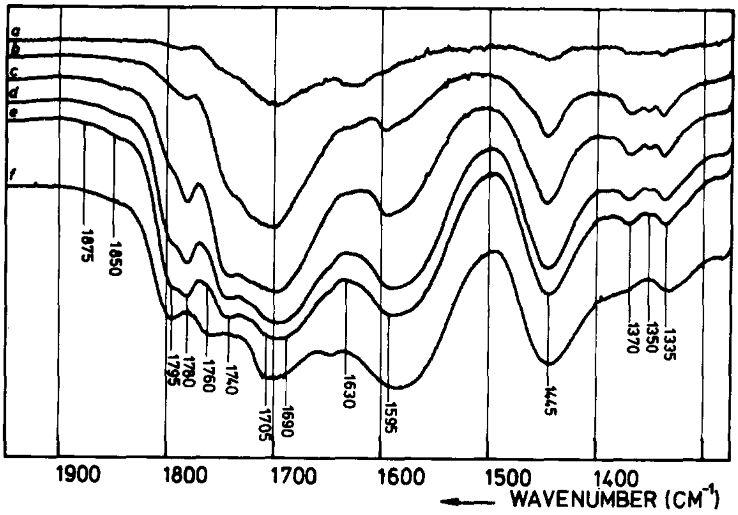

FIG. 3. Absorption spectra of 2,5*H*-furanone adsorbate at 373 K from 1950 to 1275 cm^{-1} with increasing coverage of the catalyst (a–e) and after purging with nitrogen (f).

bands arise at 1780, 1705, 1690, 1630, 1445, 1370, and 1335 cm^{-1}. The 1705 cm^{-1} band has a shoulder at 1740 cm^{-1}, and the 1630 cm^{-1} band at 1595 cm^{-1}. During further adsorption especially the 1780, 1740, 1445, 1370, and 1335 cm^{-1} bands increase with time, while the 1630 cm^{-1} band becomes covered by a band at 1595 cm^{-1}; also, additional bands arise at 1795 and 1350 cm^{-1}, and shoulders appear at 1760, 1850, and 1875 cm^{-1}. Bands typical of hydrocarbons are observed at 3100, 2930, 2820, and 2725 cm^{-1}.

Purging the IR cell with nitrogen leads to a decrease in the band intensities in the region 1800 to 1650 cm^{-1}; especially at 1780 and 1740 cm^{-1} a significant decrease occurs. The 1690 cm^{-1} band is weakened more than the 1705 cm^{-1} band. The 1445 cm^{-1} band is broadened, while the 1350 cm^{-1} band disappears (cf. Fig. 3, spectra e and f). The 3100 and 2930 cm^{-1} bands are weakened.

Easiest to identify is physisorbed 2,5*H*-furanone (3100, 2930, 1780, 1740, and 1350 cm^{-1}) which desorbs during purging with nitrogen. Further bands of this compound are at 2880, 1605, and 1450 cm^{-1} (*21*). The 2880 cm^{-1} band of 2,5*H*-furanone is very weak and may not be detected; those at 1605 and 1450 cm^{-1} are covered by other compounds.

Bands at 1795 and 1760 cm^{-1} can be assigned to another 5-substituted 2-furanone. Schroeter *et al.* (*35*) found two carbonyl bands for different 5-substituted 2-furanones; 5-hydroxy-2-furanone exhibits bands at 1793 and 1761 cm^{-1}, but other substituents may shift these bands. The small difference between both bands (35 cm^{-1}) is to be understood as an indication that they do not result from open-chain anhydrides, which absorb in the same region and have a wavenumber difference of about 60 cm^{-1}. Thus, the bands at 1795 and 1760 cm^{-1} apparently belong to a 5-substituted 2-furanone.

The very strong bands at 1705 and 1690 cm^{-1} result from different compounds. They have to be assigned to aldehyde structures. γ,β-Unsaturated acids can be excluded since they exhibit only a weak absorption band in this region. The formation of aldehydes is shown by two characteristic weak bands at 2820 and 2725 cm^{-1}. Characteristic bands for the deformation of aldehydes lie between 1415 and 1325 cm^{-1} (*36*), bands having been observed at 1335, 1350,

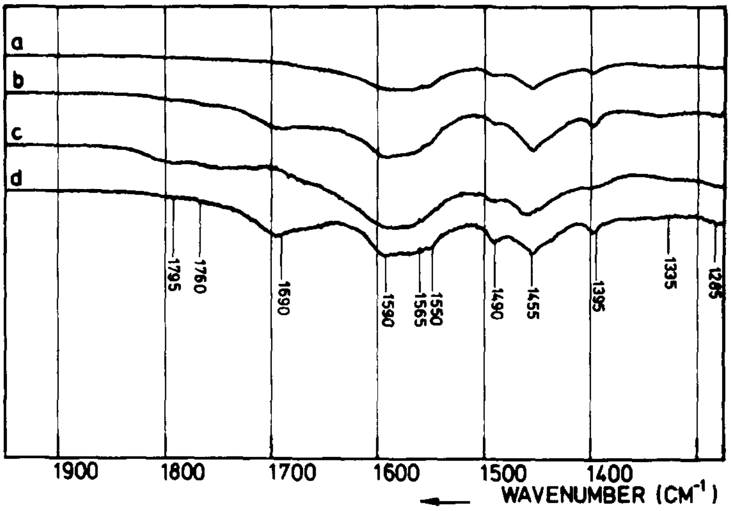

FIG. 4. Absorption spectra of furan adsorbate. (a) Spectral changes after long adsorption times at 378 K. (b) Adsorbate spectrum in the beginning of adsorption at 378 K. (c) Spectral changes after long adsorption times at 387 K. (d) Adsorbate spectrum in the beginning of adsorption at 387 K.

and 1370 cm^{-1}. The 1350 cm^{-1} band has previously been assigned to physisorbed 2,5*H*-furanone (see above). The remaining bands at 1335 and 1370 cm^{-1} can be linked to the aldehyde deformation, especially since their intensity increases with that of the carbonyl bands. The split of the carbonyl bands at 1705 and 1690 cm^{-1} may result from different conformations of the aldehyde group and the carbon double bond (*36*); the s-*cis* conformation would lead to the 1705 cm^{-1} band, while the s-*trans* conformation would absorb at 1690 cm^{-1}. Carboxylic acids also absorb around 1700 cm^{-1}; however, there should be additional bands characteristic for the hydroxyl group, one at around 3200 cm^{-1} and two weaker ones in the region 2750 to 2550 cm^{-1}, which were not detected when adsorbing 2,5*H*-furanone. Furthermore, the 2725 cm^{-1} band can be securely assigned to an aldehyde. The occurrence of a free acid therefore seems very doubtful. The bands around 1595 and 1445 cm^{-1} may be assigned to a carboxylate ion structure since similar bands (i.e., 1585 and 1445 cm^{-1}) have been observed for a carboxylate structure when MA was adsorbed; however, no final proof is possible at present.

In essence it seems reasonable to assume that during the adsorption of 2,5*H*-furanone the following compounds are formed: physisorbed 2,5*H*-furanone, another 5-substituted 2-furanone, and a 4-oxo-2-butenoic acid anion.

Adsorption of Furan

The adsorption of furan was carried out at 378 and 387 K. The respective spectra are shown in Fig. 4. At 403 K already strong bands were formed in the region from 1700 to 1850 cm^{-1}, which certainly resulted from products of furan oxidation. At 378 K very weak bands at 1795, 1760, 1335, and 1285 cm^{-1} and a little stronger band at 1690 cm^{-1} are formed in the beginning of the adsorption of furan (Fig. 4, spectrum b). The intensities of these bands did not increase with adsorption time (spectrum a). Bands at 3150–3130, 1590, 1570, 1550(sh), 1490, 1455, and 1395 cm^{-1} increase in intensity during an elongated adsorption period. A temperature increase from 378 K to 387 K did not significantly change the results at

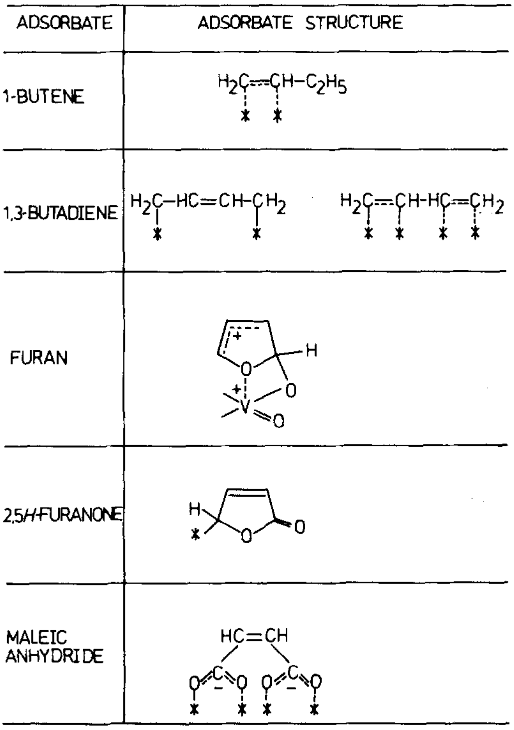

FIG. 5. Proposed structures of 1-butene, 1,3-butadiene, furan, 2,5*H*-furanone, and maleic anhydride adsorbed on a V_2O_5/P_2O_5 catalyst. *Adsorption site.

378 K (spectra c and d); however, the bands at 1850 to 1650 cm^{-1} were stronger although less pronounced than the other absorption bands. Their intensity changes were too weak to decide whether they belong to one or more compounds.

Bands at 1595, 1565, 1550(sh), 1490, 1455, and 1395 cm^{-1} are assigned to one compound. These bands are in nearly the same position as those of furan. In comparison with unadsorbed furan the 1490 cm^{-1} band is smaller, while the 1455 cm^{-1} band is stronger. As Rico *et al.* (*20*) show, substitution at the furan ring influences the position of the 1490 cm^{-1} band. This influence is strong for substitution in the 2- or 5-position of the ring, while 3- and 4-substitution has only little effect. Senechal and Saumagne (*37*) investigated several 2-substituted furans. Ring vibrations of furan appear in the range 1460 to 1530 cm^{-1}. Lowering the electron density in the ring would lead to absorption at lower wavenumber. Interaction of furan with the catalyst, as suggested by Weiss (*16*), would lead to an adsorption complex with lowered electron density in the furan ring. A cationic complex, as suggested by Weiss, would lead to the spread of one π bond over three carbon atoms. This structure is similar to a π–allyl complex, whose carbon–carbon bond absorbs at about 1458 cm^{-1} (*38*). An addition complex of the furan ring in the 2-position to the catalyst is therefore the likely structure (Fig. 5).

The remaining bands in the adsorbate spectra cannot be assigned to a single compound. They belong to other reaction products which are formed by oxidation of the adsorbate. These structures will be discussed in Part II where the adsorption results obtained under oxidizing conditions will be presented.

CONCLUSIONS

It is concluded that from 373 to 423 K no significant oxidation of the primarily formed adsorbate complexes took place. The only exception is 2,5*H*-furanone, which reacted slowly to the 4-oxo-2-butenoic acid anion even at these low temperatures. The olefins 1-butene and 1,3-butadiene formed π complexes with the catalyst surface without any further oxidation. Furan formed an addition complex in its 2-position with the catalyst, which was stable at 378 and 387 K. Maleic anhydride apparently did not undergo oxidation up to 573 K.

The spectra obtained are valuable for further discussion of the adsorption of 1-butene and its intermediates furan and 2,5*H*-furanone under oxidizing conditions which lead to maleic anhydride. The adsorbate structures derived for the various compounds are summarized in Fig. 5.

ACKNOWLEDGMENTS

This work has been supported in part by Fonds der Chemischen Industrie and by Deutsche Forschungsgemeinschaft. A. Ramstetter acknowledges personal grants awarded by both institutions. Helpful discussions with Dr. N. T. Do are appreciated.

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