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Characterisation of the structure of adsorbates An in situ DRIFTS-study of the partial oxidation of unsaturated aldehydes on Mo/V oxide catalysts

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Dedicated to Professor H. Knözinger to mark his 65th birthday.

Abstract

Mo/V oxides are interesting catalyst materials for the selective partial oxidation of unsaturated aldehydes (acrolein and methacrolein) to the corresponding carboxylic acids. Two catalyst systems — a mixed oxide and a heteropolyacid salt — were investigated by in situ DRIFT-spectroscopy. Using a novel DRIFTS cell, in which both the catalyst powder and the reference (KBr) were in the same reaction chamber, we are able to detect different adsorbates of (meth)acrolein and (meth)acrylic acid under reaction gases. The investigations showed that in the case of the adsorption of acrolein and methacrolein a significant difference in the structure of corresponding adsorbates could not be proved. This indicates that the reaction mechanism of the selective partial oxidation should be the same for both aldehydes. With these kind of investigations we gain access to a deeper insight into the reaction mechanism. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Adsorbates; DRIFTS; (Meth)acrolein; MoV mixed oxide catalysts; Selective oxidation

1. Introduction

The formation of intermediate adsorbates on catalyst surfaces is an important step in the reaction path of heterogeneously catalysed reactions. Infrared-spectroscopy (IR) is an ideal method for the characterisation of the intermediate adsorbates. The trend is now moving from IR-transmission- to DRIFT-spectroscopy, because with this technique, catalyst powders can be investigated without manipulation [1].

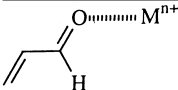
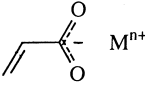
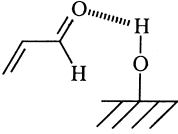
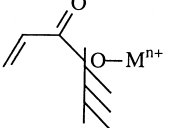
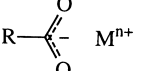
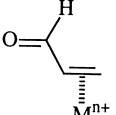
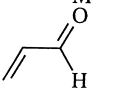
Connor [2] investigated the conversion of ethylene to ethylene oxide using silver catalysts in this way. Up to now only IR-investigations using self-supported wafers can be found in literature for the selective oxidation of either acrolein (ACR) to acrylic acid (AA) or methacrolein (MAC) to methacrylic acid (MAA). Extensive studies were carried out by Andrushkevich et al. [3] on this subject. From these investigations the authors deduced a reaction mechanism. The postulated structures of the adsorbates and the corresponding IR-vibration bands can be found in Table 1.

One of the main problems in in situ IR-spectroscopy is the differentiation between gas phase-

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Table 1
Surface compounds of ACR according to Andrushkevich et al. [3]

Structure	Name	IR absorption band in cm^{-1}
	Coordinatively bonded ACR (1) (complex) (see Fig. 1)	$\nu(\text{C}=\text{O}) = 1690\text{--}1660$ $\nu(\text{C}=\text{C}) = 1625$ $\nu(\text{C}\text{--}\text{H}) = 1370$
	Acrylate (2) (see Fig. 1)	$\nu_{\text{as}}(\text{COO}^-) = 1560\text{--}1520$ $\nu_{\text{s}}(\text{COO}^-) = 1460\text{--}1420$ $\nu(\text{C}=\text{C}) = 1640$ $\nu(\text{C}\text{--}\text{H}) = 1370$
	Hydrogen-bonded ACR (3) (see Fig. 1)	$\nu(\text{O}\text{--}\text{H}) = 3500$ $\nu(\text{C}=\text{O}) = 1705\text{--}1690$ $\nu(\text{C}=\text{C}) = 1625$ $\nu(\text{C}\text{--}\text{H}) = 1370$
	Carbonyl-bonded ACR (4) (see Fig. 1)	$\nu(\text{C}\text{--}\text{O}) = 1730\text{--}1710$ $\nu(\text{C}\text{--}\text{C}) = 1625$
	Carbonato carboxylate	$\nu_{\text{as}}(\text{COO}^-) = 1530$ $\nu_{\text{s}}(\text{COO}^-) = 1360$
	π -Complex	$\nu(\text{C}=\text{C}) = 1520\text{--}1490$
	Gaseous ACR (100°C)	$\nu(\text{C}\text{--}\text{O}) = 1731$ $\nu(\text{C}=\text{O}) = 1712$

and adsorbate vibration bands. In transmission mode gas phase spectra can be determined easily and exactly. With the DRIFTS-technology the gas phase can be measured using KBr as reference substance. These gas phase spectra, which have to be subtracted from the actual spectra of the experiment (gas phase + adsorbate + catalyst) must be measured at the same temperature, since the results of the IR-spectra depend strongly on the temperature. The subtraction of the gas phase spectra is usually carried out via a scaling factor, which Connor [2] determined e.g. on a special part of the spectra, where no adsorbate bands were expected.

In the frame of these investigations of the partial oxidation of unsaturated aldehydes to the corresponding carboxylic acids high boiling by-products unfortunately condensed on the windows of the mea-

suring cell. Since these coatings, which change with time, only appear in the presence of the catalyst the subsequent subtraction of time dependent IR spectra of the coatings is to be rejected.

In order to carry out in situ investigations, a DRIFTS-cell is favoured in which both the reference and the catalyst sample are in the same reaction chamber, both stored in sample cups on a rotating plate which can be brought into the IR-beam of the spectrometer in alternation [1]. With this technology dark coloured catalyst samples can also be easily investigated, which is not possible in transmission mode.

In this paper, we investigate the adsorption of acrolein (ACR) and methacrolein (MAC), together with acrylic acid (AA) and methacrylic acid (MAA) on a mixed oxide (MO) and a heteropolyacid salt

(Cs₂HPA) via a newly developed DRIFTS-cell [1]. The aim was to determine the structure of the intermediate adsorbates on catalyst surfaces under reaction conditions, in order to gain access to a deeper insight into the corresponding reaction mechanism.

2. Experimental

2.1. Catalysts

The investigations were carried out on the following two catalyst systems. Both samples were in powder form (average particles size: 80 µm).

2.1.1. Mixed oxide (MO)

This sample was synthesised by thermal decomposition of the corresponding ammonium salts [4–6]. Composition: Mo₉V₃W_{1,2}O_x; BET surface area: 14 m² g⁻¹.

2.1.2. Heteropolyacid salt (Cs₂HPA)

This sample was synthesised by mixing the aqueous solutions of the ammonium salts of Mo and V, CsNO₃ and H₃PO₄. After spray drying the mixture was calcinated up to 360°C under air [5,6,11]. Composition: Cs₂H₂[PVMo₁₁O₄₀]; BET surface area: 28 m² g⁻¹.

It is typical that MO is used for the partial oxidation of ACR to AA and Cs₂HPA for the partial oxidation of MAC to MAA.

2.2. Catalyst pre-treatment and experimental procedure

Both catalysts were pre-treated at 300°C with a gas mixture containing 20 vol.% O₂ in N₂ for half-an-hour in order to get a reproducible starting point for the measurements – a first (1) IR-spectrum was measured. Following this, the catalyst was cooled down to 100°C — a second (2) IR-spectrum was measured. After the injection of the probe substance — this is either 5 vol.% ACR or MAC or either 2 vol.% AA or MAA in N₂, respectively — a third (3) IR-spectrum was measured (procedure A). After an 1 h treatment of these reagents a fourth (4) spec-

trum was measured under N₂ at 100°C (procedure B). Subsequently, the sample was heated up to 300°C and a fifth (5) spectrum was measured (procedure C). Finally, we switched to a 20 vol.% O₂ in N₂ atmosphere and a sixth (6) spectrum was measured (procedure D).

Difference spectra were generally obtained by the following procedure:

Every spectrum mentioned above (1–6) was measured against KBr at identical conditions and therefore already is a difference spectrum. In addition and according to the numbering (1–6) the subsequent procedure leads to four (A, B, C, D) final difference spectra. A = 3–2; B = 4–2; C = 5–1; D = 6–1.

The total gas stream was constant at 100 ml min⁻¹. For every run fresh catalyst and reference (KBr) were used. The detailed description of the DRIFTS cell and the whole experimental set up has already been listed [1].

2.3. Spectrometer

The experiments were carried out on an FTIR-spectrometer FTS175C with a MCT detector made by BIO-RAD with a praying mantis accessory from Harrick. Every shown spectrum is the average of 1000 scans.

3. Results and discussion

In all examinations under reaction gases OH-deformation bands appeared between 1600 and 1620 cm⁻¹. They indicate an abstraction of hydrogen during the adsorption of the applied probe molecules and thus the formation of surface-hydroxyl-groups. The intensity of these bands decreases with increasing temperature. Bands caused by OH-deformation vibrations of crystal water or water of constitution are between 1400 and 1420 cm⁻¹. In this range, one can often prove bands of negative intensity, which signify a loss of these types of water. The bands of the adsorbed species are partially overwhelmed by OH-vibration bands, complicating their detection.

Different adsorbates can be observed during the examination of both catalysts. They depend on the temperature and the composition of the gaseous

Table 2
 $\nu(\text{C}=\text{O})$ -bands of the adsorbates in the experiments with ACR and MAC^a

C=O-band in cm^{-1} ACR-experiment	C=O band in cm^{-1} MAC experiment	Temperature in $^{\circ}\text{C}$	Gas-phase
Cs₂H₂[PVMo₁₁O₄₀]			
1695 (1)	1735 (8)/1700 (6) or (7)	100	N ₂ /aldehyde
1722 (4)/1703 (3)	1731 (8)	100	N ₂
1777 (5)	1780 (10)	300	N ₂
1785 (5)/1742 (5)	1786 (10)	300	N ₂ /O ₂
Mo₉V₃W_{1,2}O_x			
1692 (1)	1732 (8)/1695 (6) or (7)	100	N ₂ /aldehyde
1727 (4)/1699 (3)	1731 (8)/1688 (6) or (7)	100	N ₂
1781 (5)/1718 (5)	–	300	N ₂
1792 (5)	1792 (10)	300	N ₂ /O ₂
1731 and 1712	1727 and 1716		Gaseous aldehyde
1781 and 1768	1764		Gaseous acid

^a The assignment of the bands to surface compounds refers to the numbers given in Figs. 1 and 2.

phase. The position of the C=O vibration bands of the aldehyde-adsorbates are presented in Table 2. The assignment of these bands to different surface species is given in Table 1, a numbering of the various surface species is given in the Figs. 1–4.

3.1. Acrolein

3.1.1. Acrolein on mixed oxide

A: Under a mixture of ACR/N₂ and at 100°C coordinatively bonded ACR (1) is present. In this case, the C=O vibration shifts to lower wavenumbers as compared to the gas phase, because the oxygen atom of the carbonyl group is involved in the

adsorption. Additionally, an anti-symmetrical and symmetrical carboxylic vibration as well as C–H deformation vibrations are recognisable (1551, 1442 and 1365 cm^{-1}) [3] resulting from a surface acrylic species (2). (see Fig. 5, left)

B: After flushing with nitrogen at 100°C two different acrolein adsorbates — a hydrogen-bonded ACR (3) and a carbonyl-bonded ACR (4) — are observed. Whether these were already present under ACR/N₂ is uncertain, considering the margin of error, since they are very close to the bands of gaseous ACR. A C=C band appears under ACR/N₂ (100°C) as well as under N₂ (100°C) at approximately 1615 cm^{-1} .

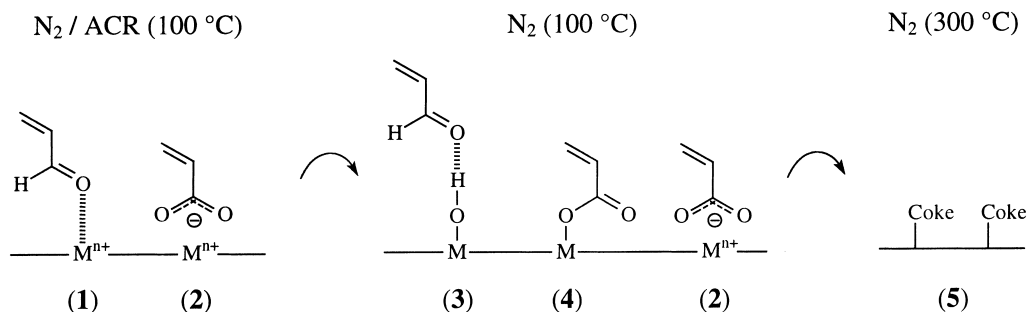


Fig. 1. Surface compounds of ACR at different gas-atmospheres and temperatures: (1): coordinatively-bonded ACR, (2): surface-acrylate, (3): hydrogen-bonded ACR, (4): carbonyl-bonded ACR, (5): coke-deposits. Species (2) can be detected on the Cs₂HPA only with low intensities.

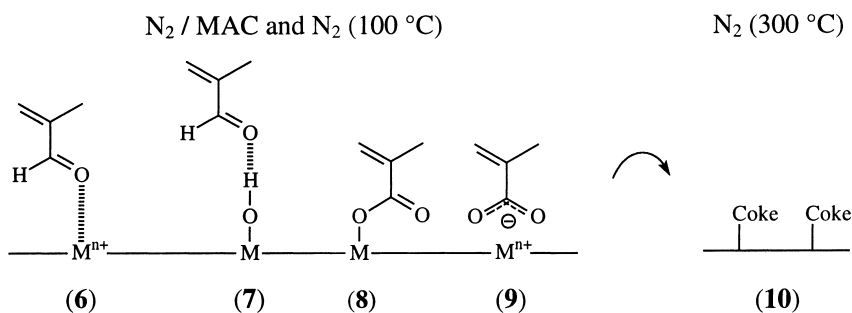


Fig. 2. Surface compounds of MAC at different gas-atmospheres and temperatures: (6): coordinatively-bonded MAC, (7): hydrogen-bonded MAC, (8): carbonyl-bonded MAC, (9): surface-methacrylate, (10): coke-deposits. On the Cs_2HPA , species (6) and (7) cannot be detected under N_2 at 100°C .

C: At 300°C under N_2 there are only the bands assignable to coke (5).

D: Switching to O_2/N_2 at 300°C shows no effect on the coke deposits. Beside the two $\text{C}=\text{O}$ bands (see Table 2) a broad band at 1599 cm^{-1} is observable, also induced by coke.

3.1.2. Acrolein on heteropolyacid salt

The treatment with ACR/N_2 at 100°C (A) as well as the subsequent N_2 -purge at the same temperature (B) produces no clearly detectable bands resulting from surface acrylic species (2) on Cs_2HPA . However, all other adsorbed species described above do appear analogously. The observations at 300°C under N_2 (C) and O_2/N_2 (D) do not differ from those made on MO. (see Fig. 5, right)

3.1.3. Discussion

Comparable adsorbates have been observed on MO and Cs_2HPA . Merely the surface-acrylate-

species (2) is weakly manifested on the Cs_2HPA . Serwicka et al. [7] postulated a mechanism for the formation of carbonyl-bonded ACR (4), in which no coordinatively bonded intermediates (1) occur. However, due to the observations in our work such intermediates are present on the Cs_2HPA .

3.2. Methacrolein

3.2.1. Methacrolein on mixed oxide

A: The treatment of the MO at 100°C with MAC/N_2 forms weak methacrylate-bands (9) at 1568 , 1456 and 1387 cm^{-1} . They are assigned to an anti-symmetrical carboxyl-, an anti-symmetrical CH_3 - and a combined symmetrical carboxylate- and CH_3 - deformation vibration [8]. This indicates that the methyl group has remained unchanged upon adsorption. Beside the carbonyl bonded MAC (8), a $\text{C}=\text{O}$ oxygen-bonded carbonyl group is observable on the catalyst. Due to the following observations

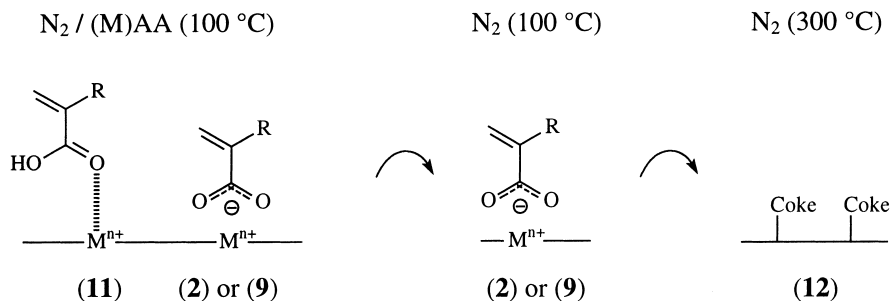


Fig. 3. Surface compounds of AA ($\text{R} = \text{H}$) and MAA ($\text{R} = \text{CH}_3$) at different gas-atmospheres and temperatures on the Cs_2HPA : (11): coordinatively-bonded acid, (2) or (9): surface-(meth)acrylate, (12): coke-deposits.

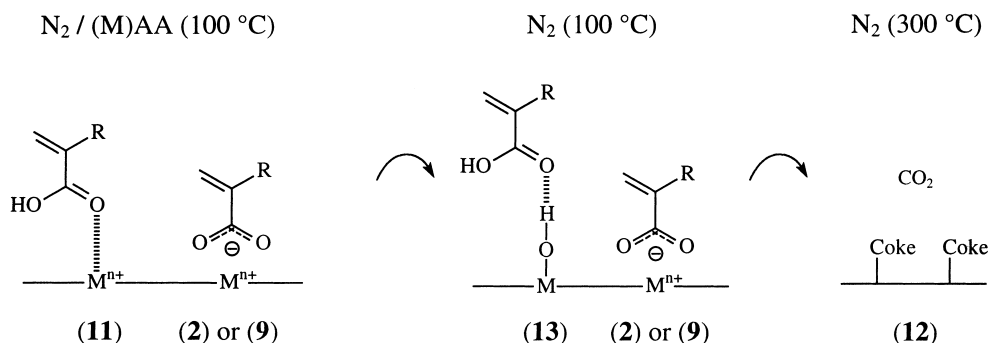


Fig. 4. Surface compounds of AA ($R = H$) and MAA ($R = CH_3$) at different gas-atmospheres and temperatures on the MO: (11): coordinatively-bonded acid, (2) or (9): surface-(meth)acrylate, (13): hydrogen-bonded acid, (12): coke-deposits.

this could be also a hydrogen-bonded MAC (7). (see Fig. 6, left)

B: While purging with N_2 at 100°C , the adsorbates are preserved. Only the $C=O$ band of the aldehyde, which is bonded over the oxygen of the $C=O$ group, is shifted to lower wave numbers but still it is clearly visible. Considering the observation made with ACR, MAC is presumably bonded over hydrogen bridges (7).

C: At 300°C it is obvious that a broad coke-band exists under N_2 at 1530 cm^{-1} .

D: Under O_2/N_2 at 300°C a narrow coke-band is assignable to 1792 cm^{-1} and a broad one at ca. 1570 cm^{-1} .

3.2.2. Methacrolein on heteropolyacid salt

A: With MAC/ N_2 at 100°C bands appear, which are comparable to those on MO, but here the methacrylate-bands are less intensive. (see Fig. 6, right)

B: At 100°C and under N_2 the band, which represents the oxygen-bonded $C=O$ group of the alde-

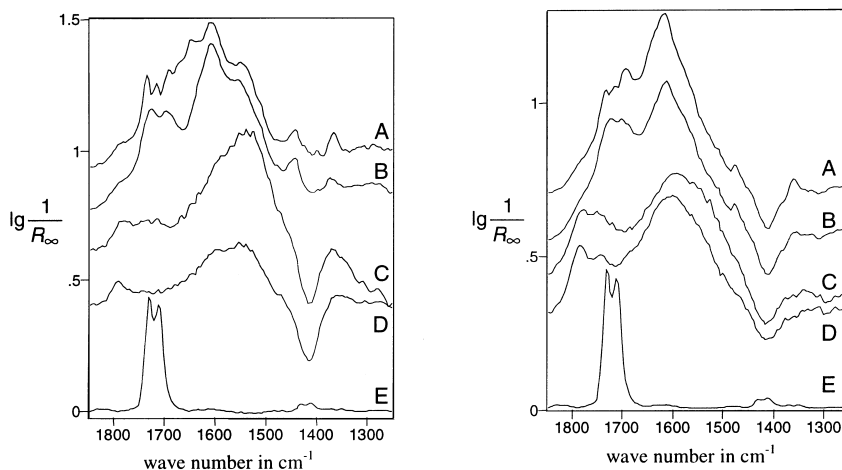


Fig. 5. Difference-spectra between the catalyst while treating it with different gases and the catalyst at the beginning of the experiment under O_2/N_2 . **A:** 5 vol.% ACR in N_2 at 100°C , **B:** N_2 -purge at 100°C , **C:** N_2 -purge at 300°C , **D:** O_2/N_2 -purge at 300°C , **E:** gaseous ACR over KBr at 100°C . The spectra are vertically shifted for better visualisation. E has been compressed for the same reason. Left: $Mo_9V_3W_{1.2}O_x$. Right: $Cs_2H_2PVMo_{11}O_{40}$.

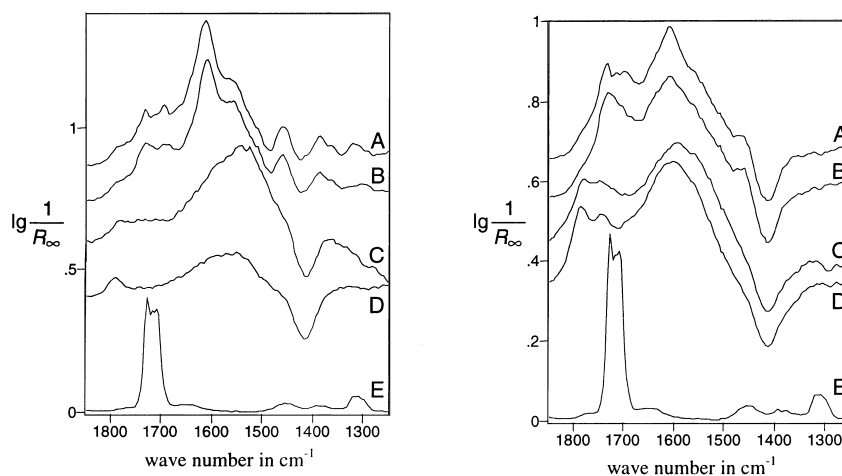


Fig. 6. Difference-spectra between the catalyst while treating it with different gases and the catalyst at the beginning of the experiment under O_2/N_2 . **A**: 5 vol.% MAC in N_2 at $100^\circ C$, **B**: N_2 -purge at $100^\circ C$, **C**: N_2 -purge at $300^\circ C$, **D**: O_2/N_2 -purge at $300^\circ C$, **E**: gaseous MAC over KBr at $100^\circ C$. The spectra are vertically shifted for better visualisation. **E** has been compressed for the same reason. Left: $Mo_9V_3W_{1.2}O_x$. Right: $Cs_2H_2PVMo_{11}O_{40}$.

hyde vanishes, while the remaining bands are preserved. Regarding the observation made with ACR, it is evident, that under MAC/ N_2 methacrolein is bonded coordinatively (**6**).

C: At $300^\circ C$ and purging with N_2 , only two bands at 1780 and 1749 cm^{-1} are found, which again represent, together with the band at 1588 cm^{-1} , coke-deposits (**10**).

D: After switching to O_2/N_2 ($300^\circ C$) the coke-bands remain with a little shift in their peak positions.

3.2.3. Discussion

On MO more intensive methacrylate-bands appear, compared to those observable on Cs_2HPA . Furthermore, MAC is presumably bonded on MO over hydrogen bridges (**7**), while on Cs_2HPA only coordinatively bound MAC is found (**6**).

3.3. Acrylic acid

3.3.1. Acrylic acid on mixed oxide

A: The band at 1692 cm^{-1} is assigned to a $C=O$ vibration of AA, which is coordinatively bound to the catalysts via the oxygen of that group (**11**). The band at 1675 cm^{-1} will be assigned either to a $C=C$ vibration of the same adsorbate or to a $C=O$ vibration of another species, which is bonded analogously

to the first, but presumably at a different site. The acrylate-bands (**2**) are found at 1638 , 1542 , 1442 , 1372 and 1275 cm^{-1} . (see Fig. 7, left)

B: At $100^\circ C$ and under N_2 only a shoulder at 1669 cm^{-1} remains from the weakly bonded surface-species (**11**). A shoulder at 1753 cm^{-1} , which is shifted to lower wave numbers due to gas-phase bands of AA (1781 and 1765 cm^{-1}), could be caused by a hydrogen-bridge bond of AA (**13**) on the oxygen surface. The acrylate-bands remain unchanged in their peak positions and intensity.

C: At $300^\circ C$ and under N_2 a broad band is visible at 1546 cm^{-1} , which belongs, together with the shoulder at 1785 cm^{-1} , to coke-deposits. In addition, a release of CO_2 ($> 1800\text{ cm}^{-1}$) appears. The required oxygen has either to originate from the catalysts or some adsorbates. Since this effect is only observed with both acids and not with the aldehydes, the CO_2 release probably has its origin in the acid adsorbates.

D: The O_2 addition at $300^\circ C$ lead to a brief intermediate rise in the CO_2 release ($> 1800\text{ cm}^{-1}$). This is due to a combustion of the adsorbates. Subsequently no more bands are verifiable.

3.3.2. Acrylic acid on heteropolyacid salt

A: At $100^\circ C$ and under AA/ N_2 a shoulder at 1714 cm^{-1} indicates a coordinatively bonded AA

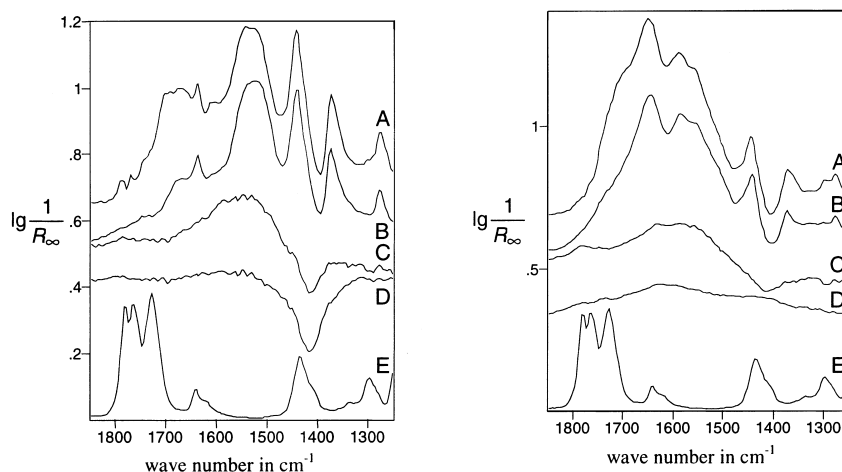


Fig. 7. Difference-spectra between the catalyst while treating it with different gases and the catalyst at the beginning of the experiment under O_2/N_2 . **A**: 2 vol.% AA in N_2 at $100^\circ C$, **B**: N_2 -purge at $100^\circ C$, **C**: N_2 -purge at $300^\circ C$, **D**: O_2/N_2 -purge at $300^\circ C$, **E**: gaseous AA over KBr at $100^\circ C$. The spectra are vertically shifted for better visualisation. **E** has been compressed for the same reason. Left: $Mo_9V_3W_{1.2}O_x$. Right: $Cs_2H_2PVMo_{11}O_{40}$.

(11). The bands at 1651, 1589, 1558 (shoulder), 1445, 1373, 1276 and 1239 cm^{-1} originate from a surface acrylate (2). They correlate very well with the peak positions that were observed by Morozova et al. [8] for the adsorption of AA on a cobalt-molybdate. The assignment of the acrylate-vibrations follows according to Table 1. (see Fig. 7, right)

B: After switching to N_2 ($100^\circ C$), the weakly bonded species (11) vanishes. All other bands remain with a maximum shift of 5 cm^{-1} .

C: At $300^\circ C$ and under N_2 bands of coke-deposits are visible at 1782 and 1560 cm^{-1} .

D: The O_2 addition at $300^\circ C$ leads to a short time rise in the CO_2 release. After that, only low quantities of coke-deposits are detectable.

3.3.3. Discussion

On both catalysts coordinatively bonded AA (11) and surface-acrylates (2) are found. With MO, at $100^\circ C$ and under N_2 AA is found to be adsorbed involving hydrogen bridges (13). Furthermore, at $300^\circ C$ and under N_2 a partial combustion of the adsorbates occur accompanied by a CO_2 release.

3.4. Methacrylic acid

3.4.1. Methacrylic acid on mixed oxide

A: At $100^\circ C$ under MAA/ N_2 bands of a methacrylate (9) at 1526, 1460, 1423, 1379 and

1245 cm^{-1} can be identified. Beside two weak $C=O$ bands of negative intensity at 1765 and 1715 cm^{-1} belonging to gaseous MAA, a $C=O$ band at 1700 cm^{-1} which is assigned to coordinatively-bonded MAA (11), is visible. A band at 1675 cm^{-1} either belongs to a $C=C$ vibration of the same adsorbate or to a $C=O$ vibration of another analogously bonded MAA (possibly at different sites). Regarding the high frequency of this band, the assignment should be favoured. (see Fig. 8, left)

B: After switching to N_2 at $100^\circ C$ only the bands assigned to methacrylate have the same intensities. A $\nu_{C=C}$ band, that also exists under MAA as a shoulder at the OH-band at 1615 cm^{-1} , now becomes clearly visible at 1636 cm^{-1} . A weak band at 1735 cm^{-1} can be assigned to a hydrogen-bonded MAA (13). Furthermore, another weak band is detected at 1794 cm^{-1} originating from coke-deposits already formed at this stage.

C: The bands of the methacrylates can be no longer identified after a N_2 -purge at $300^\circ C$. At 1546 cm^{-1} a broad band becomes visible. Together with a band at 1779 cm^{-1} it is assigned to coke-deposits. CO_2 bands ($> 1800\text{ cm}^{-1}$) can be detected exactly like those in the experiment with AA. They indicate the combustion of the adsorbates. Therefore, the oxygen required is presumably supplied from the adsorbates, too.

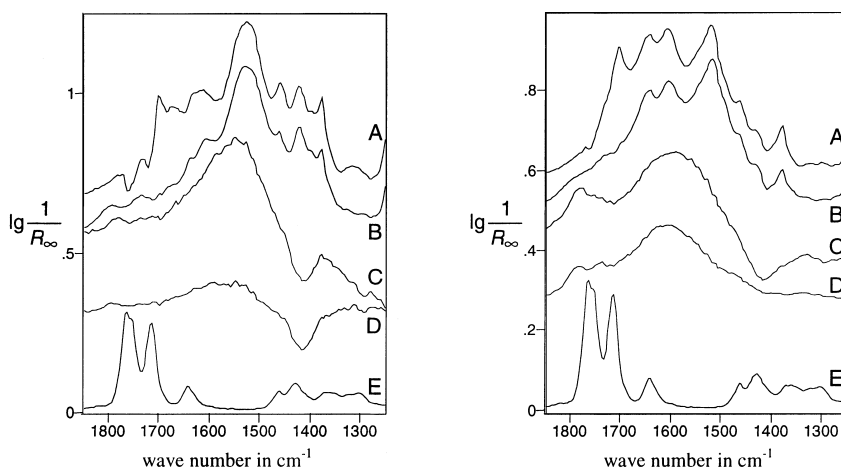


Fig. 8. Difference-spectra between the catalyst while treating it with different gases and the catalyst at the beginning of the experiment under O_2/N_2 . **A**: 2 vol.% MAA in N_2 at $100^\circ C$, **B**: N_2 -purge at $100^\circ C$, **C**: N_2 -purge at $300^\circ C$, **D**: O_2/N_2 -purge at $300^\circ C$, **E**: gaseous MAA over KBr at $100^\circ C$. The spectra are vertically shifted for better visualisation. **E** has been compressed for the same reason. Left: $Mo_9V_3W_{1.2}O_x$. Right: $Cs_2H_2PVMo_{11}O_{40}$.

D: After switching to O_2/N_2 at $300^\circ C$ the CO_2 production is increased for a short period. The intensity of the CO_2 band quickly diminishes to the value observed under N_2 at $300^\circ C$. The coke-bands, especially the broad one at 1546 cm^{-1} , clearly lose intensity.

3.4.2. Methacrylic acid on heteropolyacid salt

A: Under MAA/ N_2 at $100^\circ C$ bands of a methacrylate (**9**) can be detected at 1519, 1464, 1432, 1379 and 1245 cm^{-1} . With exception of the first band they coincide with the values, that were found by Morozova et al. [8] for the adsorption of the MAA on a cobalt-molybdate. A C=C vibration of an adsorbate is found at 1642 cm^{-1} . In the C=O region, a band at 1704 cm^{-1} is detected, that is assigned to coordinatively-bonded MAA (**11**). (see Fig. 8, right)

B: Species (**11**) can no longer be detected under N_2 at $100^\circ C$. The remaining bands show insignificant band shifts. The band intensities remain at the same level.

C: At $300^\circ C$, a broad band at 1590 cm^{-1} is detected under N_2 . It can be assigned to coke-deposits together with a band at 1782 cm^{-1} .

D: By switching to O_2/N_2 at $300^\circ C$ the CO_2 production is increased for a short period of time. However, the coke-bands, that are now located at

1782, 1738 and 1600 cm^{-1} , do not completely burn off.

3.4.3. Discussion

By treating the catalysts with MAA, effects appear analogous to those observed during the treatment with AA. The MAA-catalyst bond seems to be tighter and better stabilised on the Cs_2HPA than on the MO.

3.5. Discussion of the differences between acrolein and methacrolein

Table 2 shows that both ACR- and MAC-adsorption-species have comparable absorption bands in the C=O region. Therefore, it can be postulated that adsorbates appear during MAC-conversion analogous to those suggested by Andrushkevich [3] for ACR-adsorption in Table 1 (also see Figs. 1 and 2). Petzoldt [9] found that the conversions of ACR and MAC can be described with the same reaction-order in the kinetic model. From this fact he concluded that the reaction-mechanism of the selective oxidation to the corresponding unsaturated carboxylic acids is the same for both reactions. This is in agreement with our observations. Böhling [10] explained the difference in the selectivity of the partial oxidation of ACR and MAC on the MO with a MAC-adsorp-

tion via allyl species. In this work, we can detect an anti-symmetrical CH_3 -vibrational band upon the adsorption of MAC and MAA on both catalysts at 100°C . This could be an indication against an H-abstraction at the MAC-CH_3 - group.

3.6. Discussion of the differences between acrylic acid and methacrylic acid

Differences in adsorption could not be found between the two acids. According to Morozova et al. [8] the absorption bands of the MAA at 1464 or 1460 cm^{-1} can be assigned to an anti-symmetrical CH_3 vibration. The band at 1379 cm^{-1} belongs to a combined symmetrical C=O- and CH_3 - vibration. From these facts the methyl-group should remain intact during the adsorption of MAA at 100°C , but we cannot exclude the corresponding allyl species.

4. Conclusions

We investigated the partial oxidation of unsaturated aldehydes to the corresponding carboxylic acids on two different catalyst systems via a new DRIFTS measuring cell, in which both the catalyst powder and the reference (KBr) were in the same reaction chamber.

The first intermediate adsorbate formed is not dependent on the probe molecules and the catalyst systems under investigation. It is a species in which the oxygen atom of the C=O- group is connected to coordinatively unsaturated metal cations on the catalyst surface (Lewis acid centres) [3]. In the corresponding IR-spectra, this adsorbate can be recognised by a shift of the C=O- vibration band to lower frequencies. It is a relatively weak bonded adsorbate, which can normally only be proven under reaction gas. It disappears after the switch from reaction gas to inert gas.

In the case of ACR, surface species could be detected, which are comparable to those postulated by Andrushkevich et al. [3]. Our observations are almost identical. They differ only in the bonding strengths of the single adsorbates, which could be a result of the different surface acidity of the catalysts under investigation.

In the case of MAC it could be shown that the methyl group of the examined adsorbates remained intact under all experimental conditions. Therefore, the reaction mechanism of the selective oxidation of these educts should be the same for both ACR and MAC.

The experiments dealing with the adsorption of the acids (AA, MAA) showed, that the main adsorbate is a surface (meth)acrylate species. These adsorbates can be converted to carbon dioxide on the MO catalyst without the presence of gas phase oxygen; they are stable using the Cs_2HPA catalyst.

The investigations showed that the newly developed DRIFTS measuring cell is suitable for the reliable detection of adsorbates, under both reaction- and inert gas.

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