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The effects of residual chlorine on the behaviour of platinum group metals for oxidation of different hydrocarbons

Noel W. Cant*, Dennys E. Angove, Michael J. Patterson

School of Chemistry, Macquarie University, Sydney, NSW 2109, Australia

Abstract

The oxidation of a mixture of four hydrocarbons and carbon monoxide has been studied over alumina-supported palladium, platinum and rhodium catalysts made using chloride precursor salts. The order of the light-off temperatures for the hydrocarbons is the same for each metal (1-hexene, toluene, benzene and finally iso-octane) but the separation between each and their occurrence relative to carbon monoxide varies. The absolute values, especially for iso-octane, are strongly dependent on the pretreatment procedure. Exposure to H_2/H_2O in the place of O_2 gives much higher activity. Activation can also be achieved by repeated runs with the reactant mixture. Chlorobenzene is produced in small amounts during experiments using partially activated catalysts especially with rhodium. Other reasons for believing that the development of activity is at least partly associated with the removal of chlorine are discussed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrocarbon oxidation; Palladium; Platinum; Rhodium; Effect of chlorine; Chlorobenzene formation

1. Introduction

Catalysts containing platinum group metals (PGMs) are commonly made by impregnation of oxide supports with chlorine containing salts followed by calcination in air. Oxidative treatments are ineffective at removing residual chlorine which may then alter catalytic and isotope exchange properties [1–7]. Chlorine is removed more readily under reducing conditions but temperatures greater than 400°C may be required due to the formation of relatively stable MO_xCl_y species with both palladium [8] and rhodium [9]. Steam is needed for removal of chloride deposited on alumina during reduction or catalyst preparation [10].

The present work arose out of investigations to determine the ability of individual PGMs to oxidise different hydrocarbons in near stoichiometric mixtures. Previous work by Prigent and coworkers [11,12] and Mabilon et al. [13] had shown that within classes of unsaturated hydrocarbons light-off temperatures increased with molecular size when individual compounds were tested alone in a standard exhaust gas over both Pt–Rh and Pd–Rh catalysts. We were interested to see if this was also true with mixtures of such hydrocarbons and for the three PGMs when tested individually. Initial experiments indicated that the activities of catalysts prepared using chlorine-containing precursor salts were highly dependent on pretreatments and varied with successive runs following some pretreatments. The present work was designed to explore the extent and origin of these differences.

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*Corresponding author. Tel.: 00 61 2 9850 8285; fax: 00 61 2 9850 8313; e-mail: noel.cant@mq.edu.au

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2. Experimental

The catalysts have been described previously [14]. They were made by impregnation of standard alumina-precoated cordierite monoliths using aqueous solutions of chloride based precursor salts followed by drying and calcination in air at 500°C for ≈0.5 h. Analysis by particle induced X-ray emission (PIXE) using procedures described elsewhere [15] showed that the metal contents in the alumina washcoat were 1.5%, 1.0% and 1.0 wt% for Pd, Pt and Rh, respectively. The corresponding initial chlorine contents were 0.8%, 1.5% and 2.1%. The surface area of the alumina used was ≈140 m^2/g and that of the coated monoliths was ≈27 m^2/g. The metal surface areas were too small to measure by conventional chemisorption methods.

Testing was carried out in a flow system using 200 mg samples of monolith crushed and sieved to 106–300 µm and contained in a 4 mm i.d. Pyrex U-tube reactor. The standard test stream was a mixture containing 1.00% CO, 0.60% O_2 and 25 ppm each of 1-hexene, benzene, toluene and iso-octane (2,2,4-trimethylpentane) with a total flow rate of 100 cm^3(STP)/min. This mixture is slightly lean with a redox ratio (the ratio of the oxygen required for complete conversion to that supplied) of 0.99. The outlet gas from the reactor was analysed using a Hewlett-Packard model 5880A gas chromatograph fitted with two columns operated at 45°C. One column was a 2 m by 1/8 in. Petrocol A simulated distillation column (Supelco) which provided baseline separation of the four hydrocarbons in 6 min and could be used to detect other compounds with boiling points up to ≈160°C by extending the chromatogram to 9 min. The sensitivity using an FID detector was ≈0.02 ppm with a relative standard deviation of 0.2% when the system was operated on bypass. Carbon monoxide, carbon dioxide and oxygen were separated with a 1.8 m CTR-1 column (Alltech) comprising 5A molecular sieve and Poropak Q arranged concentrically. It was used with a thermistor-type TCD detector (Carle Inst.) which provided a sensitivity of 40 ppm and similar reproducibility to the hydrocarbon analyses. The sampling valve (Valco 10-port) was arranged so that samples were passed alternately to the two columns with an overall cycle time of 10 min.

Prior to reaction each catalyst was pretreated in either 2.2% O_2/He or reduction in 5% H_2/He or 5% H_2/0·5% H_2O/He on a temperature ramp ending at either 400°C or 500°C for 4–6 h. After cooling in He alone the activity was determined as a function of temperature using a ramp initially set at 5°C/min. This was gradually reduced to as low as 0.5°C/min during the light-off of compounds with very steep conversion versus temperature curves.

3. Results

Fig. 1 shows the light-off behaviour of the palladium catalyst following pretreatment in O_2 at 400°C. The order of removal is 1-hexene first followed by toluene, CO and benzene close together with a large gap to iso-octane, the curve for the latter exhibiting a noticeable shoulder. The curve shown for hexene is for total oxidation to carbon dioxide and water. There was some additional conversion to 2 and 3-hexenes plus small amounts of various C_6 dehydrogenation products. The latter include benzene and two other products with the same retention time which is why the benzene conversion curve is slightly negative over the temperature range 150–280°C.

Over a series of successive runs, with no additional pretreatment, the activity of the catalyst improved significantly. Fig. 2 shows the change in behaviour

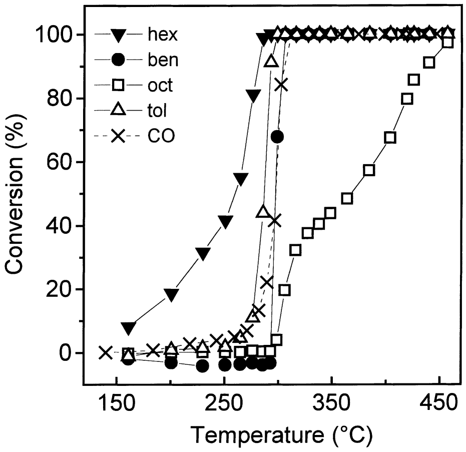

Fig. 1. Conversion versus temperature curves for the oxidation of the standard mixture over the palladium catalyst pretreated in 2.2% O_2/He for 4 h at 400°C.

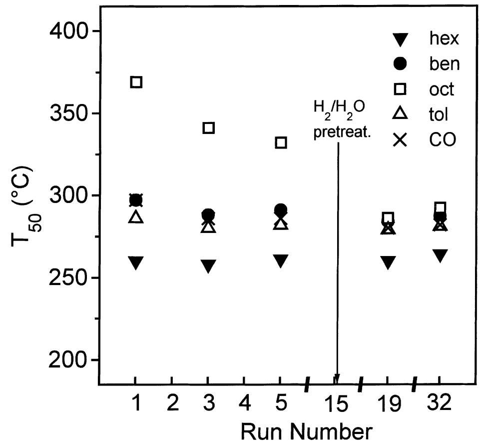

Fig. 2. Effect of repeated reaction on temperatures for 50% conversion of components in standard mixture over the palladium catalyst initially pretreated in 2.2% O_2/He for 4 h at 400°C.

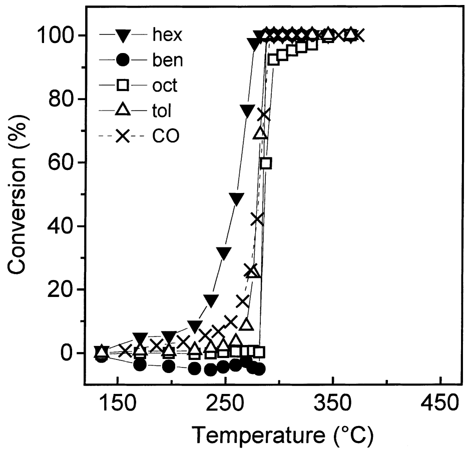

Fig. 3. Conversion versus temperature curves for the oxidation of the standard mixture over the palladium catalyst after repeated reaction and reduction in 5% H_2/0.5% H_2O/He for 4 h at 400°C as per Fig. 2.

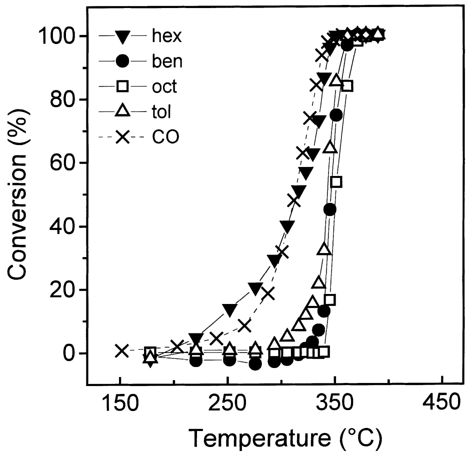

Fig. 4. Conversion versus temperature curves for the oxidation of the standard mixture over the platinum catalyst in 2.2% O_2/He for 4 h at 400°C.

in terms of the temperatures required for 50% conversion (T_{50}). Only experiments using the standard test mixture here are plotted (the missing runs used other compositions, all oxidative). While T_{50} for hexene oxidation does not change much the corresponding values for toluene, CO and benzene are steadily reduced by 10–15°C. The improvement is much larger for iso-octane (>80°C). Subsequent reduction in 5% H_2/0.5% H_2O at 400°C for 4 h produced no further change with the conversion versus temperature curves then being as shown in Fig. 3. The steep light-off for iso-octane, and its closeness to those of CO, toluene and benzene in comparison to that in Fig. 1, is striking.

The activity of the platinum containing catalyst showed less change as a result of successive experiments than did the palladium one. The behaviour following pretreatment in O_2 at 400°C is shown in Fig. 4. The activity for CO removal is significantly less than that of Pd in Fig. 1 with a T_{50} of ≈310°C versus ≈285°C. Unlike the situation with Pd, the curves for the three unsaturated hydrocarbons are at a temperature higher than that of CO. Only when all the CO has been removed does oxidation of benzene commence. This is probably because the unsaturated hydrocarbons are less able to compete for surface with CO on Pt than Pd. However, in contrast to the situation with Pd (Fig. 1), the oxidation of iso-octane on Pt commences only slightly later than that of benzene and the light-off is much sharper.

Fig. 5 shows the behaviour of the same sample of the platinum catalyst after 21 successive runs under a variety of conditions and a subsequent pretreatment in 5% H_2/0.5% H_2O at 400°C. There has been little change in the activity for removal of hexene and CO but the T_{50} values for toluene, benzene and

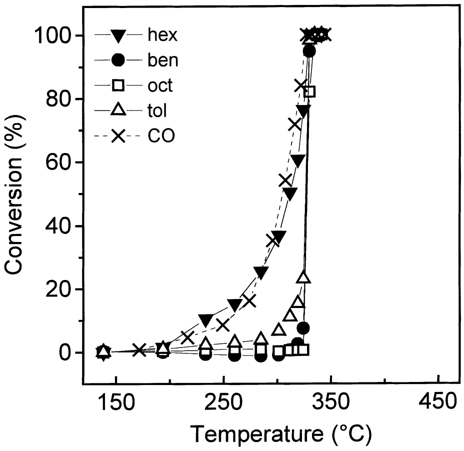

Fig. 5. Conversion versus temperature curves for the oxidation of the standard mixture over the platinum catalyst pretreated in 5% H_2/0.5% H_2O/He for 4 h at 400°C.

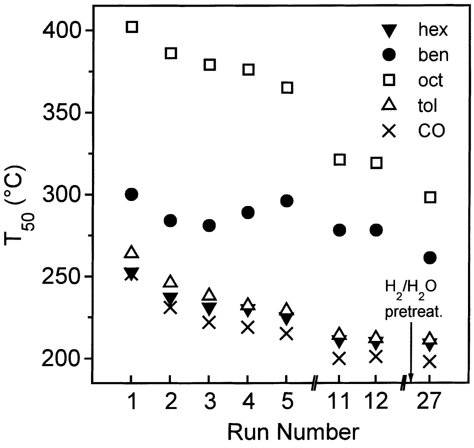

Fig. 7. Effect of repeated reaction on temperatures for 50% conversion of components in standard mixture over the rhodium catalyst initially pretreated in 2.2% O_2/He for 4 h at 400°C.

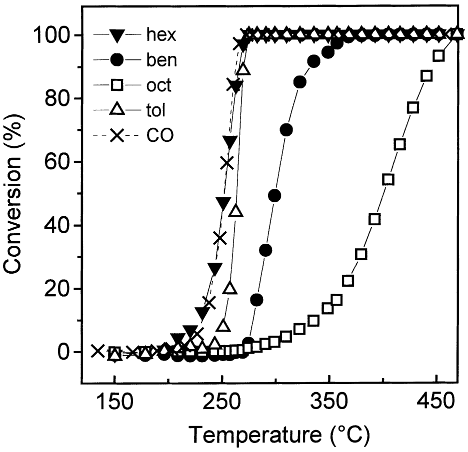

Fig. 6. Conversion versus temperature curves for the oxidation of the standard mixture over the rhodium catalyst pretreated in 2.2% O_2/He for 4 h at 400°C.

iso-octane have all been improved by 15–25°C and they now react almost simultaneously.

The rhodium catalyst exhibited a greater development of activity during successive runs than even the palladium one. Fig. 6 shows the conversion versus temperature curves with Rh following pretreatment in O_2. As with the platinum catalyst, hexene and CO react close together but with a T_{50} approximately 60°C lower. The gap to toluene is smaller than for either palladium or platinum. However, the oxidation of benzene is delayed, with little reaction until all toluene is removed. The activity for iso-octane removal is the least of the three metals after oxidative pretreatment.

The development in activity over successive runs is shown in Fig. 7. The temperatures for 50% conversion of hexene, CO and toluene improved steadily in parallel by ≈35°C over the initial 12 runs while that for iso-octane was decreased by more than 80°C. Measurements under standard conditions, following reduction in 5% H_2/H_2O at 400°C for 4 h (i.e. run 27), shows some further reduction in T_{50} for iso-octane. Most of that change was probably brought about by the intervening experiments under non-standard conditions rather than the reduction itself. Fig. 8 shows the conversion versus temperature behaviour after reduction (run 27). The general pattern for CO, hexene, toluene and iso-octane is similar to that in Fig. 6 but with the conversion versus temperature curves brought to much lower temperatures. The performance improvement for benzene is also substantial but its conversion curve shows a shoulder near half conversion which results in an increased separation from toluene at higher conversions. It is the development of this shoulder which is the reason for the smaller decrease in T_{50} for benzene in Fig. 7 as compared to the other test compounds.

Two ways in which the performance of the catalysts could have been improved by repeated reactions are reduction of partially oxidised metal present from the

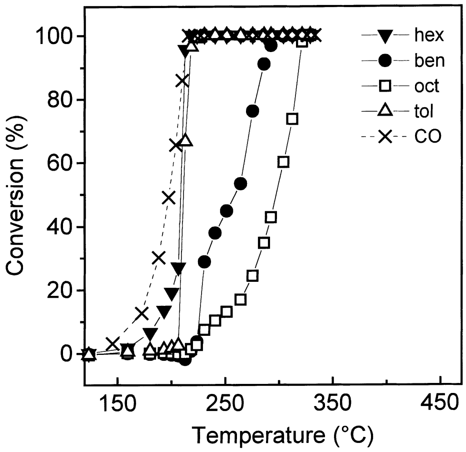

Fig. 8. Conversion versus temperature curves for the oxidation of the standard mixture over the rhodium catalyst after repeated reaction and reduction in 5% H_2/0.5% H_2O/He for 4 h at 400°C as in Fig. 7.

original oxidative pretreatment or removal of chlorine which inhibits activity. Results obtained for the rhodium catalyst after other pretreatments point to at least partial involvement of chlorine (Table 1). Row C shows that while reduction in hydrogen at 400°C does result in a substantial reduction in T_{50} relative to the initial oxidative state (A), the values are still well above those produced by repeated reaction (B), especially for iso-octane. It is known that rhodium trichloride on alumina can be completely reduced to rhodium metal in hydrogen below 200°C [16,17] but the hydrogen chloride liberated is largely taken up by the Al_2O_3. On this basis one might suspect that it is residual chlorine bound to alumina adjacent to small rhodium particles which restricts the activity of the H_2 reduced catalysts for the iso-octane reaction in particular. However, it is not entirely clear that $RhCl_3/Al_2O_3$ calcined prior to reduction can be fully converted to metal at 400°C [16] in which case traces of chlorine still present on the metal might also restrict activity. This could have a greater effect on the oxidation of iso-octane since the ensemble size required for iso-octane is likely to be greater than that for the other test compounds.

As may be seen from row D of Table 1, reduction in H_2/H_2O at 400°C brings the T_{50} values to within 12°C of those achieved by repeated reaction while use of the same pretreatment mixture at 500°C (E) results in the best performance of all for the oxidation of benzene and iso-octane. These results are consistent with the notion that water reduces deposition of the hydrogen chloride formed by reduction on alumina or aids its stripping by the reaction

$$>Al-Cl + H_2O \rightleftharpoons >Al-OH + HCl$$

According to the data of Castro et al. [10] this reaction has an equilibrium constant of $\approx 2\times10^{-3}$ at 400°C and $\approx 5\times10^{-3}$ at 500°C. Calculations using these values and assuming that equilibrium is reached, indicate that with the atmosphere used here (5% H_2/0.5% H_2O) chlorine could be largely stripped in 6 h at 500°C but only partially so in 4 h at 400°C. On this basis the improvement in catalytic performance following reduction in H_2/H_2O versus H_2 alone at 400°C (and still better activity following similar pretreatment at a higher temperature) is consistent with enhanced removal of chlorine. It is also significant that reoxidation of the catalyst produced by reduction in H_2/H_2O

Table 1
Effect of pretreatment on the activity of the rhodium/alumina catalyst

Pretreatment		Temperatures for 50% conversion (T_{50}) (°C)				
		Hexene[a]	Toluene	Benzene	Octane	CO
A	2.2% O_2, 400°C, 4 h	252	264	300	402	252
B	12 repeated reactions (as per Fig. 7)	210	212	278[b]	319	201
C[c]	5% H_2, 400°C, 4 h	225	228	297[b]	367	216
D	5% H_2/0.5% H_2O, 400°C, 4 h (after C)	220	224	267	325	210
E	5% H_2/0.5% H_2O, 500°C, 6 h (after D)	220	221	255	300	208
F	2.2% O_2 at 500°C, 6 h (after E)	214	215	255	312	203

[a] Loss of 1-hexene by total oxidation.
[b] The values here are influenced by the presence of a step in the benzene light-off curve near 50% conversion as in Fig. 8.
[c] New sample.

at 500°C caused only a small elevation in the temperature for 50% removal of iso-octane and slightly improved the values for oxidation of the other test compounds (row F versus E) even though such treatment would be expected to cause conversion of Rh to Rh_2O_3 in surface layers at least [16,18]. This indicates that either the oxidised metal alone is not adverse to activity or, more likely, that it is readily reduced at the start of reaction by the carbon monoxide in the test mixture. The latter would go undetected because the analyses are intermittent.

One way in which the catalysts could be activated by reaction is through removal of chlorine using the water produced by reaction (≈550 ppm at complete conversion) to drive the above reaction. However, we do not believe that this is the sole process for the following reason. With all three catalysts, product chromatograms in experiments following pretreatments giving incomplete development of activity consistently showed an additional peak when there was partial conversion of toluene and benzene. The size of this additional peak, which had a higher retention time than any of the hydrocarbons, fell steadily during subsequent experiments with the same catalyst. Analyses of samples of several tens of millilitres with a gas chromatograph-ion trap mass spectrometer showed that the additional peak was chlorobenzene. We can find no reference in the literature to its formation in this way. It is of particular interest because chlorobenzene is a well-known precursor to dioxins.

Fig. 9 shows plots of chlorobenzene production versus temperature following several pretreatments as listed in Table 1. The maximum amount formed exceeds 0.3 ppm after oxygen pretreatment and is largely confined to the region where conversions of the two aromatics are incomplete. Formation of chlorobenzene commences at a lower temperature following reduction in H_2/H_2O at 400°C (because the catalytic activity is higher) but does not exceed 0.2 ppm. It is barely above the detection limit in the experiment carried out after the same treatment at 500°C. The amounts of chlorobenzene formed fell steadily during the successive experiments in the series illustrated in Fig. 7. Approximate calculations indicated that the amount of chlorine removed as chlorobenzene in each such experiment was <0.3% of that present initially in the catalyst. Thus, if chlorobenzene formation is the reason for catalyst activation during repeated reactions, the removal of chlorine is unlikely to be through a generalised process involving the catalyst as a whole. Rather it must be via removal of much smaller amounts of chlorine bound to the metal itself or sufficiently close to it to hinder its catalytic properties.

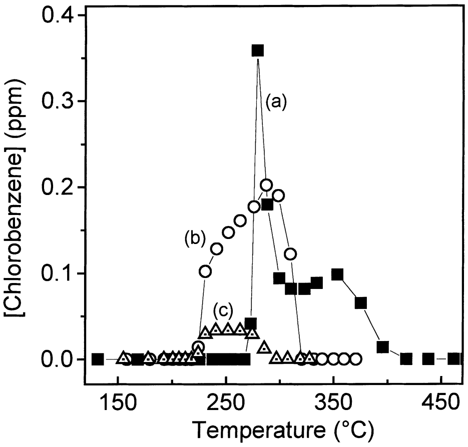

Fig. 9. Chlorobenzene production as a function of temperature during reaction of the standard mixture over rhodium catalyst pretreated as follows: (a) in 2.2% O_2/He for 4 h at 400°C; (b) in 5% H_2/0.5% H_2O for 4 h at 400°C; (c) in 5% H_2/0.5% H_2O for 6 h at 500°C.

The peak amount of chlorobenzene formed over the oxidatively pretreated palladium catalyst was a little less than with the rhodium one and confined to a narrower temperature because the separation between the light-off curves for toluene and benzene is smaller. With platinum, over which toluene and benzene react almost simultaneously (Fig. 4), chlorobenzene evolution did not exceed 0.05 ppm and was confined to a 10°C region near 335°C. Thus it seems that chlorobenzene is restricted to conditions where oxidation of the two aromatics also occurs. However, a connection between these processes, and the relative contributions of toluene and benzene to chlorobenzene formation, remains to be established.

It seems most unlikely from the present work that significant chlorobenzene could be generated during normal operation of vehicles fitted with emission control catalysts. It could occur only if the catalyst contained residual chlorine but this would be completely stripped within a few minutes by the high concentrations of steam present in exhaust once normal operating temperatures are reached. Even with residual chlorine present, chlorobenzene formation would be possible only during the short time spent at temperatures in the light-off region for aromatics. The only possible scenario for chlorobenzene formation would be during a period of continuous idling following the initial startup of a new vehicle at the factory.

4. Conclusions

The four hydrocarbons tested here are oxidised in the order 1-hexene, toluene, benzene and iso-octane over palladium, platinum and rhodium catalysts made with chlorine containing precursors. The activity improves during repeated experiments, especially for Rh and Pd, and is higher following reductive pretreatments rather than oxidative ones. The activation appears to be associated with chlorine removal. Reaction over less than fully activated catalysts is accompanied by the formation of significant amounts of chlorobenzene but the extent to which this produces activation is yet to be established.

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