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Catalytic Oxidation of 1,2-Dichlorobenzene over Supported Transition Metal Oxides

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The catalytic oxidation of 1,2-dichlorobenzene has been systematically investigated over a series of transition metal oxides (i.e., Cr_2O_3, V_2O_5, MoO_3, Fe_2O_3, and Co_3O_4) supported on TiO_2 and Al_2O_3. The activity of the different catalysts for this reaction depends on the nature of the transition metal oxide used, with Cr_2O_3- and V_2O_5-based catalysts being the most active ones. With the exception of the cobalt oxide catalysts, the TiO_2-supported systems were more active than the corresponding Al_2O_3-supported ones, indicating that the metal oxide–support interactions are significant in this reaction. Experiments conducted in the presence of water indicate an inhibiting effect for the V_2O_5- and Cr_2O_3-based catalysts and a promoting effect for Co_3O_4/TiO_2. The Fe_2O_3- and MoO_3-based catalysts were unaffected by the presence of water. Competitive adsorption between the surface species and water is suspected to be the reason for the inhibition, while the promoting effect can be attributed to the reaction of water with surface Cl^-. *In situ* FTIR studies indicate the presence of carboxylates (i.e., acetates and formates), maleates, and phenolates on the surfaces of all catalysts studied under reaction conditions. These surface species were reactive in the presence of gas-phase oxygen and are potential intermediates for the oxidation of 1,2-dichlorobenzene. © 2000 Academic Press

Key Words: **PCDD/PCDF; dichlorobenzene; oxidation; transition metal oxides.**

INTRODUCTION

The destruction of polychlorinated aromatics, such as polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), has received a lot of attention recently, due to a worldwide concern about the toxicity of these compounds (1). Thus, stringent limits (e.g., 0.1 ng of I-TEQ/Nm^3) have been imposed on the emissions of such compounds in many countries (2). One of the principal sources of PCDD/PCDF emissions, solid waste incinerators, is becoming the method of choice for waste disposal in urban areas. Catalytic oxidation is the preferred method for the destruction of PCDD/PCDFs from these incinerators.

V_2O_5/TiO_2-based catalysts, employed in most incinerators for the control of NOx emissions via its selective catalytic reduction with NH_3, are also active for the oxidation of PCDD/PCDFs (2–6). In contrast, noble metal-based catalysts, which show high activity for the oxidation of nonchlorinated organics, undergo poisoning in the presence of Cl (7, 8).

Due to the high toxicity of PCDD/PCDFs, laboratory studies in this area usually employ model compounds such as chlorobenzenes and chlorophenols to predict the dioxin destruction behavior of different catalysts (9–15). Our previous work on the oxidation of 1,2-dichlorobenzene (*o*-DCB) over vanadia supported on Al_2O_3 and TiO_2 has indicated that chlorine abstraction is probably the first step of the reaction (16) and that the rate-determining step involves a single vanadia site (10). The rate of the reaction was also affected significantly by the nature of the support, with V_2O_5/TiO_2 being more active than V_2O_5/Al_2O_3. The same effect has also been observed in the case of the oxidation of methanol (17) and butane (18) over similar catalysts.

In this paper, we present the results of our detailed kinetic and *in situ* FTIR studies of *o*-DCB oxidation over several different transition metal oxides supported on Al_2O_3 and TiO_2. The performance of these catalysts was compared with that of the vanadia-based catalysts studied in our previous work (10, 16), in an attempt to understand the role of the different transition metal oxides, and to obtain a better picture of the reaction mechanism. Activity measurements were also conducted in the presence of water, since water vapor is an integral part of the flue gas emanating from the incinerators and could affect the catalyst performance. Finally, *in situ* FTIR studies were performed both in the presence and in the absence of water, in order to understand the nature and reactivity of the various surface species formed during the reaction.

EXPERIMENTAL

Catalyst Preparation

All the catalysts used in this study were prepared by incipient wetness impregnation. Catapal-G Al_2O_3 and Kemira-95 TiO_2 were used as the supports. Chromium nitrate

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nonahydrate (Aldrich), cobalt nitrate hexahydrate (Aldrich), iron nitrate hexahydrate (Aldrich), and ammonium molybdate (Aldrich) were used as the precursors for chromium, cobalt, iron, and molybdenum oxides, respectively. Vanadium oxalate, prepared by the addition of oxalic acid (Mallinkrodt) to an aqueous solution of vanadium oxide (Strem) in ammonium hydroxide (Aldrich), was used as the precursor for V_2O_5. The metal oxide loadings were calculated such that all catalysts contained approximately the same amount of transition metal on a molar basis (see Table 1).

The impregnated catalyst samples were first dried overnight in a vacuum oven at 353 K. The dried samples were then slowly heated to 773 K in 6 h and calcined at this temperature for an additional 2 h. A slightly higher calcination temperature of 793 K was used for the vanadia samples. At these conditions, all precursors decomposed to form the corresponding oxides. The stoichiometries of these oxides are believed to be as follows: Cr_2O_3, Co_3O_4, MoO_3, Fe_2O_3, and V_2O_5 (19, 20).

The catalysts were characterized via inductively coupled plasma (ICP) spectroscopy (Galbraith Laboratories) and BET surface area measurements (Pulse Chemisorb 2000). The results of these analyses are shown in Table 1.

Activity Measurements

Activity measurements were carried out in a quartz, single-pass flow reactor which incorporated 500 mg of catalyst in the form of 80–120 mesh size particles. Experiments carried out with different particle sizes have demonstrated the absence of any internal diffusional limitations in the system. The reaction temperature was monitored using a thermocouple projecting into the catalyst bed. *o*-DCB was introduced into the vapor phase using a saturator. Nitrogen was flowed through the saturator maintained at room temperature. The saturated *o*-DCB/N_2 stream was mixed with O_2 and an additional stream of N_2 to achieve the desired concentrations of 600 ppmv *o*-DCB and 10% O_2. The reactant stream was then preheated and introduced into the reactor. The volumetric flow rate through the reactor was maintained at 445 scm^3/min (space velocity of approximately 25,000 h^{-1}). Prior to each experiment, the catalyst sample was pretreated *in situ* in O_2 at 773 K for 2 h. For measurements in the presence of water, an additional saturator maintained at room temperature was connected to the second N_2 stream.

TABLE 1

Composition and Surface Area of Catalysts Studied

Catalysts	% M_xO_y[a]	Loading[b]	SA[c]
TiO_2	—	—	85
V_2O_5/TiO_2	5.8	6.4	77
Cr_2O_3/TiO_2	5.2	6.8	87
Fe_2O_3/TiO_2	5.0	6.3	89
Co_3O_4/TiO_2	4.5	6.0	97
MoO_3/TiO_2	8.9	6.2	94
Al_2O_3	—	—	140
V_2O_5/Al_2O_3	5.6	6.2	140
Cr_2O_3/Al_2O_3	4.5	5.9	146
Fe_2O_3/Al_2O_3	4.7	5.9	139
Co_3O_4/Al_2O_3	4.7	6.3	133
MoO_3/Al_2O_3	9.0	6.3	139

[a] Metal oxide loading (wt% M_xO_y).
[b] Metal loading ($\times 10^{-4}$ mol/g catalyst).
[c] BET surface area (m^2/g).

The analysis of *o*-DCB in the reactant and product streams was performed on-line with an SRI 8610 gas chromatograph equipped with a $\frac{1}{8}$-in. silica gel packed column and a flame ionization detector. In order to protect the chromatographic column from damage due to HCl formed during the reaction, a scrubber containing an alkaline material (ALCOA Selexsorb SPCL $\frac{1}{8}$ in.) was fitted to the exit of the reactor. Initial measurements demonstrated that the alkaline scrubber becomes saturated with *o*-DCB within a few minutes, while HCl continues to react with this material. The results presented in this paper were obtained under steady-state conditions (i.e., after the *o*-DCB breakthrough was completed). Furthermore, experiments were conducted without the scrubber, and the *o*-DCB conversions observed were identical to the ones observed with the scrubber attached to the reactor outlet.

In Situ FTIR Spectroscopy

Infrared spectra were collected using a Nicolet 740 FTIR spectrometer equipped with an MCT-B detector cooled by liquid nitrogen. The spectra were collected in the single-beam mode with a 2 cm^{-1} resolution. Experiments were conducted in a stainless steel IR cell (NaCl windows), with a path length of 10 cm. The catalyst sample was in the form of a thin self-supported disk, approximately 1 cm in diameter and 16 mg in weight. The disk was placed in a sample holder and kept in the middle of the cell. Typical concentrations used for the FTIR experiments were 700 ppmv *o*-DCB and 5% O_2, with He being the carrier gas. Prior to each experiment, the sample was oxidized *in situ* at 623 K in a 10% O_2 in He mixture for 2 h. Spectra of clean surfaces taken in O_2 (for reaction studies) or He (for adsorption studies) were used as the backgrounds for the different experiments. Gas-phase subtraction of *o*-DCB was also performed on all spectra.

RESULTS AND DISCUSSION

Activity Measurements

The *o*-DCB conversions observed with different transition metal oxides supported on TiO_2 are shown as

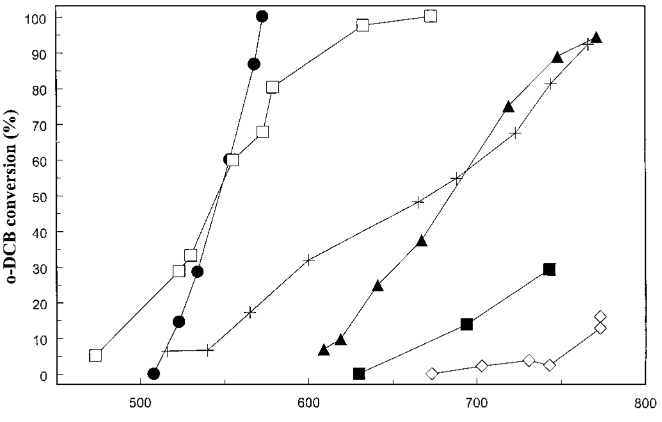

FIG. 1. *o*-DCB conversion as a function of temperature for different TiO_2-supported catalysts. (●) 5.2 wt% Cr_2O_3/TiO_2, (□) 5.8 wt% V_2O_5/TiO_2, (+) 8.9 wt% MoO_3/TiO_2, (▲) 5.0 wt% Fe_2O_3/TiO_2, (◇) 4.5 wt% Co_3O_4/TiO_2, (■) TiO_2 (600 ppmv *o*-DCB, 10% O_2, 25,000 h^{-1}).

functions of temperature in Fig. 1. Cr_2O_3, V_2O_5, MoO_3, and Fe_2O_3 exhibited relatively high activities for the reaction, with the first two being more active than the others. The TiO_2 support also exhibits some activity for the oxidation of *o*-DCB. However, the addition of the transition metal oxides—with the exception of Co_3O_4—increased the activity of TiO_2 appreciably, indicating that the transition metal oxides provide more active sites. A blank reactor experiment indicated no significant gas-phase oxidation of *o*-DCB at temperatures up to 773 K.

Our results are in general agreement with previous reports regarding the oxidation activity of these transition metal oxides. Wachs and co-workers, for example, have shown that the turnover frequency for the oxidation of methanol over V_2O_5/TiO_2 is one order of magnitude higher than that over MoO_3/TiO_2 (21). Studies conducted by other researchers on the oxidation of methanol (22–24) and 1-butene (25) have also shown similar behavior for Cr_2O_3, V_2O_5, and MoO_3 catalysts. Finally, Larrson and co-workers have shown that TiO_2-supported iron oxide is more active than cobalt oxide dispersed over the same support for the oxidation of toluene (26).

The observed steady-state activity of the Co_3O_4/TiO_2 catalyst was significantly lower than the activity of the other catalysts tested. This result appears to contradict results reported previously by Aida *et al.* (27) and Subbanna *et al.* (28), who indicated that supported cobalt oxide catalysts are highly active for the oxidation of methylene chloride and polychlorinated biphenyls (PCBs). Kießling *et al.* (29) reported the formation of volatile $CoCl_2$ during the oxidation of CH_2Cl_2 over $LaCoO_3$ and attributed an observed low steady-state activity to the loss of Co via this route. However, in our case, analysis of the spent Co_3O_4/TiO_2 catalyst does not render support to such a hypothesis under our reaction conditions (i.e., no change in the Co content was observed between the fresh and spent samples). Furthermore, X-ray diffraction patterns of the spent samples do not reveal the formation of any new crystalline phases. Results obtained in the presence of water (discussed in subsequent sections) suggest that the low activity of this sample can be attributed to the slow removal of Cl^- from the surface of the Co_3O_4/TiO_2 catalyst and, hence, the blockage of the active sites by Cl^-.

Activity measurements were also conducted at different temperatures with the Al_2O_3-supported catalysts and the results are shown in Fig. 2. Once again the transition metal oxide-containing catalysts exhibited much higher activities than the Al_2O_3 support, indicating that these oxides provide more active sites for the oxidation of *o*-DCB. A comparison between Figs. 1 and 2 shows that the TiO_2-supported catalysts exhibit higher activities than the corresponding Al_2O_3-supported ones. Similar results regarding the effect of the support have been previously reported for the oxidation of methanol over V_2O_5 (17), Cr_2O_3, and MoO_3 catalysts (25), and for the oxidation of benzene (30), but-1-ene (31), and furan (32) over vanadia catalysts. The activities of the different transition metal oxides were in general in the same order as with the titania-supported catalysts. The exception was MoO_3/Al_2O_3, which in this case was found to be at the lower end of the activity scale.

Effect of water. Activity measurements were also conducted in the presence of 1.0 and 5.0% water vapor, since water is present in significant quantities (usually around 10%) in the flue gas of different combustion processes and has been found to affect the rate of other emission control reactions over similar catalysts (33). Three different types of behavior were observed during our experiments with 1% water vapor. In the case of Cr_2O_3 (Fig. 3) and V_2O_5 catalysts, the results indicate that the presence of water inhibits

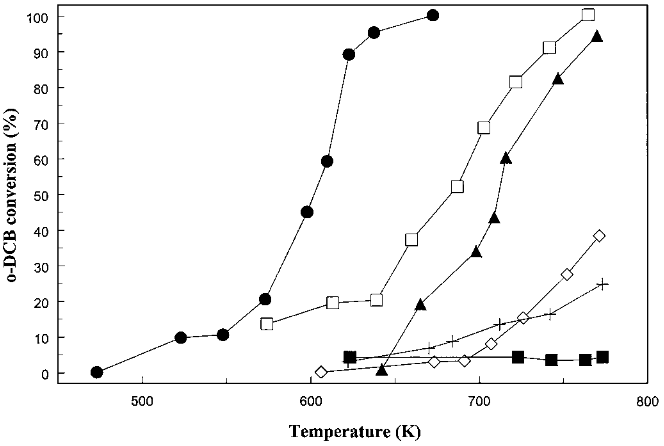

FIG. 2. *o*-DCB conversion as a function of temperature for different Al_2O_3-supported catalysts. (●) 4.5 wt% Cr_2O_3/Al_2O_3, (□) 5.6 wt% V_2O_5/Al_2O_3, (▲) 4.7 wt% Fe_2O_3/Al_2O_3, (◇) 4.7 wt% Co_3O_4/Al_2O_3, (+) 9.0 wt% MoO_3/Al_2O_3, (■) Al_2O_3 (600 ppmv *o*-DCB, 10% O_2, 25,000 h^{-1}).

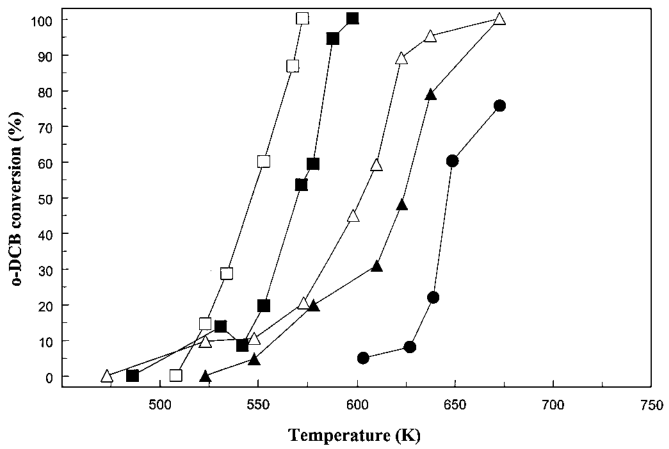

FIG. 3. Effect of water on the activity of supported Cr_2O_3 catalysts for the oxidation of *o*-DCB. (□, ■) 5.2 wt% Cr_2O_3/TiO_2, (△, ▲, ●) 4.5 wt% Cr_2O_3/Al_2O_3 ((□, △) 600 ppmv *o*-DCB, 10% O_2; (■, ▲) additional 1% H_2O; and (●) additional 5% H_2O).

the oxidation of *o*-DCB. In contrast, in the case of MoO_3 (Fig. 4) and Fe_2O_3 catalysts, as well as with Co_3O_4/Al_2O_3, the reaction was not affected by the presence of water. Finally, the activity of the Co_3O_4/TiO_2 catalyst (Fig. 5) increased in the presence of water.

Water can affect the rate of *o*-DCB oxidation in two different ways. Via a competitive adsorption mechanism it can block a number of active sites, and hence, inhibit the rate of the reaction. Our previous work with V_2O_5/TiO_2 has indeed shown that at temperatures in the range of interest in the current study, a significant amount of water is adsorbed on the active vanadia sites (33). Water can also facilitate the removal of Cl^- present on the catalyst surface by the following reaction:

$$Cl^- + H_2O \rightarrow HCl + OH^-.$$

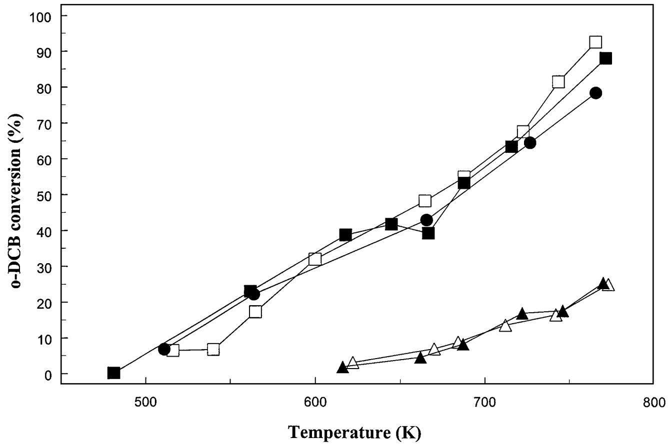

FIG. 4. Effect of water on the activity of supported MoO_3 catalysts for the oxidation of *o*-DCB. (□, ■, ●) 8.9 wt% MoO_3/TiO_2, (△, ▲) 9.0 wt% MoO_3/Al_2O_3 ((□, △) 600 ppmv *o*-DCB, 10% O_2; (■, ▲) additional 1% H_2O; and (●) additional 5% H_2O).

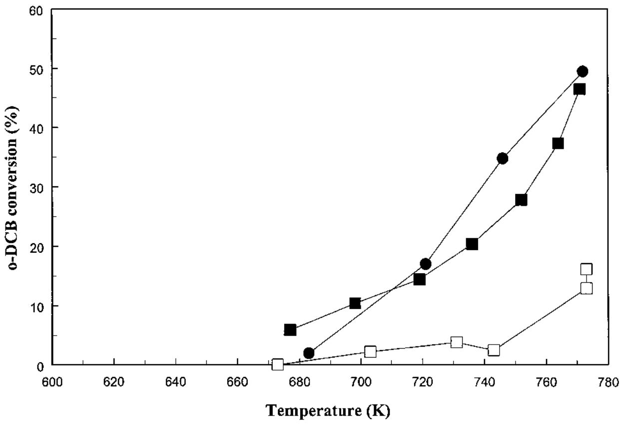

FIG. 5. Effect of water on the activity of a 4.5 wt% Co_3O_4/TiO_2 catalyst for the oxidation of *o*-DCB. (□) 600 ppmv *o*-DCB, 10% O_2; (■) additional 1% H_2O; and (●) additional 5% H_2O.

The overall observed effect of water depends on the relative importance of these two mechanisms. Cr_2O_3 and V_2O_5 catalysts are the most active ones under dry conditions, which suggests that surface Cl^- removal may not be kinetically significant in these cases. In addition, these catalysts are active at lower temperatures, at which the adsorption of water is an important issue. An increase in the water concentration from 1 to 5% further reduces the activity of Cr_2O_3/Al_2O_3 as can be observed in Fig. 3. This is consistent with the competitive adsorption mechanism, which appears to be significant under these conditions, explaining the observed reduction in the activity.

In the case of the Fe_2O_3 and MoO_3 catalysts, neither of the two proposed mechanisms appears to be important. This is further supported by the fact that no change in activity is observed with an increase in the water concentration from 1 to 5%. The fact that these catalysts operate at higher temperatures than Cr_2O_3 and V_2O_5 may explain the reduced importance of water adsorption in these cases.

Finally, the increased activity of the Co_3O_4/TiO_2 catalyst can be attributed to the removal of surface Cl^- through its reaction with water. An increase in the water concentration from 1 to 5% did not result in any further increase in activity, suggesting that most of the Cl^- is effectively removed from the catalyst surface at the 1% water level. This hypothesis is further supported by elemental analysis results obtained with the spent catalysts tested both in the presence and in the absence of water. These catalysts contained 0.25 and 1.20 wt% Cl^-, respectively.

Product selectivity. Results from previous studies on the oxidation of chlorobenzenes suggest the formation of by-products such as polychlorinated benzenes and polychlorinated biphenyls over Pt-based and $CuCl_2$-based catalysts, respectively (9, 34). In contrast, when vanadia-based catalysts were used for the oxidation of chlorinated benzenes, CO and CO_2 were the only carbon-containing products detected (10, 14). Similar results were obtained with Cr_2O_3-based catalysts for the oxidation of 1,2-dichlorobenzene (35), chlorobenzene (36), chloromethane (37), and trichloroethylene (38). During our current investigation CO and CO_2 were the only carbon-containing products detected through GC analysis. The ratio of the amounts of CO to CO_2 formed was approximately 30 : 70 in the case of Fe_2O_3, 40 : 60 in the case of Co_3O_4 and V_2O_5, and 10 : 90 in the case of Cr_2O_3. From a practical standpoint, the formation of CO or any other partial oxidation by-product does not represent a problem in this case, due to the very low concentration of PCDD/PCDFs (ppb level) in the flue gas of the incinerators and their extremely high toxicity equivalence.

Carbon balances in our study were closed to ±5%. There was, however, a trace amount of organic residue formed on the wall of the reactor. This was identified to be a polychlorinated phenol, but apparently the selectivity toward this compound is very low, and hence, its formation did not significantly affect the closure of the carbon balances.

In Situ FTIR Spectroscopic Studies

Dry conditions. *In situ* FTIR spectra of the Cr_2O_3/Al_2O_3 catalyst collected after 5 min on-stream at different temperatures are shown in Fig. 6. All the spectra show the presence of a main feature at 1577 cm^{-1} with adjoining shoulders at approximately 1550 and 1612 cm^{-1}. Also seen in all cases is a peak at 1437 cm^{-1} along with a doublet at 1389 and 1376 cm^{-1}, although the former appears to be very weak at the lower temperature. Additional peaks of low intensity are observed at 1455, 1360, 1322, and 1290 cm^{-1}. Finally, a doublet is observed at 1234 and 1217 cm^{-1} in the spectra collected at temperatures below 623 K. These spectra are similar to the ones obtained with the V_2O_5/Al_2O_3 catalyst in our previous studies (16). The strong peak at 1577 cm^{-1} (assymmetric $-COO^-$ stretching) and the doublet at 1389 (–CH bending) and 1376 cm^{-1} (symmetric $-COO^-$ stretching) can be assigned to surface carboxylates of the formate type, on the basis of previous studies of the adsorption of phenol on Cr_2O_3 (39), *n*-butane on $MgCr_2O_4$ (40), and dichloromethane on Al_2O_3 (41, 42). The shoulder at 1550 cm^{-1} (asymmetric $-COO^-$ stretching) along with peaks at 1437 (symmetric $-COO^-$ stretching) and 1360 cm^{-1} ($-CH_3$ bending) can be assigned to carboxylates of the acetate type (40, 43–46). Both types of carboxylates are formed on the transition metal site but could easily migrate to the alumina support. As can be seen in the spectra of Fig. 6, the formation of acetates becomes favored over the formates at higher temperatures, due to the lower stability of the latter. The total amount of surface carboxylates (as indicated by the broad feature at 1550–1580 cm^{-1} incorporating the main peaks of both acetate and formate species) initially increases with temperature up to 623 K, and then decreases at the higher temperature (i.e., 673 K). This behavior is the result of the increased oxidation activity of the catalyst at elevated temperatures (which leads to a higher formation rate of carboxylates) combined with the lower stability of these species at the higher temperatures (leading to their further oxidation to carbon oxides). The result is the maximum in intensity of the carboxylate peaks seen in Fig. 6.

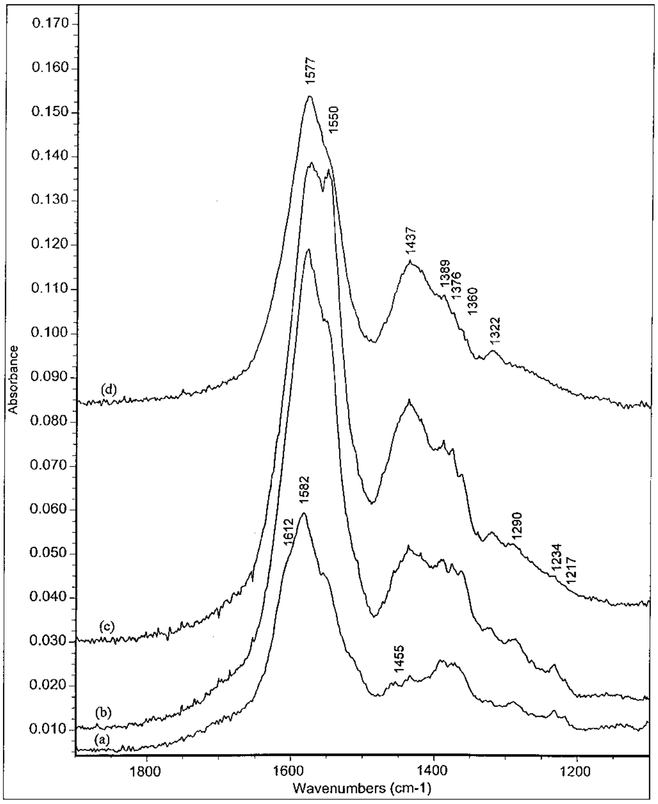

FIG. 6. *In situ* FTIR spectra of the Cr_2O_3/Al_2O_3 catalyst collected after 5 min on-stream at (a) 523 K, (b) 573 K, (c) 623 K, and (d) 673 K (700 ppmv *o*-DCB, 5% O_2, balance He).

The peak at 1322 cm^{-1} has previously been assigned to surface maleate species (47). The doublet at 1234 and 1217 cm^{-1} is characteristic of the C–O stretching vibrations of phenates (47, 48), whereas the peak at approximately 1290 cm^{-1} has previously been assigned to a C–O stretching vibration of a phenolic group on Cr_2O_3 (39, 49). Characteristic peaks of these phenate-type species were observed only in spectra collected at lower temperatures, indicating a higher reactivity of these species at elevated temperatures. In fact, spectra collected at different time intervals indicate that these species are also formed at the higher temperatures but react quickly under these conditions.

Finally, no peaks corresponding to C–Cl vibrations were observed in any of the spectra of Fig. 6, which has also been the case for V_2O_5/Al_2O_3 (16). This indicates that Cl abstraction is the first step in the activation of *o*-DCB. A similar first step for the oxidation of chlorinated organics has also been suggested by Hatje *et al.* (50) on the basis of studies of the adsorption of chlorobenzene on Pt–Y and

Pd–Y catalysts. Finocchio *et al.* (51) have further suggested that organic compounds are first activated at their weakest point (i.e., the C–H bond for hydrocarbons and the C–Cl bond for chlorinated hydrocarbons). All these results are in agreement with our assessment that the aromatic ring remains intact during the adsorption process and that the resulting adsorbed species is probably bonded through the dechlorinated carbon atoms.

Similar mechanisms have also been proposed by van den Brink *et al.* (41) and Clet *et al.* (52) for the adsorption of CH_2Cl_2 and CCl_4, respectively, on Al_2O_3. According to van den Brink *et al.*, during the adsorption of CH_2Cl_2, a Cl atom is displaced and the remaining group is attached to the alumina surface. This is quickly followed by the abstraction of the second Cl atom. The Cl atoms can either replace surface hydroxyl groups and react with the Al^{3+} ions to form aluminum chloride, or pick up protons to form HCl. A similar mechanism has also been proposed by Clet *et al.*

When the spectrum of the Cr_2O_3/Al_2O_3 sample was collected at 573 K in the absence of O_2 (Fig. 7), similar peaks were observed as in the case where O_2 was present, suggesting that the adsorbed partially oxidized species can be formed via reaction with surface oxygen. The only difference is that the intensity of most of the peaks is lower in the absence of O_2.

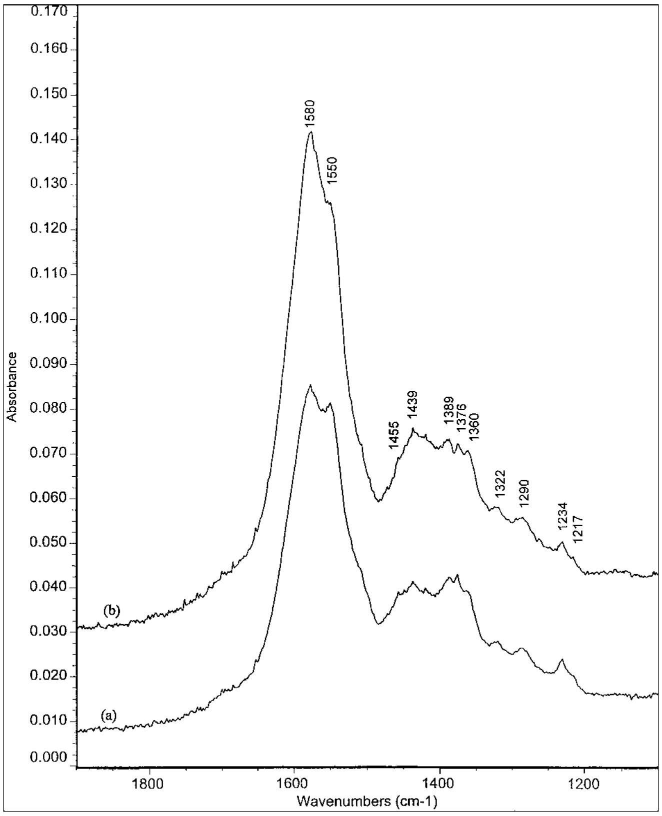

FIG. 7. *In situ* FTIR spectra of the Cr_2O_3/Al_2O_3 catalyst collected after 5 min on-stream at 573 K. (a) 700 ppmv *o*-DCB, balance He; (b) 700 ppmv *o*-DCB, 5% O_2, balance He.

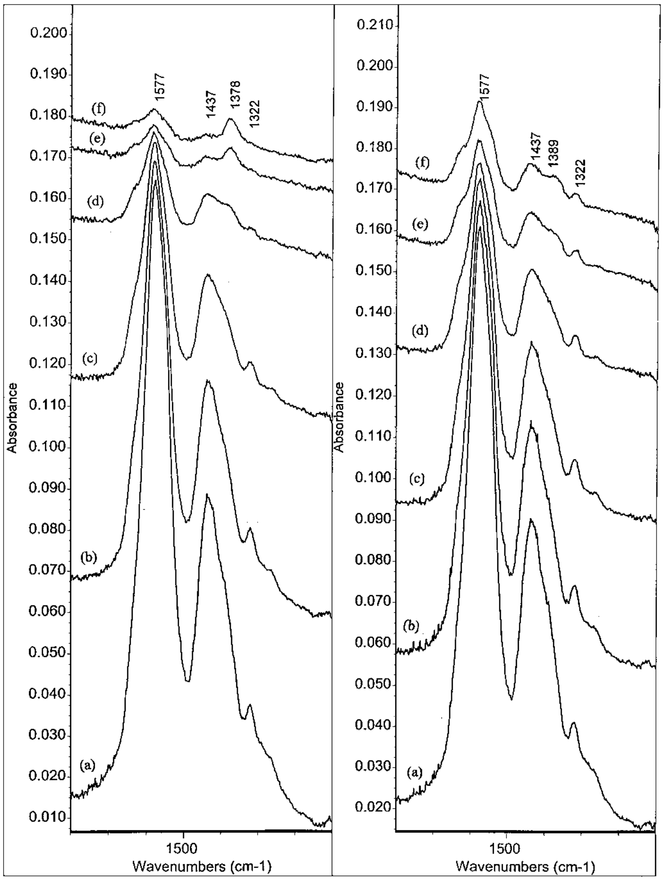

FIG. 8. (Left) *In situ* FTIR spectra of the Cr_2O_3/Al_2O_3 catalyst collected in (a) 700 ppmv *o*-DCB, 5% O_2 in He at 673 K after 30 min on-stream, followed by flushing with O_2 for (b) 1 min, (c) 5 min, (d) 20 min, (e) 60 min, and (f) 90 min. (Right) *In situ* FTIR spectra of the Cr_2O_3/Al_2O_3 catalyst collected in (a) 700 ppmv *o*-DCB, 5% O_2 in He at 673 K after 30 min on-stream, followed by flushing with He for (b) 1 min, (c) 5 min, (d) 20 min, (e) 60 min, and (f) 90 min.

The stability/reactivity of the different adsorbed species formed on Cr_2O_3/Al_2O_3 at 673 K was examined next. A sample was initially exposed to the reacting gas mixture for 30 min, in order to allow for sufficient amounts of the different surface species to be formed. At that point, the flow of the reactants was stopped, and the sample was exposed to either He or a 5% O_2 in He mixture with spectra collected at different time intervals. These spectra are shown in Fig. 8. As can be seen in the figure, the intensities of the FTIR peaks corresponding to the different surface species are reduced significantly regardless of whether He or 5% O_2/He is used. A reduction in intensity of the different peaks under He flow indicates the relatively low stability of these species at 673 K. Since the disappearance rate is more pronounced in the presence of O_2, we can conclude that all these surface species react with O_2 toward the final products, i.e., CO and CO_2. In addition, the spectrum collected after 120 min in

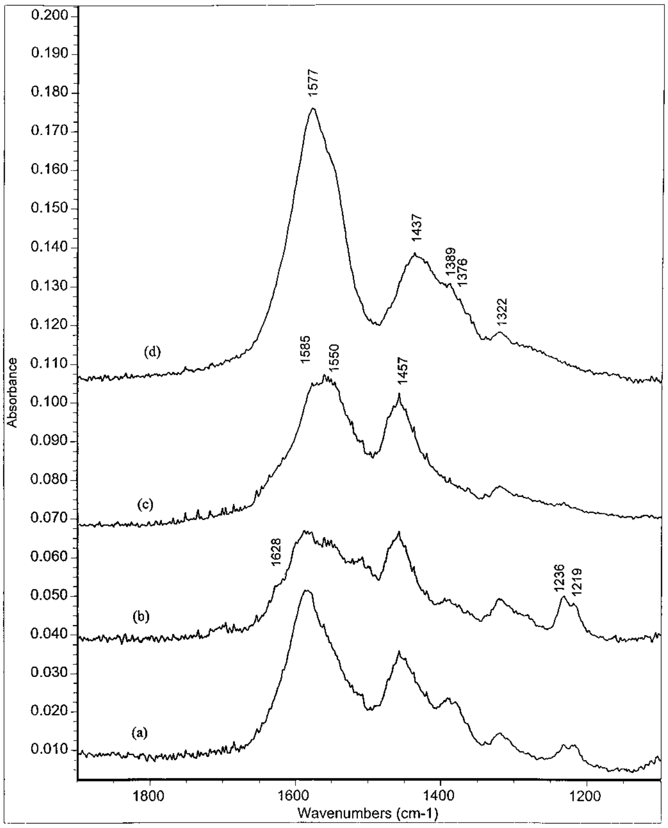

FIG. 9. *In situ* FTIR spectra collected after 5 min on-stream at 673 K: (a) Co_3O_4/Al_2O_3, (b) Fe_2O_3/Al_2O_3, (c) V_2O_5/Al_2O_3, and (d) Cr_2O_3/Al_2O_3 (700 ppmv *o*-DCB, 5% O_2 in He).

O_2 revealed the presence of a peak at 1378 cm^{-1}, which was found to be very stable on the catalyst surface. A similar peak has previously been assigned to a coke deposit (53).

A comparison of spectra collected at 673 K after 5 min on-stream for the different transition metal oxide catalysts studied is attempted in Fig. 9. The positions of the IR peaks corresponding to the different partially oxidized species were almost identical in all these spectra. The only significant difference is that the peak corresponding to the symmetric $-COO^-$ stretching of acetates was present at 1457 cm^{-1} for the V_2O_5, Fe_2O_3, and Co_3O_4 systems and was shifted to 1437 cm^{-1} for the Cr_2O_3 system. This result may be interpreted to suggest that the surface acetate species is primarily associated with Cr_2O_3 in this system and with the Al_2O_3 support in all the other cases. The doublet at 1236 and 1219 cm^{-1} corresponding to surface phenolates is observed only in the case of the Co_3O_4/Al_2O_3 and Fe_2O_3/Al_2O_3 catalysts, which can be attributed to the lower activity of these catalysts at 673 K as compared to the other two transition metal oxides. This doublet was also present in the spectra of the other transition metal oxides, when these spectra were collected at lower temperatures.

The spectra shown in Fig. 9 suggest that a similar mechanism operates over all the supported transition metal oxides studied. The first step of this mechanism is the removal of a Cl atom from the aromatic ring and its subsequent substitution with a surface oxygen, via what is probably a nucleophilic mechanism. The removal of Cl is likely affected by the nature of the support. The removal of the second Cl atom and the formation of a second carbon–surface oxygen bond follow the first step. This second step leads to the formation of an adsorbed form of dihydroxybenzene. Since no peaks corresponding to C–Cl vibrations were observed in any of the spectra, the abstraction of the second Cl atom is likely to be a fast step. The dihydroxybenzene species can react further, undergoing ring cleavage and leading to the formation of formates, acetates, and maleates. All of these surface species react with oxygen to form CO, CO_2, and H_2O. Our FTIR studies suggest that the rates of oxidation of the acetates and formates are almost one order of magnitude higher than that of the maleates.

Effect of water. *In situ* FTIR experiments were also performed to study the effect of water on the concentration of the different surface species. During these experiments, a steady state was obtained first by flowing the reactants in the absence of water over the catalyst for a certain period

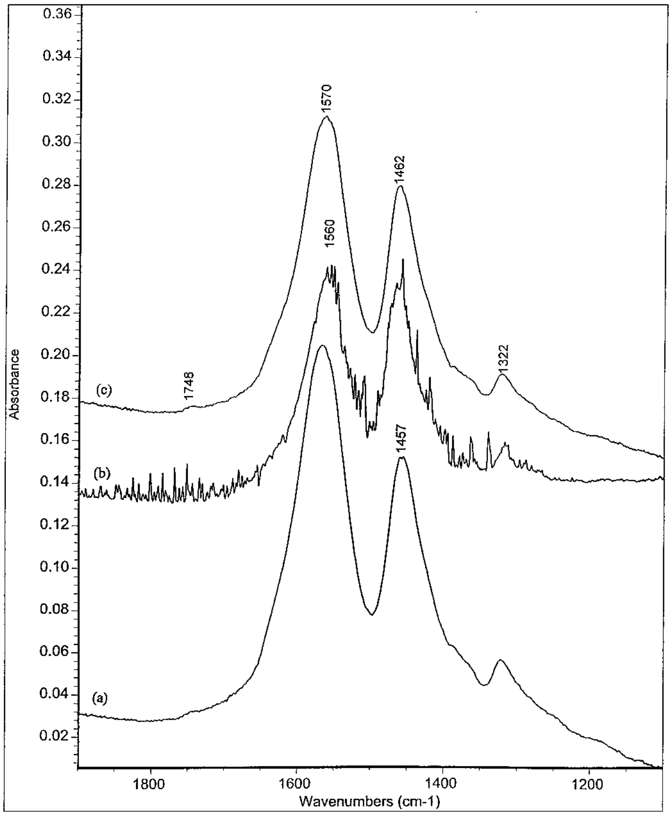

FIG. 10. *In situ* infrared spectra of the V_2O_5/Al_2O_3 catalyst collected at 623 K in (a) 700 ppmv *o*-DCB and 5% O_2 in He for 120 min, followed by (b) 700 ppmv *o*-DCB, 1.4% water, and 5% O_2 in He for 120 min, and (c) 700 ppmv *o*-DCB, 5% O_2 in He for 90 min.

of time. This was followed by the introduction of 1.4% water vapor to the reaction stream. Spectra were collected at different time intervals as the system approached a new steady state. Subsequently the flow of water was stopped and a new set of spectra was collected. The choice of the operating temperatures was such that all catalysts exhibited similar activity.

Results obtained with V_2O_5/Al_2O_3 at 623 K are shown in Fig. 10. These results indicate a decrease in the concentration of the surface carboxylates in the presence of water. This can be attributed to the formation of surface hydroxyls on the vanadia sites, which partially prevents the formation of carboxylates, thus decreasing their surface concentration. Such an explanation is consistent with the competitive adsorption mechanism utilized to rationalize the observed water effect on the catalyst activity. This effect is reversible, since the removal of water from the reacting mixture leads to a new steady-state spectrum very similar to the one obtained prior to the introduction of water.

Similar results were also observed with the other Al_2O_3-supported catalysts. In the case of the Cr_2O_3/Al_2O_3 catalyst at 523 K (Fig. 11), the presence of water resulted in the complete removal of the surface phenolates present under these conditions. Furthermore, there was an apparent change in the distribution of surface formates and acetates, with the former being significantly decreased in the presence of water. Spectra collected following water removal from the gas phase (Fig. 11c) indicate the reestablishment of the phenolate peaks, and an increase in the amount of surface acetates at the expense of the formates. A new peak was also observed at 1404 cm^{-1}, which along with a shoulder at approximately 1540 cm^{-1} (probably covered by the intense acetate peak at 1550 cm^{-1}) has previously been assigned to surface carbonates of the bidentate type (51). These changes point to a potential irreversible change of the Cr_2O_3/Al_2O_3 system upon exposure to water vapor.

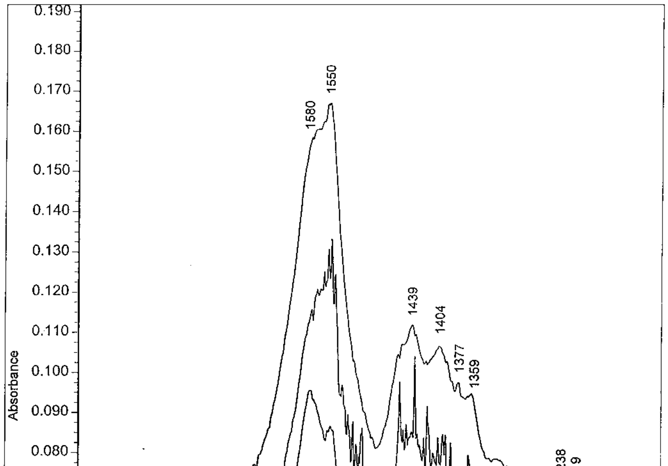

FIG. 11. *In situ* infrared spectra of the Cr_2O_3/Al_2O_3 catalyst collected at 523 K in (a) 700 ppmv *o*-DCB and 5% O_2 in He for 35 min, followed by (b) 700 ppmv *o*-DCB, 1.4% water, and 5% O_2 in He for 60 min, and (c) 700 ppmv *o*-DCB, 5% O_2 in He for 45 min.

CONCLUSIONS

A systematic kinetic and *in situ* FTIR investigation of the oxidation of *o*-DCB has been carried out over supported Cr_2O_3, V_2O_5, Fe_2O_3, MoO_3, and Co_3O_4 catalysts. Our activity measurements show that the transition metals are the active sites for this reaction. Cr_2O_3 and V_2O_5 catalysts exhibited the highest activity among the different oxides tested. The activity was also affected by the nature of the support (i.e., $M_xO_y/TiO_2 > M_xO_y/Al_2O_3$), which may indicate that the metal–oxygen–support bond is critical for this reaction.

Our *in situ* FTIR studies indicate the presence of several partial oxidation products (i.e., formates, acetates, maleates, and phenolates) on the surface of the different transition metal oxide catalysts examined. All these species can react further to form CO, CO_2, and H_2O under certain reaction conditions. Furthermore, all these partial oxidation products can be formed even in the absence of gas-phase oxygen, indicating that surface oxygen is involved in their formation. No evidence could be found in any of the spectra collected over the different catalysts for the presence of a surface species containing a C–Cl bond, indicating that Cl abstraction is the first step of the reaction. The presence of the same species over all the catalysts studied indicates that a similar mechanism operates in all cases.

The addition of water to the reaction stream had different effects on the various catalysts. The activity of Cr_2O_3 and V_2O_5 catalysts was inhibited due to the competition between *o*-DCB and water for adsorption onto the catalyst sites. In contrast, the presence of water had a promoting effect on the Co_3O_4/TiO_2 catalyst, which can be attributed to the more efficient removal of Cl^- from the surface. Finally, the addition of water had no significant effect on the activity of the MoO_3 and Fe_2O_3 catalysts, indicating that neither competitive adsorption nor the removal of surface Cl^- is kinetically important in these cases. *In situ* FTIR studies in the presence of water indicated a decrease in the concentration of the different surface species, consistent with a competitive adsorption effect.

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