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The activity and mechanism of uranium oxide catalysts for the oxidative destruction of volatile organic compounds

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Abstract

Uranium oxide based catalysts have been investigated for the oxidative destruction of volatile organic compounds (VOCs) to carbon oxides and water. The catalysts have been tested for the destruction of a range of organic compounds at space velocities up to 70 000 h^{-1}. Destruction efficiencies greater than 99% can be achieved over the appropriate uranium based catalyst in the temperature range 300–450°C. Volatile organic compounds investigated include benzene, butylacetate, cyclohexanone, toluene, methanol, acetylene, butane, chlorobutane and chlorobenzene. The catalysts are thermally stable, destroy low concentrations and mixtures of VOCs and lifetime studies indicate that deactivation during oxidation of chlorinated VOCs did not occur. A temporal analysis of products (TAPs) reactor is used to investigate the mechanism of oxidation of VOCs by uranium oxide catalysts. Studies indicated that VOCs were oxidised directly to carbon oxides on the catalyst surface. A combination of TAP pulse experiments with oxygen present and absent in the gas phase has indicated that the lattice oxygen from the catalyst is responsible for the total oxidation activity. This has been confirmed by studies using isotopically labelled oxygen which indicates that the catalyst operates by a redox mechanism. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the last several years, environmental legislation has imposed increasingly stringent limits for permitted atmospheric emission levels. In particular, the release of volatile organic compounds (VOCs) has received much attention. VOCs are a wide ranging class of chemicals derived from many sources and contain over 300 compounds as designated by the United States Environmental Protection Agency [1]. Their release has widespread environmental implications and has been linked to the increase in photochemical smog [2], the depletion in atmospheric ozone [3] and the production of ground-level ozone [4]. In addition, many VOCs are inherently toxic and/or carcinogenic. The US Clean Air Act (1990) calls for a 90% reduction in the emissions of 189 toxic chemicals, many of which are VOCs, by 1998. In 1994 it has been estimated that 706 000 t of organic pollutants were discharged to the atmosphere from the US alone [5]. Approximately 70% of these compounds can be classed as VOCs and although it cannot be determined directly, it is estimated that discharges worldwide are at least twice that of the US. In view of the magnitude of the problem presented to the chemical and processing industries, the major challenge they face is to reduce the emission of pollution without stifling economic growth.

Abatement technologies to control the release of VOCs to the environment are therefore of paramount importance. Many technologies for the treatment of

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VOC laden effluent have been developed, the most widely adopted being adsorption, often using carbon or zeolite type adsorbents. However, this process can generate considerable further waste as the adsorbent must usually be buried in landfill sites. The most widely adopted technique is thermal combustion or incineration, which requires temperatures in excess of 1000°C. Whilst it is a simple and often effective method of control, the high temperatures required culminate in a relatively fuel intensive technique with little control over the ultimate products. The latter is particularly problematic and can result in incomplete oxidation of the waste stream and the formation of toxic by-products such as dioxins, dibenzofurans and oxides of nitrogen, if conditions are not carefully controlled. Alternatively, heterogeneous catalytic oxidation offers many potential advantages. The use of a catalyst in the oxidative destruction of VOCs significantly lowers the process operating temperature, which is typically in the range 300–600°C. This reduction in temperature is advantageous, as economically little or no supplementary fuel is required to sustain combustion. Legislatively too, the process is no longer regarded as an incineration process, eliminating certain regulatory requirements. In addition, catalytic oxidation offers a much greater degree of control over the reaction products and can operate with dilute effluent streams ($<1\%$ VOC), which cannot be treated easily by thermal combustion. Hence, catalytic oxidation may be considered as a more appropriate method for end of pipe pollution control.

Two classes of catalysts are commonly used, these are noble metal and metal oxide based systems. A prospective catalyst must be active at relatively low temperatures and show high selectivity to carbon oxides. Ideally, the catalyst must also be able to destroy effectively low concentrations of VOCs at very high flow rates with little or no deactivation. Supported noble metal systems, primarily platinum and palladium, show high activity for the oxidation of many VOCs, with high selectivity to carbon oxide products. However, these tend to be relatively expensive and can be rapidly deactivated by the presence of chlorinated compounds, sulphur or other metals in the waste stream [6]. The second class of catalysts are metal oxides and some of the most active ones are based on copper [7], cobalt [8], chromium [9] and manganese [10]. Generally, these are less expensive than precious metals and show higher resistance to poisoning. However, for complete oxidation they are inherently less active. The development of oxide catalysts which may be used for the combustion of a wide range of volatile organic compounds presents a major challenge for future research.

This work outlines the advances made in the development of a new series of uranium oxide based catalysts and presents the results of transient studies using a temporal analysis of products (TAPs) reactor to unravel the reaction mechanism. Uranium oxide was initially selected as a catalyst for several reasons, in particular, U_3O_8 has uranium present in mixed oxidation states with a facile transition between states, and can also show a wide range of metal/oxygen stoichiometry. These are important features which are characteristic of other oxidation catalysts. Additionally uranium oxides have also shown relatively high activity for carbon monoxide oxidation [11]. Uranium oxide based catalysts have been widely used by the chemical industry for a considerable time. Well established procedures for the safe handling of these materials exist and these are primarily determined by issues of chemical toxicity. The results presented in this paper demonstrate that uranium oxides show high and stable activity for the destruction of a range of VOCs under industrially relevant flow rates and temperatures. Previously, uranium oxides have been considered by many as a burden on our environment; however, this work demonstrates that they can be effectively used to provide a solution to a major problem affecting the environment.

2. Experimental

2.1. Catalyst preparation and characterisation

Uranium oxide, U_3O_8, was prepared by the thermal decomposition of uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$) at 800°C in static air. A series of uranium oxide catalysts supported on silica (BDH fumed) were also prepared by impregnation of SiO_2 with the uranyl nitrate solution. An incipient wetness impregnation technique requiring 4.2 ml of $0.3952\,\text{mol}\,\text{l}^{-1}$ uranyl nitrate solution per gram of SiO_2 was used. The loading of the supported catalyst was 10 mol% U/SiO_2. The catalyst precursor was prepared by drying in air for 16 h at 100°C. The catalyst was produced by calcination of the precursor in static air at 800°C. A series of supported catalysts containing transition metal dopants were also prepared, the total catalyst active loading was 10 mol% with a U/dopant ratio of 9:1. The procedure was similar to that detailed previously, although after the initial drying stage, the precursor was impregnated with the nitrate solution of the second supported component. The resulting material was again dried at 100°C before calcination at 800°C. Bulk catalyst phases were determined using powder X-ray diffraction and identification was made by matching to the JCPDS powder diffraction file. Surface areas were determined by nitrogen adsorption in accordance with the BET method.

2.2. Steady state catalyst testing

Catalyst testing was performed using a conventional plug flow microreactor with a stainless steel reactor tube. Gas flow rates were regulated by mass flow controllers and liquid feed was introduced via a syringe pump to a vaporiser maintained at 150°C. Typically, a gas hourly space velocity of 70 000 h^{-1} (ml min^{-1} at STP/ml catalyst) was used resulting in a catalyst charge ca. 100 mg for the supported catalysts and ca. 200 mg for U_3O_8. Unless specifically stated otherwise, catalysts were pelleted to a 425–600 μm particle size before being secured in the reactor between plugs of silica wool. Heating was supplied by a furnace with a 15 cm uniform heated length, the reaction temperatures quoted are measured using a K-type thermocouple placed alongside but external to the catalyst bed. A further K-type thermocouple was placed inside the reactor tube and the temperature of the exit gas measured approximately 1 cm from the catalyst bed. In the majority of experiments, a 1% VOC concentration in air was used for catalyst screening.

Analysis of reactant and product was performed on-line using a Varian 3400 gas chromatograph with Porapak P and 5A molsieve columns and a Hiden quadrupole mass spectrometer. Conversion data was calculated using the %VOC in the outlet stream, which was detectable down to ppm levels using the mass spectrometer. Product selectivities were expressed as percentage of the converted VOC after correction for differences in carbon number, and carbon mass balances were in the range 100±6%.

2.3. TAP studies

A TAP reactor was used in continuous flow and TAP pulse modes to investigate the oxidation of a variety of VOCs including butane, benzene and chlorobutane. A detailed explanation of the design and capabilities of the TAP reactor are given elsewhere [12]. Prior to reactivity studies, detailed experiments were carried out to accurately determine the mass spectral fragmentation patterns of the VOCs and expected reaction products. This was achieved by preparing gas mixtures in a high purity (99.99%) neon standard and the fragmentation patterns collected from a continuous flow of the mixture through a reactor packed with inert quartz particles sieved to a comparable particle size distribution as that of the catalyst. These data were also used to determine the total sensitivity of reactant and products relative to the *m*/*e* peak at 20 for neon.

3. Results and discussion

3.1. Catalyst activity

Powder X-ray diffraction showed that catalysts produced by the decomposition of uranyl nitrate in air consisted of U_3O_8; furthermore, the silica supported catalysts also showed exclusively diffraction lines from U_3O_8. The catalyst BET surface areas were: U_3O_8=5.7 $m^2\,g^{-1}$; U_3O_8/SiO_2=110 $m^2\,g^{-1}$; Co_3O_4=4.2 $m^2\,g^{-1}$. The combustion activity of uranium oxide catalysts have been determined for a range of typical VOCs which are chemically different in nature. The compounds investigated include benzene, butane, butylacetate, cyclohexanone, chlorobenzene, chlorobutane, acetylene, methanol and toluene. Blank reactions in an empty reactor and using a catalyst bed of pelleted silica used to produce the supported catalysts indicated that activity for the combustion of all the VOCs at 70 000 h^{-1} was negligible. For example, benzene showed 1% conversion to CO_2 over SiO_2 at 500°C, whilst at 600°C 3% butane conversion to CO_2 was observed. Representative data for the oxidation of a range of VOCs are shown in Table 1.

The uranium oxide catalysts showed high activity and the sole carbon reaction products were carbon oxides. No partially oxygenated or other toxic hydrocarbon by-products were detected. In the case of the

Table 1
Catalytic activity of uranium oxide catalysts for the oxidation of a range of VOCs[a]

Catalyst	VOC type	Temperature (°C)	Conversion (%)	Selectivity (%)	
				CO	CO_2
U_3O_8	Benzene	400	99.9	23	77
U_3O_8/SiO_2	Benzene	400	99.9	26	74
Co_3O_4	Benzene	400	83	–	100
U_3O_8	Butane	500	3	5	95
U_3O_8	Butane	600	81	14	86
U_3O_8/SiO_2	Butane	500	99.9	37	63
Co_3O_4	Butane	500	75	–	100
Co_3O_4	Butane	600	68	–	100
U_3O_8	Chlorobenzene	350	99.7	41	59
U_3O_8/SiO_2	Chlorobenzene	400	99.9	41	59
Co_3O_4	Chlorobenzene	400	0	–	–
Co_3O_4	Chlorobenzene	600	62	16	84
U_3O_8	Chlorobutane	350	>99.5	45	55
U_3O_8	Cyclohexanone	300	99.9	29	71
U_3O_8/SiO_2	Cyclohexanone	300	99.9	34	66
Co_3O_4	Cyclohexanone	300	0	–	–
Co_3O_4	Cyclohexanone	350	99.9	4	96
U_3O_8	Butylacetate	350	99.9	23	77
U_3O_8/SiO_2	Butylacetate	350	99.9	22	78
U_3O_8/SiO_2	Butylacetate	350	99.9	3	97
U_3O_8	Methanol	300	99.9	47	53
U_3O_8	Acetylene	400	97.4	35	65
U_3O_8/SiO_2	Toluene	400	99.9	10	90

[a] 1% VOC in air; GHSV=70 000 h^{-1}.

chlorinated VOCs, HCl was the sole chlorine containing product, this is preferred to Cl_2, and can be readily removed from the effluent stream by downstream aqueous scrubbing. Comparison of catalytic activity was made with Co_3O_4 which was selected as it is recognised as a highly active catalyst for the deep oxidation of many other organic substrates [13]. In many cases comparison with the activity of Co_3O_4 has been made and it is evident that uranium oxide based catalysts show superior deep oxidation activity. The comparison for cyclohexanone and chlorobenzene is striking as the uranium oxide catalysts show high conversions at temperatures at which Co_3O_4 is inactive. With some organics the conversion is greater over U_3O_8 than Co_3O_4, and although the surface area of U_3O_8 is marginally greater than the cobalt oxide, the increased activity is not solely dependent on surface area. It is also evident that the uranium oxide catalysts are active at relatively low temperatures, generally high VOC conversion was achieved below 450°C, which compares very favourably with temperatures in excess of 1000°C which are required for thermal combustion.

Supporting uranium oxide on an inert silica had little effect on the conversion and product selectivity for VOCs like benzene, cyclohexanone and butylacetate. However, the supported catalysts did increase the activity for butane oxidation, and at 500°C butane conversion over U_3O_8/SiO_2 was 100% compared to 3% over U_3O_8. The catalyst surface area for the silica supported system is greater than U_3O_8 and although it is difficult to measure the active surface area of the supported catalyst, the uranium oxide loading was calculated to be in the region of that required for monolayer coverage. The identification of U_3O_8 crystallites with average diffracting domains in the region of 100 Å in combination with preliminary electron microscopy results, not shown in this study, indicate that monolayer coverage was not achieved, however, dispersion of the active U_3O_8 phase is relatively high and it is the increase in active surface area which gives rise to the increased activity. Although not shown here the catalytic activity of the uranium oxide catalysts can also be modified by the incorporation of low levels of metals such as copper and chromium to further enhance the catalyst activity and increase the selectivity for CO_2 >99% [14,15]. The low activity for the blank reactions indicates that the destruction of benzene and butane VOCs were, at least, heterogeneously initiated processes, with little catalytic contribution from the silica support.

In particular, it is the high activity shown by U_3O_8 for the destruction of chlorobenzene and chlorobutane which is striking, as chlorinated VOCs are in general more difficult to destroy and can lead to catalyst deactivation. Considering the high activity shown by the uranium oxide catalysts, it is important to compare their activity with other previously cited examples used for chlorinated VOC destruction. This comparison is shown in Table 2.

Catalysts of the type $CuCl/KCl/SiO_2$ have previously shown the best performance for chloro-organic destruction [16]. These catalysts operate at similar temperatures as the uranium oxide catalyst; however, low flow rates and consequently high contact times were employed. Comparison between the two systems indicates that over 230 times more VOC was destroyed by the uranium oxide catalysts than the CuCl based system in a fixed time period. Notable activity was also shown by Co–Zeolite Y and Cr_2O_3, although the former produced CO almost exclusively, whilst a considerably higher temperature was required for the latter. The only previously reported attempt to destroy chlorobenzene used a Pt/Al_2O_3 catalyst at GHSV=30 000 h^{-1} [17]. A feed stream of 398 ppm was used and although ultimate destruction limits were similar to the uranium oxide catalysts, a temperature nearly 200°C higher was required. The activity of the precious metal catalyst has been taken from values available in the open literature and are not data from a commercial catalyst; but we consider the comparison to be a valid one as the results presented for uranium oxide systems in this study are not those for fully optimised catalysts. It is therefore clear that uranium oxide based catalysts offer some advantages over other types of catalysts for VOC destruction.

3.2. *Effect of VOC concentration*

In many of the studies with different VOCs, a large hysteresis effect in the conversion was observed once the catalyst was active and then the external furnace temperature was decreased. This effect was particularly evident for benzene conversion over the U_3O_8/SiO_2 catalyst (Fig. 1).

A gradual decrease in the benzene conversion was observed on decreasing the reaction temperature from 400°C. The conversion decreased to 93% at 200°C and the catalyst became inactive when the temperature was decreased by a further 50–150°C. The conversion hysteresis and the characteristically steeply rising conversion can be attributed to the increase in the temperature of the catalyst bed during the highly exothermic benzene combustion ($\Delta H_{298}=-3302$ kJ mol^{-1}). At high conversion, the temperature of the gas stream close to the exit from the catalyst bed was consistently in the region of 30°C higher than the reactor furnace temperature. Calculations indicate that the adiabatic

Table 2
Comparison of catalytic performance for the destruction of chloro-organic compounds

Catalyst	VOC	Concentration (ppm)	Temperature (°C)	GHSV (h^{-1})	Conversion (%)	Referencces
U_3O_8	Chlorobenzene	10000	350	70000	99.7	This work
$CuCl/KCl/SiO_2$	Methylene chloride	10000	350	300	98.4	[16]
$0.1\%Pt/Al_2O_3$	Chlorobenzene	398	530	30000	92.0	[17]
Co–Zeolite Y	Trichloroethane	1500	325	2361	100	[18]
Cr_2O_3	Trichloroethane	10000	650	3600	99.7	[19]
TiO_2	CF_2Cl_2	2000	400	10500	98.0	[20]
WO_3/Al_2O_3	CF_3CF_2Cl	6700	600	15366	60.0	[21]

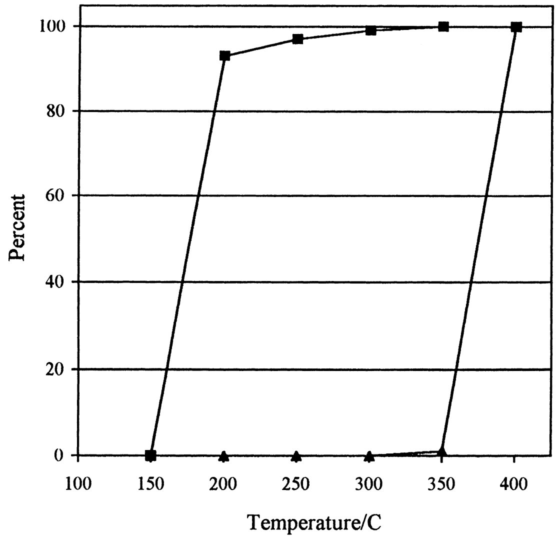

Fig. 1. Hysteresis in benzene conversion during combustion over U_3O_8/SiO_2 (1% VOC in air, GHSV=70 000 h^{-1}): (▲) increasing temperature; (■) decreasing temperature.

temperature rise within the catalyst bed was in the region of 1000°C. Very similar hysteresis were observed with many VOCs although the effect was not as great with compounds such as butane and chlorobenzene and this is a reflection of the lower enthalpies of combustion (butane, $\Delta H_{298}=-2878\,kJ\,mol^{-1}$ and chlorobenzene, $\Delta H_{298}=-3113\,kJ\,mol^{-1}$). The adiabatic temperature rise is clearly excessive, although it illustrates that the catalyst is thermally very stable as under these conditions many cycles through the hysteresis loop resulted in no discernible changes in activity. In view of the adiabatic temperature rise, we have investigated the destruction of benzene and chlorobenzene at lower concentrations, where such effects are reduced considerably. The destruction of low VOC concentrations is also an important prerequisite and one of the major advantages that a catalytic process offers over thermal combustion. The effect of decreasing benzene and chlorobenzene concentration on the destruction activity of U_3O_8 is shown in Figs. 2 and 3.

At 400°C, the benzene conversion over U_3O_8/SiO_2 decreased gradually as the concentration was reduced. The decrease in conversion was dramatic when the concentration was reduced to 0.24% as conversion was only 36%. Increasing the reaction temperature to 450°C restored the high activity as conversion over 85% was maintained. Studies were also made using a very dilute benzene feed (561 ppm). At equivalent space velocity U_3O_8/SiO_2 converted >90% benzene to carbon oxides at 400°C and this increased further to >95% at 450°C. At such low concentrations the

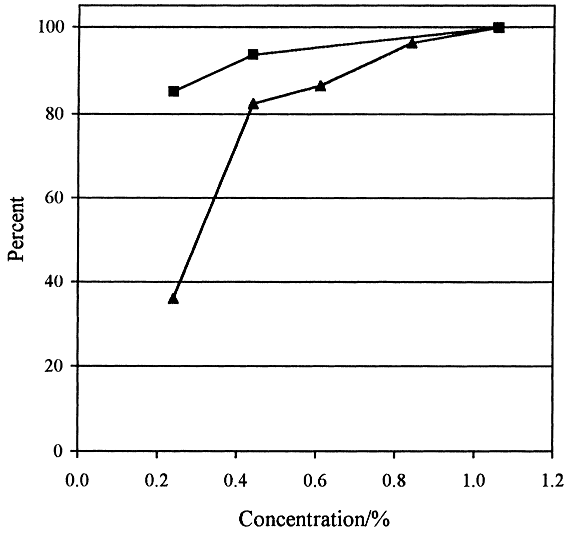

Fig. 2. Effect of benzene concentration on destruction efficiency of U_3O_8/SiO_2 at 70 000 h^{-1} space velocity: (▲) 400°C; (■) 450°C.

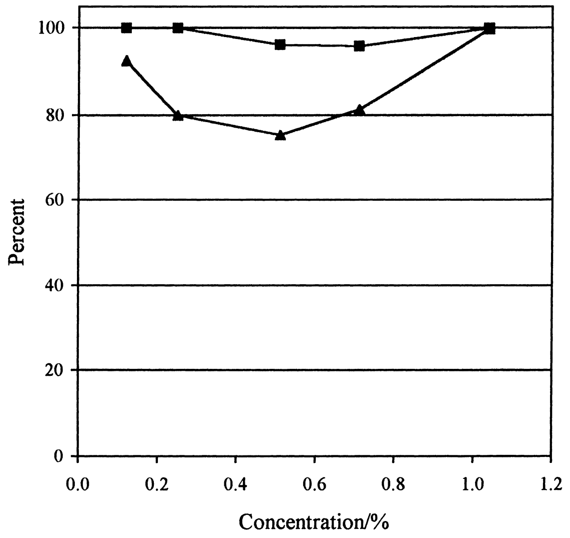

Fig. 3. Effect of chlorobenzene concentration on destruction efficiency of U_3O_8 at 70 000 h^{-1} space velocity: (▲) 350°C; (■) 400°C.

adiabatic temperature rise for the combustion reaction is around 50°C, and although the adiabatic temperature has a large effect on the conversion at higher VOC concentration, it is also evident that the catalyst still shows high inherent activity even when the reaction exotherm is greatly reduced.

Reducing the chlorobenzene concentration at a fixed temperature of 350°C was also accompanied by a general decrease in the conversion. This decrease was from 99.7% conversion at 1.04% chlorobenzene to 92.5% for 0.12% (1200 ppm) and passed through a minimum at 0.51%. Increasing the temperature by 50–400°C resulted in an increase of conversion across the concentration range. At 400°C conversion was maintained above 96% and for the majority of concentrations it was >99%. The adiabatic temperature rise for the destruction of the 1200 ppm feed stream is approximately 120°C indicating that the catalyst has high activity for chlorobenzene destruction over a wide range of concentrations. Decreasing the concentration had very little influence on the CO/CO_2 selectivity indicating that CO_2 was not predominantly produced by sequential oxidation of CO either by the catalyst surface or by homogeneous gas phase oxidation, but was an inherent product from chlorobenzene oxidation by the catalyst.

3.3. *Effect of VOC mixtures*

It is evident that the uranium oxide catalysts show high destruction activity for feed streams containing single VOC components, but when VOCs are present in mixtures, it has been observed that destruction efficiency is inhibited [22]. Such effects have been attributed to competitive adsorption of the VOCs on the catalyst surface. It is therefore important to determine the activity of the uranium oxide catalyst for the destruction of VOC mixtures. The combustion of a 1.16% benzene/chlorobenzene mixture (1:1.29) over U_3O_8 is shown in Fig. 4.

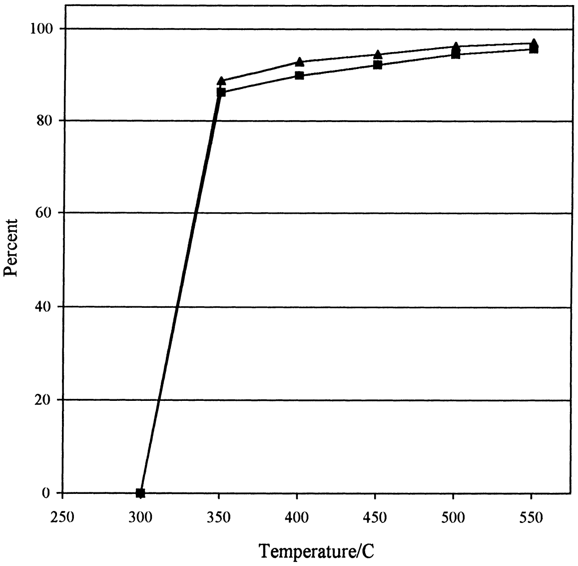

Fig. 4. Destruction of a 1.16% benzene/chlorobenzene mixture (1:1.29) over U_3O_8 at GHSV=70 000 h^{-1}: (■) benzene conversion; (▲) chlorobenzene conversion.

At 300°C trace conversion was observed and this increased rapidly to 89 and 86% at 350°C for benzene and chlorobenzene, respectively. The conversion of benzene over U_3O_8 when present as a single component at similar concentration was zero and thus the destruction of benzene in the VOC mixture was enhanced relative to the pure component. The conversion of chlorobenzene at 350°C was not adversely affected by the mixture and was of equivalent magnitude to the pure component at approximately the same concentration. The increased combustion of benzene is most probably associated with the increase in temperature within the catalyst bed once chlorobenzene combustion was initiated. In studies using solely chlorobenzene the light off temperature over U_3O_8 was 350°C whilst it was 400°C for benzene. Above 350°C the conversion of both components increased as the temperature increased. However, the increase in activity was small and ultimate conversions of benzene and chlorobenzene at 550°C were 97 and 96%, respectively. The gradual increase in conversion at temperatures above 350°C is indicative of a reaction rate limited by mass transport effects. This type of behaviour which shows two distinct regions of reactivity, one of which is mass transport limited, has been commonly observed for catalytic VOC combustion reactions [23] and such limitations can be resolved by reactor engineering. Similar behaviour was also observed when the total VOC concentration varied. Increasing the total concentration to 1.72% had no effect, but when it was decreased to 0.68%, higher conversion was observed which was >99% at 500°C and above.

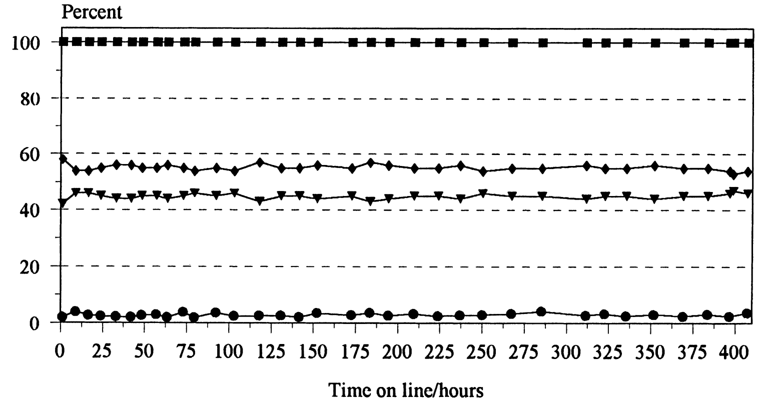

Fig. 5. Time on line studies for 0.12% chlorobenzene destruction over U_3O_8 at 450°C and 70 000 h^{-1} space velocity: (■) chlorobenzene conversion; (●) oxygen conversion; (◆) carbon monoxide selectivity; (▼) carbon dioxide selectivity.

3.4. Extended catalyst lifetime studies

One of the main reasons for developing oxide based catalysts is the increased tolerance to deactivation and long term stable activity compared to noble metal catalysts. Studies using a 1% feed have indicated that the U_3O_8 catalyst shows excellent thermal stability. It is also important that the catalysts used for VOC destruction applications show long term stable activity. Therefore, initial studies for the destruction of 1200 ppm chlorobenzene oxidation at 450°C have been performed to assess the effect of time on line (Fig. 5).

Chlorobenzene conversion remained at 99.9% for the duration of the study which lasted for over 400 h. During the test period, there were no fluctuations in CO and CO_2 selectivities outside those of experimental error. The duration of the study was relatively short in comparison to the lifetime required for a commercial catalyst, but the time on line studies indicate that significant deactivation did not take place in the presence of a chlorinated VOC or the HCl product.

3.5. Catalytic mechanism

TAP experiments were carried out with a range of VOCs and many similarities between different VOCs were observed. A typical TAP response for pulsed butane oxidation in anaerobic conditions (19.8% butane, 80.2% neon) over U_3O_8/SiO_2 at 479°C is shown in Fig. 6.

There are several important observations from the TAP pulse experiment. The first is that oxidation takes place in the absence of gas phase oxygen, suggesting that oxygen species from the catalyst are active in the oxidation cycle. All the catalysts were vacuum treated in situ at >500°C prior to pulse experiments, and consequently, the concentration of adsorbed oxygen would be minimal. The activity was maintained after many thousands of pulses, indicating that lattice oxygen was the active species. Secondly, analysis of the TAP data indicated that the response maximum for the products and reactants as a function of time increased and are all significantly broader than that of inert neon. As there are no diffusion effects in the TAP reactor system, this would indicate that the products and reactants interact with the catalyst surface and are adsorbed to varying degrees. This observation provides an indication that the reaction is occurring on the catalyst surface and not via gas phase processes.

It is also evident that the only carbon containing products were carbon monoxide and dioxide, which is consistent with the steady state reactor studies. The TAP reactor is particularly suited to the detection and identification of gas phase intermediate species which cannot be detected readily in conventional steady state studies. In the TAP system, the relatively low number of molecules passing through the catalyst bed and the absence of a carrier results in molecular beam transport through the bed, thus minimising collision between reactants and products. Consequently, highly reactive and short lived intermediates which are not

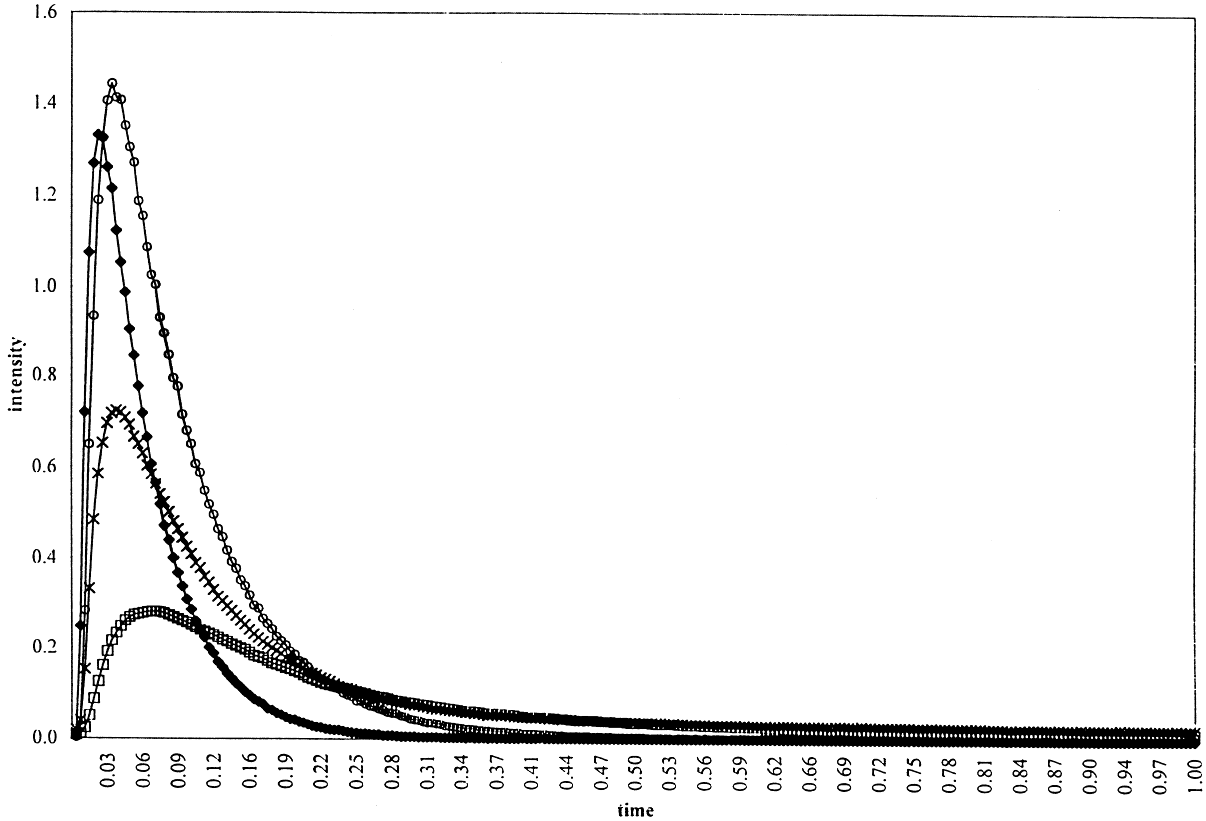

Fig. 6. TAP pulse response for butane oxidation at 479°C in the absence of gas phase oxygen: (◆) neon; (○) butane; (□) carbon dioxide; (×) carbon monoxide.

detected by conventional steady state techniques are readily observed in the TAP reactor. The absence of any partially oxidised intermediates in these studies indicates that the fundamental reaction pathway for the oxidation of these VOCs by U_3O_8 based catalysts takes place on the catalyst surface. The surface reaction pathway is unclear and it may be via a partially oxygenated intermediate; however, such intermediates do not desorb to the gas phase as they would be detected in these studies. This clearly contrasts with many other TAP studies which have identified a series of reaction intermediates. Direct comparison can be made with other systems for the oxidation of butane such as vanadium phosphate catalysts. Under similar conditions, TAP studies with VPO catalysts have identified a series of reaction intermediates, such as butadiene and maleic anhydride, during the oxidation of butane to the thermodynamically more stable carbon oxides [24].

Similar TAP pulse studies have also investigated oxidation under aerobic conditions and the results with all VOCs are the same as the anaerobic experiments. The normalised response in the absence of gas phase oxygen can be superimposed on the response in the presence of oxygen. In the non-steady state conditions of the TAP reactor this indicates that there is no difference in conversion with gas phase oxygen present and absent. It can therefore be concluded that the oxygen species which is utilised in total oxidation of benzene is derived from the catalyst surface.

During the oxidation of chlorobutane, no chlorine containing product was observed, although reactant was still converted to carbon oxides. It therefore appears that there is a build up of chlorine species on the

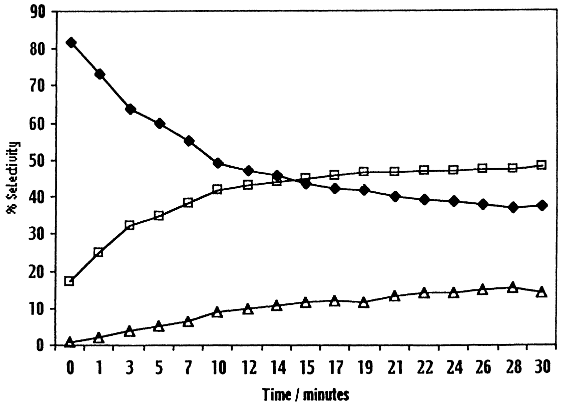

Fig. 7. Isotopic selectivity of CO_2 species during continuous flow of $C^{16}O/^{18}O_2$ over U_3O_8/SiO_2 at 596°C: (◆) $C^{16}O_2$; (□) $C^{16}O^{18}O$; and (Δ) $C^{18}O_2$.

catalyst surface. The pulse size is small in comparison with the number of sites on the catalyst surface and a large number of pulses would be required before chlorine products are liberated into the gas phase. Steady state studies in a microreactor have shown that HCl is the only chlorine containing product formed from chlorobutane and that the concentration of chlorine on the catalyst surface reaches a steady state demonstrated by the long term stable oxidation activity under steady state conditions. Prolonged TAP pulse studies using more highly chlorinated products, such as trichloroethane, showed that after many pulses, HCl was observed as the only chlorine containing product.

In order to confirm the origin of the oxygen in the oxidation products a model study has investigated the oxidation of CO with isotopically labelled oxygen. These studies were performed with a continuous flow of $C^{16}O/^{18}O_2$ (25% $C^{16}O$, 25% $^{18}O_2$, 50% neon). Data are shown for CO oxidation over U_3O_8/SiO_2 at 596°C (Fig. 7).

Carbon dioxide is the only reaction product and initially only ^{16}O is observed. This is again consistent with oxidation by lattice oxygen. With time on line, the concentration of $C^{16}O_2$ decreased and the concentration of the isotopically labelled product, $C^{16}O^{18}O$, increased. This type of behaviour indicates that the catalyst is operating by a redox mechanism with re-oxidation of the catalyst by the gas phase $^{18}O_2$. Some $C^{18}O_2$ is also observed, however in comparison, levels are relatively low. The $C^{18}O_2$ product may be derived either from oxidation of a $C^{18}O$ species derived from exchange of oxygen in $C^{16}O$ once the surface is enriched with ^{18}O, or it may be derived from oxygen exchange of the CO_2 product with the surface. Identical behaviour was also observed with the U_3O_8 catalyst indicating that it also operated via a redox mechanism involving lattice oxygen. A more comprehensive investigation of the mechanism of oxidation by uranium oxide catalysts is given elsewhere [25].

4. Conclusions

The activity observed for the destruction of a range of VOCs over uranium based catalysts indicates that there is good potential for the broad application of such materials in VOC abatement systems. The use of high gas hourly space velocities in the laboratory testing enables a more meaningful comparison to be made between laboratory and process scale. The uranium oxide catalysts show high activity for the destruction of a diverse range of VOCs to carbon oxides. In particular, they show an affinity for the destruction of chlorobenzene, which is a typical VOC, producing high selectivity towards HCl. The catalysts also show flexibility to changes in operating conditions and are able to treat effluent streams of varying concentration and those containing VOC mixtures. Lifetime studies demonstrate that stable and high activity is maintained during prolonged combustion of chlorobenzene and showed no evidence of catalyst deactivation.

Studies using a TAP reactor have proved a valuable approach in starting to understand the mechanism of uranium oxide catalysts for the oxidation of VOCs. Investigations using a continuous flow method have shown that benzene, butane and chlorobenzene are combusted directly to carbon oxides with no partially oxidised species. Further studies using a combination of TAP pulse experiments in the presence and absence of gas phase oxygen and with isotopically labelled gas phase oxygen demonstrates that the active oxygen species are derived from the lattice of the oxide catalyst which operates via a redox mechanism.

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