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Catalytic oxidation of 1,2-dichlorobenzene over V_2O_5/TiO_2-based catalysts

Sundaram Krishnamoorthy[a], Julia P. Baker[b], Michael D. Amiridis[a,*]

[a]*Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA*
[b]*Department of Chemistry, Winthrop University, Rock Hill, SC 29733, USA*

Abstract

A systematic investigation of the oxidation of 1,2-dichlorobenzene (*o*-DCB) was conducted over a series of vanadia/titania catalysts with different V_2O_5 loadings (i.e. 0.8, 3.6 and 5.8 wt%). The TiO_2 support was also found to be active for this reaction, but its activity was significantly lower than that of the surface vanadia species. Reaction rates per vanadium atom (i.e. turnover frequencies) were calculated for these catalysts and found to be independent of the vanadia coverage. Kinetic measurements showed that under excess oxygen conditions, the reaction is approximately first order in *o*-DCB and zero order in oxygen. Carbon monoxide and carbon dioxide were the only products detected. The selectivity towards CO was approximately 40–45% and was found to be independent of vanadia loading and temperature. No deactivation of the catalyst was observed even after 100 h of operation at 723 K. Addition of WO_3, MoO_3 and ZnO to the V_2O_5/TiO_2 system was found to have no significant effect on its activity for *o*-DCB oxidation. © 1998 Elsevier Science B.V.

Keywords: Vanadia/titania; Chlorinated VOCs; Oxidation; Dichlorobenzene; Dioxin

1. Introduction

Various air pollutants are present in the flue gas generated from municipal and medical waste incinerators due to the diversity and complexity of the incinerated waste. Such units are widely used today as an ''environmentally friendlier'' alternative to the traditional land disposal of waste. In addition to standard combustion byproducts such as CO, NO_x and SO_x, trace amounts of chlorinated volatile organic compounds (VOCs), including polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), have been detected in the flue gas of such incinerators [1]. The 1990 Clean Air Act Amendments (CAAA) have placed stringent regulations on the emission of such pollutants.

Several control strategies apply in general to the control of VOCs, such as catalytic and thermal oxidation and adsorption on activated carbon [2]. These can also be utilized for PCDD/PCDF emission control. The high toxicity and low concentration of these compounds in the exhaust gas makes catalytic destruction to CO_2 and HCl the method of choice.

Noble metal-based catalysts, in general, exhibit the highest activity for oxidation of volatile organics [3]. Such catalysts however are not particularly suited for the destruction of chlorinated VOCs, since they undergo deactivation due to halide poisoning of the noble metal [4]. Improved Cl-resistant formulations of

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*Corresponding author. E-mail: amiridis@sun.che.sc.edu

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noble metal-based catalysts have been introduced recently to overcome this shortcoming [5,6]. Alternatively, the use of transition metal oxides such as Cr_2O_3, MnO_2, CuO, Co_3O_4, TiO_2, WO_3 and V_2O_5, has been proposed [7–11]. Among these systems, chromia/alumina has the highest activity [12], but the high toxicity of chromium causes serious disposal problems with this system. Other classes of catalysts, such as zeolites, pillared clays, molten salt-based systems and perovskites, have also been considered for chlorinated VOC control [13–18].

NO_x emissions from municipal waste incinerators are currently controlled via the Selective Catalytic Reduction (SCR) of NO by NH_3. V_2O_5/TiO_2-based catalysts are considered state-of-the-art for this application [19]. Field measurements have indicated that incinerator units fitted with commercial NO_x control catalysts show a reduction of dioxin emission [20,21]. However, there is virtually no information currently available regarding the fundamental chemistry of the catalytic destruction of PCDD/PCDF over these catalysts. Only recently, Jones and Ross [22] have carried out the oxidation of chlorinated organics, primarily ethyl chloride, over supported vanadia catalysts.

In this work, we investigated the catalytic destruction of 1,2-dichlorobenzene (*o*-DCB), which is structurally similar to the more toxic 2,4,7,8-tetrachlorodibenzodioxin. A detailed kinetic analysis of this reaction was performed. In addition, we investigated the effect of catalyst parameters such as the vanadia loading and the presence of a second transition metal oxide (i.e., WO_3, MoO_3 and ZnO). It should be noted that the present experiments were conducted in the absence of other gases that may be present in a typical flue gas (e.g. H_2O, SO_2, NH_3), which may affect the kinetics and bias some of the results presented in this paper. Our long term goal is the design of an improved catalyst for the combined control of NO_x and dioxin emission and this work represents just the first step in this direction.

2. Experimental

2.1. Catalyst preparation

All catalysts used in this investigation were prepared via incipient wetness impregnation. Vanadium oxalate, 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), was used as the vanadia precursor. The TiO_2 support (Kemira-905) was impregnated with the appropriate amounts of precursor solution to incipient wetness and dried overnight at 353 K in a convection oven. The catalyst samples were then heated from 308 to 723 K in 2 h, followed by subsequent heating to 793 K in 6 h. The catalysts were finally calcined at 793 K for 2 h.

For the preparation of promoted catalysts, aqueous solutions of ammonium metatungstate, ammonium molybdate and zinc acetate were used as the precursors for WO_3, MoO_3 and ZnO, respectively. Equal amounts of 0.8% V_2O_5/TiO_2 catalyst were impregnated with the appropriate amounts of precursor solutions to incipient wetness and then dried and calcined according to the same protocol followed for the unpromoted samples.

All catalysts used in this investigation were subjected to elemental analysis by inductively coupled plasma (ICP) spectroscopy (Galbraith Laboratories) and BET surface area measurements (Pulse Chemisorb 20000). The results are reported in Table 1.

2.2. Activity measurements

Kinetic experiments were carried out in a stainless steel, single-pass, fixed bed reactor. *o*-DCB was chosen as a model compound because of its structural similarity to the part of dioxin that is most difficult to

Table 1
Composition and surface area of catalysts studied

Catalysts	V[a]	V[b]	M[c]	M[d]	SA[e]
TiO_2	—	—	—	—	85
V_2O_5/TiO_2	0.8	0.9	—	—	70
V_2O_5/TiO_2	3.6	4.0	—	—	69
V_2O_5/TiO_2	5.8	6.4	—	—	77
V_2O_5–MoO_3/TiO_2	0.9	1.0	4.9	3.4	69
V_2O_5–WO_3/TiO_2	0.8	0.9	7.3	3.1	80
V_2O_5–ZnO/TiO_2	0.8	0.9	2.5	3.1	68

[a] Vanadia loading (wt% V_2O_5).
[b] Vanadium loading (mol V/g catalyst$\times 10^{-4}$).
[c] Additive loading (wt% MO_x).
[d] Additive loading (mol M/g catalyst$\times 10^{-4}$).
[e] BET surface area (m^2/g).

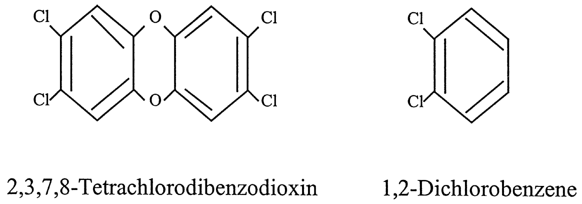

Fig. 1. Chemical structure of dioxin and *o*-DCB.

be oxidized (Fig. 1). *o*-DCB was introduced to the reactor by the passage of a N_2 stream through a saturator maintained at room temperature. The saturated stream was mixed with O_2 and N_2 to achieve the desired concentrations, preheated, and introduced to the reactor. The volumetric flow through the catalyst bed 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. Activity measurements were also conducted with different particle sizes from 45–60 to 120–170 mesh. These measurements demonstrated the absence of any intraparticle diffusional limitations in the 473–673 K temperature range.

Analyses of reactants and products were performed on-line using two gas chromatographs (SRI 8610) equipped with flame ionization and thermal conductivity detectors. The analyses of *o*-DCB and CO/CO_2 were conducted through 1/8 in. silica gel and Carbosieve S-II columns, respectively. Prior to its introduction to the gas chromatograph (GC), 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 columns. For the purpose of identifying all reaction products, experiments were also conducted with the product gas stream directly injected into the GC.

3. Results and discussion

3.1. *Activity of* V_2O_5/TiO_2 *catalysts*

The *o*-DCB conversion over V_2O_5/TiO_2 catalysts with different vanadia loadings is shown as a function of temperature in Fig. 2. The TiO_2 support was also found to exhibit some activity for the reaction, which

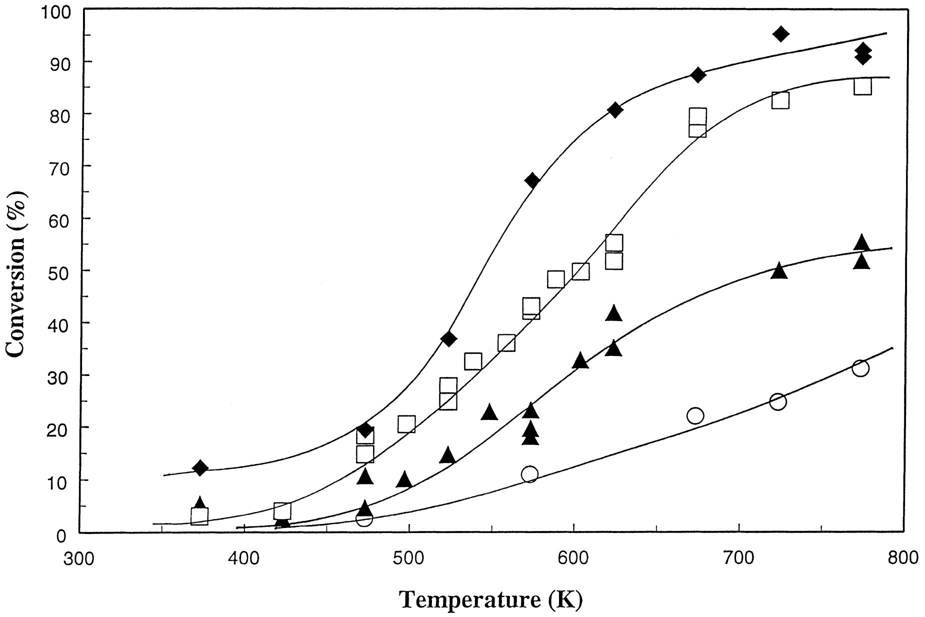

Fig. 2. Effect of temperature on the activity of V_2O_5/TiO_2 catalysts of variable vanadia loading for *o*-DCB oxidation: (◆) 5.8% V_2O_5/TiO_2; (□) 3.6% V_2O_5/TiO_2; (▲) 0.8% V_2O_5/TiO_2; (○) TiO_2 (600 ppm *o*-DCB, 10% O_2).

is in agreement with previous results reported for methylene chloride oxidation [23]. The conversion of *o*-DCB however, shows a significant enhancement with the addition of vanadia to the support, and increases with increasing vanadia loading in the range studied. This confirms that the vanadia sites are more active for the oxidation of dichlorobenzene. V–O and V–Cl bond energies are in the order of 121 kJ/mol [13]. These values are lower than that for most other transition metals (e.g. 289 and 213 kJ/mol for Ti–O and Ti–Cl, respectively; 159 and 117 kJ/mol for Co–O and Co–Cl, respectively; 167 kJ/mol for Cr–Cl, etc), which could explain the high oxidation activity of vanadia for this class of organics.

Reaction rates per vanadium atom (i.e. turnover frequencies) at the inlet *o*-DCB concentration were calculated next 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 equations:

$$r_V = k_V C_{o\text{-DCB}}, \quad (1)$$

$$k_V = -(Q/\eta_V)[\ln(1 - x_{V/T}) - [\ln(1 - x_T)](1 - f_V)], \quad (2)$$

where

- r_V is the turnover frequency of *o*-DCB oxidation over vanadia at the inlet conditions,
- k_V is the first order rate constant for *o*-DCB oxidation over vanadia,
- $C_{o\text{-DCB}}$ is the inlet *o*-DCB concentration,
- Q is the volumetric flow rate to the reactor,
- η_V is the total number of V^{5+} mol in the reactor (calculated from the mass of the catalyst and the vanadia loading),
- $x_{V/T}$ is the fractional conversion of *o*-DCB across the reactor for the V_2O_5/TiO_2 catalyst,
- x_T is the fractional conversion of *o*-DCB across the reactor for the TiO_2 support, and
- f_V is the fractional coverage of V_2O_5 (calculated from the vanadia loading and a monolayer coverage of 13 μmol V^{5+}/m^2 [20]).

These expressions assume that vanadia is fully dispersed on the titania support, in agreement with previous studies which showed this to be the case at submonolayer coverages [24,25].

It is interesting to compare the turnover frequencies thus obtained for the three vanadia catalysts studied,

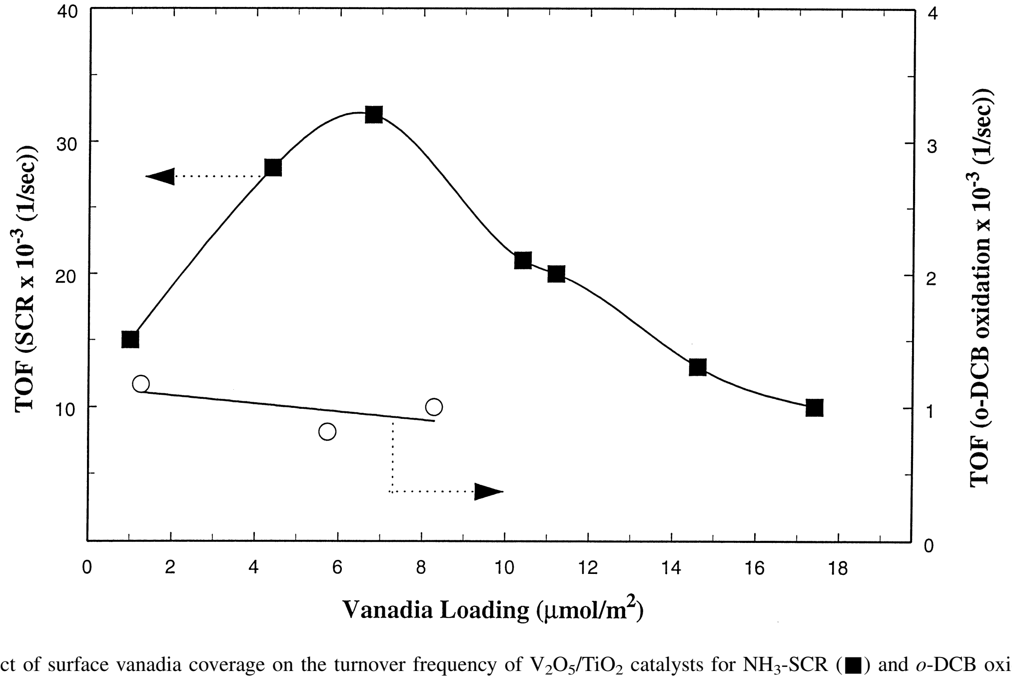

Fig. 3. Effect of surface vanadia coverage on the turnover frequency of V_2O_5/TiO_2 catalysts for NH_3-SCR (■) and *o*-DCB oxidation (○) (623 K; SCR conditions as in [26]; *o*-DCB conditions as in Fig. 2).

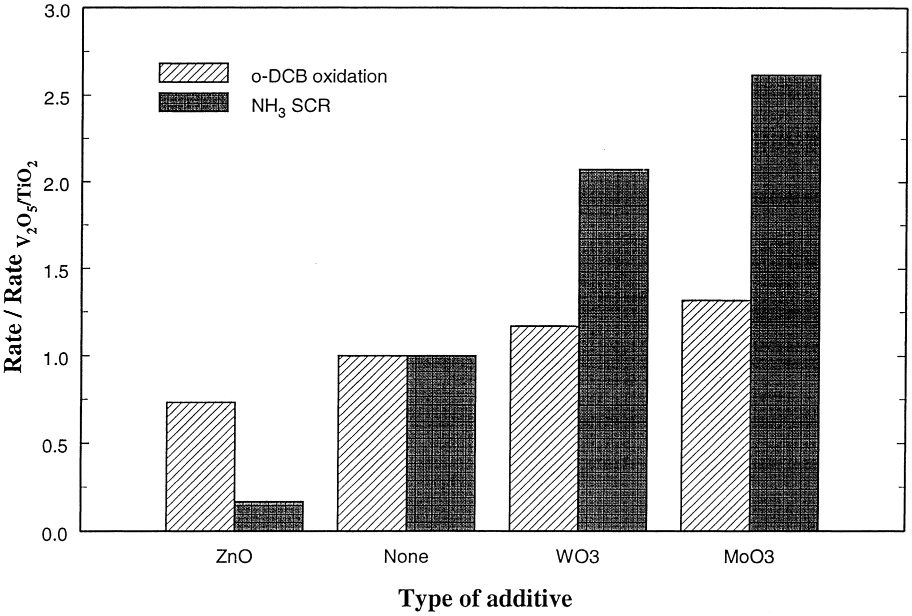

Fig. 4. Effect of additives on the rate of NH_3-SCR and *o*-DCB oxidation over the 0.8% V_2O_5/TiO_2 catalyst (623 K; SCR conditions as in [32]; *o*-DCB conditions as in Fig. 1).

especially in view of the fact that vanadia in this system is known to exist in different structural forms depending on vanadia coverage [24–28]. At low coverages, vanadia exists primarily as an isolated tetrahedrally coordinated surface vanadyl species. At higher coverages, the vanadyl monomers combine to form polymeric vanadyl species that share an oxygen bridge. Finally, at coverages exceeding a monolayer (approximately 13 μmol V^{5+}/m^2) microcrystallites of vanadia start growing on the surface.

We have previously shown that the SCR activity of V_2O_5/TiO_2 catalysts varies as a function of the vanadia coverage ([26]; Fig. 3). These changes in activity have been attributed to differences in the activity of the monomeric and polymeric species, as well as changes in acidity with vanadia coverage [26,29,30]. On the contrary, as shown in the same figure, the turnover frequency for the catalytic oxidation of *o*-DCB is independent of the vanadia coverage in the range of coverages studied. Similar results have been reported for methanol oxidation over the same catalysts [24]. The results of Fig. 3 demonstrate that the factors that control SCR activity are not equally important for the oxidation of *o*-DCB. They further suggest that in contrast to SCR, where both redox and acid sites are believed to be kinetically important, a single redox site is participating in the rate determining steps of *o*-DCB oxidation.

Consistent with these arguments, the addition of a second transition metal oxide to V_2O_5/TiO_2 had different effects on its activity for SCR and *o*-DCB oxidation. Such additives are usually present in V_2O_5/TiO_2-based commercial SCR formulations for a variety of reasons including a promoting effect on SCR activity [19,31,32]. The effect of three such additives (MoO_3, WO_3 and ZnO) on the normalized rates of SCR and *o*-DCB oxidation is shown in Fig. 4. Changes in SCR activity have been correlated with changes in the Brønsted acidity of the catalyst [32]. As can be seen in Fig. 4 however, the presence of these oxides did not significantly alter the *o*-DCB oxidation activity of the V_2O_5/TiO_2 catalyst.

3.2. *Kinetic studies*

The effect of the concentrations of the two reactants on the rate of *o*-DCB oxidation was studied at two different temperatures and vanadia coverages. The concentration of *o*-DCB was varied in the 100–1000 ppm range, while the corresponding concentra-

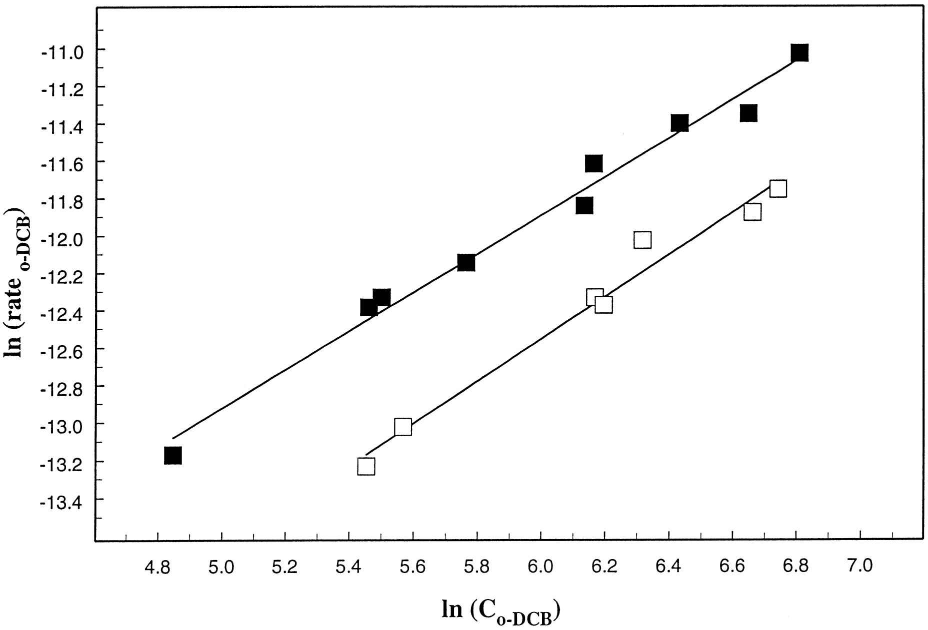

Fig. 5. Rate of *o*-DCB oxidation over the 3.6% V_2O_5/TiO_2 catalyst as a function of *o*-DCB concentration (10% O_2; (□) 523 K, and (■) 573 K).

tion of O_2 was varied between 1000 ppm and 10%. During these studies, the reactor was operated under differential conditions and the rate was calculated according to the following equation:

$$r_{o\text{-DCB}} = -QC_{o\text{-DCB}}x/m, \tag{3}$$

where m is the mass of the catalyst.

The observed rates were found to give a good fit to a simple power law expression. An example is given in Fig. 5, which shows the rate of *o*-DCB oxidation as a function of the *o*-DCB concentration over the 3.6% V_2O_5/TiO_2 catalyst at 523 and 573 K. The kinetic parameters thus obtained are summarized in Table 2. As can be seen in this table, the rate of *o*-DCB oxidation was found to be approximately first order in *o*-DCB and zero order in O_2, regardless of temperature or vanadia coverage. At low concentrations of O_2, however, the *o*-DCB oxidation rate becomes dependent on the oxygen concentration as shown in Fig. 6. All commercial applications for this reaction, however, are expected to operate under excess O_2 conditions.

Table 2
Kinetic parameters for *o*-DCB oxidation
$r = kC_{o\text{-DCB}}{}^{a}\,C_{O_2}{}^{b}$

Vanadia loading	a		b	
	523 K	573 K	523 K	573 K
0.8%	1.3	0.9	0.3	0.1
3.6%	1.1	1.0	0.2	0.0

Table 3
Activation energies for *o*-DCB oxidation over different V_2O_5/TiO_2 catalysts

Catalyst	Activation energy (kJ/mol)
0.8% V_2O_5/TiO_2	37
3.6% V_2O_5/TiO_2	31
5.8% V_2O_5/TiO_2	30

Finally, activation energies for the reaction were calculated based on the turnover frequencies for the different V_2O_5/TiO_2 catalysts and are shown in Table 3. The calculated values are between 30 and 37 kJ/mol. These values are similar to those reported previously for the oxidation of methylene chloride over sulfated transition metal oxides (35–43 kJ/mol)

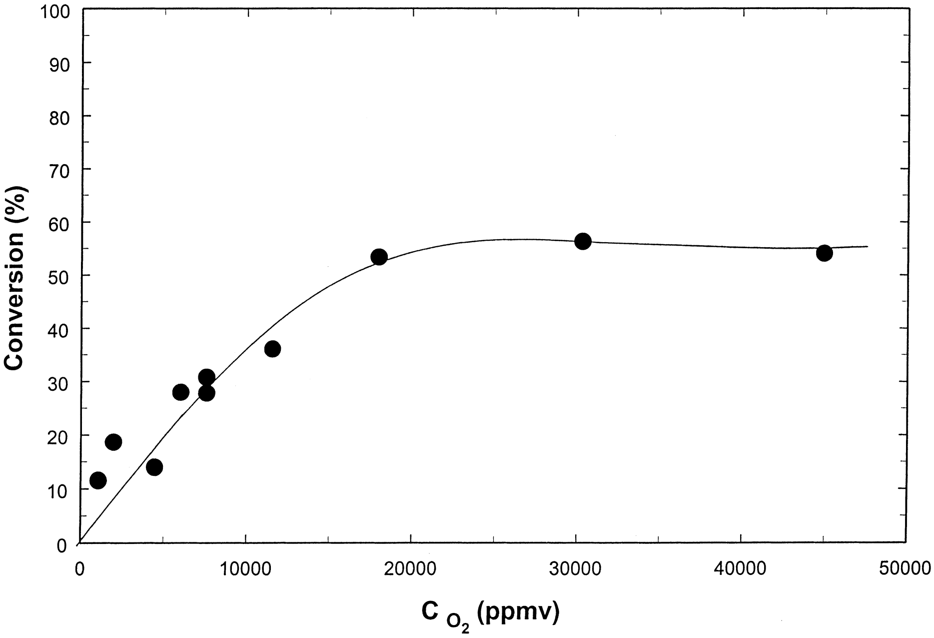

Fig. 6. Effect of O_2 concentration on *o*-DCB oxidation at 573 K over the 3.6% V_2O_5/TiO_2 catalyst (600 ppm *o*-DCB).

[23]. On the contrary, they are significantly lower than the activation energies reported for *o*-xylene oxidation over vanadia-based catalysts (115–120 kJ/mol) [33]. This difference could be attributed to the lower energy of C–Cl bonds as compared to the substituted C–H bonds in similar molecules (approximately 63–84 kJ/mol less) [34].

3.3. Product selectivity

The chromatographic analysis performed on the product stream identified the formation of CO and CO_2 and also quantified their production. In recent studies of *o*-DCB oxidation over $CuCl_2$-based catalysts, poor carbon balances were obtained in the concentration range 1000–10 000 ppm and incomplete combustion products (i.e. $C_{12}HCl_9$) were formed on the walls of the reactor [17]. During our experiments, carbon balances were closed within ±5% and only CO and CO_2 were detected in the analysis of the product stream. The selectivities of the V_2O_5/TiO_2 catalysts towards CO formation were found to be in the order of 40–45%, independent of temperature and vanadia coverage, and were affected slightly by changes in the concentration of oxygen and *o*-DCB. CO formation has also been reported in the literature for the oxidation of polychlorinated biphenyls and methylene chloride over copper and chromium oxide-based catalysts, respectively [35,36].

With the exception of *o*-DCB no other chlorine-containing organics were detected during the chromatographic analyses, even when the reaction products were directly injected into the GC (i.e. without scrubbing). Jones and Ross [22] have reported that under similar conditions, HCl is the only chlorine-containing product of the oxidation of chlorobenzene over $V_2O_5/ZrO_2–Al_2O_3$. Since in a typical run of our current study, a scrubber containing an alumina-based material was utilized to remove all HCl formed, before the introduction of the product stream to the chromatographic column, the closure of the chlorine balance becomes problematic. Furthermore, elemental analysis of spent catalyst after 80 h of operation indicates the presence of a significant amount of Cl on the catalyst (0.76 wt%). However, the presence of Cl on the catalyst does not appear to affect its performance, since no change in activity was observed even after 100 h on stream at 623 K.

4. Conclusions

The catalytic oxidation of *o*-DCB has been investigated over a series of V_2O_5/TiO_2-based catalysts. Although the TiO_2 support is active for this reaction, the addition of vanadia significantly enhances the activity of the catalysts. Unlike the selective catalytic reduction of NO by NH_3, the turnover frequency for the oxidation of *o*-DCB is independent of the surface vanadia coverage, suggesting that only a single surface redox site participates in the kinetically significant step(s). Similarly, the addition of a second transition metal oxide to the V_2O_5/TiO_2 catalyst has no significant effect on the reaction rate. A kinetic investigation showed the reaction to be approximately first order in *o*-DCB and zero order in O_2 under excess oxygen conditions. Activation energies of 29–37 kJ/mol were calculated in the 473–673 K temperature range. Dichlorobenzene is oxidized to CO and CO_2 and no other incomplete combustion product were detected. The selectivity towards CO is approximately 40–45% and is not affected by changes in temperature and vanadia coverage.

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References

[1] K. Olie, P.L. Vermeulen, O. Hutzinger, Chemosphere 6 (1977) 445.
[2] J.J. Spivey, J.B. Butt, Catal. Today 11 (1992) 465.
[3] J.J. Spivey, Ind. Eng. Chem. Res. 26 (1987) 2165.
[4] I.M. Freidel, Proceedings of the 1992 Incineration Conference, vol. 287, 1992.
[5] I.M. Freidel, A.C. Frost, K.J. Herbert, F.J. Meyer, J.C. Summers, Catal. Today 17 (1993) 367.
[6] H. Muller, K. Deller, B. Despeyroux, E. Peldszus, P. Kammerhoffer, W. Kuhn, R. Spielmannleitner, M. Stoger, Catal. Today 17 (1993) 383.
[7] H. Nagata, T. Takakura, S. Tashiro, D. Kishida, K. Mizuno, I. Tamori, K. Wakabayashi, Appl. Catal. B 5 (1994) 23.
[8] H. Windawi, M. Wyatt, Platinum Metals Rev. 37(4) (1993) 186.
[9] L. Jin, M.A. Abraham, Ind. Eng. Chem. Res. 30 (1991) 89.
[10] S. Imamura, H. Tarumoto, S. Ishida, Ind. Eng. Chem. Res. 28 (1989) 1449.
[11] S.L. Hung, L.D. Pferfferle, Environ. Sci. Tech. 23(9) (1989) 1085.
[12] G.R. Lester, Proceedings of the 1989 Annual AWMA Meeting, Anaheim, vol. 96 A, 1989.
[13] H. Shaw, Y. Wang, T.-C. Yu, A.E. Cerkanowicz, ACS Symp. Ser. 518 (1993) 358.
[14] G. Wendt, M. Hackenberger, D. Kieling, R. Schneider, Kraak, Proceedings of the Fourth International Conference on Advanced Materials, Po-274, Oxidation Catalysis, Cancun, Mexico, 1995.
[15] L. Storaro, R. Ganzerla, M. Lenarda, R. Zanoni, J. Mol. Catal. A 97 (1995) 139.
[16] H.L. Greene, D.S. Prakash, K.V. Athota, Appl. Catal. B 7 (1996) 213.
[17] R.M. Lago, M.L.H. Green, S.C. Tsang, M. Odlyha, Appl. Catal. B 8 (1996) 107.
[18] B. Ramachandran, H.L. Greene, S. Chatterjee, Appl. Catal. B 8 (1996) 157.
[19] C.J. Pereirra, M.D. Amiridis, ACS Symp. Ser. 587 (1995) 1.
[20] R. Boos, R. Budin, H. Hartl, M. Stock, F. Wurst, Chemosphere 25 (1992) 375.
[21] K.B. Carlsson, Chemosphere 25 (1992) 135.
[22] J. Jones, J.R.H. Ross, Catal. Today 35 (1997) 97.
[23] X. Jiang, L. Zhang, X. Wu, L. Zheng, Appl. Catal. B 9 (1996) 229.
[24] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 323.
[25] I.E. Wachs, J. Catal. 124 (1990) 570.
[26] M.D. Amiridis, I.E. Wachs, G. Deo, J. Jehng, D.S. Kim, J. Catal. 161 (1996) 247.
[27] I.E. Wachs, G. Deo, B.M. Weckhuysen, A. Andreini, M.A. Vuurman, M. de Boer, M.D. Amiridis, J. Catal. 161 (1996) 211.
[28] G.E. Went, L.-J. Leu, A.T. Bell, J. Catal. 134 (1992) 479.
[29] N.-Y. Topsøe, H. Topsøe, J.A. Dumesic, J. Catal. 151 (1995) 226.
[30] G.T. Went, L.-J. Leu, R.R. Rosin, A.T. Bell, J. Catal. 134 (1992) 492.
[31] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.
[32] M.D. Amiridis, R.V. Duevel, I.E. Wachs, Appl. Catal. B (submitted).
[33] G.C. Bond, P. Konig, J. Catal. 77 (1982) 309–322.
[34] CRC Handbook of Physics and Chemistry, 48th ed., The Chemical Rubber, 1967–1968.
[35] P. Subbanna, H.L. Greene, Environ. Sci. Tech. 22 (1988) 557.
[36] S.K. Agarwal, J.J. Spivey, J.B. Butt, Appl. Catal. A 82 (1992) 259.