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Catalysis Today 54 (1999) 3–12

CATALYSIS TODAY

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A temporal analysis of products study of the mechanism of VOC catalytic oxidation using uranium oxide catalysts

Catherine S. Heneghan [a], Graham J. Hutchings [a], Shane R. O'Leary [a],
Stuart H. Taylor [a,*], Vicki J. Boyd [b], Ian D. Hudson [b]
[a] Department of Chemistry, University of Wales Cardiff, PO Box 912, Cardiff CF1 3TB, UK
[b] BNFL Research and Technology, Springfields, Preston PR4 OXJ, UK

Abstract

A temporal analysis of products (TAP) reactor is used to investigate the mechanism of oxidation of volatile organic compounds by uranium oxide catalysts. Continuous flow studies indicated that butane, benzene and chlorobutane VOCs were oxidised to carbon oxides and no partially oxidised products were observed. 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. It is proposed that the catalysts operates by a redox mechanism utilising lattice oxygen and the high activity shown by U_3O_8 is due to the facile uranium redox couple and the non-stoichiometric nature of the oxide. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: VOC; Catalytic oxidation; Uranium oxides; TAP reactor

1. Introduction

The application of catalytic technology for protection of the environment has in recent years become increasingly important. In particular, the destruction of volatile organic compounds (VOCs) by catalytic oxidation has been widely adopted. In general, two classes of catalyst are employed industrially, these are supported noble metal systems and metal oxide based catalysts. Recently, we have demonstrated that catalysts based on uranium oxide are exceptionally active for the destruction of a range of VOCs [1,2]. These catalysts have proved versatile and they are able to destroy mixtures of VOCs and are efficient over a wide VOC concentration range. Uranium oxide catalysts show long term stable activity with complete selectivity to carbon oxides. This latter observation is crucial for an effective VOC destruction catalyst, particularly for the oxidation of chlorinated VOCs, as partial oxidation products can be highly toxic. It is clear that uranium oxides are potentially important catalysts for VOC destruction, however, further work is needed to probe the absence of partially oxidised compounds and little is known about the mechanism of these catalysts.

Many catalytic reactions involve numerous steps which may encompass chemisorption of one or more reactants, reaction of the chemisorbed species and the desorption of reaction products. The mechanism of transformation can also involve a number of intermediates which may react via sequential or parallel pathways and which may or may not be desorbed from the surface. The majority of such intermediates exist in low concentration and are short lived, however, unless these species can be detected and their production

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[*] Corresponding author.

PII: S0920-5861(99)00162-5

and reactivity routes determined an understanding of the complete reaction mechanism is unobtainable. The most appropriate technique to unravel complex reaction schemes is by transient techniques which involve perturbation of the reacting catalytic system. Most commonly this takes the form of a concentration change by the introduction of a gas pulse whilst monitoring the response of reactants and products. One of the most powerful reactor systems for mechanistic determination is the temporal analysis of products (TAP) reactor. TAP studies have been used extensively for the study of oxidation reactions, in particular, they have involved selective oxidation reactions and have proved useful in the elucidation of the mechanisms of methane oxidation to methanol and formaldehyde [3], butane oxidation to maleic anhydride [4] and propene oxidation to acrolein [5].

In this study the mechanism of uranium oxide catalysts for VOC destruction has been addressed and the results of TAP studies are presented for the catalytic oxidation of butane, benzene and chlorobutane VOCs.

2. Experimental

2.1. Catalyst preparation

The uranium oxide catalysts used in this study were U_3O_8 and silica supported U_3O_8. The former was prepared by thermal decomposition of $UO_2(NO_3)_2 \cdot 6H_2O$ in static air at 800°C. The majority of results in this study were obtained using the silica supported catalyst (U_3O_8/SiO_2). This was prepared by an incipient wetness impregnation technique requiring 4.2 ml of 0.3952 mol l^{-1} uranyl nitrate solution per g of SiO_2 (BDH fumed silica 278 $m^2\,g^{-1}$). The loading of the supported catalyst has a uranium to silica ratio of 10 mol%. The catalyst precursor was prepared by drying the impregnated silica in air for 16 h at 100°C and the final catalyst was produced by calcination of the precursor in static air at 800°C. The calcination temperature of 800°C was required to form the supported U_3O_8 phase. The supported uranium oxide phase was crystalline and identified as orthorhombic U_3O_8 by powder X-ray diffraction. The catalyst surface area was 110 $m^2\,g^{-1}$ and the average U_3O_8 crystallite size was 103 Å determined by X-ray line broadening. The catalysts were pelleted to a 150–425 μm particle size range for use in the TAP reactor.

2.2. TAP studies

The 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 [6]. 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 the catalyst. This data was also used to determine the total sensitivity of reactant and products relative to the *m*/*e* peak at 20 for neon.

Two experimental methods were adopted using the TAP reactor; (i) continuous flow studies and (ii) TAP pulse experiments. Prior to experiments the catalysts were pre-treated in the vacuum system of the TAP by heating in air to 300°C followed by prolonged heating in the vacuum at reaction temperature. Continuous flow studies used a VOC/oxygen/neon ratio ca. 1/10/10. The gas pulsing valve was opened fully and the gas flow into the reactor controlled by a fine leak valve. The catalyst activity was investigated over a temperature range and mass spectra collected by scanning over a suitable mass range with 0.1 amu resolution. The data from continuous flow studies were used to determine the temperature required to produce an acceptable level of conversion for TAP pulsing experiments.

Two types of pulsing experiments were performed. The first were single pulse experiments involving the introduction of pulse into the reactor either from valve A or valve B. The response to the pulse at the exit of the reactor was measured by a mass spectrometer tuned to detect at a single *m*/*e* value. Repeat pulses were made to determine the response for each reactant/product. The *m*/*e* values monitored were determined from the fragmentation patterns measured previously and were selected such that there was no interference between the reactants and different reaction products. The *m*/*e* values used to identify reactants and products were; *m*/*e* 20 – neon, *m*/*e* 28 – carbon monoxide, *m*/*e* 32 – oxygen, *m*/*e* 43 – butane, *m*/*e* 44 – carbon dioxide, *m*/*e* 56 – chlorobutane, *m*/*e* 77 – benzene.

Multipulse studies used a time delay between pulses from valve A and valve B. In these studies a pulse from valve A was followed after 0.5 s by a pulse from valve B. The reactants and products were monitored by mass spectrometry tuned to a single ion using the method employed for single pulse experiments.

3. Results and discussion

3.1. Continuous flow experiments

A series of continuous flow experiments was used to study the reaction products during VOC oxidation over the U_3O_8/SiO_2 catalyst. The mass spectra for butane oxidation using 0.0510 g catalyst and 1/9.7/8.5 butane/oxygen/neon in the temperature range 478–604°C. The butane conversion increased from 25% at 478°C to 51% at 604°C and the only carbon containing products formed were those from total oxidation to carbon monoxide (*m*/*e* 28) and carbon dioxide (*m*/*e* 44). With the exception of water no other reaction products were identified and all *m*/*e* peaks were attributable to fragmentation of unreacted butane, oxygen and neon with intensities matching the previously determined standard fragmentation patterns.

Similar conclusions can be drawn from the results of the oxidation of benzene VOC continuous flow over U_3O_8/SiO_2 in the temperature range 314–366°C. The conversion of benzene increased from 4 to 46% over the temperature range. The oxidation of benzene in the TAP reactor occurred at a lower temperature compared with butane and this is consistent with our observation using steady state microreactor studies [1]. The only reaction products identified under these conditions were again those of total oxidation.

The destruction of chlorinated VOCs is particularly desirable as their release into the environment has been linked with the formation of smog and destruction of the ozone layer. Chlorobutane is used in this study as it represents a typical chlorinated VOC, and oxidation was investigated by continuous flow experiments over U_3O_8/SiO_2 in the temperature range 294–480°C. The chlorobutane conversion at 294°C was 10% increasing to 89% at 480°C. In common with the previous observations for the oxidation of butane and benzene, carbon monoxide and carbon dioxide were the only carbon containing products from chlorobutane oxidation. This is an important criterion for the total oxidation of chloro-organics which can be partially oxidised to form toxic by-products such as $COCl_2$ which has been observed during oxidation over other catalysts used for VOC destruction [7]. Particular attention has been made to identify the production of any partially oxidised species. To the limits of detection on the TAP system none were observed. 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 minimising collision between reactants and products. Consequently highly reactive and short lived intermediates which are not 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 (VPO) 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.

3.2. TAP pulse studies

Initial single TAP pulse experiments were carried out using benzene in the presence and absence of gas phase oxygen. The pulses were passed over a

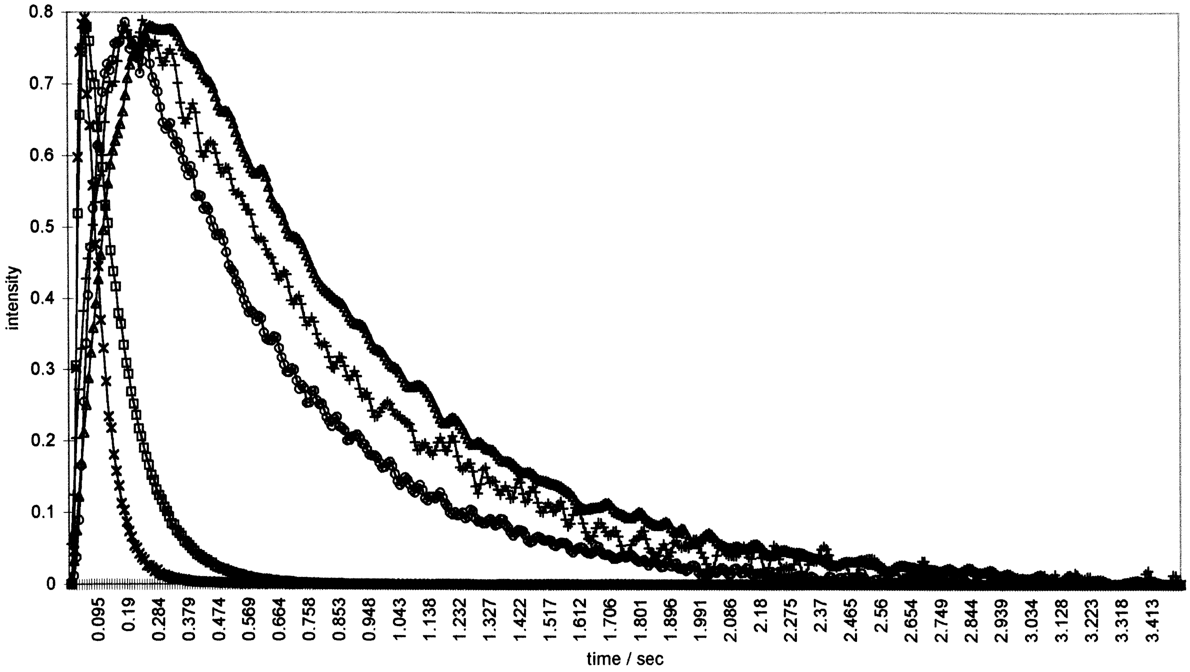

Fig. 1. TAP pulse response for benzene oxidation at 366°C: in the presence of gas phase oxygen: □ neon; ○ benzene; ▲ carbon dioxide; + carbon monoxide; * oxygen.

Table 1
Gas mix composition for TAP pulse studies investigating benzene oxidation in the presence and absence of gas phase oxygen

	Valve A (Torr)	Valve B (Torr)
Benzene	84	81
Oxygen	809	–
Neon	901	1716

U_3O_8/SiO_2 catalyst at 366°C, this temperature was determined previously to produce a level of conversion suitable for study. The gas mixtures used in these studies are detailed in Table 1.

The results of the TAP pulse from valve A is shown in Fig. 1.

The first observation that can be made about the qualitative analysis of the TAP data is that the response for the products and reactants as a function of time 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 a gas phase process. Identical observations were also apparent for the oxidation of butane and chlorobutane in the TAP reactor.

An identical response was observed when a benzene pulse without gas phase oxygen was injected into the reactor. The same type of behaviour was also seen when butane and chlorobutane were pulsed into the reactor in the presence and absence of gas phase oxygen. During the oxidation of chlorobutane no chlorine containing product was observed. It therefore appears that there is a build up of chlorine species on the catalyst surface. The pulse size is small in comparison with the number of sites on the catalyst surface and large number of pulse 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 long term stable oxidation activity [1,2]. These TAP data indicate that benzene, butane and chlorobutane are converted to CO_2 and CO both in the presence and absence of gas

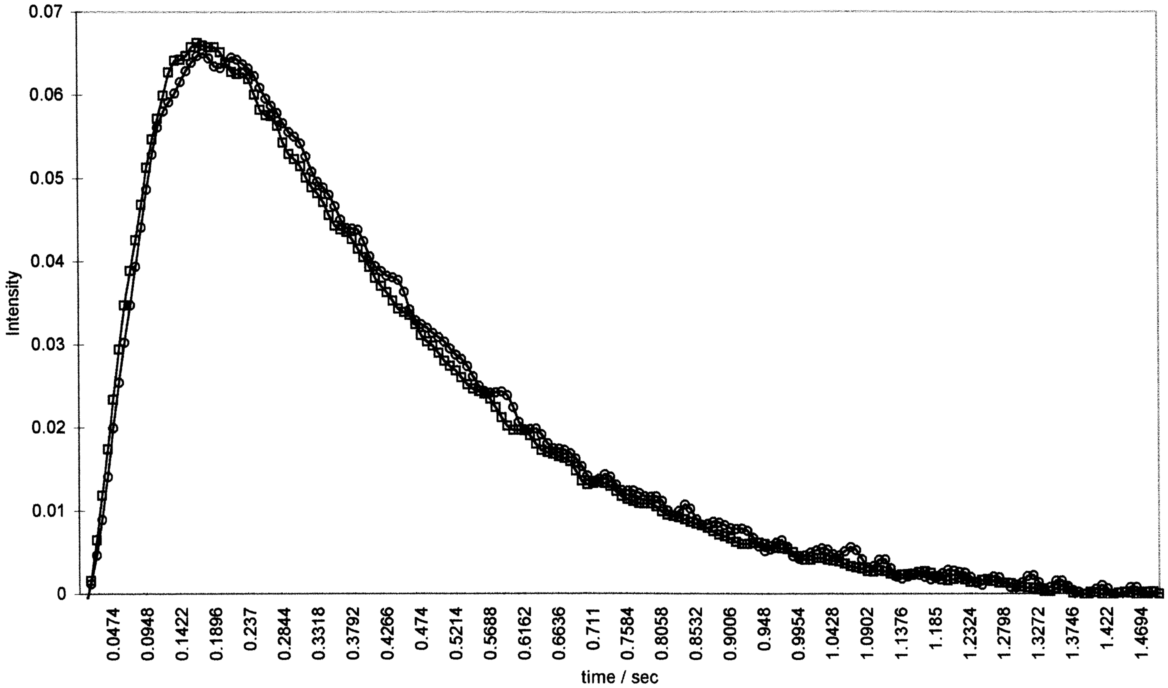

Fig. 2. Normalised TAP pulse response for carbon dioxide production from benzene in the presence and absence of gas phase oxygen at 366°C: □ gas phase oxygen; ○ no gas phase oxygen.

phase oxygen. In agreement with the continuous flow studies CO_2 and CO were the only reaction products. Using benzene the selectivity for CO_2 was 86% in the presence of oxygen and 88% with no oxygen in the pulse, the balance of product was CO.

The normalised response for carbon dioxide, the major product from benzene oxidation, with and without oxygen in the feed gas are shown in Fig. 2.

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 and not directly from the gas phase. The oxygen source could be either from and adsorbed surface species or from the lattice of the oxide. Considering the vacuum pre-treatment of the catalyst the concentration of adsorbed oxygen will be relatively low and therefore supply of oxygen from the lattice would appear more likely.

Table 2
Gas mix composition for TAP multipulse studies investigating butane oxidation at 478°C

	Valve A (Torr)	Valve B (Torr)
Butane	160	0
Oxygen	0	705
Neon	650	697

3.3. TAP multipulse studies

The investigation of the origin of the oxygen species for the oxidation of butane and benzene over a U_3O_8/SiO_2 catalyst has been extended by a series of multipulse experiments. In these experiments a pulse of gas is introduced to the reactor followed after a fixed time period by a second pulse of different composition. The results in this section detail studies using butane, although as was highlighted previously the same kind of behaviour is also shown during benzene oxidation. The gas compositions used in these multipulse experiments are detailed in Table 2.

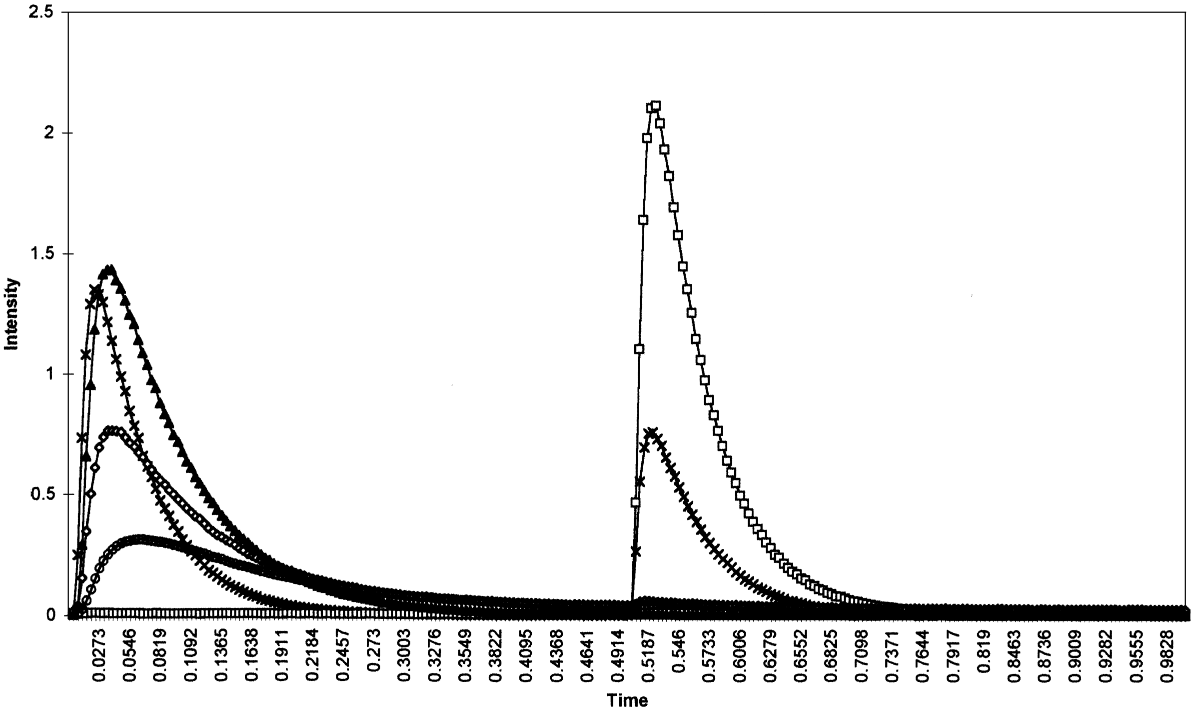

Fig. 3. TAP multipulse response for a U_3O_8/SiO_2 catalyst at 478°C using a butane /neon pulse followed after 0.5s by an oxygen/neon pulse: × neon; ☐ oxygen; ▲ butane; ○ carbon dioxide; ◇ carbon monoxide.

The experiments detailed here used a delay of 0.5 s between the initial and second pulse. A catalyst bed temperature of 478°C was found to give a satisfactory level of conversion for the pulsing reactions. Before use in the multipulsing experiments, the catalyst was heated in oxygen at 478°C and then in a vacuum to remove any absorbed surface species and establish that the catalyst was in an oxidised state at the start of the experiment.

Initial multipulsing experiments used a butane/neon pulse followed by an oxygen/neon pulse, results for the fresh catalyst are shown in Fig. 3.

The most significant mechanistic observation from these data is that carbon oxides are again produced in the absence of gas phase oxygen. Studies on the fresh catalyst showed that no products were formed as a consequence of the oxygen pulse following the butane. However, as the catalyst was exposed to more multipulse sequences carbon oxides were produced during the oxygen pulse. Data for the production of carbon monoxide are shown in Fig. 4, and although not shown here, similar data were observed for the production of carbon dioxide.

The level of carbon oxides produced during the oxygen only pulse are significantly reduced compared to the primary butane pulse, however, a real quantifiable effect is observed. There is no gas phase butane within the catalyst under these conditions and although the butane pulse is broadened by passing over the catalyst as detectable butane levels reach those of the background approximately 0.4 s after the introduction of the initial pulse. Consequently these results indicate that there is some form of carbon containing species present on the catalyst surface which is generated from the butane and this is oxidised by gas phase oxygen to form carbon oxides which are desorbed from the catalyst surface.

The oxygen conversion for the first multipulse sequence shown in Fig. 4. is 44%, this increased to 66% after further pulse sequences and is consistent with the replenishment of the lattice oxygen which is the major oxidising species utilised under the anaerobic

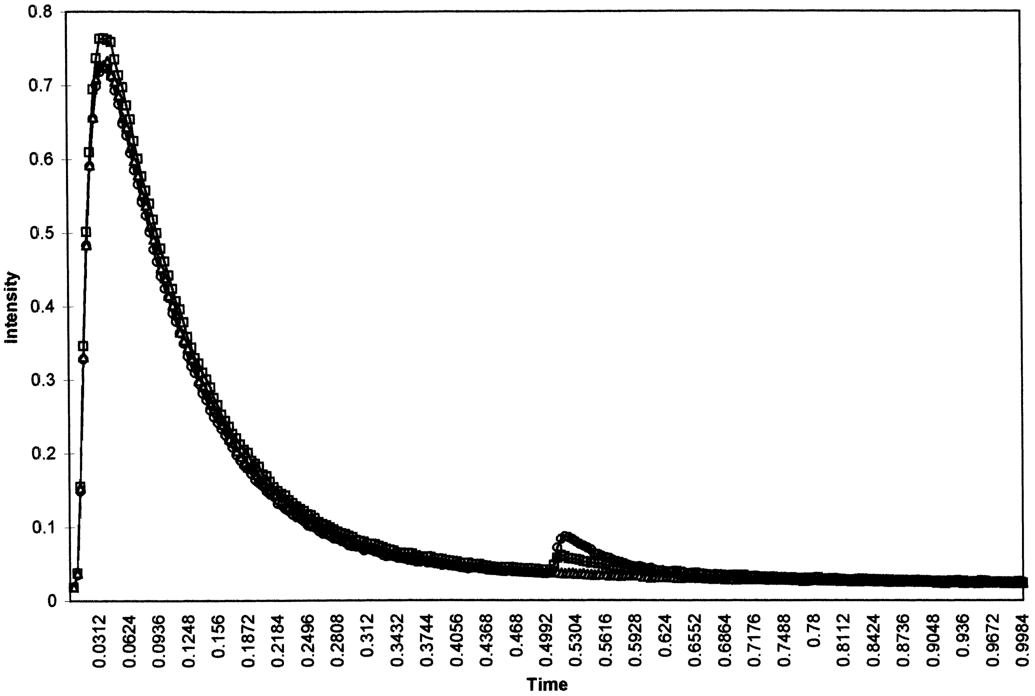

Fig. 4. The formation of carbon monoxide from TAP multipulse experiments for a U_3O_8/SiO_2 catalyst at 478°C using a butane /neon pulse followed after 0.5 s by an oxygen/neon pulse. ○ 0 min; ■ 15 min; △ 30 min.

conditions of butane oxidation. This being the case prolonged butane oxidation in the absence of gas phase oxygen should have the effect of stripping oxygen from the catalyst lattice, these effects have been studied and results are shown in Fig. 5.

The conversion of butane remains relatively constant as the number of butane/neon pulses are increased. The butane pulse after 30 min continuous pulsing can be superimposed on the pulse response from the fresh catalyst. A similar observation is also made for the carbon monoxide response as data after prolonged butane pulsing can be superimposed on the data for the fresh catalyst, although it should be noted that after 15 min pulsing there was a slight increase in carbon monoxide. Differences were observed for the carbon dioxide response. A gradual decrease in the carbon dioxide peak area was evident as the number of butane pulses increased.

Based on the butane responses it appears that rapid deactivation of the catalyst during TAP pulse anaerobic studies does not take place. The same conclusion can also be drawn from the carbon monoxide data and it is readily apparent that a reservoir of oxygen species is readily accessible to sustain oxidation in the absence of gas phase oxygen. It would appear unlikely that such long term oxidation in anaerobic conditions could be sustained by adsorbed oxygen species and the oxygen source is most likely derived from the oxide lattice. This being the case the depletion of the lattice oxygen does however, seem to influence oxidation to carbon dioxide. The decreased carbon dioxide production could indicate a decrease in oxygen available for oxidation although carbon monoxide production was not influenced in the same way and this may suggest that two types of active oxygen species may exist for butane oxidation, one responsible for carbon dioxide formation and the other for carbon monoxide.

Consequently due to the depletion of oxygen from the lattice there should also be an effect on the oxygen conversion once gas phase oxygen is reintroduced into the catalytic cycle. Data for the oxygen pulses after prolonged pulsing from butane/neon are shown in Fig. 6.

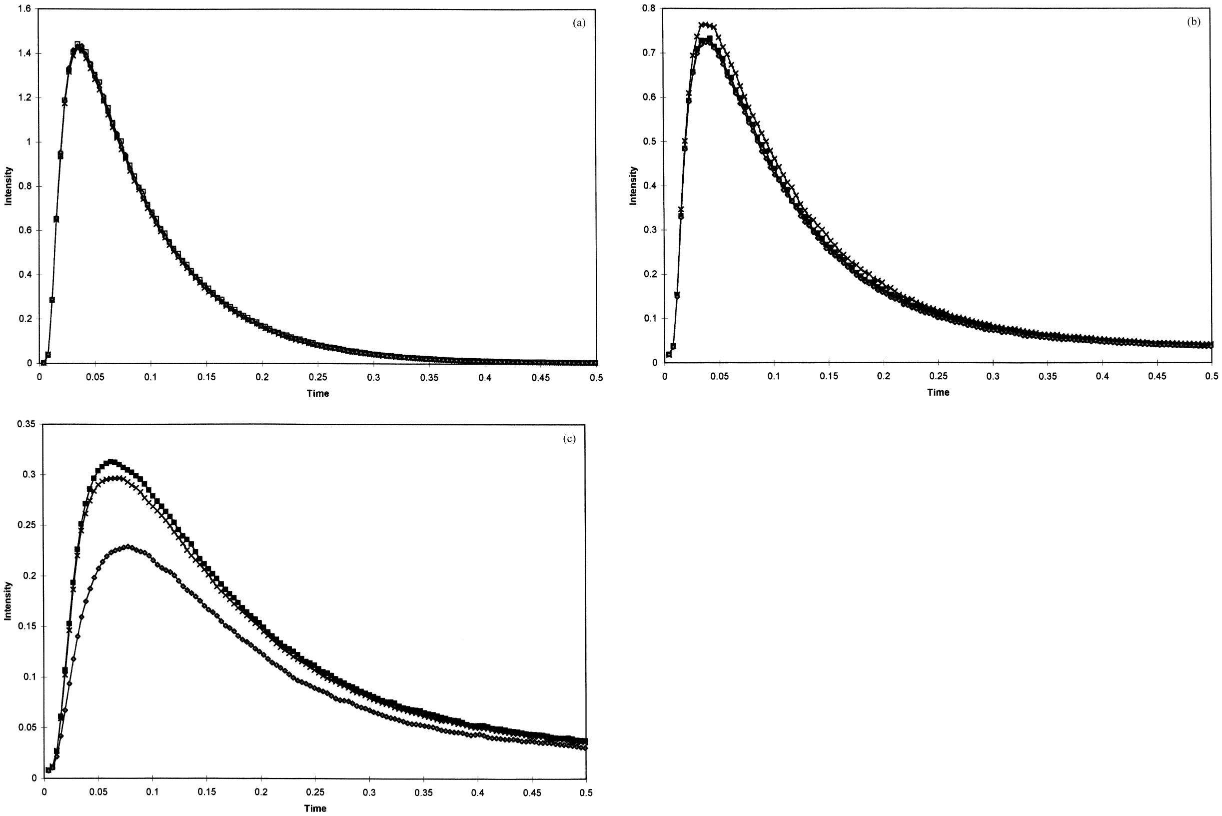

Fig. 5. TAP response for pulsing butane/neon over U_3O_8/SiO_2at 478°C (a) butane (b) carbon monoxide (c) carbon dioxide. ■ 0 min; × 15 min; ◆ 30 min.

There is significant variation in the normalised areas of the oxygen pulse directly after the catalyst has undergone prolonged pulsing with a butane/neon atmosphere. It is evident that the oxygen content in the gas phase exiting the reactor is dependent on the duration of the butane/neon pre-treatment. The intensity of the oxygen signal decreases, indicating that there is greater uptake of oxygen by the catalyst after increasing time of butane/neon pulses. This is consistent with the replenishment of oxygen from the oxide lattice by gas phase oxygen. A redox mechanism for the reaction may therefore be proposed, and the reduction and oxidation steps in the catalytic cycle can be probed using the TAP reactor.

In order to confirm the origin of the oxygen in the oxidation products the oxidation of butane has been carried out using multipulse studies with isotopically labelled oxygen, These studies were performed using a gas mix of 160 Torr butane/650 Torr neon in valve A and 137 Torr 102/668 Torr neon in valve B. Valve B followed the pulse from valve A by 0.5 s. The response for the production of carbon dioxide is shown in Fig. 7.

The oxidation products contained exclusively ^{16}O confirming that the oxygen source is supplied by the lattice of the catalyst. Prolonged multipulsing studies, which are not detailed here [8], have shown that ^{18}O from the gas phase is incorporated into the oxide lattice and is eventually observed in the oxidation products with increasing concentration as the reaction time is increased.

Previous studies of the uranium oxide catalyst show that the silica supported catalyst which has been investigated predominantly in the TAP reactor is supported U_3O_8, which has been observed ex and in situ [9]. The activity of the catalyst and the mechanism by which it operates can be rationalised by considering

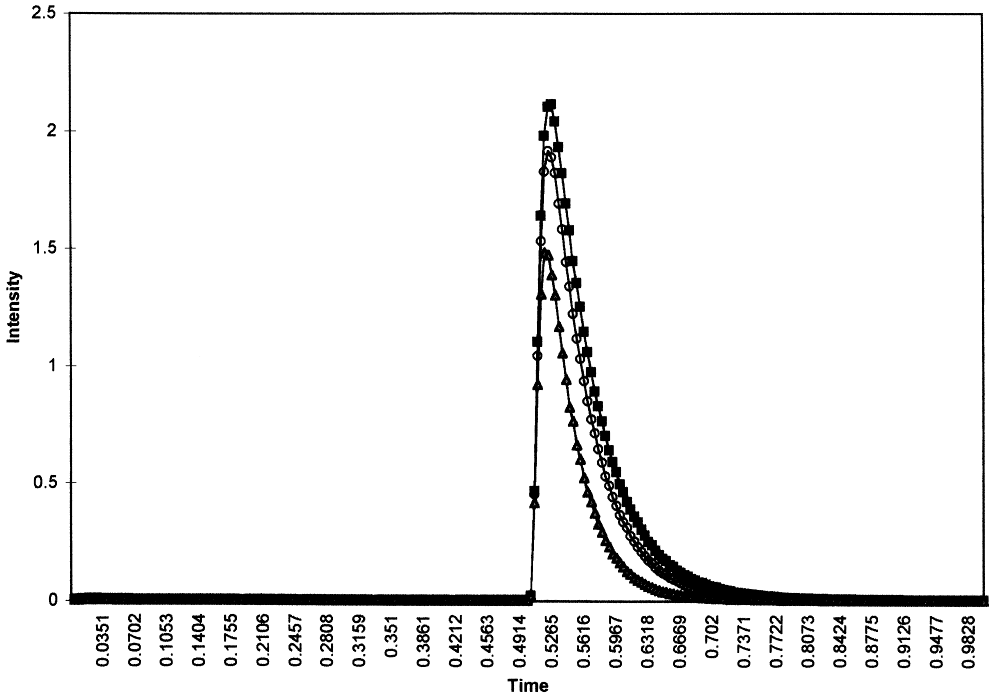

Fig. 6. TAP response for pulsing oxygen/neon over U_3O_8/SiO_2at 478°C after pulsing butane/neon: ○ 0 min; ■ 15 min; △ 30 min.

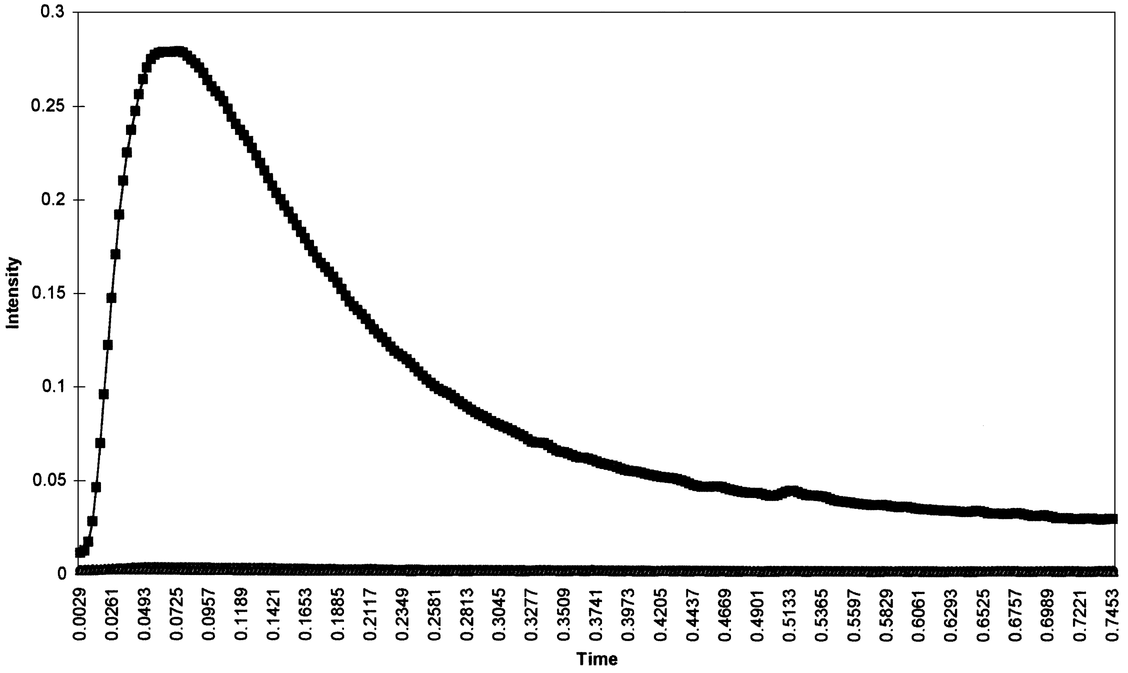

Fig. 7. The production of carbon dioxide from butane oxidation at 484°C using isotopically labelled gas phase oxygen: ■ $C^{16}O_2$; ○ $C^{16}O^{18}O$; △$C^{18}O_2$.

the chemistry of uranium oxides. The uranium oxygen system is one of the most complex with at least 17 phases identified in the UO_2–UO_3 stoichiometric ratio [10]. This abundance of phases is in part due to the multiplicity of oxidation states and the fact that deviations from stoichiometry is common. Many of the oxide phases, for example UO_2 can accommodate over 10% excess oxygen in interstitial sites. Recently it has been proposed that uranium cations in close proximity to the interstitial species have higher oxidation states compared to the stoichiometric oxide [11]. These types of features are common in many uranium oxides as is the transition between oxidation states which is a facile process. Specifically U_3O_8 has two distinct uranium environments, with uranium in +4 and +6 oxidation states which exhibit a low energy for transition between these states. It thus appears that the reaction mechanism is dependent on the readily available supply of lattice oxygen, and as this is utilised the oxide structure can easily accommodate the changing metal cation/oxygen anion ratio due to the facile uranium redox couple and the availability of interstitial oxygen species. It has been proposed that UO_3 operates in this manner for the oxidation of ethylene to acetaldehyde [12]. We have investigated the oxidation activity of UO_3 and found it to be significantly less active than U_3O_8 for total oxidation reactions. Structurally U_3O_8 and UO_3 are very similar but the latter does not contain uranium in mixed oxidation states. We therefore believe that the presence of the mixed oxidation state in U_3O_8 is a more important factor than structure in directing activity towards total oxidation and not selective oxidation. A similar hypothesis has also been eluded to by Nozaki and Ohki [13] during the oxidation of carbon monoxide over U_3O_8. Further investigation of the influence of the redox behaviour of uranium oxides and the influence on catalytic activity and mechanism is currently being made and particular attention is focusing on the characterisation of the active catalyst using in situ laser Raman and X-ray diffraction techniques.

4. Conclusions

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. This behaviour can be explained in terms of the solid state chemistry of the active uranium oxide phase.

Acknowledgements

We would like to acknowledge the assistance of Dr Horst W. Zanthoff at the University of Bochum, Germany, who provided access, help and advice on using the TAP reactor.

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