Catalytic Destruction of Halogenated Volatile Organic Compounds

MECHANISMS OF PLATINUM CATALYST SYSTEMS

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Halogenated volatile organic compounds are associated with a broad range of industrial processes, but when discharged into the atmosphere they constitute a major source of air pollution. Recognition of the potentially damaging effects that these emissions can have on the environment is leading to increasing demands for their control. Catalytic combustion appears to offer advantages over thermal destruction, resulting from lower incineration temperatures and higher destructive efficiencies. While platinum metals catalyst systems are known to be the most effective for the catalytic destruction of non-halogenated volatile organic compounds, only a relatively small amount of data has been published on their performance for destroying halogenated volatile organic compounds; this paper reports on an investigation of catalysts developed for this purpose.

Environmental and health concerns about the emission of halogenated volatile organic compounds, VOCs, that is, those containing fluorine, chlorine and bromine, are leading to demands for stricter emission control regulations. Although the C1 and C2 chlorocarbons are dominant, a wide range of halocarbons find industrial and commercial application and the level of concentration permitted depends upon the toxicity of each compound. A selection of halocarbons, typically used as solvents and cleaners (except for vinyl chloride which is the precursor for polyvinylchloride, PVC), and permitted exposure levels, are given in Table I. The low permissible levels for some of the compounds emphasises the need for highly efficient pollution abatement methods, with the preferred products of combustion being carbon dioxide, water and hydrogen halides.

Over the years significant information has been collected about the catalytic destruction of VOCs discharged from stationary sources, including such diverse operations as food processing, the manufacture and use of paints and varnishes, printing, metal degreasing and plas-

tics moulding (1). During the last two decades this knowledge has been applied to, and supplemented by, data from the catalytic oxidation and abatement of hydrocarbon emissions from automotive spark ignition internal combustion engines. As a general rule, the ease of oxidation of VOCs increases in the order:

$$\text{methane} < \text{paraffins} < \text{aromatics} < \text{olefins} < \text{oxygenates}.$$

Platinum metals catalysts are the most effective for the catalytic incineration of VOCs, ensuring high conversion rates at low temperatures with high combustion efficiencies. Furthermore all the catalysts currently used for controlling automotive emissions contain platinum metals.

The catalytic incineration of halogenated VOCs is now receiving increased attention, in view of the potential technological and economic advantages it provides compared to thermal combustion systems. The catalytic process must, however, be selected for the complete destruction of all the halocarbons, including the toxic halogenated by-products that can result from incomplete combustion of the parent

halocarbon. The catalyst must also overcome the reversible attenuation of catalyst activity which can result from the presence of halides on the surface of the catalyst.

Unlike the well reported catalytic destruction of non-halogenated VOCs there is relatively little data in the literature on the use of platinum metals catalysts for the combustion of halogenated VOCs. One of the most frequently referenced works is that by Bond and Sadeghi who, some 18 years ago, used platinum catalysed alumina granules in a fixed bed reactor to investigate destructive efficiencies for several chlorocarbons (3). At moderate temperatures, typical conversions were greater than 90 per cent. More recently this work has been compared with other catalytic processes, which did not employ platinum metals, and which used vastly different process parameters and catalyst geometries (4). The present authors believe that such comparisons have led to conflicting, or at best confused, conclusions about the performance of platinum metals catalysts.

The purpose of the work summarised here is to establish the performance of platinum metal catalysts for the destruction of halogenated VOCs. Although Johnson Matthey markets, and is continuing to develop, catalysts containing other platinum metals for this purpose, this paper will only consider the characteristics of platinum catalysts, and the optimisation of both the catalysts and the process parameters for the catalytic incineration of halogenated VOCs.

Experimental Work

The catalysts were prepared by conventional methods, involving the deposition of the platinum component onto a washcoat layer on ceramic honeycomb supports, and aged at temperatures above 600°C in a tubular quartz reactor for 165 hours in a chlorinated hydrocarbon gas stream containing air and moisture. Unless otherwise indicated, the data discussed here are for aged catalysts. Reactivity studies were undertaken in a laboratory tubular quartz flow reactor under simulated field conditions. Halocarbon species, in concentrations of 10 to 1500 ppm, were quantified by gas chromatography. The

Table 1
U. S. Occupational Safety and Health Administration Permissible Exposure Limit-Time Weighted Average Levels (2)

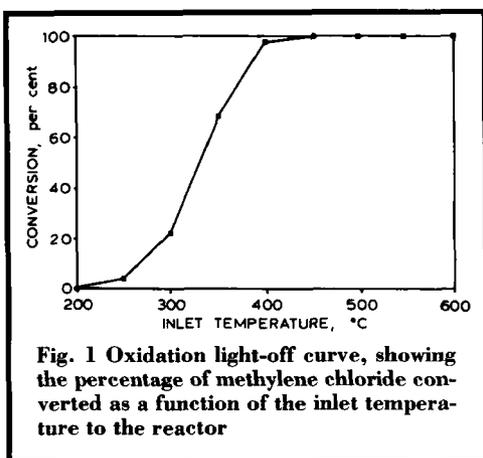| Halocarbon	PEL-TWA, ppm
Phosgene	0.1(TLV)
Vinyl chloride	1
1,1 -Dichloroethylene	1
1,2-Dichloroethane	1
1,1,2,2-Tetrachloroethane	1
Carbon tetrachloride	2
Chloroform	2
1,1,2-Trichloroethane	10
Tetrachloroethylene	25
Methyl chloride	50
Trichloroethylene	50
Chlorobenzene	75
1,2-Dichloropropane	75
Methylene chloride	100
1,1,1-Trichloroethane	350

TLV Threshold Limiting Value

gas hourly space velocity was set at 26,000 per hour. Field tests were carried out on side streams from industrial processes utilising the Johnson Matthey "Minicat", a self-contained catalytic incinerator for pilot testing (5) and (6).

Temperature Effects

The effect of temperature on the oxidation efficiency of a catalyst is best illustrated by showing the rise in conversion which occurs with increasing temperature — the light-off curve. A light-off curve for the oxidation of methylene chloride over a platinum catalyst is shown in Figure 1. Light-off curves are generally characterised by two parameters: T50 (the temperature for 50 per cent conversion, is often referred to as the light-off temperature), and T90 (the temperature for 90 per cent conversion). T50 is used to rank the catalysts and to compare catalyst activity for various gaseous species. T90 is a function of the physical dimensions of the catalyst, and is usually controlled by mass transfer of the unconverted species from the bulk gaseous phase to the catalyst surface.

Light-off characteristics for other types of

Fig. 1 Oxidation light-off curve, showing the percentage of methylene chloride converted as a function of the inlet temperature to the reactor

chlorocarbon compounds over a platinum catalyst are shown in Table II. One similarity between these and the light-off characteristics for non-halogenated VOCs is that the oxidation of C1 compounds is more difficult than the oxidation of saturated C2 compounds. However, there are three distinguishing characteristics of halogenated chlorocarbons:

[a] The ease of destruction via catalytic incineration is remarkably similar for all the halogenated C1 compounds, and does not change with an increase of chlorine:carbon ratio in the molecule. The oxidation of saturated C2 compounds occurs more readily, and also appears to be insensitive to the number of chlorine atoms in the molecule.

The catalytic oxidation of hydrocarbons is thought to proceed via dissociative chemisorption of the molecule followed by reaction of the abstracted hydrogen with co-adsorbed oxygen, with hydrogen abstraction being the step that limits the rate of reaction. Thus the relative ease of oxidation of these molecules has been correlated with the strength of the carbon-hydrogen bond (7). Since an increase in the chlorine:carbon ratio weakens the carbon-chlorine bond in the molecule, the observed oxidation characteristics for the halogenated C1 and saturated C2 molecules suggest that the rate determining step is not a carbon-chlorine bond rupture.

This behaviour, however, changes when washcoat, A, is replaced by a second washcoat, B. The light-off temperatures for these two catalyst types are compared in Table III. The data show that the rate limiting step for the oxidation of some halocarbons over Pt/B catalyst can be the same as for the oxidation of non-halogenated hydrocarbons. However, the oxidation characteristics for unsaturated halocarbons are not explainable by these mechanisms, and will be discussed next.

Table II
Light-off Characteristics for Combustion of C1 and C2 Halocarbons over Fresh Platinum Catalysts

Halocarbon	T50,°C	T90,°C
Methyl chloride	325	390
Methylene chloride	310	355
Chloroform	310	350
Carbon tetrachloride	320	370
Chloroethane	245	310
Dichloroethane	250	310
1,1,1-Trichloroethane	250	310
1,1,2-Trichloroethane	215	320
1,1,2-Trichloroethylene	445	520
Tetrachloroethylene	490	570

Table III

Table III
Light-off Characteristics for Combustion of C1 and C2 Halocarbons
over Fresh Platinum Catalysts

Halocarbon	T50 for Pt/A,°C	T90 for Pt/B,°C
Methyl chloride	325	360
Methylene chloride	310	330
Chloroform	310	290
Carbon tetrachloride	320	220
Chloroethane	245	280
Dichloroethane	250	330
1,1,1-Trichloroethane	250	210
1,1,2-Trichloroethane	215	245
1,1,2-Trichloroethylene	445	370
Tetrachloroethylene	490	430

[b] The oxidation of unsaturated chlorinated compounds is more difficult than the oxidation of saturated compounds, which is in direct contrast to the oxidation of unsaturated non-halogenated hydrocarbons.

For unsaturated non-halogenated compounds, the C=C double bond is readily reacted on the active site on the surface of the platinum group metal catalyst. For the halogenated compounds, however, the high electronegativity of the halide atom causes a redistribution of electron charge on the individual atoms of the adsorbed molecule, and can change the orientation of the molecule relative to the catalyst surface. The relatively large size of the halide atom and the high electron affinity can produce severe steric and electronic hindrances to the dissociative adsorption of unsaturated halogenated molecules on the active sites of the catalyst.

[c] As noted previously, the oxidation of saturated C2 compounds is fairly rapid and occurs at relatively low temperatures. However, this fast oxidation is often accompanied by the generation of unsaturated by-products which, as previously noted, require higher temperatures for complete oxidation. Figure 2 shows the formation of dichloroethylene during the oxidation of trichloroethane. The dichloroethylene

is then further oxidised at higher temperatures. This less rapid oxidation of the unsaturated by-products parallels the high light-off temperatures for unsaturated chlorinated C2 compounds shown in Table II. Thus, while the dissociation of the saturated C2 chlorocarbons (adsorption and abstraction of hydrogen and chlorine from the saturated molecules) can occur readily, even on non-catalysed alumina surfaces (8), the molecules are not totally destroyed at low temperatures and the more stable unsaturated C2 chlorocarbons can be produced, which require higher temperatures for their complete destruction.

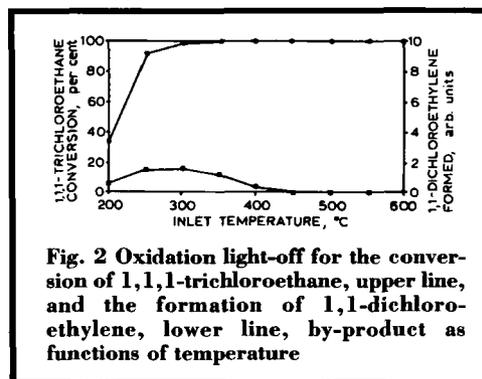The above discussion clearly demonstrates

Fig. 2 Oxidation light-off for the conversion of 1,1,1-trichloroethane, upper line, and the formation of 1,1-dichloroethylene, lower line, by-product as functions of temperature
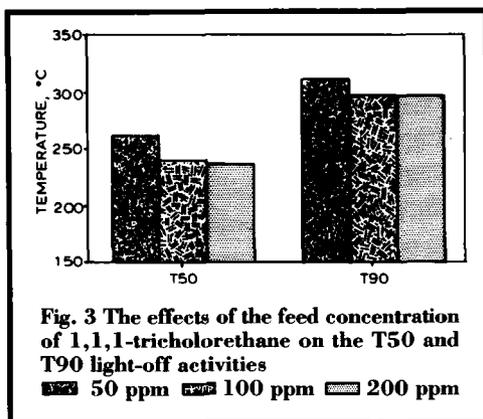
Fig. 3 The effects of the feed concentration of 1,1,1-tricholorethane on the T50 and T90 light-off activities
50 ppm 100 ppm 200 ppm

that an integrated approach is needed to understand the overall mechanisms for a particular catalyst system, and cannot be based solely on data/conclusions from the oxidation of C1 compounds (4).

This paper will concentrate on understanding the oxidation characteristics for the Pt/A catalyst system.

Concentration Effects

The effects of increasing the feed concentration on the light-off characteristics of both trichloroethane and on the resulting dichloroethylene by-product generated at temperatures of incomplete combustion are shown in Figures 3 and 4, respectively. The oxidation of trichloroethane improves slightly with an increase in concentration — the T50 and T90 values decrease. However, dichloroethylene is

formed at a disproportionately higher rate than is accounted for by the increase in concentration of the trichloroethane. This behaviour may be understood by examining the effects of feed concentration on the light-off characteristics of trichloroethylene, Figure 5, which shows that increasing the concentration of trichloroethylene decreases the performance. The improvement in performance on increasing the concentration, which was observed for the oxidation of trichloroethane, may be attributed to the increased acidity (9) of the surface by the resulting higher concentration of chlorine on the catalyst surface. The increased chlorine concentration, however, appears to decrease the effectiveness of the catalyst towards both suppression of the unsaturated dichloroethylene by-product, Figure 4, and the oxidation of trichloroethylene, Figure 5. This effect may be attributed to the high electronegativity of the chlorine.

The high electron affinity of an adsorbed chlorine relative to that of a co-adsorbed oxygen causes a reduction in the electronic charge on the co-adsorbed oxygen. The reduction in charge forces charge transfer from the C=C double bond to the platinum group metal site through the co-adsorbed oxygen, and reduces the probability for C-C bond scission. This process could suggest that the rate of removal of chlorine from the catalyst surface is the rate limiting step in the oxidation of unsaturated halogenated VOCs. However, this does not rule out dissociative chemisorption as being the rate limiting step, because high concentrations of
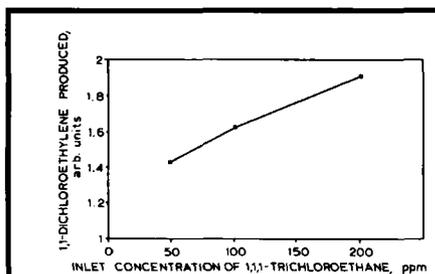

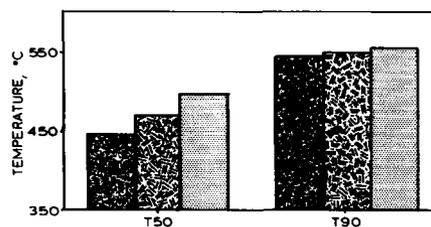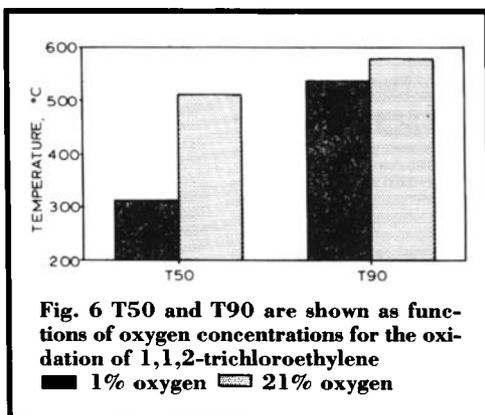Fig. 4 1,1-Dichloroethylene produced, normalised to the 1,1,1-trichloroethane feed concentration

Fig. 5 The effects of the concentration of 1,1,2-trichloroethylene on the T50 and T90 light-off activities
50 ppm 100 ppm 200 ppm

Fig. 6 T50 and T90 are shown as functions of oxygen concentrations for the oxidation of 1,1,2-trichloroethylene
■ 1% oxygen ▨ 21% oxygen

halides can also reduce dissociative chemisorption of the halocarbon.

The above discussion suggests that increasing the concentration of unsaturated halocarbons, whether they are the primary pollutant or the by-product of incomplete combustion, may require relatively higher temperatures for the complete destruction, but the temperatures needed are still well below those needed for thermal destruction.

Oxygen Effects

The effects of increasing the concentration of oxygen are similar to those for increasing the halocarbon feed concentrations. Figure 6 shows the effect of increasing oxygen concentration on the light-off characteristics for the oxidation of trichloroethylene. The light-off temperature increases dramatically when the oxygen concentration is increased from 1 to 21 per cent (air).

High oxygen concentration in the gas stream increases the concentration of oxygen atoms adsorbed on the catalyst surface. The high concentration of co-adsorbed oxygen atoms can behave analogously to a high concentration of adsorbed chlorine (though not necessarily to the same degree, because of differences in electron affinity and size). The results, therefore, lend credence to the suggestion that it is the removal of the halide from the catalyst surface, and not the dissociative chemisorption of the halocarbon, that is the probable rate limiting

step in the oxidation of halocarbons. The results also suggest that for some halocarbons in high oxygen streams, it may be necessary to operate the catalyst at higher temperatures than for streams containing low oxygen levels.

Water Effects

The presence of water (steam) in the gaseous stream can have significant effects on the destructive properties of the catalyst and on the product composition. Some major effects are discussed below.

Hydrogen Chloride Selectivity

In practice, it is more desirable to treat effluent streams containing hydrogen chloride rather than those containing chlorine, since the former is easily scrubbed via caustic absorption, and also less corrosive and less toxic. The selectivity towards hydrogen chloride as against chlorine is dependent on the presence of water (steam) and is governed by the Deacon reaction:

$$2Cl_2 + 2H_2O \Longleftrightarrow 4HCl + O_2$$
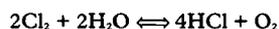
The formation of hydrogen chloride is favoured at high water levels and at high temperatures.

By-products

The oxidation of some chlorocarbons can lead to the formation of unwanted by-products, such as phosgene (carbonyl chloride). The mechanisms for phosgene formation may proceed via a secondary step involving a "Cl_2" intermediate on the catalyst surface and by carbon monoxide formed from the incomplete oxidation of the halocarbon:

$$\text{"}Cl_2\text{"} + CO \rightarrow COCl_2$$

This route is used in the large-scale manufacture of phosgene under very dry conditions.

As discussed above, hydrogen chloride formation is favoured over chlorine as a product from the combustion of chlorinated VOCs in the presence of steam. In addition, phosgene hydrolyses readily to hydrogen chloride and carbon dioxide in the presence of moisture (10). These mechanisms suggest that the presence

Table IV Phosgene Suppression by Water during Halocarbon Combustion over Fresh Platinum Catalysts at 450 to 500°C		
Halocarbon	Phosgene, ppm	
	0% H_2O	5% H_2O
Carbon tetrachloride	0.15	0
Methylene chloride	0.5	0
Trichloroethylene	0.3	0
Chloroform	0	0

of excess steam in process effluent streams is likely to suppress the formation of phosgene in a catalytic destruction process. Table IV demonstrates the desirable effect of steam on eliminating the small amount of phosgene formed by the destruction of halocarbons over several platinum group metal catalysts.

Another example of the beneficial effect of steam in suppressing the formation of by-products is demonstrated for the oxidation of trichloroethane, see Figures 2 and 7. Dichloroethylene is formed as a by-product of the oxidation of 1,1,1-trichloroethane. Figure 7 shows that as the concentration of steam is increased, the amount of dichloroethylene formed is suppressed. This suppression appears most effective at high temperatures.

Destruction Mechanisms

As discussed previously, the halides are larger, more electronegative and are less strongly bonded to carbon than to hydrogen. The halides are also strong attenuators of catalytic activities, and at high concentrations can poison the catalytic activity. No reaction is expected between the halide and an adsorbed oxygen, unlike hydrogen, and since hydrogen evolving from the dissociated molecule can readily react with oxygen, the rate at which the halide is removed from the catalyst surface may limit the combustion process.

The presence of steam is effective in removing the halide from the catalyst surface and promoting the destruction of unsaturated halo-

genated C2 compounds. This supports the conclusion that the rate limiting step in the oxidation of halogenated VOCs over platinum supported on alumina catalysts is likely to be controlled by the removal of the halide from the surface. Although dissociative chemisorption does not appear to be the limiting step for the oxidation of C1 and saturated chlorinated C2 compounds, it cannot be ruled out, particularly for the unsaturated C2 compounds, and for other platinum group metal catalysts.

Catalyst Durability

An important aspect of the performance of platinum group metals catalysts is their ability to withstand corrosive halide environments. The durability of these catalysts can be affected in several ways.
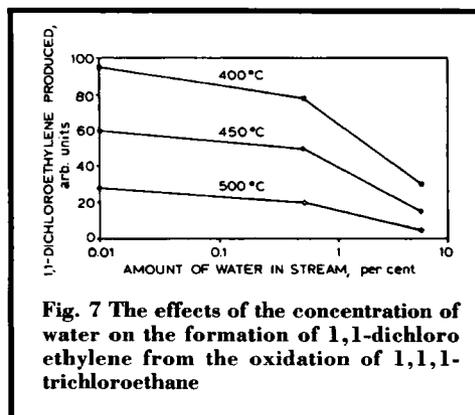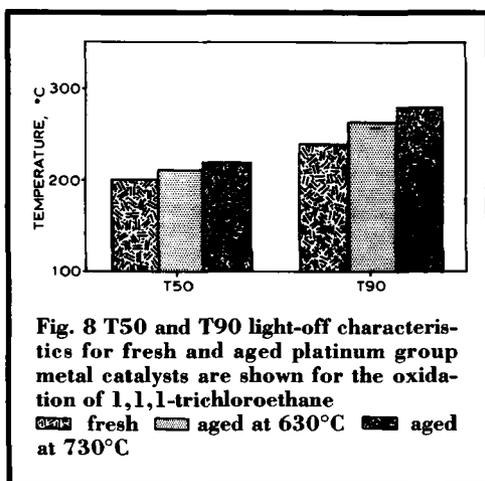
(i) The active sites can be poisoned by the

Fig. 7 The effects of the concentration of water on the formation of 1,1-dichloro ethylene from the oxidation of 1,1,1-trichloroethane

Fig. 8 T50 and T90 light-off characteristics for fresh and aged platinum group metal catalysts are shown for the oxidation of 1,1,1-trichloroethane
▨▨▨ fresh ▨▨▨ aged at 630°C ▨▨▨ aged at 730°C

halides; this is a reversible effect since the halide can easily be removed by treating with steam and/or high temperatures.

(ii) The dispersion of the platinum group metals can be affected by the halides: the presence of halides can increase (and maintain) the dispersion of the metals under typical process conditions (11), particularly in the presence of steam.

(iii) The halides can react with the platinum group metals. Dispersed platinum group metals are, however, not likely to form stable halides, particularly at high temperatures and in the presence of steam and at the low halide concentrations typically present.

(iv) The halides can react with the substrate and affect its integrity; this is particularly important for base metal catalysts and metallic supports.

The performance of platinum catalysts aged at several ageing temperatures, and under conditions previously described is shown in Figure 8. Little decrease in activity is observed. High durability for platinum group metals catalysts is presently being observed in actual field applications. Pilot tests for such catalysts in a pharmaceutical application with C2 chlorinated gas streams (ethylene chloride) achieved better than design conversion levels without forming by-products of combustion, and with no decrease in activity after four months of continuous operation; similarly for a ground water and soil remediation trial treating perchloroethylene and trichloroethylene.

In another industrial process remarkably similar durability for treating dichloropropane and trichloroethane after four years in operation has been observed.

Conclusions

Following laboratory investigations, a supported platinum catalyst has been developed for the specific destruction of halogenated VOCs. The results of on-going field trials indicate that this catalytic process offers both economic and technical advantages compared to established thermal incineration methods, which in addition to being energy intensive may even produce unwanted greenhouse gases during the oxidation of industrial waste gases.

References

1 J. H. Houdry and C. T. Hayes, *Platinum Metals Rev.*, 1958, **2**, (4), 110; G. J. K. Acres, op. cit., 1970, 14, (1), 2; G. J. K. Acres, *op. cit.*, 1971, **15**, (1), 9; T. H. Snape, *op. cit.*, 1977, **21**, (3), 90; A. E. R. Budd, *op. cit.*, 1980, 24, (1), 12; T. J. Lawton, *op. cit.*, 1989, **33**, (4), 178

2 E. J. Calabrese and M. Kenyon, "Air Toxics and Risk Assessment", Lewis Publishers, Chelsea, Michigan, 1991

3 G. C. Bond and N. Sadeghi, *J. Appl. Chem. Biotechnol.*, 1975, **25**, 241

4 G. R. Lester, *Air Waste Manage. Assoc.*, Anaheim, CA, June 25, 1989

5 D. M. VanBenschoten, *Air Waste Manage. Assoc.*, Kansas City, Missouri, 21st June, 1992

6 D. McKeon and T. Roden, *Film Foil Converter*, May 1992, 141

7 Y. F. Y. Yao, *IEC Prod. Res. Dev.*, 1980, **19**, 293

8 T. H. Ballinger and J. T. Yates, *J. Phys. Chem.*, 1992, **96**, 1417

9 H. C. Yao, H. K. Stepien and H. S. Gandhi, *J. Catal.*, 1981, 67, 231

10 "Encyclopedia of Chemical Technology", Kirk-Othmer, John Wiley & Son, 1982, Vol. 17, p.416

11 M. J. D'Aniello, D. R. Monroe, C. J. Carr and M. H. Krueger, *J. Catal.*, 1988, **109**, 407