Selective oxidation of toluene and *o*-xylene on MgF_2-supported monolayer vanadium oxide catalyst

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Information on the reactions of selective oxidation of toluene and *o*-xylene on monolayer V_2O_5/MgF_2 catalyst was obtained using IR spectroscopy. Also adsorption of aldehyde derivatives of these reagents, i.e. benzaldehyde and *o*-tolualdehyde, was investigated in order to identify intermediate species, which were formed during the oxidation process. The measurements were carried out at different temperatures, under conditions similar to that of the catalytic reaction. On the surface of the catalyst many intermediate species, as aldehyde-like, keton-like and benzoate species, were detected. On the basis of the data obtained the mechanism of these reactions has been proposed.

Keywords: Selective oxidation; toluene; *o*-xylene; benzaldehyde; *o*-tolualdehyde

1. Introduction

Selective oxidation of hydrocarbons over oxidic vanadia catalysts was extensively studied in many papers. A great part of them were connected with kinetic investigations, which have been made in order to obtain information on the mechanism of oxidation reactions. Additional and even more direct evidence for the mechanism of catalytic reactions can often be obtained by investigation of an interaction of reactants and products with the catalyst surface on the basis of IR spectra. For instance, this method was used to identify the intermediate species in oxidation reactions of alkenes, alkynes [1,2] and alcohols [3–5]. So far only a few publications concerning the IR study aiming at identification of surface structures which form during oxidation of aromatic hydrocarbons have appeared. Niwa et al. [6,7] investigated the adsorption of toluene and xylenes on V_2O_5/Al_2O_3 catalyst, as well as the adsorption of the corresponding aldehydes on the uncovered Al_2O_3. These authors performed the experiments at relatively high temperature (400°C), and that is why only the bands originating from adsorbed benzoate species were observed in IR spectra. No information was given on the structure of the intermediate species and reaction paths.

Hengstum et al. [8] studied by IR method the mechanism of oxidation of toluene

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and *o*-xylene over V_2O_5/TiO_2 catalyst under conditions similar to that of catalytic reaction. Interaction of these hydrocarbons and their oxidation products with the surface of the support resulted in formation of adsorbed aldehydes, carboxylate-like and benzoate species observed in the IR spectra. These species were intermediate complexes in the reaction of oxidation of toluene and *o*-xylene, and on that basis the authors have proposed the mechanism of these reactions.

In the present work the IR method was used to study the selective oxidation of toluene and *o*-xylene over vanadium oxide monolayer supported on MgF_2 catalyst.

2. Experimental

2.1. PREPARATION OF CATALYSTS

The V_2O_5/MgF_2 catalysts were prepared by precipitation from a solution of ammonium metavanadate onto a suspension of freshly precipitated magnesium fluoride. Details of the experimental procedure were described in ref. [9]. The sample was hereafter denoted by the symbol MFV_5, where 5 equaled the atomic ratio V/Mg expressed as a percent. The surface area as determined by BET method from the adsorption isotherm of nitrogen at liquid nitrogen temperature amounted to 55 m^2/g. The results of structural studies of V_2O_5/MgF_2 catalysts by XRD, XPS, EPR and IR are described in ref. [10].

2.2. INFRARED SPECTRA

The IR spectra were recorded by use of a Brucker IFS 113 v spectrometer in the range 1300–1800 cm^{-1}, using a vacuum cell equipped with sodium chloride windows. The catalysts in the form of compressed wafers were outgassed under a pressure of 10^{-3} Pa at 623 K for 3 h. Several portions of oxygen were introduced successively during this period. Then samples were cooled to room temperature.

Subsequently, the reactant mixture obtained by saturating air with toluene or *o*-xylene at a temperature of 290 K was introduced into the evacuated infrared cell at different temperatures (20, 50, 90, 120, 200°C). After adsorption on the surface of the catalyst during 0.5 h, the system was outgassed for 5 min and the spectrum was recorded.

In the experiments with benzaldehyde and *o*-tolualdehyde, only the vapours of adsorbates were introduced into the evacuated infrared cell. After adsorption on the surface of the catalyst at different temperatures (20, 50, 90, 120, 200°C) during 0.5 h, the system was outgassed for 5 min and the spectrum was recorded.

3. Results and discussion

Our previous study on the structure of MgF_2-supported vanadium oxide catalysts has revealed [10] that at low vanadium oxide loadings the isolated VO_4 tetrahedra appear at the surface, which undergo polymerization to form chains of $(VO_3)_n$ tetrahedra of the metavanadate type, or trigonal bipyramid islands. At higher concentrations polyvanadate species with octahedrally coordinated vanadium were deposited on the surface. These polymerized species were responsible for the activity of V_2O_5/MgF_2 for redox reactions [11], which was observed only at higher vanadate coverage.

In the present work we tried to explain the mechanism of the oxidation of toluene and *o*-xylene on V_2O_5/MgF_2 catalyst on the basis of adsorption experiments. In order to do this we have employed IR spectroscopy, and on the basis of the performed study, some information about the nature of intermediate species which form during this process has been found. The results obtained after adsorption of aldehyde derivatives of these reagents, i.e. benzaldehyde and *o*-tolualdehyde, were helpful for identification of the intermediate species formed during the oxidation reactions. Our investigations were performed in the range of infrared adsorption bands between 1300–1800 cm^{-1}.

In fig. 1 the IR spectra of toluene recorded during selective oxidation in gas phase on MFV_5 sample, are presented. The experiments were performed at a temperature range of 20– 200°C. The employment of such low temperatures was necessary to obtain information on intermediate products formed in the first reaction period. The conditions as described above, also made possible obtaining more clear

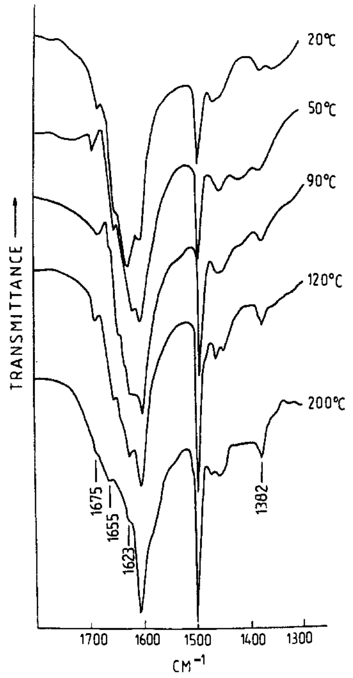


Fig. 1. IR spectra of toluene adsorbed at the temperature range 20–200°C, and subsequently oxidized on MFV_5 catalyst (after 0.5 h of the reaction).

results than those at the catalytic reaction temperatures [12]. After all, the bands in the range between 1200 and 1380 cm^{-1}, originating from unknown contaminants irreversibly adsorbed on NaCl vacuum cell windows [8] were observed.

A typical benzene ring vibration band at about 1600 cm^{-1} was observed in IR spectra at all temperatures. This indicates, that during the adsorption/oxidation process of aromatic hydrocarbons the benzene ring remained unaffected. The frequencies of the vibration bands characteristic of the interaction of the surface of the catalyst with the side chain of the aromatic hydrocarbon, observed during experiments are given in table 1. After adsorption/oxidation of toluene at the temperature of 20°C apart from the band at ~ 1600 cm^{-1} many additional bands (~ 1400, ~ 1500, ~ 1630, 1650 and ~ 1670 cm^{-1}) were observed. When different temperature conditions of adsorption were employed, only the band at ~ 1600 did not change its intensity. With the increase of temperature the intensity of the bands at ~ 1630, ~ 1650 and ~ 1670 cm^{-1} decreased. At the same time the intensity of the band at ~ 1500 increased significantly, and at the temperature of 200°C it became the biggest one. Similar behaviour was observed for the band at ~ 1400 cm^{-1}, but the intensity of this band was lower.

In order to attribute an appropriate structure to each band the adsorption of benzaldehyde was used. The choice of this compound was due to the fact that it is one of the side products of the oxidation reaction of toluene. Adsorption of benzaldehyde did not produce two characteristic bands, of high intensity at 2700 and 2850 cm^{-1}, originating from aldehyde C–H bonds, and stretching vibrations bands of C=O at around 1710 cm^{-1}, characteristic of free aldehyde group. Deficiency of the bands between 2700 and 2850 cm^{-1} strongly indicates that adsorbed aldehyde

Table 1
Position of characteristic infrared adsorption bands (in cm^{-1}) observed during adsorption of benzaldehyde and adsorption/oxidation of toluene on V_2O_5/MgF_2 catalyst at different temperatures

T (°C)	1400	1500	1630	1650	1670	1700
toluene						
20	1381	1495	1627	1652	1673	–
50	1379	1496	1618	1650	1679	–
90	1381	1496	1626	1650	1679	–
120	1382	1496	1626	1652	1679	–
200	1382	1496	1623	1655	1675	–
benzaldehyde [a]						
20	1398	1494	1635	1655	–	1688
50	1395	1491	1623	1655	–	1691
90	1393	1489	1623	1658	–	1694
120	1397	1492	1621	1660	–	1694
200	1400	1492	1623	1657	–	1694

[a] According to the literature the band at ~ 1400/ ~ 1500 originates from the benzoate species, and the others from the aldehyde-like or keton-like species of different structures, see fig. 6.

species did not contain typical C–H bonds. Hence, not only the carbonyl group but also the hydrogen atom interacted with the surface of the vanadia catalyst.

After adsorption of benzaldehyde at room temperature, intensive bands in the range of 1398–1688 cm^{-1} (fig. 2, table 1) were observed. Namely, in this region the bands at ~ 1630, ~ 1650 and ~ 1700 cm^{-1} were observed, and they decreased with increasing temperature. Simultaneously in the same region the bands at ~ 1400 and ~ 1500 cm^{-1} were recorded, which showed the reverse trend, i.e. the highest intensity for these bands was observed at a temperature of 200°C. A similar view of the IR spectra appeared after adsorption of benzaldehyde on the V_2O_5/TiO_2 catalyst [8].

The bands observed in this work had somewhat different frequencies than those registered for V_2O_5/TiO_2 [8]. The reason for the shift in frequency was probably the employment of MgF_2 as a support. In our investigation, after adsorption of benzaldehyde (fig. 2) on MFV_5, the bands recorded at around 1700 cm^{-1} were most probably produced by coordinatively adsorbed aldehyde or keton species. The authors of ref. [5], who studied oxidation of alcohols over vanadium–titanium oxide, and Hengstum et al. [8] investigated the adsorption of benzaldehyde and *o*-tolualdehyde over V_2O_5/TiO_2. They all have reported similar structures. The rest of the bands (table 1, fig. 2) we attributed, as in ref. [8], to the other adsorbed hydrocarbon species.

The results given in fig. 2 suggest that with the increase of the adsorption tem-

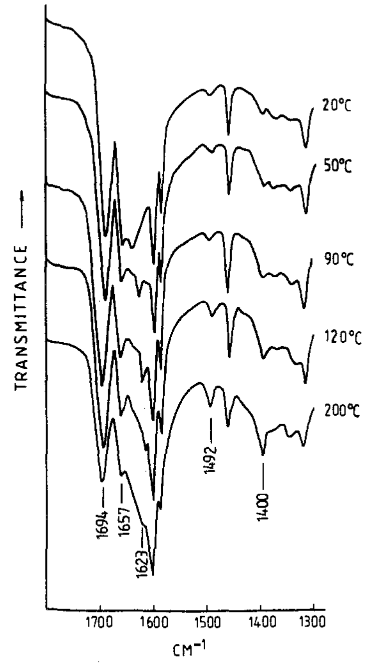


Fig. 2. IR spectra of benzaldehyde adsorbed on MFV_5 catalyst at the temperature range 20–200°C.

perature coordinatively adsorbed complexes with the bands at ~ 1630, ~ 1650, ~ 1700 cm^{-1} (after adsorption of benzaldehyde) converted themselves to another species with a band at about 1400/1500 cm^{-1}. These bands were found to be due to asymmetric and symmetric vibrations of the benzoate group. Similar bands have been recorded by many investigators after adsorption of toluene, benzaldehyde or benzoate acid on V_2O_5/oxide catalysts [6,7,13]. Frequencies of these bands depend on the catalyst used in the adsorption experiments.

One can see the big similarity between IR spectra obtained after adsorption/oxidation of toluene and adsorption of benzaldehyde on the surface of the MFV_5 catalyst. In both cases bands with similar IR frequencies (table 1) were observed. Only the band at ~ 1670 cm^{-1} present in the IR spectrum after oxidation of toluene was not recorded after adsorption of benzaldehyde under identical conditions. The comparison between the spectra of adsorption/oxidation of both compounds (figs. 1 and 2, table 1) revealed also an agreement in the changes of the intensities of each band. This indicates that in both cases similar species were present on the surface of the catalyst. (It should be noticed that the species attributed to the band at ~ 1670 cm^{-1} observed after adsorption/oxidation of toluene, during adsorption of benzaldehyde was also present, but due to the short lifetime the band originating from this surface complex was not observable in the IR spectrum.) Thus in the adsorption/oxidation process of aromatic hydrocarbons similar intermediate complexes were formed on the surface of the catalyst.

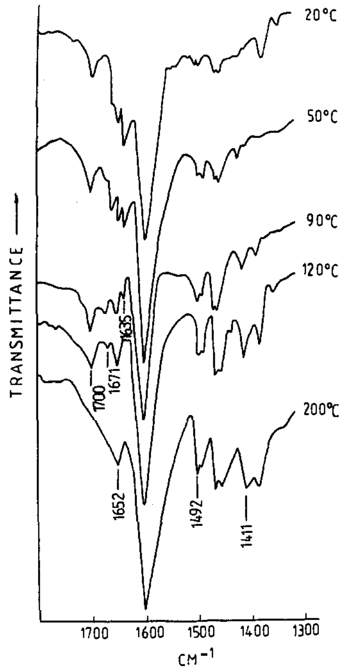


Fig. 3. IR spectra of *o*-xylene adsorbed at the temperature range 20–200°C, and subsequently oxidized on MFV_5 catalyst (after 0.5 h of the reaction).

The same method of study as in the case of toluene and benzaldehyde was employed for the oxidation reaction of *o*-xylene. During adsorption/oxidation of *o*-xylene on the MFV_5 catalyst (fig. 3, table 2) the band at ~ 1600 cm^{-1} originating from the vibrations of the benzene ring was observed. The intensity of this band did not change with varying temperatures. Furthermore the bands at ~ 1420, ~ 1500, ~ 1630, ~ 1670 and ~ 1700 cm^{-1} were also observed. Similarly to the oxidation of toluene changes of the intensity of these bands with growth of temperature were observed. The bands at ~ 1630 and ~ 1670 cm^{-1} significantly decreased and finally disappeared at higher temperatures. The band at ~ 1700 cm^{-1} seemed unchanged under various conditions, but at the temperature of 200°C it vanished. On the other hand the bands at ~ 1400 and ~ 1500 cm^{-1} were enhanced with the increase of temperature. For the band at ~ 1650 cm^{-1} it was very difficult to specify the trend of the change in intensity.

Adsorption of *o*-tolualdehyde (fig. 4, table 2) proceeded in the same way as the adsorption of benzaldehyde. After adsorption of *o*-tolualdehyde the band originating from the C=O of the free aldehyde group (~ 1700 cm^{-1}) and typical bands originating from the C–H bonds (2700–2850 cm^{-1}) were not observed. The band at ~ 1700 cm^{-1} shown in fig. 4 originated rather from the intermediate products formed during the adsorption process, than from the C=O vibrations. This was concluded from the decrease of intensity of this band till it decayed at a temperature of 200°C, while the band originating from the C=O group is usually sharp and very intensive.

Adsorption of *o*-tolualdehyde at room temperature brought the bands in the range of 1490–1710 cm^{-1}. At higher temperatures also appeared the band at ~ 1400 cm^{-1}. Contrary to the adsorption of *o*-xylene, in this case the bands at

Table 2
Position of characteristic infrared adsorption bands (in cm^{-1}) observed during adsorption of *o*-tolualdehyde and adsorption/oxidation of *o*-xylene on V_2O_5/MgF_2 catalyst at different temperatures

T (°C)	1400	1500	1630	1650	1670	1700
xylene						
20	1420	1498	1636	1650	1671	1700
50	1419	1497	1636	1652	1671	1700
90	1407	1496	1635	1658	1675	1700
120	1410	1496	1637	1652	1671	1700
200	1411	1492	–	1652	–	–
o-tolualdehyde						
20	–	1490	1623	–	–	1710
50	–	1488	1623	–	–	1708
90	1396	1490	1632	–	–	1708
120	1396	1488	1639	–	–	1705
200	1396	1489	–	–	–	–

[a] According to the literature the band at ~ 1400/ ~ 1500 originates from the benzoate species, and the others from the aldehyde-like or keton-like species of different structures, see fig. 6.

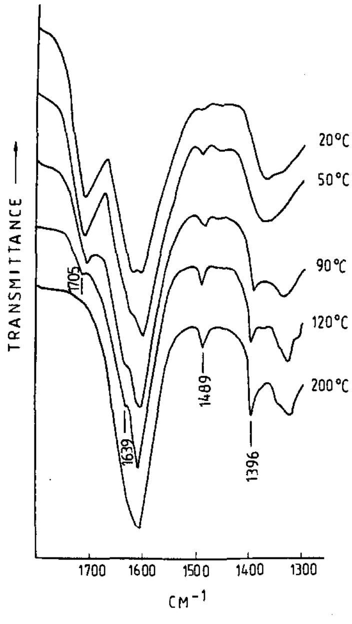


Fig. 4. IR spectra of *o*-tolualdehyde adsorbed on MFV_5 catalyst at the temperature range 20–200°C.

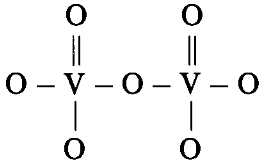
~ 1650 and ~ 1670 were not observed, which was probably caused by the short lifetime of both species attributed to these bands. The bands presented in fig. 4 changed intensity at different adsorption temperatures. The bands at ~ 1630 and ~ 1700 cm^{-1} decreased, while the others (~ 1400 and ~ 1500 cm^{-1}) increased when the temperature of the process grew up. As in the case of the adsorption of benzaldehyde, following the changes of the intensity of appropriate bands to which the species of different structures could be attributed [8], we concluded that with the growth of the adsorption temperature one kind of the adsorbed species was converted into the other (decrease of the intensity of the bands at ~ 1630 and ~ 1700 cm^{-1}, and increase of the bands at ~ 1400 and ~ 1500 cm^{-1}). Comparing the results of the IR study of adsorption/oxidation of *o*-xylene and adsorption of *o*-tolualdehyde, one can say that as in the case of toluene and benzaldehyde bands of similar frequencies appeared, which indicated that similar intermediate complexes were present by both the oxidation of *o*-xylene and adsorption of *o*-tolualdehyde. Furthermore a good agreement of the trend of the changes of intensities of each bands was also observed.

Analysis of the changes of intensities of respective bands in dependence on the temperature of the oxidation processes of toluene and *o*-xylene on the MFV_5 sample was useful for estimation of the reaction mechanism of these compounds. On the basis of literature data [8] it was possible to attribute to the appropriate IR bands observed after adsorption of benzaldehyde and *o*-tolualdehyde on the V_2O_5/

MgF_2 catalyst the intermediate complexes with different structures. The bands with similar IR intensities, which means similar species, were observed after adsorption/oxidation of toluene and *o*-xylene on this catalyst. The changes of intensities of the bands with the growth of temperature gave the view of the changes that the species underwent on the surface of the catalyst. The decrease of the intensity of some bands and the increase of the others was found to be due to the conversion of the less stable complexes into other complexes, more stable under current conditions. In other words, with growth of the temperature the equilibrium of the reaction was shifted towards the benzoate species ($\sim$ 1400/1500 cm^{-1}). So the recorded species showed the individual steps of the reactions in a "slow motion", i.e. also the steps of the reaction which are difficult to see or cannot be observed under normal reaction conditions because of the fast transformations of the respective structures into the others. On the basis of the results obtained for adsorption/oxidation of toluene and *o*-xylene we have tried to explain the mechanism of these reactions.

The observation of the change of intensity of the respective bands in dependence on the temperature of the oxidation process of toluene and *o*-xylene over MFV_5 sample and the data on the frequency of the IR vibrations attributed to different intermediate species on V_2O_5/TiO_2 [8], made it possible to propose a mechanism for these reactions on V_2O_5/MgF_2 catalyst.

On the basis of our previous work, in which the structure of V_2O_5/MgF_2 was studied [10], it is known, that the MFV_5 surface is covered by a $(VO_3)_n$ tetrahedrons layer of metavanadate type or trigonal bipyramid islands. Thus, it can be concluded, that monolayer islands of these surface species give active sites for oxidation of hydrocarbons. Characteristic elements of such monolayers are:



$$\begin{array}{ccccccccc} & & O & & & & O & & \\ & & \| & & & & \| & & \\ O & - & V & - & O & - & V & - & O \\ & & | & & & & | & & \\ & & O & & & & O & & \end{array}$$

with the bridging oxide ions playing the role of active sites [14] which oxygen ions are inserted into the hydrocarbon molecule during the oxidation reaction. In fig. 5 such $(VO_3)_n$ tetrahedrons adsorbed on MgF_2 surface at sites with a positive charge are presented. Species a at the [001] crystal plane of MgF (fig. 5A) is formed as an effect of the polymerization of VO tetrahedrons located on two coordinatively unsaturated (cus.) Mg ions (after removal of OH groups with $-1/5$ electric charge) with species adsorbed on one Mg_{cus} ion (after removal of OH groups with $-3/5$ electric charge) [10]. However, at [110] crystal plane (fig. 5B) the $(VO_3)_n$ tetrahedrons are produced by association of two VO_4 tetrahedrons coordinated with two Mg_{cus} ions (after removal of OH groups with $-1/5$ electric charge) with the tetrahedrons located on two other Mg_{cus} ions (after removal of hydroxyl groups with $-2/3$ electric charge) – species b. On this plane there can also occur c type structures, formed in the polymerization process of VO_4 tetrahedrons of which top oxy-

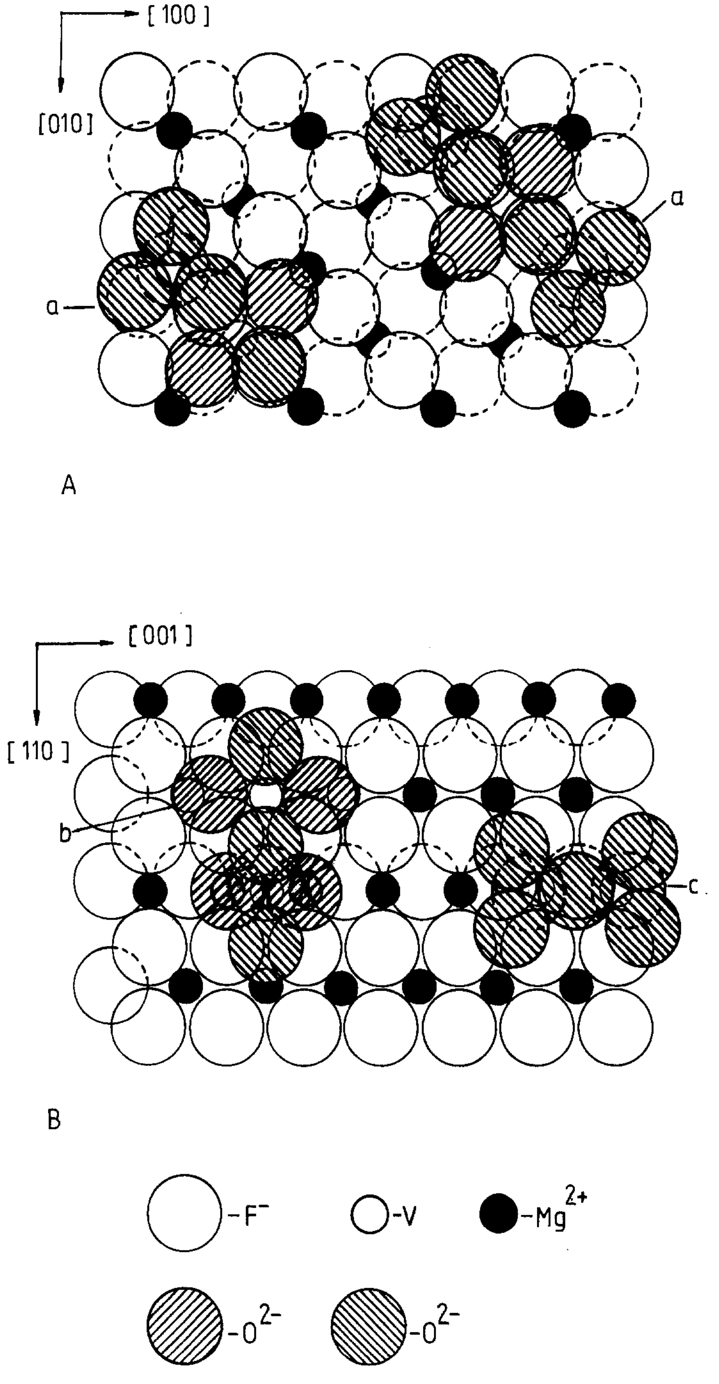


Fig. 5. Tetrahedrons of $(VO_3)_n$ located on the MgF_2 surface: (A) at crystal plane [001], (B) at crystal plane [110].

gen ions are located on Mg_{cus} ions (after removal of hydroxyl groups with −2/3 electric charge).

On the above described $(VO_3)_n$ surface complexes the oxidation process of toluene and *o*-xylene can proceed. At the first step of the reaction a hydrogen atom of the methyl group of a hydrocarbon is abstracted [8], and then the created radical is adsorbed on vanadium species giving an intermediate complex (fig. 6 I). The next step is the abstraction of another hydrogen, and the structure transforms itself into IIa (1670 cm^{-1}) or IIb (1630 cm^{-1}) intermediate complexes. The two latter complexes are converted into the intermediate complex III (1400/1500 cm^{-1}), which gives the final products. Furthermore, the IIa and IIb structures can transform into structures IIIa (1700 cm^{-1}) for xylene or IIIb (1650 cm^{-1}) in the case of xylene and toluene. These structures seem to be the intermediate species in the process of formation of the side products of these reactions, i.e. aldehydes. Different

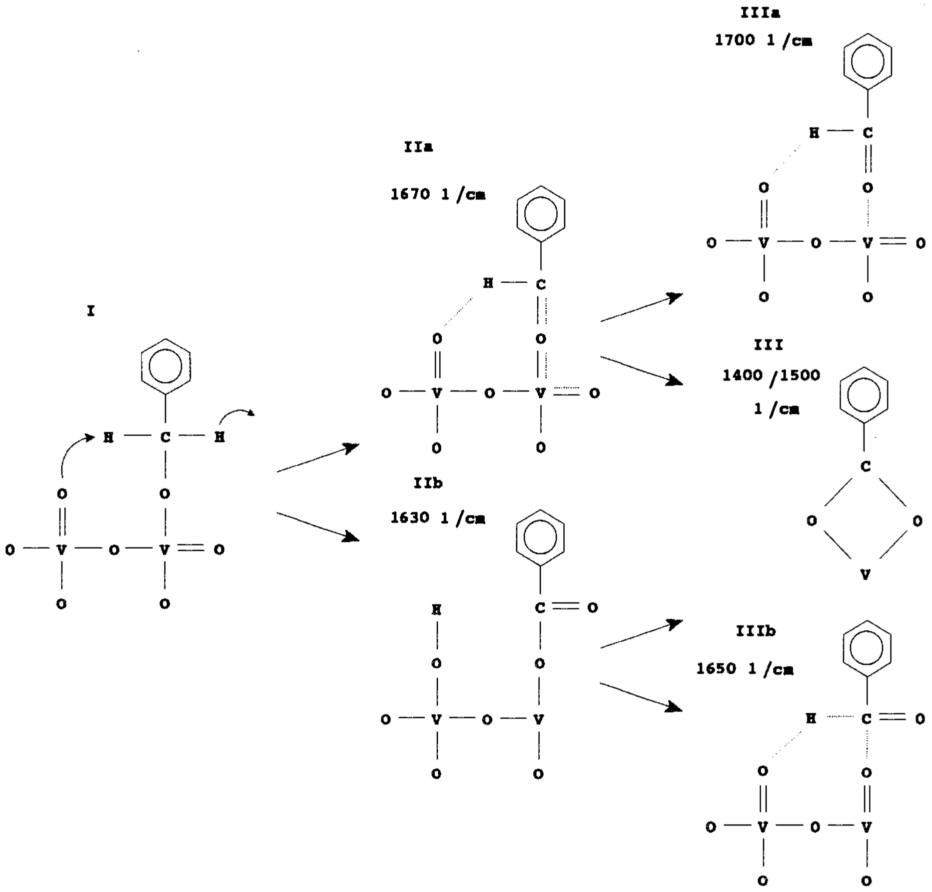


Fig. 6. Proposed mechanism of the reaction of oxidation of toluene and *o*-xylene on monolayer V_2O_5/MgF_2 catalyst.

behavior of *o*-xylene and toluene in oxidation process may be a result of a stabilization effect of the second methyl group in ortho position, which results in the possibility of creation of the structure IIIa. During the final step the complex III converts itself into products of the reaction, i.e. in the case of toluene it forms benzoic acid, while in the case of *o*-xylene the two neighbouring complexes give phthalic anhydride.

In conclusion, oxidation of toluene and *o*-xylene over V_2O_5/MgF_2 catalyst seemed to run in a different path than over V_2O_5/TiO_2 preparation [8]. In our work, an intermediate complex with bridging structure and the IR band at around 1410/1545 cm^{-1} for V_2O_5/TiO_2 was not observed.

4. Conclusion

The reactions of selective oxidation of toluene and *o*-xylene over MgF_2 supported monolayer vanadium oxide catalyst have been studied, using IR spectroscopy. On the basis of the results obtained and literature data, the appropriate frequencies of vibrations were assigned to different intermediate complexes, which were formed during adsorption/oxidation of the listed hydrocarbons. Finally, mechanisms of oxidation of toluene and *o*-xylene over V_2O_5/MgF_2 catalyst have been proposed, as a result of observations of changes in the intensity of IR bands.

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