Benzene formation during the oxidation of cyclohexene in the presence and absence of thiophene over a supported palladium catalyst

Emwajee Kullavanijaya [a], Noel W. Cant [a,b] and David L. Trimm [a,*]

[a] *Department of Chemical Engineering and Industrial Chemistry, University of New South Wales, NSW 2052, Australia*
E-mail: d.trimm@unsw.edu.au
[b] *Department of Chemistry, Macquarie University, NSW 2109, Australia*

The catalytic oxidations of cyclohexene and thiophene, singly and together, have been studied over a $Pd/CeO_2/Al_2O_3$ monolith catalyst. On a freshly reduced sample, the oxidation of cyclohexene on its own commences below $100\,°C$ with benzene as the major product over a considerable temperature range, even when O_2 is in large excess. Benzene is still produced when cyclohexene and thiophene are co-oxidised and the reaction exhibits oscillations, associated with accumulation and removal of sulfur, at high conversions. The oxidation of thiophene is self-poisoned to some degree and sulfur accumulated during it considerably reduces the activity of the catalyst for the subsequent oxidation of cyclohexene. However, the maximum yield of benzene remains high.

KEY WORDS: cyclohexene; benzene; oxidation; palladium; thiophene

1. Introduction

The catalytic combustion of volatile organic compounds for pollution control purposes is well-established technology [1]. The process is usually operated continuously but intermittent operation can be more energy efficient for the treatment of gas streams with low concentrations of odorous compounds [2]. The compound is accumulated on a suitable adsorbent until close to breakthrough and then desorbed onto the heated catalyst, with total combustion over a short period of time, before cooling for the next adsorption. In recent work we have investigated a range of adsorbents and catalysts for suitability with this type of system using four model compounds, namely, cyclohexene, methylmethacrylate, diethylamine and thiophene [3]. Activated carbon was found to be the most suitable adsorbent for use with humid streams while a palladium-based catalyst was somewhat more active than platinum and rhodium systems although it was subject to some deactivation when used with a sulfur-containing feed.

During the course of the above work, partial oxidation products were sometimes seen, especially when using cyclohexene in combination with palladium. Undesired formation of benzene was suspected but the gas chromatographic system available at the time was unsuitable for its analysis especially when using mixed feeds. The aims of the present work were firstly to identify positively the product from cyclohexene oxidation and secondly, to determine how the characteristics of its formation were affected by sulfur, present through prior or concurrent oxidation of thiophene.

There is no previous work of this type under oxidative conditions with gaseous feeds. However, disproportionation of cyclohexene to cyclohexane and benzene is well-known with various supported palladium catalysts in the absence of oxygen in both batch liquid phase experiments [4] and for continuous-flow gas phase conditions [5,6]. In the liquid phase, oxygen increases yields of benzene with a maximum selectivity of $\sim 80\%$ using 6 atm O_2 with ethanol as the solvent [4]. Dehydrogenation of cyclohexene to benzene is also well established under non-oxidative conditions on Pd(111) at low pressure [7] and on other platinum group metals as well [8,9].

2. Experimental

Reactions were carried out in a single-pass flow system operated at atmospheric pressure. The feed stream, at $100\,cm^3/min$, contained 20% O_2 in helium with cyclohexene and/or thiophene supplied from separate saturators to give concentrations of ~ 3000 and ~ 2200 ppm, respectively, as determined by analysis of the CO_2 produced at total combustion. The catalyst was a commercial monolith from Johnson Matthey CSD (Australia) with 1.8 g/l Pd in a 5 wt% CeO_2/Al_2O_3 washcoat supported on a cordierite honeycomb with 64 cells per cm^2. The BET surface area was $34\,m^2/g$. All experiments reported here were carried out using a single cylindrical sample, 10 mm diameter by 15 mm in length, weighing ~ 600 mg. This was packed between plugs of quartz wool in a 12 mm OD Pyrex tube. It was reduced in 25% H_2/He on a temperature ramp ending with 12 h at $300\,°C$ prior to the first experiment and again

*To whom correspondence should be addressed.

between some experiments as indicated later. Each reaction was carried out starting with the sample at room temperature, ramping quickly to ~90 °C and then at ~2 °C/min until complete conversion was reached and CO_2 analyses were stable.

The gas stream leaving the test system was analysed by two gas chromatographs and by mass spectrometry. One chromatograph, fitted with a 4% Carbowax plus 0.8% KOH on Carbograph 1 column held at 90 °C and a FID detector, was used for the analysis of cyclohexene and thiophene. It could also separate benzene from cyclohexene but not from thiophene. The second chromatograph, fitted with a CTR-1 column (Alltech Associates) at 60 °C and a TCD detector, was used for analysis of oxygen and carbon dioxide. The reproducibility of the analyses were approximately ±3%. Mass spectrometric analyses were carried out with a Balzers Thermostar quadrupole instrument with multiple ion monitoring. Electron multiplier and/or Faraday cup signals were acquired on a ~20 s cycle at $m/z = 28$ (for CO), 32 (O_2), 44 (CO_2), 64 (SO_2), 67 (C_6H_{10}, principal fragment), 78 (C_6H_6), 80 (C_6H_8), 82 (C_6H_{10}) and 84 (C_4H_4S). The mass spectrometer was fast, sensitive and quite stable during the course of a single day. However, it did show substantial variations in absolute and, to a lesser extent, relative sensitivities from one day to the next. The data is best processed in relative terms, *i.e.*, for the reactant(s) with respect to signals of the feed on bypass, and for the products, CO_2 and SO_2, with respect to their signals at complete conversion. In the case of benzene, the signal was normalised against the gas chromatography data for its peak concentration relative to feed cyclohexene. With CO, the $m/z = 28$ signal was first corrected for background drift and fragmentation of CO_2 and then processed relative to the CO_2 signal at complete conversion allowing for the difference in intrinsic sensitivity as determined with a mixture containing CO and CO_2 in known concentrations.

3. Results and discussion

Figure 1 shows the relative concentrations and atom balances for the temperature-programmed oxidation of cyclohexene alone over a freshly reduced $Pd/CeO_2/Al_2O_3$ sample. Leaving aside the spikes associated with operation of the sampling valves, there is excellent agreement between the mass spectrometer results (small open symbols) and the gas chromatographic ones (larger closed symbols). Oxidation of cyclohexene starts below 100 °C with benzene formed initially followed by CO_2 at temperatures above ~160 °C. The maximum yield of benzene (~90%) is astonishingly high bearing in mind the high O_2/C_6H_6 ratio at the time (>50). The probable reason is that cyclohexene adsorbs strongly in preference to benzene so that oxidation of the latter is minimal until cyclohexene is completely converted. The carbon atom balance is complete within experimental error so loss of carbon to the catalyst is minimal throughout.

Mass spectrometer results for the oxidation of thiophene alone over the same sample without further reduction are
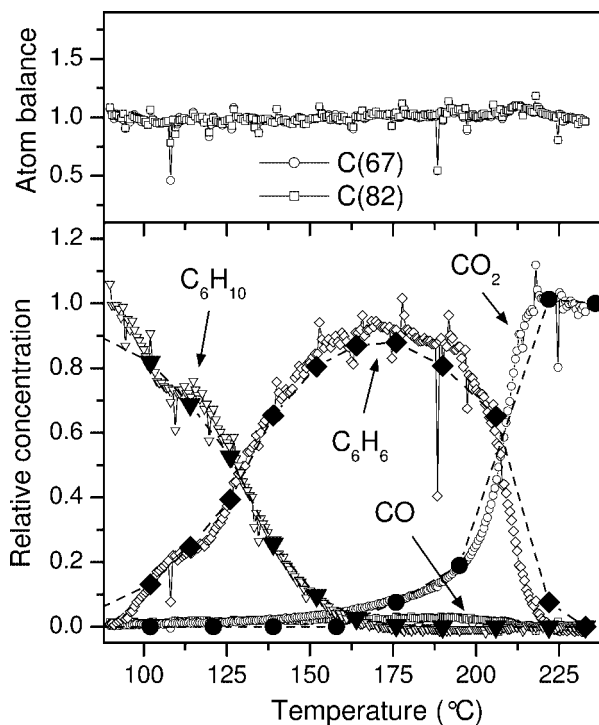

Figure 1. Relative concentrations and atom balances as a function of temperature during the oxidation of 3000 ppm of cyclohexene in 20% O_2/He over 0.6 g of freshly reduced $Pd/CeO_2/Al_2O_3$ monolith with total flow rate of 100 cm^3/min. Open symbols: mass spectrometer data; closed symbols: gas chromatograph data; C(67) – carbon balance calculated using signal for fragment ion with m/z of 67 for cyclohexene, C(82) – carbon balance calculated using signal for parent ion with m/z of 82 for cyclohexene.
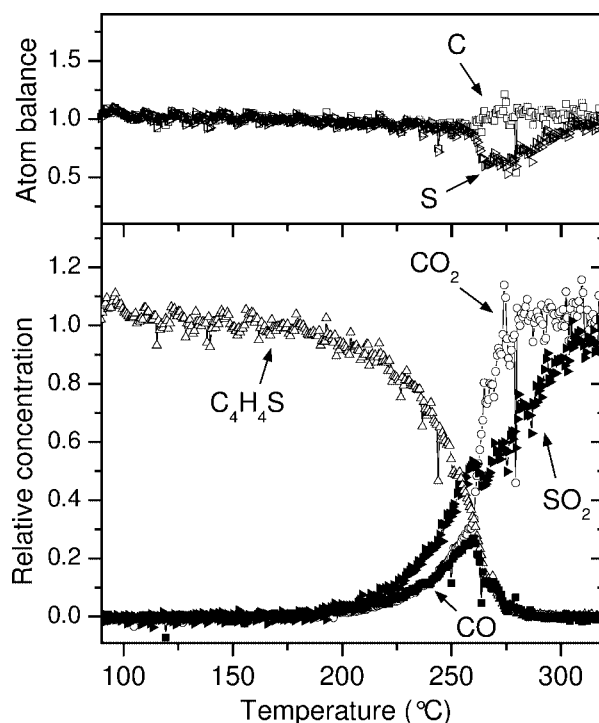

Figure 2. Relative concentrations and atom balances calculated from mass spectrometer data for the oxidation of 2200 ppm of thiophene in 20% O_2/He with total flow rate of 100 cm^3/min over 0.6 g of $Pd/CeO_2/Al_2O_3$ monolith following experiment illustrated in figure 1.
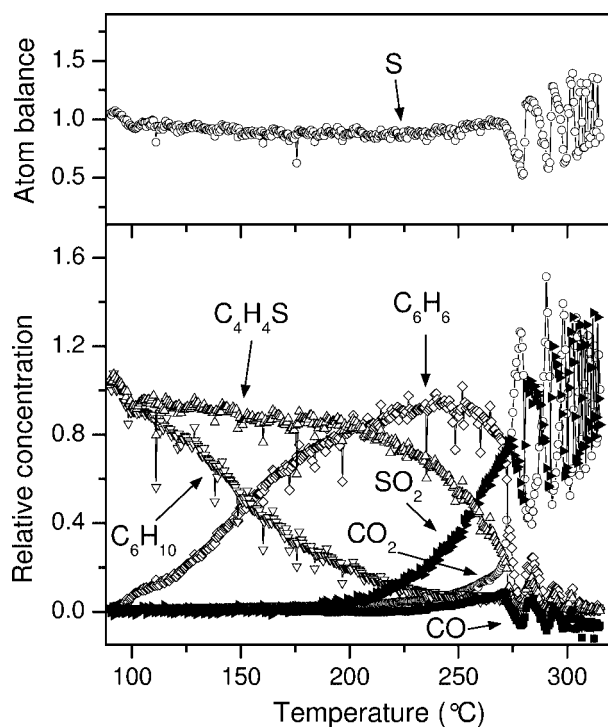
Figure 3. Relative concentrations and atom balances for the oxidation of a mixture of 3000 ppm cyclohexene and 2200 ppm of thiophene in 20% O_2/He with total flow rate of 100 cm^3/min over 0.6 g of Pd/CeO$_2$/Al$_2$O$_3$ re-reduced monolith following experiment illustrated in figure 2.
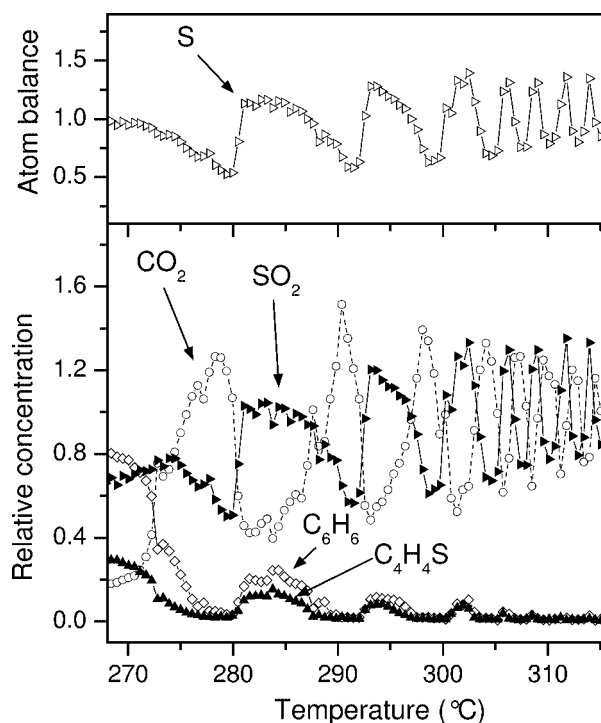
Figure 4. Expanded scale section of figure 3 for the oxidation of a mixture of 3000 ppm cyclohexene and 2200 ppm of thiophene in 20% O_2/He with total flow rate of 100 cm^3/min over 0.6 g of reduced Pd/CeO$_2$/Al$_2$O$_3$ monolith.

shown in figure 2. Gas chromatographic determinations were similar but are omitted from now on for reasons of simplicity. Oxidation of thiophene commences at $\sim$200 °C and is complete by 300 °C. Unlike cyclohexene, some CO is made as well as CO_2 with a maximum yield of $\sim$25% at 260 °C but none at complete conversion. Formation of SO_2 lags that of CO + CO_2 at high conversions indicating some uptake of sulfur. This is also apparent from a significant deficit in the S atom balance between 250 and 300 °C.

Figure 3 shows the result of a subsequent experiment in which a mixture of cyclohexene and thiophene was oxidised over the same sample following re-reduction in H_2/He. Based on previous tests, this is sufficient to restore the behaviour of the catalyst for the individual reactions to that shown in figures 1 and 2. With thiophene present, oxidation of cyclohexene still commences near 100 °C. The maximum yield of benzene is similar to that for the individual reaction (figure 1) but occurs at a higher temperature ($\sim$250 versus 175 °C). Oxidation of thiophene in the mixture is similar to the individual reaction (figure 2) up to 275 °C but shows fluctuations above that as does formation of CO_2 and SO_2, and the atom balance in sulfur.

An expanded scale plot of this region is shown in figure 4. Repeated oscillations of similar magnitude are apparent which become more frequent as the temperature rises. The process commences as conversions of benzene and thiophene first approach 100% near 275 °C. Production of CO_2 then starts to exceed unity in relative concentration terms, reflecting combustion of accumulated carbonaceous matter,

while that of SO_2 commences to decline. Clearly sulfur is being stored on the catalyst as is also obvious from the sulfur atom balance. This accumulation poisons the catalyst and CO_2 production falls with re-emergence of some benzene and thiophene. SO_2 formation now rises rapidly with the atom balance going above unity. The removal of adsorbed sulfur species is eventually sufficient to restore activity for oxidation of benzene and thiophene. The cycle is then repeated many times on an increasingly shorter time scale reflecting faster reaction steps at higher temperature.

Definition of the surface processes driving the system is necessarily speculative but they must involve both cyclohexene and thiophene since oscillations are absent when the latter is oxidised alone. Thiophene dissociates on Pd(111) with formation of a C_4H_4 species and a strongly bound adsorbed sulfur [10] which is likely to be the poisoning sulfur species in the present system. Disproportionation of cyclohexene to benzene and cyclohexane over Pd/sepiolite undergoes continuous deactivation at temperatures from 150 to 250 °C which is associated with the adsorption of benzene and species derived from it [6]. Hence the alternate accumulation and burn-off of such deposits are more likely to be the source of the oscillations in CO_2 than are the C_6H_9 and C_6H_8 intermediates through which cyclohexene is known to be converted to benzene on single crystal surfaces of Pd and Pt [7–9].

Figure 5 shows the results obtained in a fourth experiment in which thiophene was oxidised alone over the same sample
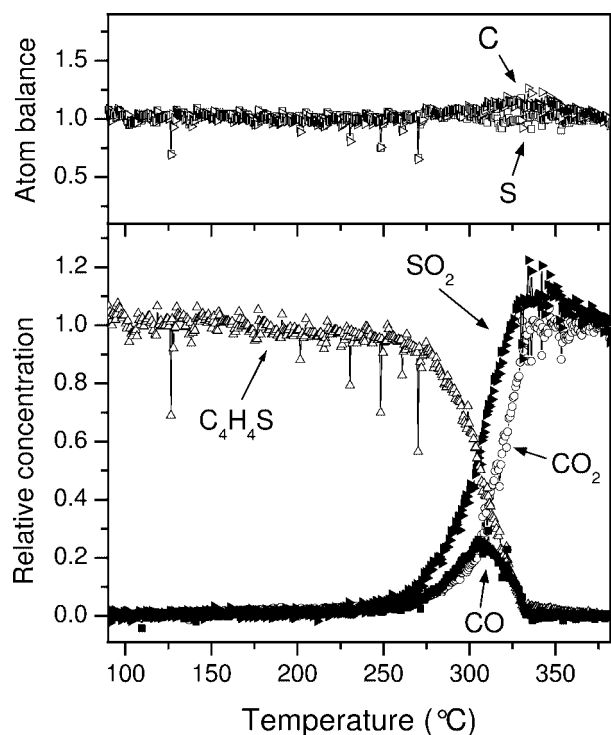
Figure 5. Relative concentrations and atom balances for the oxidation of 2200 ppm of thiophene in 20% O_2/He with total flow rate of 100 cm^3/min over 0.6 g of Pd/CeO$_2$/Al$_2$O$_3$ monolith previously used for experiment illustrated by figure 3.
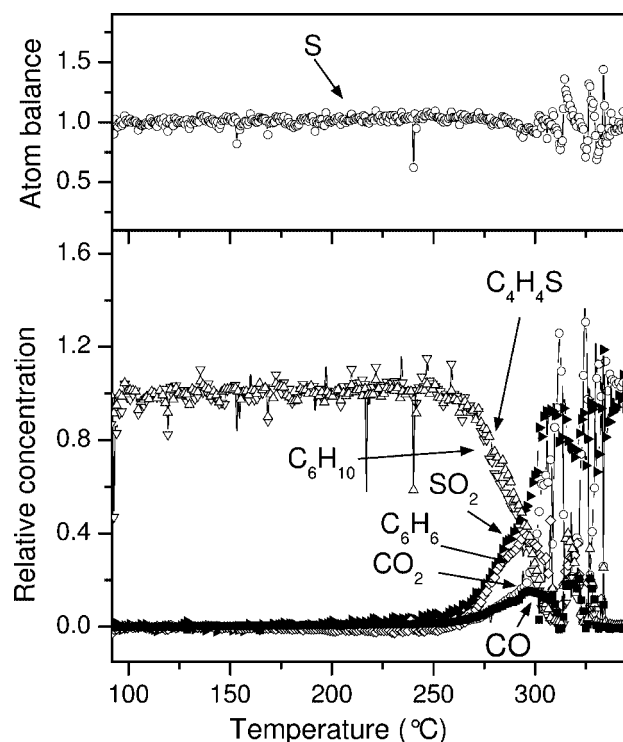

Figure 6. Relative concentrations and atom balances for the oxidation of a mixture of 3000 ppm cyclohexene and 2200 ppm of thiophene in 20% O_2/He with total flow rate of 100 cm^3/min over 0.6 g of Pd/CeO$_2$/Al$_2$O$_3$ monolith previously used for experiment illustrated by figure 5.

of Pd/CeO$_2$/Al$_2$O$_3$ without an intervening reduction. Reaction now commences close to 250 °C with complete reaction at ∼350 °C and a temperature for 50% conversion (T_{50}) of ∼306 °C. This is more than 50 °C higher than found for oxidation over the same sample when not previously exposed to sulfur (*i.e.*, figure 2). Thus thiophene exhibits significant self-poisoning due to the retention of sulfur from the previous experiment in which the mixture was oxidised (*i.e.*, as per figures 3 and 4). It is also apparent that, unlike the data in figure 2, the sulfur atom balance in figure 5 appears complete throughout, indicating no major additional accumulation of sulfur.

The results of a further reaction using a cyclohexene/thiophene mixture over the same catalyst sample, again without intervening pretreatment, are illustrated in figure 6. The two exposures to a sulfur-containing feed have greatly poisoned the activity for cyclohexene oxidation which does not commence until 250 °C compared to below 100 °C when the catalyst was freshly reduced. The yield of benzene, partially hidden behind the data for SO$_2$, is also much less, with a maximum of ∼40% at 290 °C. However, the reaction of thiophene, although requiring a much higher temperature than for the sulfur-free catalyst of figure 2, is slightly faster than when it was oxidised alone on the used catalyst (figure 5). The values for T_{50} are 293 and 306 °C, respectively. Thus co-oxidation of cyclohexene has aided reaction slightly, presumably due to some removal of sulfur using hydrogen atoms derived through dissociative desorption. As in figure 3, oscillations in SO$_2$ and CO$_2$ concentrations, and in
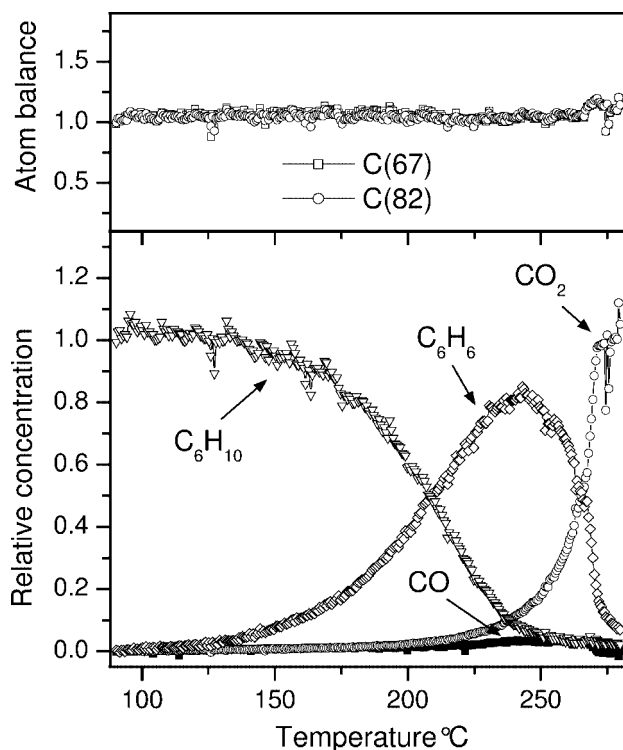

Figure 7. Relative concentrations and atom balances for the oxidation of a mixture of 3000 ppm cyclohexene in 20% O_2/He with total flow rate of 100 cm^3/min over 0.6 g of Pd/CeO$_2$/Al$_2$O$_3$ monolith previously used for experiment illustrated by figure 6.

the sulfur atom balance, become evident as conversion of the mixture approaches 100%. While the phasing between the various species is the same as for the first reaction with the mixture the oscillations are rather less regular and smaller in magnitude.

Figure 7 shows plots for a further reaction of cyclohexene alone over the same sample without reduction so that there have now been three exposures to sulfur. The temperature for 50% removal is now 210 °C compared with 287 °C for the previous experiment with the mixture and 128 °C with the freshly reduced catalyst (figure 1). Production of benzene is again high with a maximum yield of about 80% at 240 °C. Formation of CO is still not significantly greater than the experimental error.

Other experiments carried out as part of this study have shown that the behaviour of thiophene-exposed $Pd/CeO_2/Al_2O_3$ catalysts for cyclohexene oxidation can be fully returned to their initial state, as illustrated in figure 1, by a standard reduction in hydrogen.

4. Conclusions

The oxidation of cyclohexene over reduced $Pd/CeO_2/Al_2O_3$ is very selective towards the formation of benzene even when O_2 is in great excess. Benzene is still produced, but at higher temperatures, when cyclohexene is co-oxidised with thiophene and that reaction exhibits oscillations in CO_2 and SO_2 near complete conversion which are associated with the alternate accumulation and removal of sulfur and of carbonaceous matter, that is probably derived from benzene.

Oxidation of thiophene is self-poisoning to some extent. Residual sulfur from that reaction has a considerable effect on the activity of the catalyst for the subsequent oxidation of cyclohexene but benzene remains the dominant initial product.

References

[1] R.M. Heck and R.J. Farrauto, *Catalytic Air Pollution Control: Commercial Technology* (Van Nostrand Reinhold, New York, 1995).
[2] V. Meeyoo, J.H. Lee, D.L. Trimm and N.W. Cant, Catal. Today 44 (1998) 67.
[3] E. Kullavanijaya, D.L. Trimm and N.W. Cant, Stud. Surf. Sci. Catal. 130A (2000) 569.
[4] Z. Cvengrosova and M. Hronec, J. Mol. Catal. 94 (1994) 181.
[5] R.B. Borade, B. Zhang and A. Clearfield, Catal. Lett. 45 (1997) 233.
[6] M.A. Aramendia, V. Borau, I.M. Garcia, C. Jimenez, A. Marinas, J.M. Marinas and F.J. Urbano, J. Mol. Catal. A 151 (2000) 261.
[7] D.E. Hunka, T. Picciotto, D.M. Jaramillo and D.P. Land, Surf. Sci. 421 (1999) L166.
[8] C.L.A. Lamont, M. Borbach, R. Martin, P. Gradner, T.S. Jones, H. Conrad and A.M. Bradshaw, Surf. Sci. 374 (1997) 215.
[9] X. Su, K.Y. Kung, J. Lahtinen, Y.R. Shen and G.A. Somorjai, J. Mol. Catal. A 141 (1999) 9.
[10] T.E. Caldwell, I.M. Abdelrehim and D.P. Land, Surf. Sci. 367 (1996) L26.