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Kinetic and in situ FTIR studies of the catalytic oxidation of 1,2-dichlorobenzene over V_2O_5/Al_2O_3 catalysts

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Abstract

A systematic investigation of the catalytic oxidation of 1,2-dichlorobenzene (*o*-DCB) was conducted over a series of supported vanadia/alumina catalysts. The reaction was found to be first-order in *o*-DCB and zero-order in O_2 under excess oxygen conditions. Deactivation studies conducted with a 5.6% V_2O_5/Al_2O_3 catalyst at 773 K indicated a 15% loss in activity after 75 h on-stream. In situ FTIR studies suggest that the benzene ring remains intact during the adsorption of *o*-DCB, while no surface species containing C–Cl bonds were detected. Thus, it is suggested that chlorine abstraction is the first step in the reaction. Several partial oxidation products, namely phenolates, maleates and carboxylates were observed on the catalyst surface under reaction conditions. All of these species with the exception of the maleates can react with gas phase oxygen.

Keywords: Vanadia; Dichlorobenzene; Oxidation; FTIR

1. Introduction

Thermal incineration of municipal and medical wastes is widely employed in large residential areas due to its significant advantages over the traditional waste disposal methods. During the incineration process, small amounts of toxic chlorinated compounds such as polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) are formed, in addition to standard combustion byproducts (e.g., CO, NO_x, SO_x) [1]. The emissions of PCDDs/PCDFs are tightly regulated. Catalytic oxidation to HCl, carbon oxides and H_2O is the most viable and economic mode of destruction of these toxic compounds.

Supported noble metal catalysts are known for their high activity for the oxidation of organic compounds including aromatics. Their applicability towards the destruction of chlorinated organics however, is limited due to deactivation of the noble metal in the presence of Cl [2]. Oxides of transition metals such as Cr, Cu and V represent viable alternatives, since they resist deactivation to a large extent [3–5]. V_2O_5/TiO_2-based catalysts, which are considered state of the art for the control of NO_x emissions from the same incinerator units, have been found to be active for the oxidation of PCDDs/PCDFs in field measurements [6,7]. However, the surface chemistry of this reaction over vanadia-based catalysts remains largely unknown, and the first fundamental studies were only recently published [8–10].

Jones and Ross [8] examined the applicability of supported vanadia catalysts for the combined removal

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of NO and chlorinated VOCs. Ethyl chloride and chlorobenzene were the model VOCs used in that study. Zirconia doped with alumina was found to have the highest activity among all the supports studied for the simultaneous removal of NO (via its selective catalytic reduction by ammonia) and ethyl chloride (via its catalytic oxidation). Jones and Ross also showed that the removal of NO and ethyl chloride are independent of each other, and the presence of both compounds in the same reaction mixture has no effect on the catalyst activity for either reaction. CO_2, H_2O and HCl were the only oxidation products detected with either ethyl chloride or chlorobenzene. Catalyst activity was found to be stable and was not affected by the presence of HCl.

Our previous work on the oxidation of 1,2-dichlorobenzene (*o*-DCB) over V_2O_5/TiO_2-based catalysts confirmed that the surface vanadia sites exhibit significant activity for the oxidation of *o*-DCB [9]. CO and CO_2 were the only carbon containing products detected, with the selectivity towards CO being approximately 40%. Analysis of the spent catalyst indicated the presence of a significant amount of chlorine on the catalyst surface (0.76 wt%). Surface chlorine however, did not affect the catalyst activity, which was stable over a period of 100 h on-stream.

Different vanadia species are present on the surface of supported vanadium oxide catalysts depending on the vanadia surface coverage [11–15]. At low coverages, vanadia is present in the form of isolated, tetrahedrally coordinated vanadyl species, while at higher coverages, these species form polymeric chains. Our previous work has shown that the turnover frequency of the vanadia/titania catalysts for the SCR reaction varies as a function of the vanadia coverage, and exhibits a maximum at approximately half a monolayer [13]. On the contrary, our study on the oxidation of *o*-DCB showed that the turnover frequency is almost independent of the vanadia coverage in the submonolayer region [9]. As a result, it was suggested that only a single vanadia site is involved in the rate-determining step of *o*-DCB oxidation, while a more complex mechanism involving multiple sites operates for NH_3-SCR. Similarly, it is believed that a single site is involved in the rate-determining step of the oxidation of *o*-xylene and methanol over the same type of catalysts [11].

Finally, we had also investigated the effect of the addition of tungsten, molybdenum and zinc oxides on the activity of V_2O_5/TiO_2 for *o*-DCB oxidation. Such transition metal oxides are frequently added in commercial vanadia/titania formulations for a number of reasons, including promotion of the catalyst activity [16–18]. Changes in SCR activity caused by the presence of these oxides, have been correlated with changes in the Brønsted acidity of the catalyst [18]. However, we did not observe any significant change in the activity of the V_2O_5/TiO_2 catalysts for *o*-DCB oxidation in the presence of these oxides, which further supports the idea that a single vanadia site is involved in the rate-determining step of *o*-DCB oxidation.

In this paper, we expand our studies of the catalytic oxidation of *o*-DCB to a series of vanadia catalysts supported on Al_2O_3. Kinetic data were complemented by in situ infrared spectra of the same catalysts collected under reaction conditions. The results provide an insight into the mechanism of *o*-DCB oxidation over vanadia-based catalysts under dry conditions. An understanding of the surface chemistry of this reaction coupled with the fairly well documented fundamental chemistry of NH_3-SCR over the same catalysts can eventually lead to the applicability of vanadia-based catalysts for the combined destruction of dioxins and NO_x.

2. Experimental

2.1. Catalyst preparation

All catalysts used in this investigation were prepared via incipient wetness impregnation of vanadium oxalate onto Catapal-G Al_2O_3. The vanadia precursor was prepared by the addition of oxalic acid (Mallinkrodt, 99.99% purity) to an aqueous solution of vanadium oxide (Strem, 99.5% purity) and ammonium hydroxide (Aldrich, 99.99% purity). The catalyst samples were dried overnight at 353 K in a vacuum oven. They were then slowly heated to 793 K in 8 h and calcined at this temperature for 2 h. Elemental analysis via ICP spectroscopy (Galbraith) and BET surface area measurements (Pulse Chemisorb 20000) were used to characterize the catalysts. Vanadia surface coverages were calculated

Table 1
Composition and surface area of catalysts studied

Catalysts	% V_2O_5[a]	V^{5+} concentration[b]	$\theta_{V_2O_5}$[c]	SA[d]
Al_2O_3	–	–	–	140
V_2O_5/Al_2O_3	3.2	2.5	0.19	140
V_2O_5/Al_2O_3	5.2	4.4	0.34	131
V_2O_5/Al_2O_3	5.6	4.5	0.35	138
V_2O_5/Al_2O_3	7.2	5.7	0.44	140
V_2O_5/Al_2O_3	10.2	8.0	0.62	140

[a] Vanadia loading (wt% V_2O_5).
[b] Vanadium surface concentration (μmol V/m^2 catalyst).
[c] Fraction of vanadia monolayer.
[d] BET surface area (m^2/g).

based on a monolayer coverage of 13 μmol V^{5+}/m^2 and the assumption that vanadia remains fully dispersed in the submonolayer region, in agreement with previous reports [11,14]. These results are summarized in Table 1.

2.2. Kinetic and FTIR studies

Kinetic experiments were carried out in a stainless steel, single-pass, fixed bed reactor. *o*-DCB was introduced to the reactor by the passage of nitrogen through a saturator maintained at room temperature. This saturated stream was mixed with O_2 and N_2 to achieve the desired concentrations, preheated, and introduced to the reactor. The volumetric flow rate through the reactor was held constant at 450 scm^3/min. The reaction temperature was measured using a thermocouple projecting into the catalyst bed. Each run utilized approximately 500 mg of the catalyst in the form of 80–120 mesh particles. Prior to each run, the catalyst was oxidized in situ at 723 K for 2 h.

Analysis of *o*-DCB was performed on-line using a SRI 8610 gas chromatograph (1/8″ silica gel packed column) equipped with a flame ionization detector. The reaction rates were calculated based on the conversion of *o*-DCB. Prior to its introduction to the gas chromatograph, the reactor outlet stream was passed through a scrubber fitted with an alkaline material (ALCOA-Selexsorb SPCL 1/8″) to remove any HCl or Cl_2 formed during the reaction. This measure was deemed necessary for the protection of the chromatographic column.

In situ infrared spectra were collected using a Nicolet 740 FTIR spectrometer equipped with a MCT-B detector cooled by liquid nitrogen. Transmission spectra were collected in the single beam mode with a resolution of 2 cm^{-1}. A stainless steel IR cell (path length 10 cm), with NaCl windows cooled by water flowing around them, was used for the experiments. The catalysts were in the form of self-supported wafers, approximately 1 cm in diameter and 15–20 mg in weight and were placed in a sample holder in the middle of the cell. A heating element was wrapped around the cell and the temperature was monitored by a thermocouple kept in close proximity with the catalyst sample. Prior to each experiment, the catalyst was oxidized at 623 K in 10% O_2/He for 2 h. Typical concentrations used during the collection of the IR spectra were 700 ppmv *o*-DCB and 5% O_2, with He as the carrier gas. *o*-DCB was introduced with the help of a saturator maintained at room temperature. The total volumetric flow rate through the cell was 100 scm^3/min. Reference spectra of the clean surfaces taken in He or 5% O_2/He were used as the background. Gas phase subtraction was performed on all spectra.

3. Results and discussion

3.1. Kinetic studies

Fig. 1 shows the activity of two V_2O_5/Al_2O_3 catalysts of different vanadia loading, as well as the activity of the Al_2O_3 support at different temperatures for *o*-DCB oxidation. CO (45%) and CO_2 (55%) were the only C-containing products detected during on-line GC analyses of the product stream and carbon balances were closed within ±5%. Previous studies by Lago and co-workers [5] on *o*-DCB oxidation over copper chloride-based catalysts have shown the formation of polychlorinated biphenyls (e.g. $C_{12}HCl_9$) leading to poor carbon balance closure. Although we cannot eliminate the possibility of formation of such biphenyls or other partial oxidation products (especially in view of the FTIR results discussed later in this paper), we are confident that if these products are indeed formed, then they are present in trace amounts as indicated by the absence of unknown peaks in the GC analyses and the good closure of the carbon balances.

The results (i.e., increase in activity with vanadia loading and inactivity of the support) confirm that

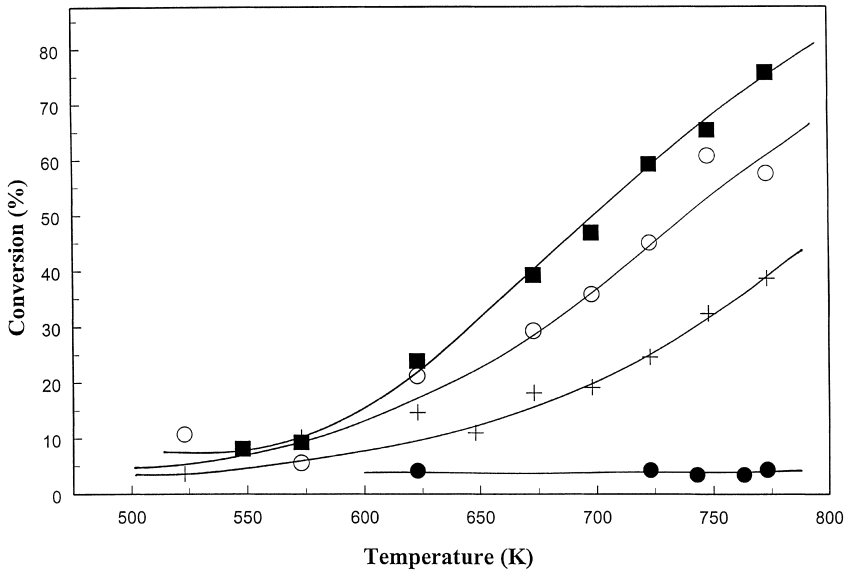

Fig. 1. Effect of temperature on the activity of V_2O_5/Al_2O_3 catalysts of variable vanadia loading for *o*-DCB oxidation: (■) 7.2% V_2O_5/Al_2O_3, (○) 5.2% V_2O_5/Al_2O_3, (+) 3.2% V_2O_5/Al_2O_3, (●) Al_2O_3 (600 ppmv *o*-DCB, 10% O_2).

vanadia is the active catalytic component. Comparison with a V_2O_5/TiO_2 catalyst of similar vanadia loading shows the V_2O_5/Al_2O_3 catalyst to be less active (Fig. 2), indicating that the rate of the reaction is affected by the nature of the support. Similar results have been obtained in the case of the partial oxidation of methanol over the same catalysts [11].

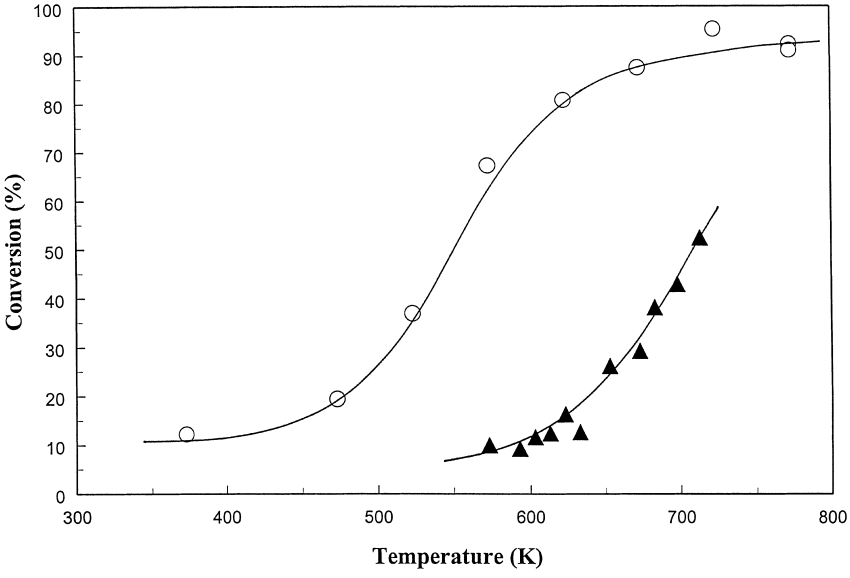

Fig. 2. Effect of temperature on the activity of a 5.8% V_2O_5/TiO_2 catalyst (○) and a 5.6% V_2O_5/Al_2O_3 catalyst (▲) for *o*-DCB oxidation. (Conditions as in Fig. 1.)

Table 2
Turnover frequencies and activation energies for *o*-DCB oxidation over different V_2O_5 catalysts

Catalyst	TOF at 623 K ($\times 10^{-3}$ s^{-1})	TOF at 698 K ($\times 10^{-3}$ s^{-1})	Activation energy (kJ/mol)
3.2% V_2O_5/Al_2O_3	0.18	0.24	45
5.2% V_2O_5/Al_2O_3	0.17	0.31	45
5.6% V_2O_5/Al_2O_3	0.11	0.36	53
7.2% V_2O_5/Al_2O_3	0.14	0.32	46
10.2% V_2O_5/Al_2O_3	–	0.30	–

Turnover frequencies (i.e. rates per vanadium site) can be calculated from the results shown in Fig. 1, since vanadia is known to be fully dispersed on alumina at sub-monolayer coverages [12]. These values were calculated by treating the reactor as an integral or plug flow reactor and utilizing a first-order dependence on *o*-DCB (in agreement with the results presented later), according to the following equation:

$$r = -(Q/\eta_V) * C_{o\text{-DCB}} * [\ln(1-x)], \quad (1)$$

where r is the turnover frequency of *o*-DCB oxidation at the inlet conditions, Q the volumetric flow rate to the reactor, η_V the total moles of V^{5+} in the reactor, $C_{o\text{-DCB}}$ the inlet *o*-DCB concentration and x is the fractional conversion of *o*-DCB across the reactor.

The results are presented in Table 2, and indicate that the turnover frequency is not affected by the vanadia loading. Similar results were obtained previously with V_2O_5/TiO_2 [9]. However, the turnover frequency of *o*-DCB oxidation at 623 K is approximately one order of magnitude lower for the V_2O_5/Al_2O_3 catalysts. Since the structure of vanadia is the same on both Al_2O_3 and TiO_2, this difference could be attributed to the effect of vanadia-support interactions on the redox properties of vanadia. A similar conclusion has been reached by Deo and Wachs based on Raman and temperature-programmed reduction studies of the oxidation of methanol and butane over supported vanadia catalysts [11,19]. Activation energies calculated for the V_2O_5/Al_2O_3 catalysts for *o*-DCB oxidation were in the 45–53 kJ/mol range, while the corresponding values for the V_2O_5/TiO_2 catalysts were in the 29–36 kJ/mol range.

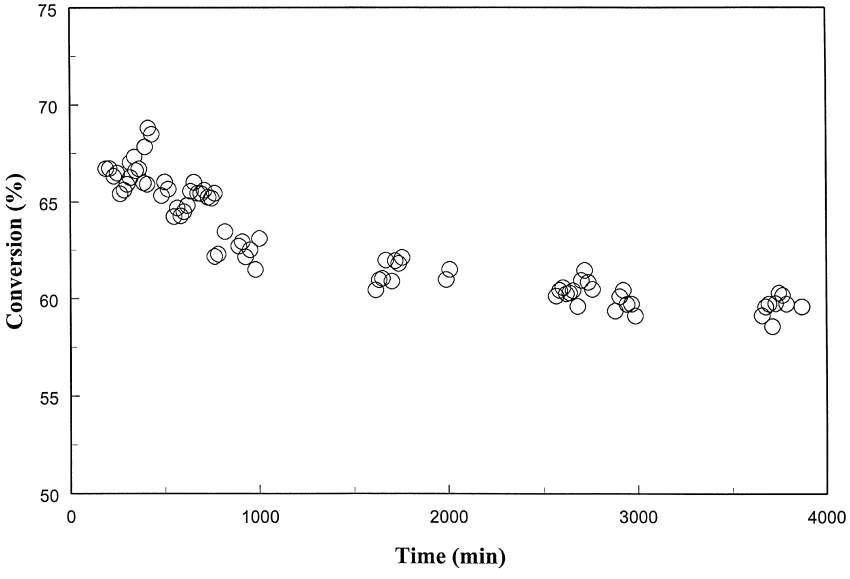

Fig. 3. Activity of the 5.6% V_2O_5/Al_2O_3 catalyst for *o*-DCB oxidation at 773 K, as a function of time on-stream. (Conditions as in Fig. 1.)

Table 3
Kinetic parameters for *o*-DCB oxidation; $r=k\ C_{o\text{-DCB}}{}^{a}\ CO_2{}^{b}$

Catalyst	*a*		*b*	
	673 K	723 K	673 K	723 K
5.6% V_2O_5/Al_2O_3	1.2	1.1	0.1	0.1

The effect of the concentration of the two reactants on the rate of *o*-DCB oxidation was studied over the 5.6% V_2O_5/Al_2O_3 catalyst at two different temperatures (673 and 723 K). The concentration of *o*-DCB was varied in the range 100–1000 ppmv, while the corresponding O_2 concentration was varied between 1% and 10%. The reactor was operated under differential conditions and the rate was calculated according to the following equation:

$$r_{o\text{-DCB}} = C_{o\text{-DCB}} * Q * x/m, \quad (2)$$

where m is the mass of the catalyst.

The kinetic parameters thus obtained are summarized in Table 3. As can be seen, *o*-DCB oxidation was found to be approximately first-order in *o*-DCB and zero-order in O_2 regardless of temperature. The same results were also obtained previously with V_2O_5/TiO_2 catalysts [9], indicating that a similar mechanism operates in both cases.

Catalysts used for the oxidation of chlorinated organics are susceptible to deactivation due to the presence of chlorine. Furthermore, it has been suggested that a slow change in the selectivity of the

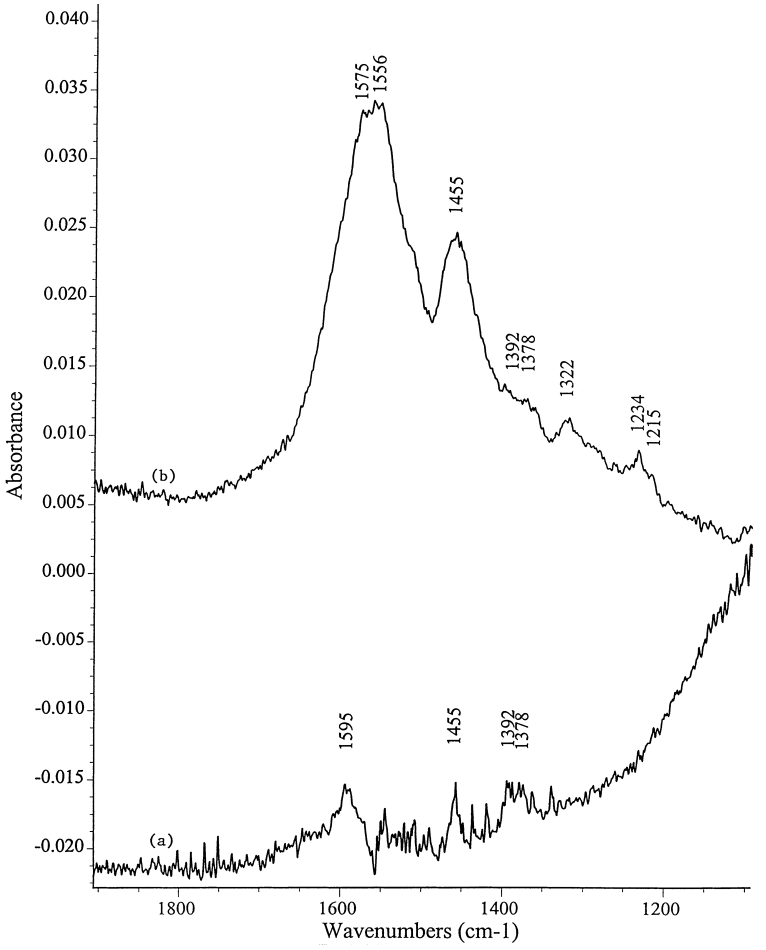

Fig. 4. In situ infrared spectra of (a) Al_2O_3 and (b) 5.6% V_2O_5/Al_2O_3 samples, collected at 573 K in 700 ppmv *o*-DCB and 5% O_2 in He after 20 min on-stream.

catalyst and formation of partially oxidized and incomplete combustion products may take place over a long period of catalyst exposure to the reactants [20,21]. The *o*-DCB conversion for the 5.6% V_2O_5/Al_2O_3 catalyst at 773 K is shown as a function of time on-stream in Fig. 3. A 15% reduction in catalyst activity was observed after 75 h of operation. While the surface areas of the spent and the fresh catalyst samples were identical, elemental analysis of the spent catalyst indicates a Cl concentration of 0.52% by weight, suggesting that some Cl is retained on the catalyst. However, no peaks corresponding to aluminum or vanadium chloride were observed in the X-ray diffraction pattern of the spent catalyst, suggesting that if a chloride is formed, it is either amorphous or has a small crystallite size. Studies by Butt and coworkers [22] have further shown that coking could be another reason for the deactivation of transition metal oxide catalysts during chlorinated VOC destruction. It is thus evident that for the V_2O_5/Al_2O_3 catalysts examined in our work, further studies are required in order to understand the origin and the mechanism of the deactivation process observed.

3.2. FTIR studies

In situ infrared spectra of Al_2O_3 and V_2O_5/Al_2O_3 samples, collected in our case after 20 min on stream under reaction conditions at 573 K, are shown in Fig. 4. These spectra exhibit several peaks in the 1200–1600 cm^{-1} range. Similar IR peaks have been observed by others during FTIR studies of oxidation

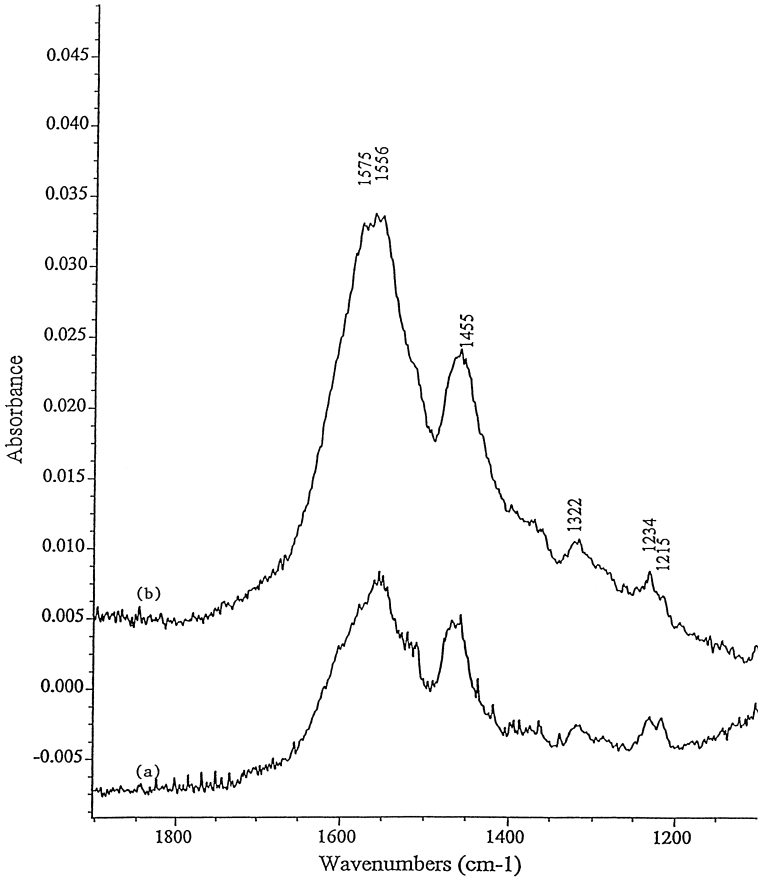

Fig. 5. In situ infrared spectra of a 5.6% V_2O_5/Al_2O_3 sample collected at 573 K in (a) 700 ppmv *o*-DCB in He, (b) 700 ppmv *o*-DCB, 5% O_2 in He, after 20 min on-stream.

reactions over supported vanadia catalysts and have been assigned to surface carboxylates and/or carbonates. Chintawar and Greene [23], for example, conducted adsorption/reaction studies of 1,1-dichloroethane over a Cr–Y zeolite and have assigned peaks at 1576 cm^{-1} (asymmetric –COO^- stretching) and ~1445 cm^{-1} (symmetric –COO^- stretching) to surface carboxylates of the acetate type. Busca et al. [24] and Vigue et al. [25] have assigned IR peaks at 1595 cm^{-1} (asymmetric –COO^- stretching) and a doublet at 1398 (–CH bending) and 1377 cm^{-1} (symmetric –COO^- stretching) to surface formates. These were observed during the adsorption/reaction of formaldehyde and chloromethane, respectively, over γ-Al_2O_3. Escribano et al. [26] studied the adsorption/reaction of allyl alcohol over V_2O_5/TiO_2 and have assigned IR peaks at 1550 (more intense) and ~1450 cm^{-1} (less intense) to surface carboxylates. Finocchio et al. [27] observed an IR peak at 1520 cm^{-1} during the adsorption of methane on $MgCr_2O_4$ and assigned it to a surface carbonate species of the bidentate type. Busca and co-workers [28] have shown the presence of a peak at ~1330 cm^{-1} during the reaction of benzene adsorbed on V_2O_5/TiO_2 with gas phase oxygen. This was assigned to a surface maleate species, which is also observed during in situ oxidation of butadiene over similar catalysts [29]. Furthermore, FTIR studies on phenol adsorption over vanadia-based catalysts have shown C–O stretching vibrations corresponding to

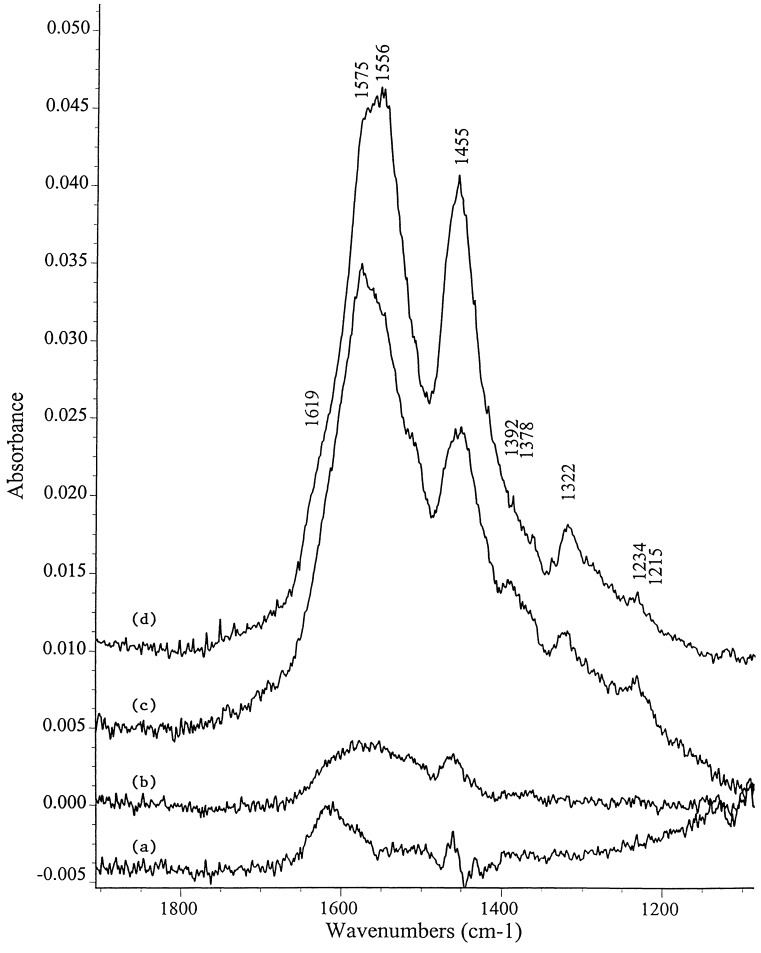

Fig. 6. In situ infrared spectra of a 5.6% V_2O_5/Al_2O_3 sample collected at (a) 523, (b) 573, (c) 623 and (d) 673 K, in 700 ppmv *o*-DCB, 5% O_2 in He after 5 min on-stream.

surface phenolate species to be present in the 1230–1210 cm^{-1} range [28,30].

Based on these reports, we have made the following assignments: the peaks at 1575, 1556, 1455 cm^{-1} and the doublet at 1392 and 1377 cm^{-1} in the V_2O_5/Al_2O_3 spectrum, to surface carboxylate groups; the shoulder at 1510 cm^{-1} to a surface carbonate; the peak at 1322 cm^{-1} to a surface maleate species; and finally, the doublet at 1234 and 1215 cm^{-1} to a surface phenolate species. On the contrary, no peaks characteristic of C–Cl vibrations are present in the 1100–1200 cm^{-1} region.

When the spectrum of the V_2O_5/Al_2O_3 catalyst is collected in the absence of gas phase oxygen at the same temperature after 20 min (Fig. 5), similar peaks are observed indicating that surface vanadia oxygen reacts with *o*-DCB to form the various adsorbed partial oxidation products. The intensity of the carboxylates however, is lower in the absence of oxygen indicating further growth of these species in the presence of gaseous O_2.

In contrast to the spectrum of the V_2O_5/Al_2O_3 catalyst, the spectrum of the Al_2O_3 support (Fig. 4) exhibits only three low intensity peaks assigned to surface carboxylate groups at 1595 and 1455 cm^{-1} as well as the doublet at 1392 and 1377 cm^{-1}. The absence of intense peaks associated with oxidation products is not surprising, since according to the kinetic results, the alumina support shows very low activity for the oxidation of *o*-DCB.

Peaks at 1619 and 1455 cm^{-1} corresponding to stretching vibrations of an adsorbed aromatic ring

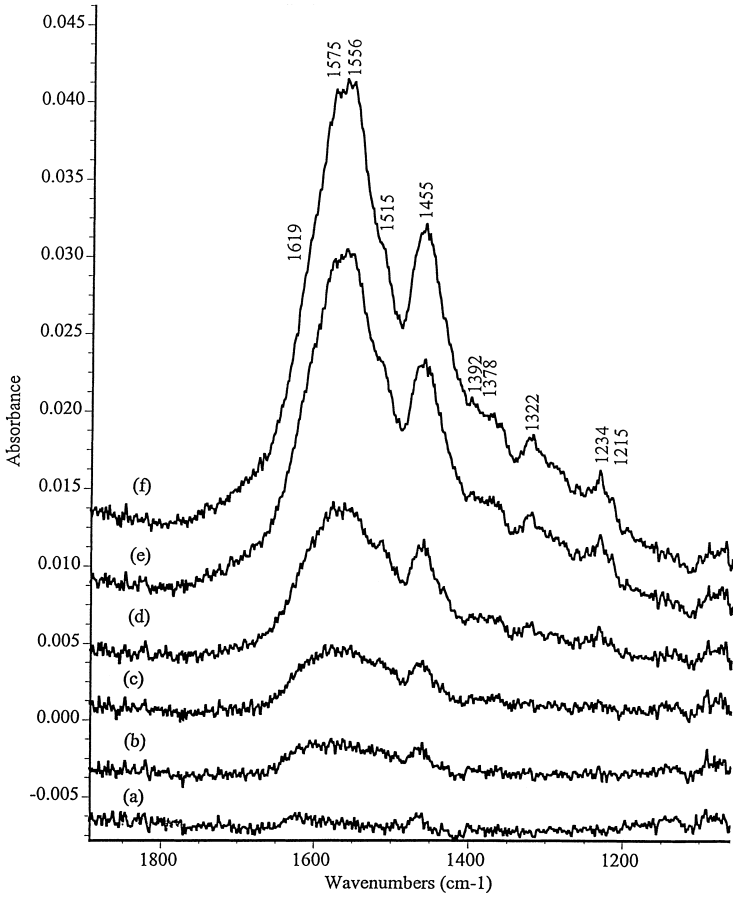

Fig. 7. In situ infrared spectra of a 5.6% V_2O_5/Al_2O_3 sample collected in 700 ppmv *o*-DCB and 5% O_2 in He at 573 K after (a) 1, (b) 3, (c) 5, (d) 10, (e) 15 and (f) 20 min on-stream.

[29], are clearly noticeable in the spectra collected at low temperatures (Fig. 6). In fact, these peaks are also present as weak shoulders in the spectra of Fig. 5, but their detection is problematic because of the high intensity of the carboxylate peaks in the region. Fig. 7 further demonstrates the growth of the carboxylate peaks over the ring vibration peaks at 573 K, under reaction conditions as a function of time. This, along with the absence of any C–Cl vibrations assigned to surface species, suggests that chlorine abstraction is the first step of the reaction process. A similar conclusion has been reached for the oxidation of chlorinated aliphatic compounds [23]. These results further suggest that the aromatic ring remains intact during the adsorption process and that the adsorbed species is probably bonded through the dechlorinated carbon atoms.

A comparison of the spectra collected at different temperatures is attempted in Fig. 6. At 523 K, only weak peaks corresponding to the ring vibrations are present, indicating that at this temperature only adsorption and no significant reaction is taking place. This is in agreement with the kinetic data of Fig. 1. When the temperature exceeds 573 K (beyond which point the reaction takes off according to the kinetic data), one can observe significant amounts of partial oxidation products on the catalyst surface. Finally at 673 K, we observe further growth of the peaks corresponding to the carboxylate and maleate species, but a slight decrease of the phenolate doublet, which may

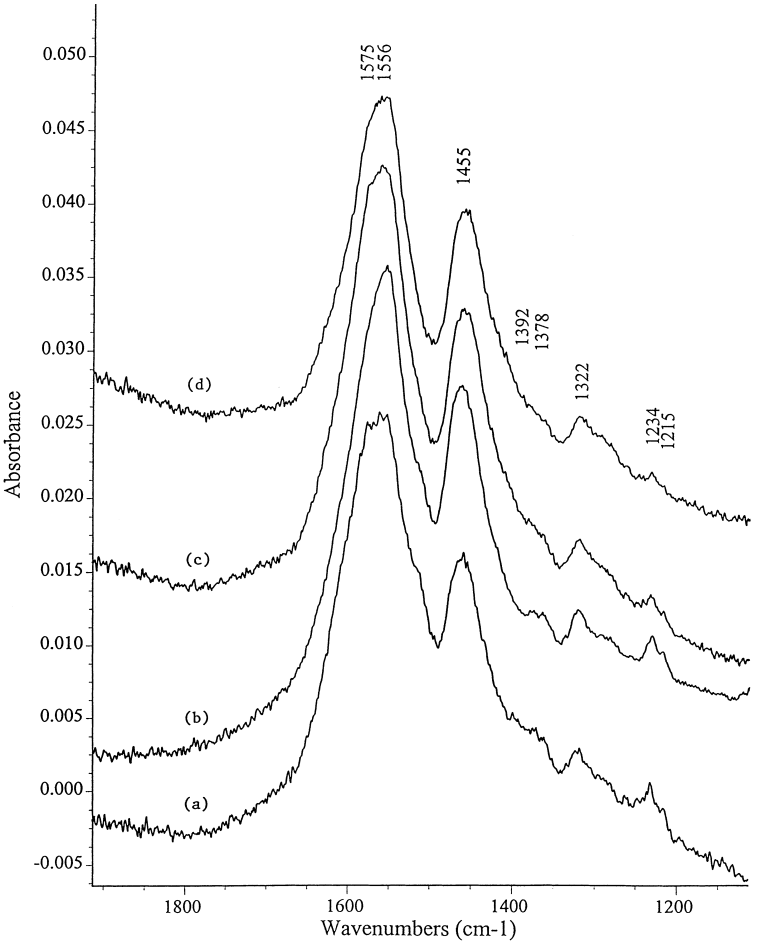

Fig. 8. In situ infrared spectra of a 5.6% V_2O_5/Al_2O_3 sample collected in 700 ppmv *o*-DCB and 5% O_2 in He at 623 K after 20 min on-stream (a), followed by flushing with He for 20 min (b), 5% O_2 in He for 20 min (c), and 5% O_2 in He for 60 min (d).

suggest that the phenolate group is the most active among the observed surface species, at least at high temperatures.

The stability of the various adsorbed species was studied at 573 K, by conducting a series of desorption and reaction experiments, in the presence of helium and oxygen, respectively (Fig. 8). The intensity of all peaks corresponding to surface species decreases when the cell is flushed with either helium or 5% oxygen in helium, with the exception of the peak corresponding to the surface maleates which remains constant. This indicates that the majority of the surface species (i.e., carboxylates, phenolates and the adsorbed aromatic ring) can either desorb or react with gas phase oxygen. The decrease in intensity however, is more pronounced in the presence of oxygen, indicating that the rate of reaction is higher than the rate of desorption under these conditions.

At 673 K, the reaction between gas phase O_2 and the adsorbed species becomes faster as indicated by the spectra shown in Fig. 9. Furthermore, under these conditions, a new peak appears at approximately 1636 cm^{-1}, which can be assigned, to deformation vibrations of adsorbed water [27,31,32], formed as a reaction product. Another weak peak is observed at 1748 cm^{-1}. Peaks in this region have been previously assigned to adsorbed carbonyl (C=O) groups [23]. The species responsible for this peak is also believed to be an oxidation product that further reacts with gas phase O_2 and eventually disappears at longer reaction times (Fig. 9(e)). Even at this elevated temperature, the intensity of the peak assigned to surface maleates

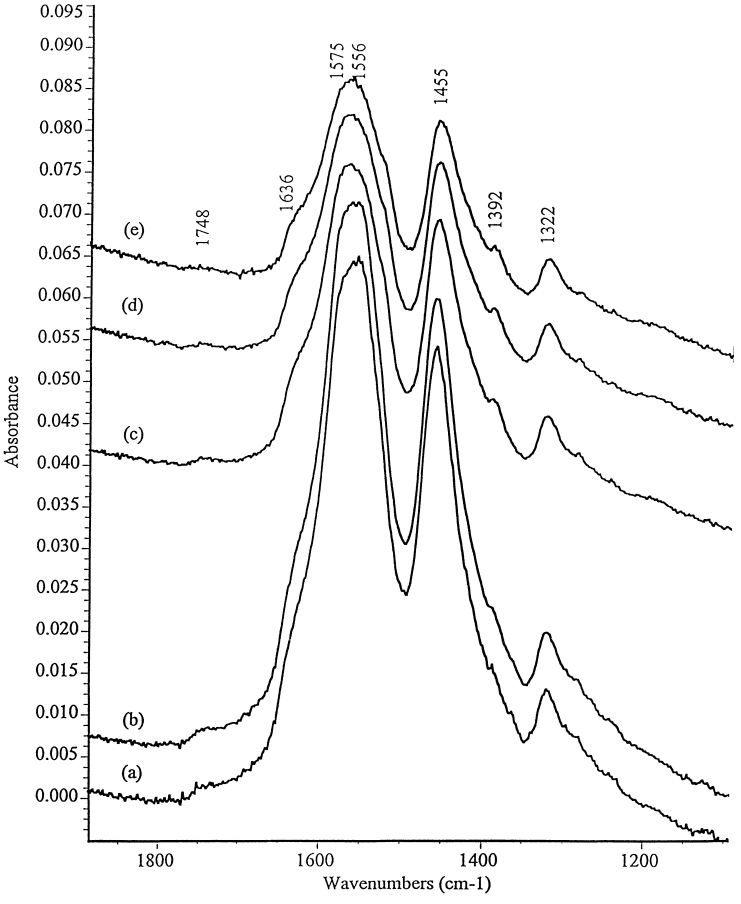

Fig. 9. In situ infrared spectra of a 5.6% V_2O_5/Al_2O_3 sample collected in 700 ppmv *o*-DCB and 5% O_2 in He at 673 K after 20 min on-stream (a), followed by flushing with 5% O_2 in He for 1 (b), 10 (c), 20 (d) and 60 min (e).

remained constant, indicating that this species is very stable and is probably a spectator rather than an intermediate in the *o*-DCB oxidation process.

4. Conclusions

Kinetic and in situ FTIR studies of the oxidation of *o*-DCB have been performed over V_2O_5/Al_2O_3 catalysts. Activity measurements demonstrated that V_2O_5/Al_2O_3 catalysts are less active than the corresponding V_2O_5/TiO_2 catalysts. The reaction was found to follow first-order kinetics in *o*-DCB and zero-order in oxygen under excess oxygen conditions. CO and CO_2 were the only carbon-containing products detected. A 15% loss of activity was observed at 773 K over a period of 75 h on-stream. In situ infrared spectroscopic studies show the formation of several surface species (including carboxylates, maleates and phenolates) under reaction conditions. All surface species (with the exception of the maleates) are reactive at temperatures above 523 K in the presence of gas phase O_2.

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