In situ observation of structural changes in polycrystalline silver catalysts by environmental scanning electron microscopy

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Morphology changes induced in polycrystalline silver catalysts as a result of heating in either oxygen, water or oxygen–methanol atmospheres have been investigated by environmental scanning electron microscopy (ESEM), FT-Raman spectroscopy and temperature programmed desorption (TPD). The silver catalyst of interest consisted of two distinct particle types, one of which contained a significant concentration of sub-surface hydroxy species (in addition to surface adsorbed atomic oxygen). Heating the sample to 663 K resulted in the production of 'pin-holes' in the silver structure as a consequence of near-surface explosions caused by sub-surface hydroxy recombination. Furthermore, 'pin-holes' were predominantly found in the vicinity of surface defects, such as platelets and edge structures. Reaction between methanol and oxygen also resulted in the formation of 'pin-holes' in the silver surface, which were inherently associated with the catalytic process. A reaction mechanism is suggested that involves the interaction of methanol with sub-surface oxygen species to form sub-surface hydroxy groups. The sub-surface hydroxy species subsequently erupt through the silver surface to again produce 'pin-holes'.

Introduction

Polycrystalline catalysts are used extensively for the partial oxidation of methanol to formaldehyde. Although they exhibit excellent selectivity to formaldehyde there remains a need to further increase the methanol conversion efficiency. Consequently, a large amount of research has been directed towards the elucidation of the reaction mechanism[1−3] and the nature of the active site. However, controversy still exists, owing primarily to the complex morphological changes that occur in the silver structure during catalytic conditions.[4,5] Bao *et al.*[6] showed that the interaction of oxygen with an Ag(111) surface at temperatures >800 K resulted in profound surface reconstruction Furthermore, it was suggested that oxygen became incorporated into sub-surface sites and concomitantly caused a slight expansion of the uppermost silver layer. Interaction of sub-surface oxygen with hydrogen promotes the formation of hydroxy species,[7] which are thought to react subsequently to produce water molecules which then erupt through the silver surface.[7,8] Similarly, reaction of sub-surface oxygen with methanol also results in strong surface facetting.[8]

One of the most significant features observed after either the catalytic reaction or reduction of the silver surface by hydrogen, is the formation of 'pin-holes'. It has been hypothesised that these holes are due to recombinative desorption of sub-surface hydroxy species,[7,8] and moreover, it appears that these holes are concentrated in the vicinity of surface defects. Clearly, these holes might play a central role in the activity of silver catalysts. Therefore, it is desirable to monitor hole evolution under *in situ* conditions.

Conventional electron microscopic techniques are not suitable in this context since they normally operate under high vacuum conditions. Environmental scanning electron microscopy (ESEM) surmounts this problem and actually allows imaging of a sample at pressures of up to 2.67 kPa, and at temperature between 253 and 1273 K. Although the aforementioned technique has found applications in biological and material sciences,[9] it has not been used to image a catalytic process to the best of our knowledge. This paper reports an

ESEM investigation of oxygen, water and methanol (components of a methanol oxidation stream) interaction with polycrystalline silver catalyst, and correlates this data with information concerning the nature of surface species obtained by FT-Raman spectroscopy and temperature programmed desorption (TPD) methods.

Experimental

Polycrystalline silver catalyst (99.999% as verified by ICP analysis) was supplied by ICI Resins, New Zealand and was used without any further pretreatment. The BET surface area was approximately 70 cm^2 g^{-1}. ESEM images were obtained using an Electroscan ESEM model 20A instrument and an accelerating voltage of 30 kV. For more detailed information regarding the operating principles of ESEM the reader is referred to the work of Danilatos.[10] A typical experiment involved placement of *ca.* 400 mg of silver catalyst onto a heating stage located in the ESEM chamber, followed by evacuation to high vacuum. The specimen was then introduced to *ca.* 0.5 kPa of either oxygen, water, methanol (BDH, AnalaR grade) or a methanol–oxygen mixture produced using a methanol saturator. Images were continuously acquired using a conventional videocamera and individual snapshots taken with a videoprinter. The temperature of the sample was accurately controlled by a temperature programmable controller, which produced a heating rate of *ca.* 10 K min^{-1}. More detailed pre- and post-reaction images were collected using JEOL 890 and 6400 field emission scanning electron microscopes (FESEM).

In order to gain data pertinent to the nature of the oxygen species present in the silver system, FT-Raman spectra were recorded using a Perkin–Elmer 2000R spectrometer. Spectra were acquired using an incident laser power of 200 mW, a spectral resolution of 4 cm^{-1} and averaging over 64 scans. Spectral manipulation was performed using GramsResearch software. Support for the Raman assignments was also provided by use of apparatus designed to facilitate TPD studies. Briefly, approximately 500 mg of silver catalyst was placed in a 4 mm id stainless-steel tube located in an electrically heated furnace. Samples were heated linearly at 20 K min^{-1} in a

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stream of ultra-high-purity helium and effluent gases continuously monitored by a Balzers Thermocube quadrupole mass spectrometer.

Results

Raman spectroscopy of fresh catalyst

Fig. 1 illustrates the typical morphology of the silver catalyst before reaction. In general, two distinct types of structure could be identified. First, relatively featureless grains, containing only slight signs of surface cracks and some platelet construction [Fig. 1(b), (d)], were present, the size of which varied between 10 and 40 μm, on average. More interestingly, intermingled with the aforementioned large grained structures, were silver particles consisting of a complex mixture of elongated globular crystallites [Fig. 1(a)]. These latter moieties were typically of between 3 and 6 μm in length and *ca.* 1.5 μm in diameter, and were always present as components of a large agglomerate with overall size in the order of tens of micrometres [Fig. 1(a), (c)].

The corresponding FT-Raman spectrum of the silver sample is shown in Fig. 2(a). Bands were identified at 235, 382, 554, 706, 773, 860 and 1042 cm^{-1}. Benndorf *et al.*[11] observed a peak at 220 cm^{-1} in the EELS spectrum of oxygen adsorbed on Ag(111) ascribed to the ν(Ag—O) mode of dissociatively adsorbed oxygen. Similarly, Kondarides *et al.*[12] and Millar *et al.*[13] also noted the presence of a band at 240 cm^{-1} in the Raman spectrum of oxygen adsorbed on polycrystalline silver, again assigned to a vibration of atomically adsorbed oxygen. In addition, the observed shoulder on the 240 cm^{-1} peak in Fig. 2(a) might be indicative of a vibration of molecularly adsorbed oxygen.[12] Consequently, the maximum at *ca.* 235 cm^{-1} in this study is proposed to be a combination of vibrations for both atomically and molecularly adsorbed oxygen on silver. The sharp peak at 1054 cm^{-1} was characteristic for the ν_1 vibration of adsorbed carbonate (produced by the reaction of CO_2 with chemisorbed atomic oxygen).[14] The Raman spectrum was dominated by an intense feature at 773 cm^{-1}. Ertl and co-workers[15,16] demonstrated that an oxygen-reconstructed silver single crystal displayed Raman bands at *ca.* 630 and 803 cm^{-1} assigned to the ν(Ag—O) vibrations for sub-surface and strongly bound atomic oxygen species, respectively. Corresponding peaks have also been observed in Raman spectra of polycrystalline silver catalysts[13] and significantly their vibrational frequency was influenced by the presence of other adsorbates. In contrast, Kondarides *et al.*[12] attributed a band at 815 cm^{-1} to the O—O stretching mode for a molecularly adsorbed oxygen species, this assignment being based upon the observation of a shift to lower wavenumber with ^{18}O isotopic substitution. XPS data reported by Pettinger *et al.*,[15] and more convincingly the thermal stability of this species beyond 830 K,[13,15] support the assignment of the 773 cm^{-1} peak to atomic oxygen. Millar *et al.*[13] have argued that this species is actually Ag^{III}=O, by analogy with the vibrational frequency for the isoelectric PtO (851 cm^{-1}). The shift to lower wavenumber is attributed to the influence of sub-surface species on the bonding properties. Bao *et al.*[17] exposed either water or hydrogen to an oxygenated Ag(111) single crystal to produce species identified by Raman bands at 554 and 985 cm^{-1}. At elevated temperatures, these bands were shifted to 575 and 860 cm^{-1}. These pairs were ascribed to the ν(Ag—OH) and δ(OH) vibrations for hydroxy groups on the surface and in the sub-surface region, respectively. The bands present at 860 and 554 cm^{-1} in the spectrum of the polycrystalline silver sample are thus attributed to sub-surface hydroxy species. In harmony with this assignment are the results of Iwasaki and co-workers,[18] who reported bands at 560 and 860 cm^{-1} following the reaction of water with bulk Ag_2O.

Two bands remain unassigned, 382 and 706 cm^{-1}. It is proposed that the lower wavenumber band is characteristic of an oxygen species dissolved in the bulk silver structure. Comparison with the Raman band for AgO, which appears at 390–430 cm^{-1} supports this hypothesis. Assignment of the 706 cm^{-1}
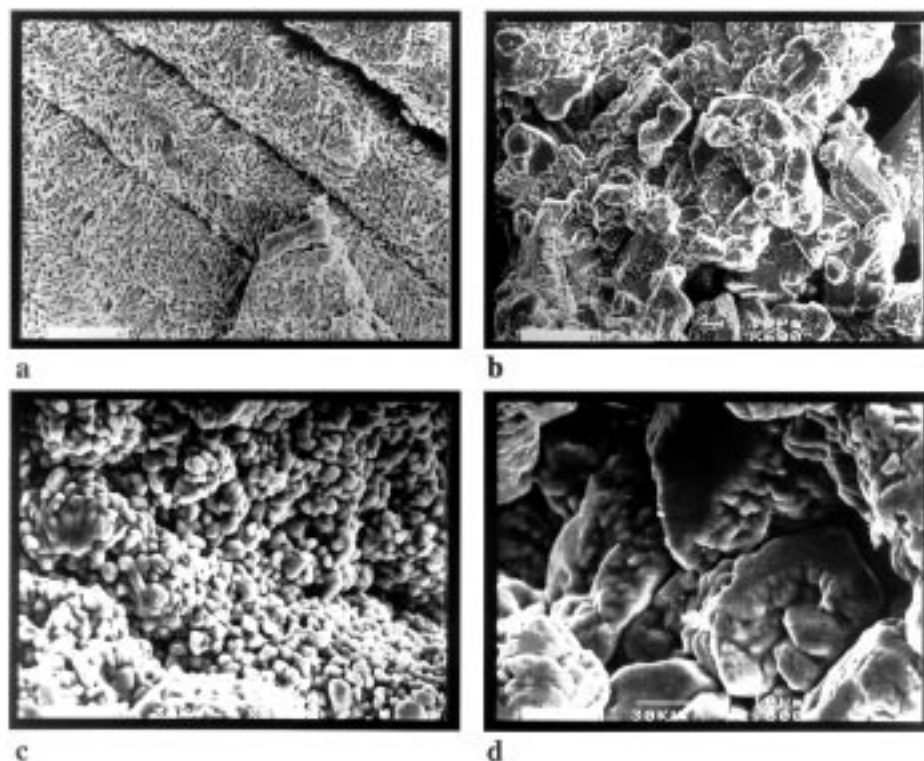

Fig. 1 FESEM images of polycrystalline silver illustrating the two distinct types of morphology identified
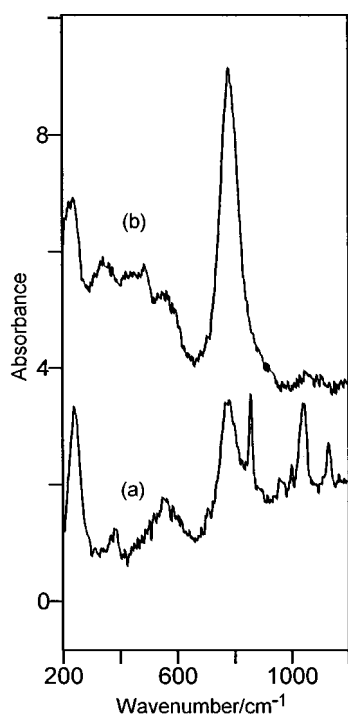
Fig. 2 FT-Raman spectra of: (a) fresh silver catalyst, and (b) silver catalyst following use in an industrial plant for methanol oxidation

band to the ν_4 mode associated with the vibration of adsorbed unidentate carbonate might be plausible, as this is expected to be quite weak.[19] Consequently, we conclude that the present catalyst contains atomically adsorbed surface oxygen, molecularly bound surface oxygen and a significant concentration of sub-surface hydroxy groups.

Temperature programmed desorption

Further identification of the surface adsorbates present was achieved by the use of desorption measurements. The silver catalyst was linearly heated in a stream of purified helium and the gaseous products continuously monitored by on-line mass spectrometry. The resultant TPD trace is shown in Fig. 3. A complex water desorption profile was recorded along with a simpler carbon dioxide pattern, which exhibited desorptions at *ca.* 633, 753 and 1050 K. Deconvolution of the water outline revealed the presence of a minimum of three species at
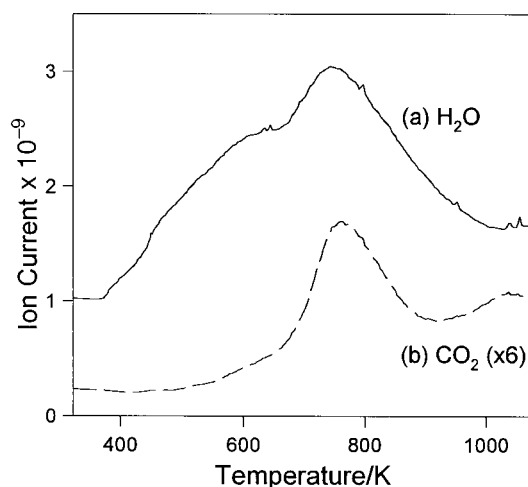
413, 629 and 751 K. The first desorption presumably corresponded to the removal of physisorbed water from the silver surface. The remaining two losses indicated the presence of hydroxy groups, which was in agreement with the Raman data that suggested the presence of substantial concentrations of sub-surface hydroxy species (Fig. 2). Lefferts *et al.*[20] have noted the desorption of water at 673 K from polycrystalline silver when hydrogen species were dissolved in the silver lattice in addition to sub-surface oxygen. Although these authors postulated the existence of hydroxy species no definite conclusion could be attained due to the lack of spectroscopic evidence. The nature of the two distinct hydroxy species identified is revealed below when examination of the ESEM data is performed.

ESEM studies

Interaction of silver with water vapor. Silver catalyst was placed in the ESEM chamber then exposed to water vapor (0.5 kPa) at ambient temperature. Images were then recorded continuously during heating of the catalyst at a rate of *ca.* 10 K min^{-1} from 298 to 973 K (Fig. 4). Heating the catalyst to 623 K produced slight changes in the surface topography as the catalyst began to sinter. When the catalyst temperature was raised above *ca.* 713 K, pin-holes started to appear in the silver structure [Fig. 4(b)]. This behaviour correlated with the appearance of water in the TPD profile (Fig. 3) thus indicating that the desorption of sub-surface hydroxy groups might be responsible for the 'pin-holes'. Increasing the catalyst temperature to 773 K resulted in a slight increase in the concentration of pin-holes [Fig. 4(c)], and it is apparent that they are mainly associated with the small globular particles. Also evident was the fact that considerable sintering of the smaller silver grains was occurring, a process that produced a rather undulating, comparatively smooth silver surface. Substantial promotion in the extent of pin-hole formation happened at 828 K and, significantly, hole evolution was also initiated on the relatively defect free, large silver crystallites [Fig. 4(d)]. Inspection of the TPD profile (Fig. 3) again revealed substantial water evolution and again it must be inferred that the pin-hole formation is associated with the desorption of sub-surface hydroxy species. Elevation of the catalyst temperature to 923 K caused further sintering of the catalyst surface. In addition, the pin-hole concentration not only increased but also the holes themselves became of larger average size. Finally, the catalyst temperature was raised to 973 K (the upper limit for the industrial methanol oxidation reaction) [Fig. 4(e)] and held at the same temperature for another 35 min. The number of holes recorded in the silver surface decreased at 973 K (compared with the situation at 923 K), although their mean size did increase slightly. After 10 min at 973 K the pin-hole concentration decreased again, an effect accompanied by the remaining holes again assuming slightly greater diameters. The images obtained after 15 and 35 min reaction time at 973 K contained approximately the same hole size and number distribution, which suggested the system has equilibrated. However, striking evidence was gained for the dynamic nature of this catalyst. The formation of new holes in an originally flat surface could be seen [Fig. 4(f)], as well as the disappearance of already established pin-holes (thus indicating a very mobile silver surface at this temperature). Moreover, some existing holes could also be discerned to increase dramatically in size during the reaction [Fig. 4(f)].

It is of particular interest to evaluate the effect of the water treatment upon other areas of the silver catalyst, in order to determine if the hole formation is widespread. Fig. 5 shows ESEM images of selected regions of the catalyst before and after exposure to water vapor. Apparently, the structural changes observed for the small globular particles are not as
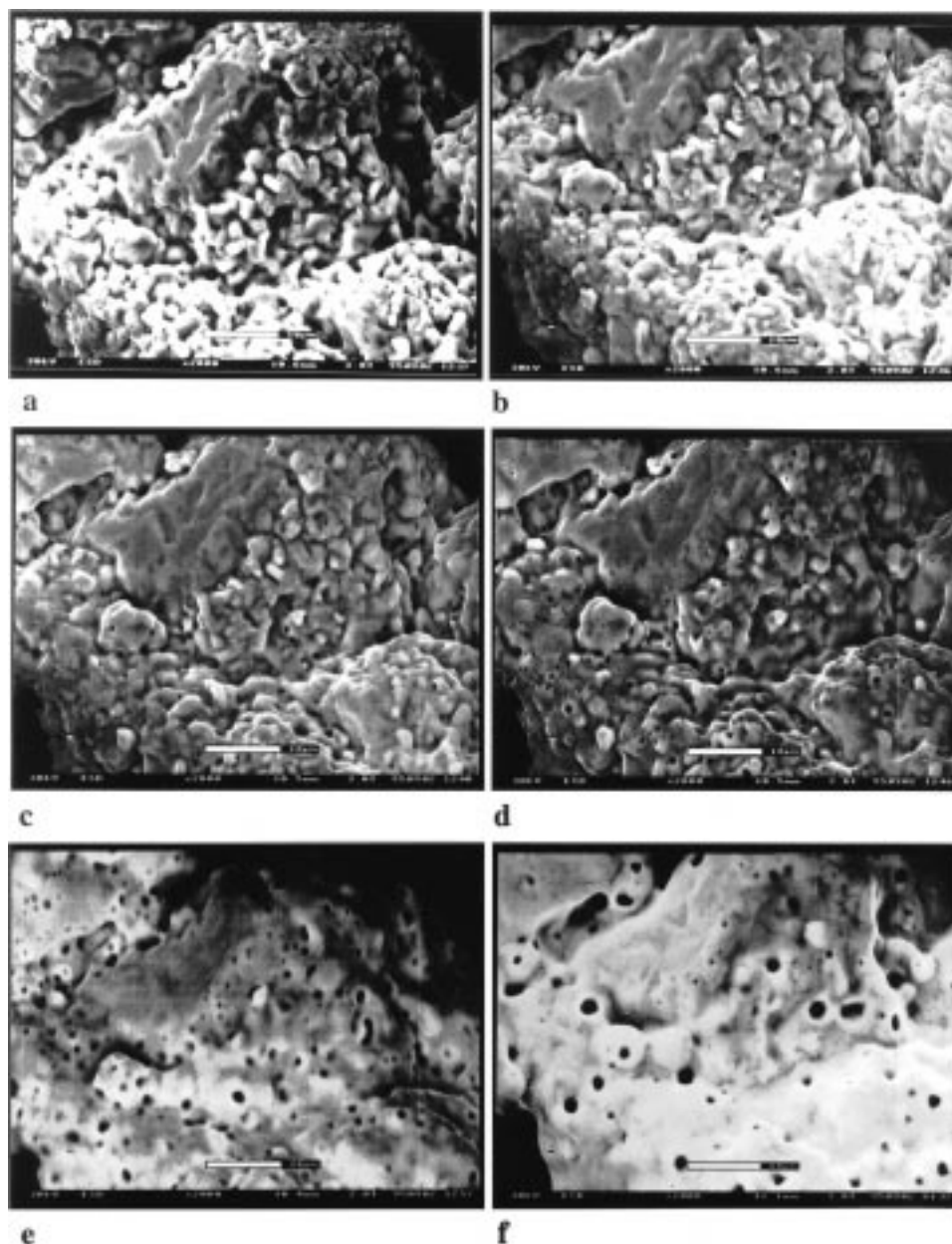

Fig. 3 TPD of: (a) H_2O, and (b) CO_2 from polycrystalline silver

Fig. 4 ESEM videomicrographs of silver catalyst in water vapour at: (a) 273, (b) 713, (c) 773, (d) 828, (e) 973, and (f) the catalyst was held at the last temperature for a further 35 min

prevalent in the larger silver grains. However, holes are still evident in the silver surface albeit at a lower concentration. Smoothing of the platelet edges was also detected [Fig. 5(a)]. Another feature suggested in Fig. 5 is that the hole formation appears to occur predominantly in the vicinity of cracks in the silver or at the edges of platelets. This observation has also been reported by Lefferts et al.,[7] who concluded that the formation of holes in silver occurred at grain boundaries. In addition, they also indicated that after TPD measurements, the silver surface became flattened,[7] which is in accordance with the present study.

The question arises as to the source of the hole production in silver catalyst. Bao et al.[8] proposed that hole formation was caused by sub-surface reaction between hydroxy groups. Therefore, to test the role of water vapor in the catalytic reaction (steam is added to the industrial reactant gas stream to regulate bed temperature) ESEM experiments were conducted using either nitrogen or oxygen atmospheres. As in the case with water vapor (Fig. 4) no discernible change in the morphology was detected until a temperature of ca. 663 K was

attained whereupon pin-holes in the silver surface appeared in addition to smoothing and agglomeration of the originally small silver particles. Further heating resulted in a structure comparable with that obtained after reaction with water vapor. Therefore, it must be concluded that the holes are formed as a result of reaction between sub-surface hydroxy species already present in the silver structure. The TPD profile for the silver catalyst (Fig. 3) strongly supported this conclusion.

Indirect evidence and a hypothesis have been previously given,[7,8] to indicate that the holes in the silver surface were formed as a consequence of a surface explosion. To confirm this theory FESEM images of silver, which had been subjected to reaction in the ESEM chamber, were obtained (Fig. 6). In the near vicinity of every hole considerable debris consisting of small silver fragments is found [Fig. 6(a), (b)], which provides complete support for the theory that a violent eruption had occurred. In addition, images were obtained that showed that the hole formation did indeed occur predominantly along the edges of platelets or cracks in the surface [Fig. 6(a), (d)].
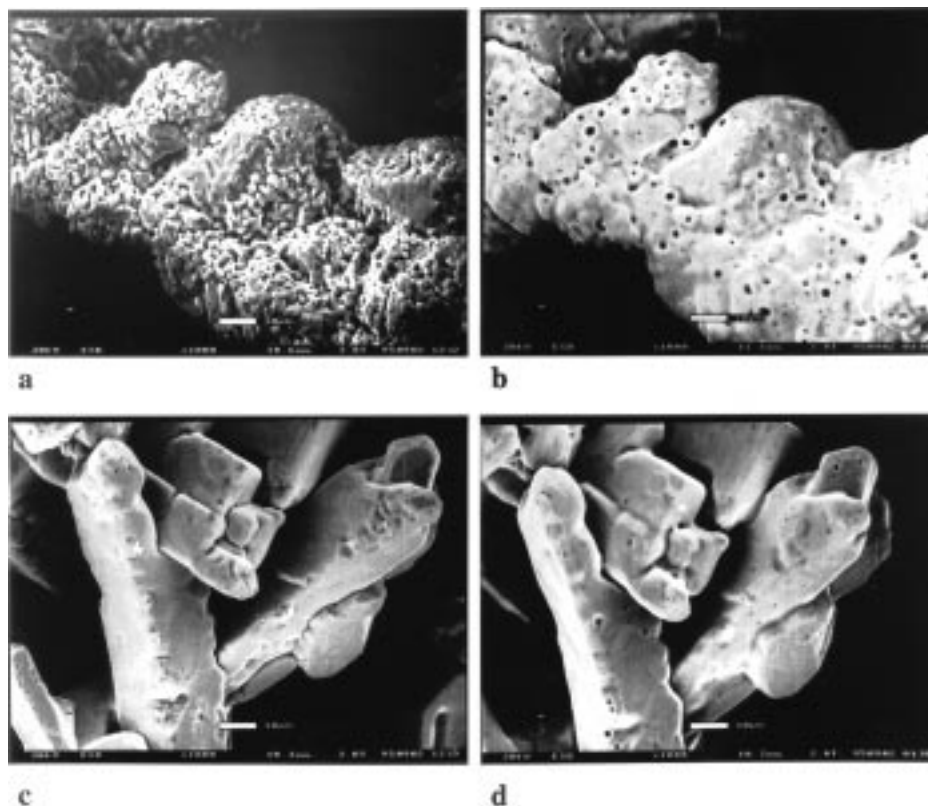
Fig. 5 ESEM videomicrographs of silver catalyst in water vapour: (a) and (c) before heating, and (b) and (d) after heating to 978 K

Reaction of silver catalyst with methanol

ESEM studies. Silver catalyst was placed in the ESEM chamber and exposed to a mixture of methanol vapor and oxygen. Images were continuously acquired during heating to 923 K (Fig. 7). The first notable change occurred between 633 and 668 K where pin-holes began to form. As the catalyst was heated to 738 K the pin-hole production accelerated, and these pin-holes were of significantly greater concentration than those observed when methanol was absent (*cf.* Fig. 4). Increasing the catalyst temperature induced sintering of the catalyst as evidenced by the substantial coalescing of the small

silver particles. More dramatic surface reconstruction was apparent when the catalyst was heated from 753 to 855 K. Several effects were determined. First, the appearance of pin-hole defects became more pronounced. Secondly, the silver surface became covered in 'nodules', which ultimately disappeared at higher temperatures with simultaneous pin-hole formation. Thirdly, the silver surface further sintered, which indicated that the silver surface was relatively mobile in the reaction environment. As the catalyst approached simulated industrial conditions the surface became intensely perforated. Allowing the catalyst to equilibrate at 923 K resulted in the
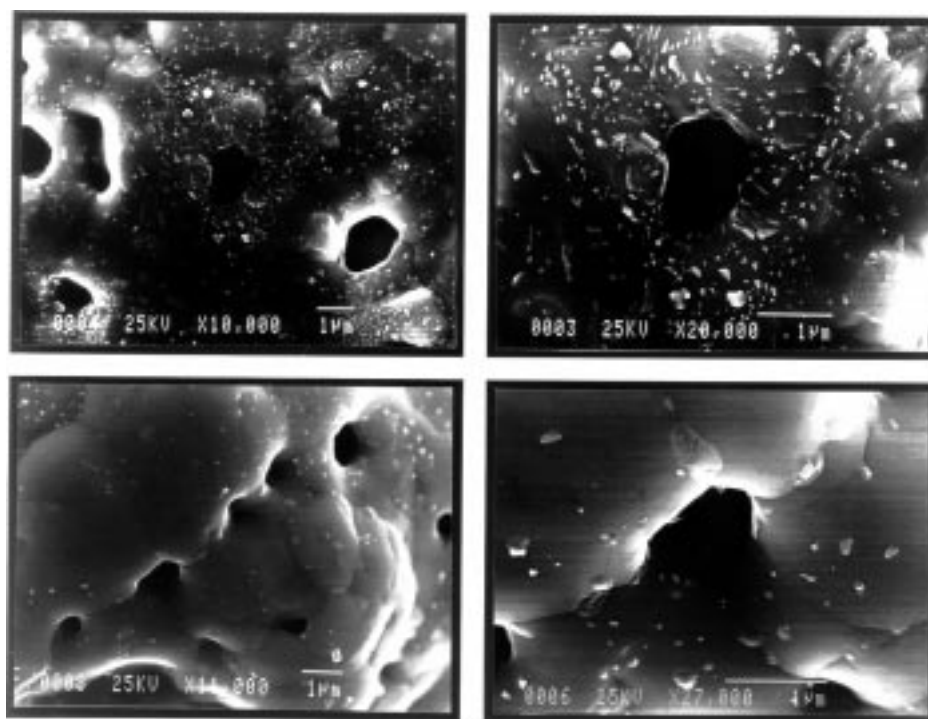

Fig. 6 FESEM images of the holes formed in the silver surface following heat treatment in water vapor

25 °C   390 °C

470 °C   600°C

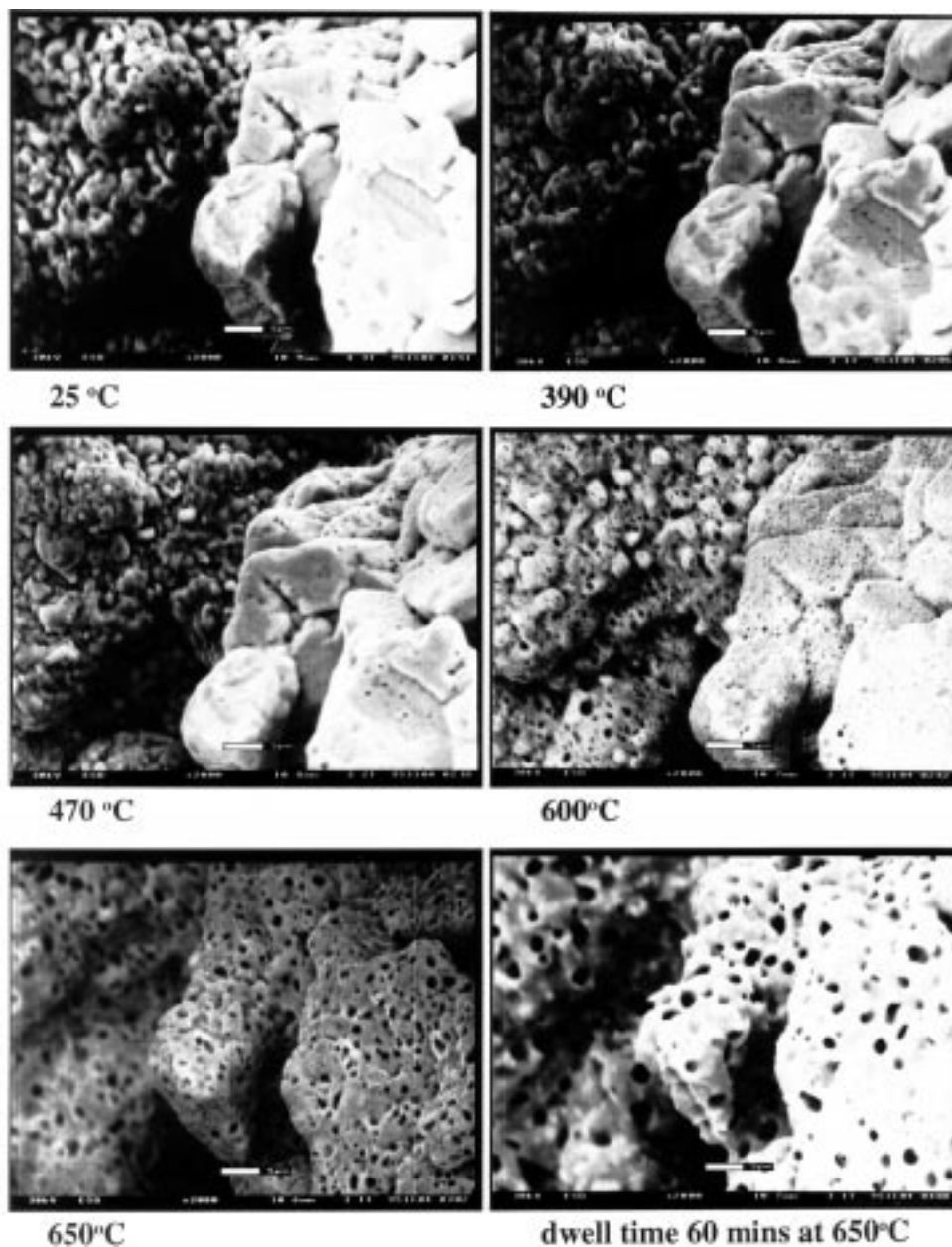650°C   dwell time 60 mins at 650°C

Fig. 7 ESEM videomicrographs of silver catalyst in methanol–oxygen at temperatures as indicated

average size of the pin-hole defects increasing and sub-micrometre grains of silver formed as a consequence of coalescence of debris from the surface explosions.

Raman spectroscopy. An experiment was performed wherein a catalyst sample was exposed to a methanol–air mixture under high temperature conditions for a sustained period and was then subsequently transferred for characterisation by FT-Raman spectroscopy. The Raman spectra thus obtained are presented in Fig. 8. Heating to 473 K induced few changes to the observed species. Only a hint of the features at 380 and 550 cm^{-1} are still prominent, as evidenced by the sharp peak at 860 cm^{-1} The appearance of this band may be associated with the complex mechanism of the surface enhanced Raman effect for silver. Further heating to 573 K resulted in the loss of all the spectral features except the low-wavenumber peak for weakly adsorbed atomic and/or molecular oxygen species. It is most likely that oxygen has been readsorbed during sample transfer. The absence of the hydroxy peaks is in good agreement with the TPD data (Fig. 3), which indicated that extended heating at 573 K should promote the desorption of sub-surface hydroxy species. Reaction at 673 K for a period of

several hours results in the growth of bands at 570 and 780 cm^{-1}, ascribed to sub-surface hydroxy and strongly bound atomic oxygen species, respectively. At 773 K, ESEM experiments demonstrated a more extensively reconstructed surface and prominent blisters over the entire surface. This behaviour correlates well with the accumulation of the sub-surface hydroxy and oxygen species, indicated by intense Raman features centred at 560 and 600 cm^{-1}, following reaction at 773 K. Interestingly, a band is now discerned at 950 cm^{-1}. Some discrepancy remains over the assignment of this band since both molecularly adsorbed oxygen and surface hydroxy species have been proposed to give rise to it. Bao *et al.*[17] observed that the migration of surface hydroxy species to the sub-surface region occurred at temperatures in excess of 600 K. It is therefore unlikely that this species would emerge through high temperature reaction. Experiments cited by Bao *et al.*[17] equally demonstrated that an oxidised polycrystalline silver surface did not react upon exposure to water at room temperature. Wu *et al.*[21] advanced the idea that stabilisation of molecular oxygen is intimately related to the presence of surface defects in the structure. In addition, this band is found at a lower wavenumber than usual, suggesting substantial communication with sub-surface species. It seems plausible
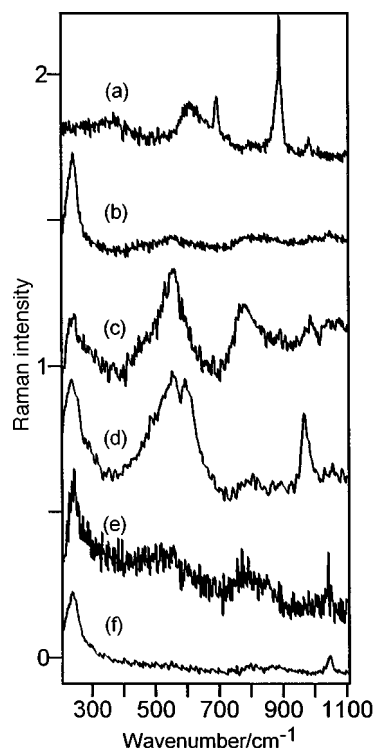
Fig. 8 FT-Raman spectra of silver catalyst following exposure to methanol–oxygen at: (a) 473, (b) 573, (c) 673, (d) 773, (e) 823, and (f) 873 K

Fig. 9 TPD of: (a) CO_2, (b) H_2O, and (c) H_2 from silver catalyst after exposure to methanol–oxygen at 773 K for 3 h

that the peak at 950 cm^{-1} can be assigned to the $v(O{-}O)$ mode for adsorbed molecular oxygen and that its occurrence is the result of adsorption subsequent to reaction induced restructuring of the silver surface. By 823 K, the silver surface under on-going reaction exhibits dynamic surface morphology changes, increasing at 873 K to cover the entire surface with pin-holes. The absence of sub-surface species further inhibits readsorption of molecular oxygen.

TPD of reaction intermediates

The samples previously evaluated with Raman spectroscopy following exposure to methanol–oxygen mixtures at various reaction temperatures were also studied by TPD methods. The treated catalyst was heated linearly in purified helium while continuous monitoring of the evolved gases by on-line mass spectrometry was performed. The catalyst sample, which had been exposed to methanol–air at 773 K, was evaluated and the resultant TPD spectrum is displayed in Fig. 9. Two distinct water peaks can be discerned at *ca.* 473 and 643 K and the second of these features was accompanied by some carbon dioxide evolution. Hydrogen also desorbed at a maximum rate at 792 K. The detection of substantial water formation is in accordance with the FT-Raman data, which clearly illustrates the presence of sub-surface oxygen species in silver (Fig. 8) that presumably recombinatively desorb at elevated temperatures. It is interesting to note that the dominant species present was the hydroxy species associated with surface defects. The low temperature peak is higher than that predicted for simple physisorption of water to the catalyst surface, therefore, it is tentatively proposed that this species might be stabilised by physisorption to the reconstructed silver surface. This theory is supported by the fact that the evolution temperature is typical for that of water of hydration from numerous inorganic complexes, thus indicating some sort of bonding to the silver catalyst. Hydrogen has been shown by Wachs and Madix[2] to desorb at temperatures of approximately 325 K or lower. Consequently, it is difficult to
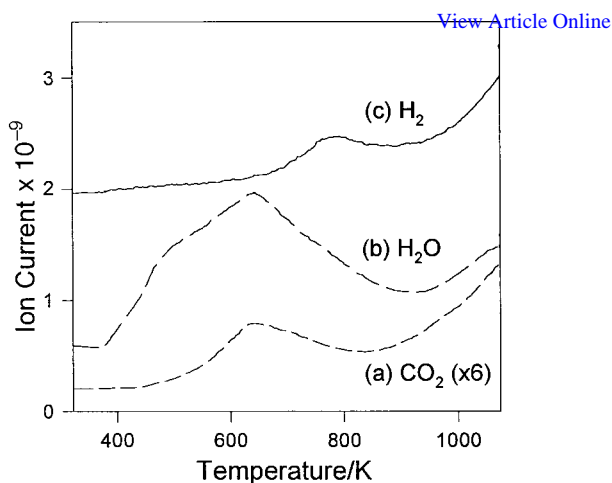
assign the observed high temperature hydrogen desorption profile as arising from surface adsorbed atomic hydrogen species. In contrast, it appears reasonable to conclude that these hydrogen species were actually located in the sub-surface layer of silver (in a similar manner to sub-surface oxygen and hydroxy species). The concurrent evolution of carbon dioxide with the high temperature water peak is puzzling. The concentration of the carbon dioxide was considerably less than the amount of water produced and thus it is unlikely that they occur from the same intermediate. However, it may be that they are released *via* the same surface reconstruction process (*e.g.*, surface explosion).

Finally, it is noted that at very high temperatures (*ca.* >1000 K) the traces for all three illustrated species showed a dramatic increase in intensity (although no maximum was observed due to experimental limitations). Lefferts *et al.*[20] have shown that dissolved species in the bulk silver structure are not removed until temperatures in excess of 1073 K. Consequently, it can be seen that under high temperature reaction conditions vast concentrations of dissolved hydroxy, oxygen and hydrogen species exist in the bulk silver structure.

Spent catalyst

It was of interest to examine subsequently the morphology of the catalyst used in this study after it has been subject to methanol oxidation in an industrial plant for several months. FESEM images (Fig. 10) revealed that the silver now consisted of relatively large particles characterised by an extensive layered or platelet structure.

The FT-Raman spectrum of the spent silver catalyst (Fig. 2) contained bands at 240, 353, 448, *ca.* 565 and 783 cm^{-1}. As discussed previously the peak at 240 cm^{-1} can be attributed to atomic oxygen species adsorbed on silver. Likewise, the extremely broad shoulder on the 240 cm^{-1} suggests a significant quantity of molecular oxygen species might also be present. The intense band at 783 cm^{-1} has been observed by several authors[12,13,16,22] although there exists controversy to its assignment. Vayenas and co-workers[12,22] proposed that this band was due to a vibration of chemisorbed molecular oxygen. However, Bao *et al.*[16] showed that molecular oxygen was actually characterised by a band at *ca.* 954 cm^{-1}, a view also shared by Millar *et al.*[13] Furthermore, Bao *et al.*[16] also suggested that a band at 802 cm^{-1} should be assigned to a vibration involving sub-surface oxygen species. In contrast, Millar *et al.*[13] agreed that this band corresponded to an oxygen reconstructed surface but ascribed this peak to a mode for Ag=O species located on sites created by sub-surface oxygen. The broad band centred at *ca.* 565 cm^{-1} is due to a
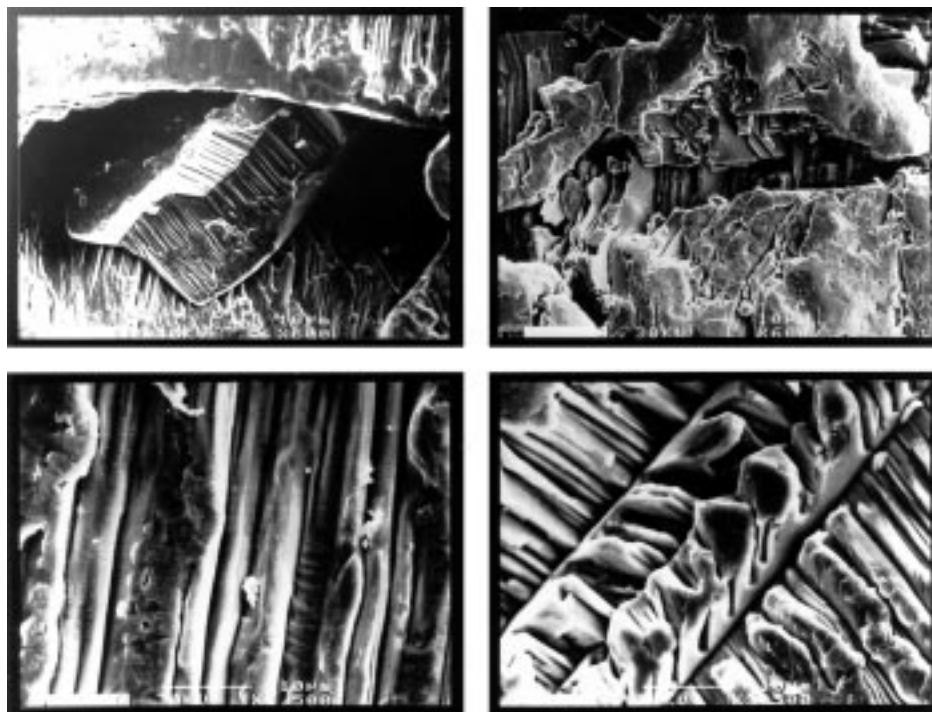
Fig. 10 FESEM images of silver catalyst after use in an industrial methanol oxidation plant for a period of several months

vibrational mode for sub-surface hydroxy species and the broad bands at 353 and 488 cm^{-1} are typical for highly dissolved atomic oxygen in silver, which resemble the structures of 'AgO' and 'Ag$_2$O', respectively.[13]

Discussion

The observation of two distinct types of particle morphology within the same silver sample could be of substantial influence upon the subsequent catalytic activity. This is particularly evident when the ESEM images are examined. First, the majority of the hole formation occurs in the silver particles, which are composed of the elongated globular structures, indeed some of the larger grains show almost no hole production. To appreciate the significance of this result it is necessary to discuss the mechanism of hole formation and its relevance to methanol oxidation.

FT-Raman spectra for the fresh silver catalyst indicate the presence of sub-surface hydroxy species, which by necessity must have been incorporated in the silver catalyst during manufacture. Upon heating to 663 K they presumable recombined *via* the reaction

$$OH(sub) + OH(sub) \rightarrow H_2O(g) + O(sub)$$
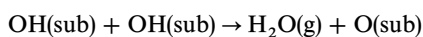
Lefferts *et al.*[7] determined by TPD methods that sub-surface hydroxy species desorbed with maximum rate at 673 K, which is in excellent agreement with the observations of this study. Moreover, Lefferts *et al.*[7] were not able to produce definitive data to support the theory that the hydroxy species were definitely sub-surface (although they had considerable indirect evidence for this conclusion). However, the ESEM and FESEM images, in conjunction with the FT-Raman spectra, provide confirmation that the hydroxy species are indeed sub-surface. Furthermore, in accordance with Bao *et al.*[8] the 'driving power' for such sub-surface explosions is proposed to be the hydrostatic pressure generated by the product water vapor. One aspect of importance was the detection of two distinct hydroxy species in the silver catalyst, one of which was associated with defects in the silver structure. The second was considerably more stable and did not desorb

appreciably until the silver atoms became mobile due to attainment of the Tammann temperature.

An interesting aspect of the ESEM study was that the observed 'annealing' of the silver surface was also initiated at about 663 K [Fig. 3(b)]. It might be tempting to suggest that the heat of reaction for sub-surface hydroxy recombination is sufficient to mobilise the silver surface atoms. This postulate is at best only tentative, especially with the fact that the system is at a temperature corresponding to the Tammann temperature of silver (643 K, calculated as 5.52T where T = melting point of silver). Therefore, it is reasonable to expect that the shape of small silver crystallites will change significantly at *ca.* 663 K due to the mobility of the lattice atoms (which is assumed to occur at the Tammann temperature). This proposal is in agreement with the study of Meima *et al.*,[23] who concluded that surface facetting of silver occurred at temperatures of 598 K or above.

The observation that the size of the holes increases from *ca.* 0.5 to 1 μm in diameter, upon further heating to typical industrial conditions [Fig. 3 (b), (c)] correlates with the investigation of Lefferts *et al.*[7] where the hole size increased with the number of TPR measurements. Very large holes have also been imaged in a silver catalyst that had undergone prolonged reaction with an oxygen–methanol mixture.[7] It might be that the initial hole formation creates the defects in the silver surface which then, in turn, act as sites for subsequent sub-surface hydroxy formation. Naturally, sub-surface explosions again occur, resulting in enlargement of the original hole. This theory is in accord with the mechanism of Bao *et al.*,[8] where it was proposed that bulk reaction at defects caused the formation of new defects.

The *in situ* Raman studies of Millar *et al.*[13] demonstrated that sub-surface hydroxy species were formed, by the interaction of methanol and sub-surface oxygen, very rapidly on a defected silver sample, whereas hydroxy formation was extremely slow on a large grained, smooth silver sample. Consequently, it can be seen that the initial extent of hole formation when the silver catalyst is activated could be critical to the subsequent catalytic activity in the industrial plant. Therefore, the hypothesis regarding the role of hole formation would certainly explain why some silver catalysts 'light off'

within a few hours in a methanol oxidation plant, whereas others may take several days. This latter effect is probably due to the well known effect of reaction-induced facetting of the catalyst surface.

The spent catalyst exhibited a pronounced layered structure (Fig. 10) resembling the morphology of a polycrystalline silver foil following reaction in a methanol–oxygen mixture at 920 K,[8] which consisted of a distinct terrace-and-step structure. This pattern was rationalised in terms of large scale surface reconstruction due to the inclusion of atomic species into sub-surface locations.[6,8] The FT-Raman spectrum for the spent catalyst provides support for this theory since a strong band at 783 cm^{-1} was recorded [Fig. 2(b)]. Bao *et al.*[16] have shown that this species only developed when a silver single crystal underwent dramatic reconstruction at high temperature to a phase incorporating both sub-surface oxygen atoms and a new atomically adsorbed species. Whether or not the band due to sub-surface oxygen (*ca.* 630 cm^{-1}) or the peak ascribed to Ag=O species (*ca.* 800 cm^{-1}) dominates the Raman spectrum, appears to be a function of the surface crystal plane. For Ag(111) planes the 800 cm^{-1} band is prevalent, likewise the 630 cm^{-1} peak is more intense for Ag(110) planes. This effect is probably due to the complex mechanism associated with the surface enhanced Raman effect for silver, the theory of which is beyond the scope of this paper. However, it is sufficient to say that the spent catalyst apparently consists of a structure resembling an Ag(111) surface structure. This conclusion is in accordance with the study of Bao *et al.*,[6] which indicates that the reconstructed phase is comparable to a slightly expanded Ag(111) surface.

Reaction between CH$_3$OH and O$_2$ resulted in the appearance of holes in the silver structure that resembled those formed by the interaction of sub-surface hydroxy species, both in size and location. Recent studies[24] have found that in a methanol atmosphere the formation of pin-holes is suppressed and thus catalytic etching must be responsible for the features seen in the current ESEM images. It has already been suggested that sub-surface oxygen is the active species for the oxidation of methanol to formaldehyde.[13] This hypothesis is in agreement with the current data, which can be interpreted by the following reactions

$$CH_3OH(ads) + O(sub) \rightarrow OH(sub) + CH_3O(ads)$$

$$OH(sub) + OH(sub) \rightarrow H_2O(g) + O(sub) + \text{'pin-hole'}$$
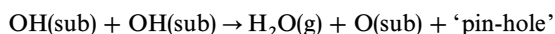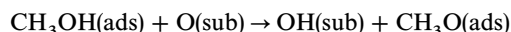
Comparison of the concentration of pin-holes present in the silver surface and methanol oxidation activity has revealed a remarkable correlation,[24] thus lending considerable support to this mechanism. The recombination of sub-surface hydroxy species produces water, which exerts a hydrostatic pressure. This hydrostatic pressure acting against the silver surface induces the surface to adopt a more stable configuration, *i.e.*, it adopts a hill-and-valley structure (manifested as 'nodules' in Fig. 7). The release of this pressure is proposed to be the source for the observed hole formation. In addition, it is apparent that these holes might then themselves act as active sites for the continuing selective oxidation of methanol to formaldehyde since these defects can act as rapid diffusion paths for oxygen to migrate to sub-surface positions. This latter hypothesis is supported by the TPD profile (Fig. 9) for the catalyst that had been exposed to methanol–oxygen at 773 K, wherein the dominant sub-surface hydroxy species was associated with defects in the silver lattice. This observation is in contrast to the fresh catalyst, which exhibited substantial quantities of hydroxy species located beneath smoother regions of the silver surface.

The observation of carbon dioxide evolution at the same instance as water production in the TPD patterns was curious in that the stability of carbonate species (which could possibly be the source of carbon dioxide) is known to be relatively low.[13,19] However, it is known that the silver samples employed in this study contained appreciable quantities of carbonaceous deposit when supplied (Raman spectroscopy identified the characteristic D and G bands for amorphous and graphitic carbon, respectively). It could be that sub-surface oxygen recombined with the carbon deposits to form carbon dioxide during the TPD process and, in parallel with the effect of hydrostatic pressure of water, the CO$_2$ would explode through the catalyst surface. It is emphasised that this effect is substantially less prevalent than the case with sub-surface hydroxy groups, and in addition this process is not expected to be significant during industrial reaction conditions.

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