Catalysis Letters 28 (1994) 383–395

On the mechanism of the selective oxidation of methanol over elemental silver

H. Schubert, U. Tegtmeyer and R. Schlögl

Fritz Haber Institut der Max-Planck Gesellschaft, Faradayweg 4–6,
D-14195 Berlin, Germany

Received 30 July 1994; accepted 10 August 1994

We analysed previously the interaction of silver with oxygen and characterised three different atomic oxygen species. The present communication uses TPRS data to assign a chemical function to each of these three species prepared on a sample of practical electrolytic silver particles. With stationary and instationary conversion experiments close to practical conditions we confirmed the conclusions from the TPRS data also to hold qualitatively for the stationary operating catalyst. Surface oxygen was found to react in an oxydehydrogenation reaction with adsorbed methanol with a significant selectivity to total oxidation. "Sub-surface" oxygen catalyses the dehydrogenation of the adsorbed methanol with no selectivity to total oxidation. Dissolved atomic oxygen from the bulk replenishes both surface species via "sub-surface" oxygen. The interconversion of all three species at the high reaction temperatures required to overcome the barriers for the formation and motion of the various atomic oxygen species limits the overall selectivity of the formaldehyde production.

Keywords: oxygen on silver; methanol oxidation; temperature-programmed reaction spectroscopy (TPRS); ion–molecule-reaction mass spectrometry (IMR-MS); dehydrogenation; oxydehydrogenation

1. Introduction

One way for the industrial production of formaldehyde from methanol is the selective oxidation over elemental silver as catalyst. The process is carried out in a water–methanol atmosphere under adiabatic conditions at about 950 K and atmospheric pressure. The extremely fast reaction conditions (few millimetres active catalyst bed) and the high throughput (above 0.1 kg cm^{-2} h^{-1} methanol) required for efficient production [1] indicate that the reaction is kinetically controlled. Conversion and selectivity values above 95% are possible despite of the fact that, at 950 K in oxygen, the total oxidation of methanol is thermodynamically far more favourable.

© J.C. Baltzer AG, Science Publishers

The main reactions in the system are [2]:

$$CH_3OH \rightleftharpoons CH_2O + H_2 \tag{1}$$

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O \tag{2}$$

$$2CH_3OH + 3O_2 \rightarrow CO_2 + 2H_2O \tag{3}$$

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{4}$$

$$2H_2 + O_2 \rightarrow 2H_2O \tag{5}$$

$$CH_3OH + O_2 \rightarrow HCOOH + H_2O \tag{6}$$

$$CH_2O \rightarrow CO + H_2 \tag{7}$$

The dehydrogenation equilibrium (1) is of practical importance, as a main component of the reactor effluent gas is hydrogen. The oxydehydrogenation (2) seems also to occur as the hydrogen production is understoichiometric. This may, however, be accounted for by a consecutive reaction (5). The production of steam resulting from either reaction (2) or (5) is practically observed to balance the hydrogen gas production. The preferred operation of reaction (5) over reaction (2) would help to shift the equilibrium (1) to the side of the desired product. The main total oxidation reactions (3) and (4) can be suppressed efficiently by the mode of operation of the reactor [1]. They are required to occur to a certain extent in order to maintain the adiabatic operation at 950 K as reaction (1) is endothermic ($\Delta H = +84$ kJ/mol [3]). Formation of formic acid (6) can be suppressed at the high temperatures of reaction. Decomposition of formaldehyde into hydrogen and CO, which is highly efficient at the high reaction temperatures, has to be avoided by a very rapid quench-cooling of the effluent gas phase immediately after the converted bed.

The catalyst is essential for the formaldehyde production. It was further found that the presence of oxygen is also essential [4] for the reaction, which excludes the possibility that reaction (1) alone describes the mechanism of formaldehyde production. One way to get access to the reaction mechanism is to study the interaction of oxygen with silver at reaction conditions.

We investigated this interaction under conditions of UHV in addition to extensive literature studies [5–8] and under conditions close to those of technical operation in detail [9] and found three species of atomic oxygen to be present under reaction conditions. Using a combination of analytical techniques, a profile of physical properties of each species was established [10]. One essential difference between the species is their location either on the surface (α species), or dissolved in the bulk of the metal (β species) or incorporated in the top atom layer of the silver as "sub-surface" or γ species. This latter species was found to interact most strongly with the silver atoms which are, however, not oxidised to a binary oxide. Formation of the γ species causes the surface of silver to reconstruct [11,24] in order to accommodate the lattice mismatch between the enlarged top atomic layer and the bulk of the silver. It was further found that silver at high temperatures and in the presence of oxygen forms facets of the (111) orientation irrespective of the crystal orientation of the starting material [11]. This facetting is not only characteristic of single crystals, but occurs also with foils or even powder samples. The driving force for this oxygen-induced restructuring is the minimisation of the surface free energy, which is also indicated by the complete suppression of silver evaporation at 950 K in oxygen [11].

The purpose of the present communication is to show that the various species of atomic oxygen react differently with methanol. Previous studies using single crystals and low pressure gas conditions arrived at the conclusion that the oxidation step (2) is the primary reaction pathway [12] although practical exit gases contain significant amounts of elemental hydrogen. Earlier work under more practical conditions [4] concluded that both reactions (1) and (2) occur simultaneously over the catalyst. This discrepancy indicates extrapolation problems when UHV data and high pressure reaction experiments are directly compared.

We used temperature programmed desorption (TPD) [13] and reaction (TPR) profiles [14] and compared their results to selectivity data obtained with a reactor operating at steady state under atmospheric pressure with practical gas feed conditions as isothermal process. In this way it was possible to isolate the conversion reactions in the temperature programmed low pressure mode and to correlate the results with data obtained under practical conditions.

2. Experimental

The experiments were all carried out using electrolytic silver particles of about 0.3 mm diameter kindly supplied by BASF (Ludwigshafen).

The TPD-TPRS data were measured in a quartz cell reactor attached to a gas inlet system allowing us to dose purified molecular oxygen at atmospheric pressure and methanol vapour (saturation pressure of liquid methanol at 310 K) and to a Hiden Analytical quadrupole mass spectrometer which operated either in UHV or in a methanol atmosphere supplied from the reactor at 10^{-7} mbar. Care was taken to eliminate background reaction from steel, thermocouples or evaporated silver. External heating was provided by a high-power mini furnace surrounding the quartz reactor, which was operated by a software-controlled power supply to guarantee linear heating ramps in all segments of the heating range from 300 to 1000 K. The heating rate was always 1 K s^{-1}.

The microreactor experiments were carried out in an air-heated quartz reactor housing a 15 mm diameter 10 mm thick bed of the catalyst particles. It was operated at 890 K with 50% methanol/water feed at a load of 1.0 g methanol cm^{-2}

min^{-1}. Oxygen was fed with 10% understoichiometry relative to methanol. Under steady state conditions a maximum conversion of 85% and a maximum formaldehyde selectivity of 86% were achieved. An IMR-MS ATOMIKA 100 mass spectrometer was used as on-line gas detector allowing to monitor simultaneously oxygen, CO, CO_2, water, methanol, formaldehyde and formic acid using both Kr and Xe as primary ions. The time resolution for a full analysis was 10 s.

The instationary experiments were done after keeping the catalyst for 100 h on stream. The gas feed was replaced for 3 min by nitrogen and then the methanol/water feed was switched back. A nitrogen gas stream balanced the gas throughput to the previous value. Only the IMR-MS detector with its extreme sensitivity of below 0.1 vppm for molecular oxygen allowed us to exclude that traces of molecular oxygen could have interfered with the experiment.

3. Results and discussion

The exact shape of all TPD/TPRS data depends on the history of the sample. Reproducible data can only be obtained after cycling a sample 50 times through an oxygen loading–reaction loop.

In fig. 1 the detection of the three atomic oxygen species is shown in trace A. The sharp peak arises from surface oxygen (α species). This peak has been observed in single crystal studies before [5,15,16] with the correct kinetic analysis remaining controversial [12,16,17]. The shoulder at higher temperatures can become dominant over the main line for heavily aged samples or very low heating rates and indicates diffusion-limited desorption from the silver bulk (β species). The novel γ species gives rise to the high temperature peak. An increase in the exposure time changes little the intensities, increased exposure pressures increase the abundance of the β species.

A TPRS experiment with molecular hydrogen was carried out (traces A + B) in order to study a possible discrimination of the reactivity of the different species. Only the surface oxygen and some bulk oxygen replenishing the surface oxygen reacted with hydrogen to form water, not, however, the tightly held γ species. The shape of the water evolution curve, which is not an echo of the oxygen desorption profile, indicates that within the timescale of the experiment an interchange between bulk and surface oxygen is possible. In this interconversion of species also the γ species is involved, which is, however, a less efficient reservoir for oxygen than the bulk. The efficient diffusion of oxygen in the bulk [13] of silver as well as the blocking influence of a surface limitation of this diffusion (by formation of the more stable γ species) have been described in a recent study of the application of silver as a selective oxygen separator [18]. We state that reaction (5) is not efficiently carried out with the sub-surface species and that even surface oxygen reacts only rather slowly with molecular hydrogen.

In fig. 2 we illustrate using a different batch of the catalyst after extensive ageing

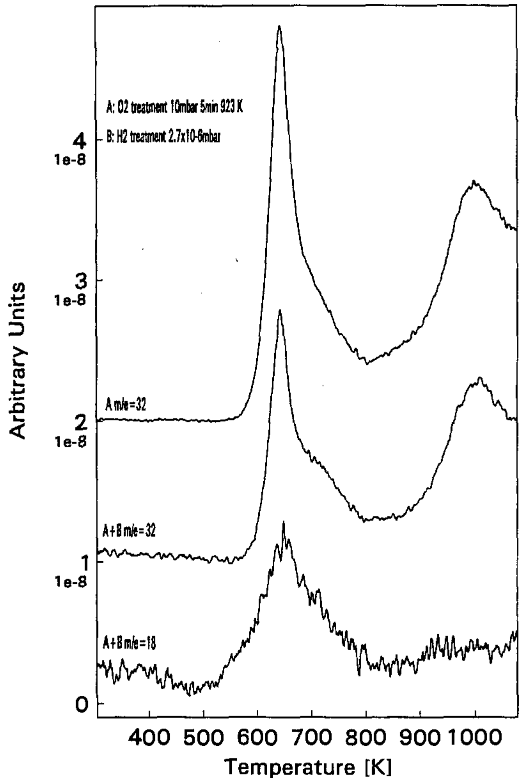

Fig. 1. The interaction of molecular oxygen with silver. A mildly aged (10 cycles) batch of catalyst (210 mg) was loaded at 923 K with 10 mbar oxygen for 5 min (standard conditions chosen to saturate the surface oxygen species). Trace A: UHV TDS (heating rate 1 K s^{-1}) of the oxygen-loaded sample. Traces A + B: TPRS in hydrogen.

that the formation of formaldehyde in a TPRS experiment is coupled with the simultaneous presence of methanol and the oxygen loaded silver catalyst. Traces 1 and 3 illustrate that homogeneous reaction in the quartz reactor under the present reaction conditions is negligible. Trace 2 shows that the catalyst without oxygen loading is inefficient and rules out catalysis of reaction (1) by elemental silver.

Trace 4 shows the formation of formaldehyde when methanol and the oxygen loaded catalyst are heated together. It is most significant that the formaldehyde production occurs exactly at the peak temperatures of the atomic oxygen desorptions seen in fig. 1. This indicates that chemisorbed oxygen is involved in the formation of the formaldehyde and rules out any participation of the gas phase in the reaction (either in an Eley–Rideal mechanism or as homogeneous catalysis involving silver atoms or clusters in the gas phase). This co-incidence of desorption and reaction further strongly implies that the rate-limiting step in the overall reaction is the generation of the activated oxygen species.

Fig. 3 shows a complete TPRS experiment. The catalyst was preloaded with 10 mbar oxygen at 923 K. The interconversion of atomic oxygen species allowed to

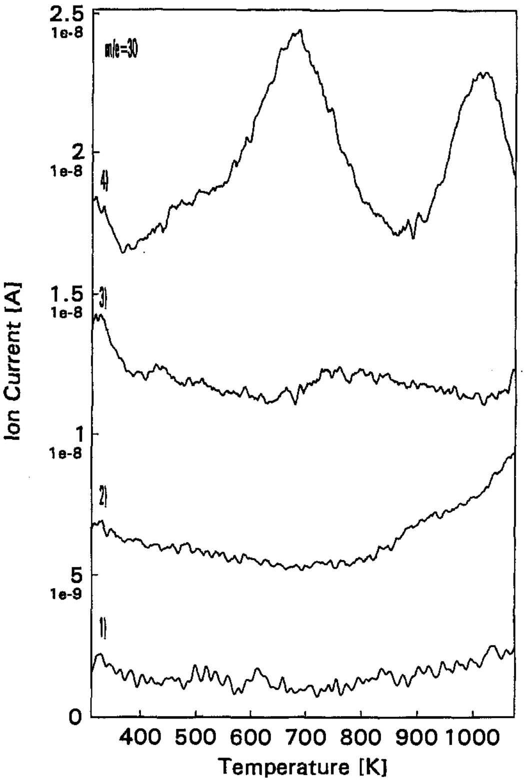

Fig. 2. The formation of formaldehyde in the TPRS system. All experiments were carried out at a constant partial pressure of 2×10^{-7} mbar methanol and an aged catalyst sample. Trace 1: Empty reactor filled with quartz wool; trace 2: Reactor filled with aged silver catalyst. The formaldehyde formation above 850 K is due to residual oxygen segregating out of the bulk of the silver. Fresh catalysts show no formaldehyde activity up to the melting point of the sample. Trace 3: Empty reactor filled with quartz wool and molecular oxygen (1×10^{-6} mbar). Under these conditions massive total oxidation was observed. Trace 4: Reactor with catalyst loaded with oxygen under standard conditions.

find atomic oxygen desorbing at temperatures below the exposure temperature in exactly the same way as shown in fig. 1.

The top trace shows the consumption of methanol in three different temperature regimes namely at above 400 K, at 700 K and at 980 K. The products formed were formaldehyde, carbon dioxide and water besides hydrogen, which was not detected here. Formaldehyde was formed in all three temperature regions. Carbon dioxide was formed only in the low and medium temperature region, not, however, in the high temperature region. This proves that formaldehyde is produced by partial oxidation with limited selectivity from α and (after diffusion to the surface) from β oxygen. The γ species produces formaldehyde in a different reaction mechanism with ideal selectivity.

The different reaction mechanisms are also reflected in the water evolution trace showing water as a product of total and partial oxidation at 700 K and not to occur

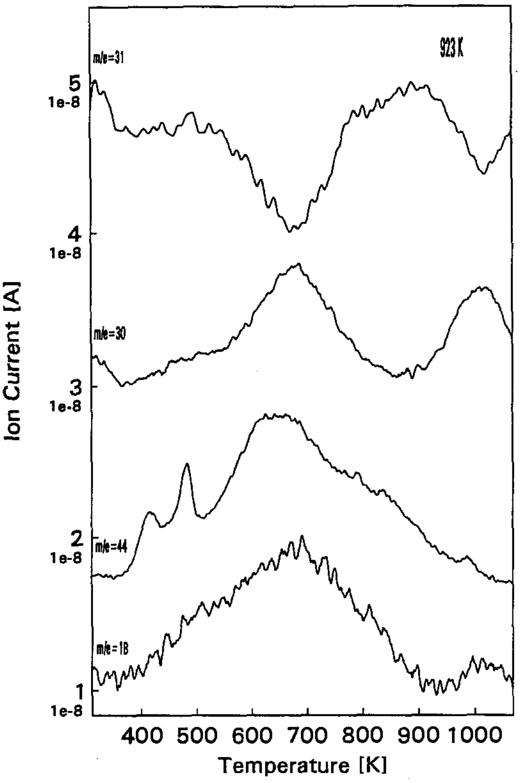

Fig. 3. TPRS experiment with a methanol and an oxygen pre-loaded catalyst. The experimental conditions were as stated in the captions of figs. 1 and 2. The data are uncorrected except for the water curve, which was corrected for a background desorption from the empty reactor system.

at 980 K. This allows to identify the 700 K route as the oxydehydrogenation reaction and the reaction at 980 K as following the dehydrogenation route. The fact that the methanol-to-formaldehyde reaction is discriminated in two different reaction pathways provides clear evidence for the simultaneous participation of silver, different oxygen species and methanol in the rate-determining step. This is important in the light of the failure to ever observe chemisorbed methanol on clean or oxygen-covered silver surfaces to be present or even react at temperatures above 180 K [19].

The fundamental difference in the mode of action of the two atomic oxygen species is rationalised in terms of their differing location on top and incorporated into the silver surface and the resulting significant difference in chemical bonding between silver and oxygen [6,7].

The *m/e* 44 trace in fig. 3 contains additional structures compared to those arising from the main conversion processes. The two sharp peaks at 410 and 485 K are attributed to the decomposition of surface formate [20] and surface carbonate [14]. These spectator species were formed by reaction of methanol with the oxygensaturated surface in line with earlier reports on "induced adsorption" [14,17]. The shoulder at around 800 K arises from the decomposition of three-dimensional basic silver carbonates ("black silver oxide" forming from oxygen, water and carbon dioxide at around 400 K) as it was concluded from TPD runs at lower heating rates and independent synthesis experiments [21].

The level of conversion rises with the number of cycles carried out with one catalyst batch, until it reaches a stable regime after more than 100 cycles. Under these conditions the shape of the 700 K formaldehyde peak has changed into a broad base and a superimposed sharp line, a pattern which can be seen to emerge in the data of fig. 3. Comparison with the shape of the water evolution curve, which does not exhibit the sharp part of the formaldehyde profile, indicates a significant contribution of the dehydrogenation reaction without simultaneous formation of water. After calibrating the sensitivity factors for water and formaldehyde it is possible to subtract the inselective reaction contribution from the total formaldehyde conversion and to arrive at the contribution of the selective dehydrogenation pathway to the total conversion. This is compared in fig. 4 to the oxygen desorption spectrum recorded in UHV for identical loading conditions. First, we note the perfect correspondence between the oxygen desorption features and the selective formation of formaldehyde via dehydrogenation. The irregular peak profiles compared to the earlier experiments are due to the rough shape of the catalyst surface, which has undergone massive surface restructuring in the state of stable conversion visible by the bare eye.

The results presented in fig. 3 allow us to use the selective formation of formaldehyde as chemical probe for the presence of γ-oxygen. Comparison of figs. 3

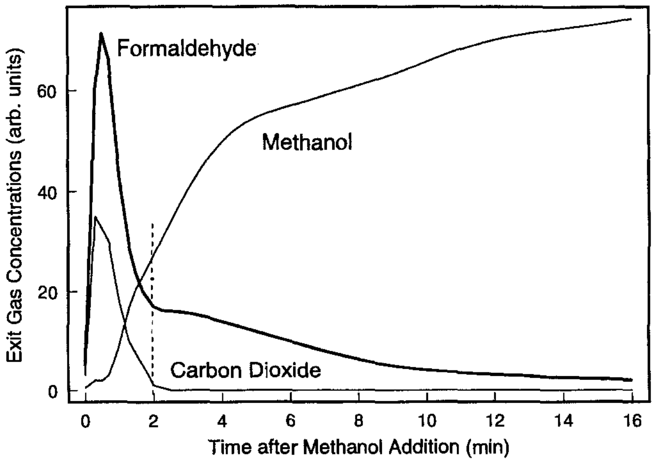

Fig. 4. Comparison between TPRS and TDS experiments for the fully aged catalyst sample used for the data in fig. 3 (129th catalysis cycle). The formation of formaldehyde via the oxydehydrogenation route was removed by subtraction of the weighted water evolution profile. The weighting accounted for the sensitivity factors for water and formaldehyde in the mass spectrometer. The shift in the oxygen desorption maxima compared to the values in fig. 1 is due to the surface restructuring.

and 4 allows us to conclude that the ageing of the catalyst gave rise to the formation of γ oxygen at lower temperatures in the region of the desorption of surface and bulk oxygen. Surface restructuring with the formation of (111) facets [22] is thus a pre-requisite for the formation of γ oxygen. The fact that we observe in fig. 4 two distinct peaks of activity for the formation of formaldehyde implies that a reaction channel must exist which reduces the abundance of γ oxygen in the temperature interval between 700 and 850 K under our conditions of low gas phase pressure of oxygen. Raman experiments [7,21] showed earlier that in this temperature range in the absence of gas phase oxygen the γ oxygen is converted into atomic oxygen dissolved in the bulk (β species). The reaction maximum above 1000 K indicates that at these temperatures the segregation of bulk dissolved oxygen to the surface dominates the dissolution process. This is in line with the observation of a jump in the oxygen permeability through a silver membrane from 198 cm^3 m^{-1} h^{-1} at 878 K to 1330 cm^3 m^{-1} h^{-1} at 1020 K [23].

In summary, the TPRS experiments have clearly shown that the two different surface α and γ species of atomic oxygen react either as oxydehydrogenation centres (α) or as dehydrogenation centres (γ). This is in line with integral kinetic data [4] suggesting the simultaneous action of both reaction pathways. The data further clearly show that the reaction is a conventional surface Langmuir–Hinshelwood type reaction with short-lived organic intermediates accumulating under reaction conditions to amounts insufficient to be detected by spectroscopy. The fact that the reaction to formaldehyde and the desorption of pre-adsorbed oxygen coincide on the temperature (energy) scale is a strong confirmation for the dominating influence of the silver–oxygen interaction on the overall reaction kinetics. The failure of many previous studies [11] to observe these results, although they used the same techniques as the present investigation, is due to the fact that the partial pressure effect of oxygen on the nature of the silver–oxygen species was overlooked due to experimental difficulties. In the discussion of the review by Barteau and Madix [14] it is, however, stated that adsorption pressures may have an important effect on the course of the partial oxidation reaction.

The data also highlight the participation of structural effects (oxygen-induced facetting as on-line activation process) and the equilibration of oxygen concentrations on the surface and in the bulk of the catalyst as functions of temperature and gas phase partial pressure of oxygen.

These conclusions may be criticised as being again experimentally far from the "real" system. For this purpose an instationary kinetic experiment with the "real" system under operating conditions close to practical conditions was designed in order to prove the action of two independent reaction pathways. This was possible due to the knowledge of the behaviour of α and γ oxygen at surfaces under high temperature and high and low partial pressures of molecular oxygen from previous ISS [10] and in situ Raman experiments [24]. These data show that at high partial pressures of oxygen both atomic oxygen species are present in large abundances. Removal of surface oxygen by reaction or ion bombardment brings the abundance of α oxygen quickly to low values, whereas γ oxygen is accumulating at very low partial pressures of molecular oxygen by segregation of bulk β oxygen to the initially clean surface. Only after reaching a steady state surface abundance after about 35 min at 900 K is the interconversion of γ oxygen into the surface α species observed by XPS and UPS [10].

Fig. 5 summarises and instationary (see also Experimental section) conversion experiment. It occurs that two regimes of reactivity are present. In the first 2 min of the reaction the formation of formaldehyde via the oxydehydrogenation mechanism with limited selectivity is the dominating process. After this period the selectivity rises steeply to 100% indicative of the now exclusive operation of the dehydrogenation mechanism. This is in full agreement with the oxygen chemisorption behaviour on silver outlined above.

Interruption of the stationary feed leaves a surface covered with both oxygen species. The top surface atomic oxygen reacts after addition of the organic substrate and is consumed stoichiometrically by the formation of both water and carbon dioxide. After removal of the α species the remaining firmly held (see fig. 1) γ oxygen acts as fully selective dehydrogenation agent. It is, however, progressively consumed and converted most likely to water (where it cannot be analysed due to the excess of steam in the system). The long tail of the conversion curve after 10 min indicates the re-formation of the γ oxygen from segregated atomic oxygen from the bulk. It takes more than 90 min until the formaldehyde production has come to a complete end. The fact that the conversion falls to zero in the absence of oxygen supports the experiments of fig. 2 as being significant for practical reaction conditions.

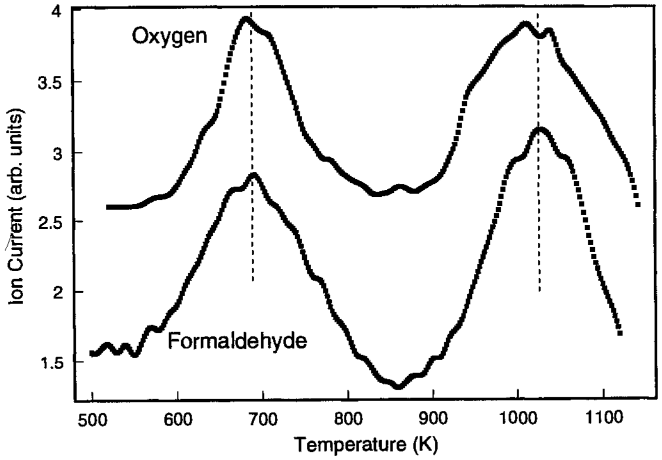

Fig. 5. Conversion experiments in the microreactor: IMR-MS response curves for an instationary experiment. After prolonged steady-state operation the reactor was flushed with preheated nitrogen until no educts or products were detectable. Then, at time = 0 the methanol–water feed was applied together with a nitrogen stream balancing the total flow for the omitted oxygen gas stream. Note that 55% of the total formaldehyde formation occurred at 100% selectivity.

If the findings in fig. 4 about two distinct temperature regimes of selective dehydrogenation are also valid under practical conditions, then we should observe two peaks in the selectivity curve of our steady state experiment. This is indeed the case as can be seen from the formaldehyde selectivity pattern displayed in fig. 6. A section through the parameter space with the temperature and the ratio of redox equivalents (methanol as reducing agent and atomic oxygen as oxidising agent) being the variables. The maximum selectivity is reached at slightly understoichiometric redox equivalents indicating the participation of the dehydrogenation in the overall reaction. As function of temperature we observe the expected two-peak structure at temperatures close to the TPRS experiments. In addition, a regime of catalyst operation exists at low temperatures and highly understoichiometric feed where good selectivities are achieved. This further confirms the relevance of the dehydrogenation pathway in the overall conversion process. These conditions are, however, unfavourable for practical operation as the conversion of methanol under fixed flow conditions is significantly lower than in the region of the parameter space (almost stoichiometric feed, high temperatures), where the catalyst is operated practically.

4. Conclusion

The reactivity of silver loaded with oxygen under practical partial pressures in the methanol to formaldehyde reaction was studied. Evidence was found for the

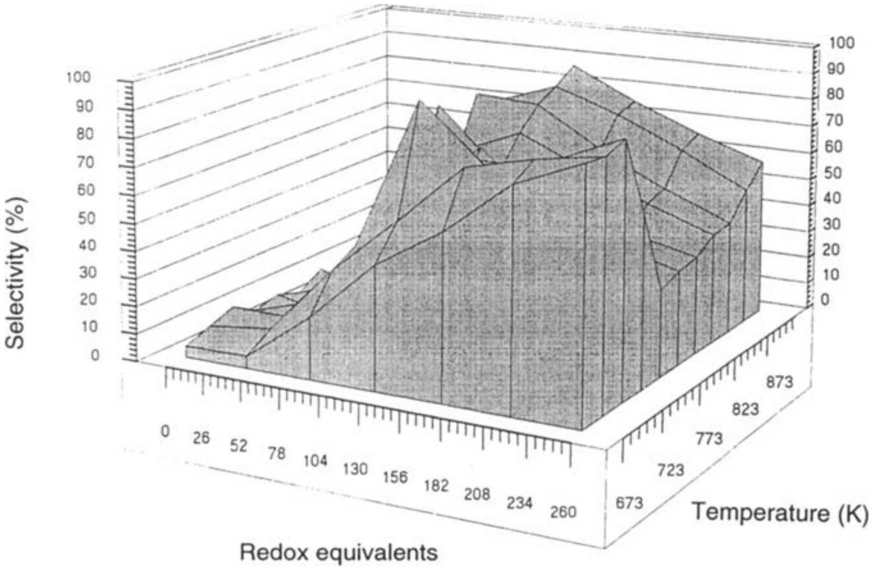

Fig. 6. Conversion experiments in the microreactor: section through the operating parameter space presented as formaldehyde selectivity. Each data point is averaged from two independent experiments and was checked for steady-state for 24 h. The catalyst mass, total gas stream and feed loading (from a 45% water–methanol mixture) were fixed. The two x-axis variables were the catalyst temperature and the ratio of redox equivalents (methanol to oxygen, ×100). The low selectivity to formaldehyde at oxygen-rich conditions is due to extensive total oxidation.

participation of three different atomic oxygen species in the reaction sequence. These three species were identified earlier as to exhibit different locations and hence chemical bonding to the substrate. For this reason it is not surprising that their mode of operation in the methanol conversion is also different. Surface oxygen acts as oxydehydrogenation agent and is stoichiometrically consumed as water or carbon dioxide. The firmly held sub-surface species acts as strong Lewis base and catalyses dehydrogenation with 100% selectivity. Its reactivity to the primary product hydrogen is low (see fig. 1) so that catalytic amounts of this species are sufficient. Under conditions of low partial pressures of molecular oxygen the atomic oxygen dissolved in the bulk segregates to the surface and replenishes the pool of sub-surface oxygen without contributing significantly to the formation of surface atomic oxygen. Earlier Raman studies and the data in fig. 1 show that sub-surface oxygen is converted only in the absence of a reactive species in the gas phase to surface atomic oxygen.

The present data allow us to assign a specific catalytic function to each of the spectroscopically characterised oxygen species. This assignment is also valid under practical reaction conditions. The present findings do not contradict the conjecture in the literature [14] about two qualitatively different atomic oxygen species chemisorbed on the surface as explanation for the selectivity of the partial oxidation reaction. Arguments of adsorbate–adsorbate interaction and hence coverage effects were made responsible for the postulated different mode of chemical bonding between silver and oxygen causing different degrees of Lewis basicity to the two species. Our results are also full support for the conclusions by Lefferts [25], who pointed out the catalytic relevance of a strongly bonded oxygen species (our γ oxygen) which he detected in very small amounts in his TDS patterns.

It cannot be decided on the basis of the present results how much of the total conversion is contributed by each of both reaction channels. The obvious fast reaction of surface oxygen is to be compared to the catalytic action of the sub-surface oxygen and not to the slow kinetics of its formation. As all species interconvert into each other under steady state conditions, it will remain a difficult task to determine relevant kinetic constants. Of importance will further be the spatial distribution of sub-surface oxygen sites and surface oxygen sites which can be translated into the fractional coverage of the real catalyst with (111) facets. Work is in progress to determine this quantity.

The present results are of relevance in a study on experimental possibilities for the closure of the pressure gap between essential UHV characterisation data and practical reaction conditions by a combination of problem-adapted measurements.

Acknowledgement

We acknowledge collaborative discussion with the BASF group, namely Drs. Diercks, Marosi, Essig, Krösche and with Professor Ertl and Drs. Bao and Muhler at the Fritz Haber Institute. The work was financially supported by the BASF AG and by the University of Frankfurt, where most of the experimental work was done.

References

[1] H. Sperber, Chem. Ing. Techn. 41 (1969) 962.
[2] Ullmann, *Encyclopedia of Industrial Chemistry* (Verlag Chemie, Weinheim), Vol. 21 (1982) p. 311; Vol. A11 (1988) p. 619.
[3] E. Jones and G.G. Fowlie, J. Appl. Chem. 3 (1953) 206.
[4] V.J. Atoschenko and I.P. Kusnharenko, Int. Chem. Eng. 4 (1964) 581.
[5] G. Rovida, F. Pratesi, M. Maglietta and E. Ferroni, Surf. Sci. 43 (1974) 230.
[6] R.J. Ekern and A.W. Czanderna, J. Catal. 46 (1977) 109.
[7] A.M. Bradshaw, H.A. Engelhardt and D. Menzel, Ber. Bunsenges. Phys. Chem. 76 (1972) 500.
[8] H. Albers, J.M.M. Droog and G.A. Bootsma, Surf. Sci. 64 (1977) 1.
[9] C. Rehren, M. Muhler, X. Bao, R. Schlögl and G. Ertl. Z. Phys. Chem. 174 (1991) 11.
[10] X. Bao, M. Muhler, B. Pettinger, R. Schlögl and G. Ertl, Catal. Lett. 22 (1993) 215.
[11] X. Bao, G. Lehmpfuhl, G. Weinberg, R. Schlögl and G. Ertl, J. Chem. Soc. Faraday Trans. 88 (1992) 865.
[12] I.E. Wachs and R.J. Madix, Surf. Sci. 76 (1978) 531.
[13] C. Rehren, G. Isaak, R. Schlögl and G. Ertl, Catal. Lett. 11 (1991) 253.
[14] M.A. Barteau and R.J. Madix, in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Vol. 4, eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1982) p. 95.
[15] H.A. Engelhard and D. Menzel, Surf. Sci. 57 (1976) 591.
[16] G. Rovida, J. Phys. Chem. 80 (1976) 150.
[17] M. Bowker, M.A. Barteau and R.J. Madix, Surf. Sci. 92 (1980) 528.
[18] R.A. Outlaw, D. Wu, M.R. Davidson and G.B. Hoflund, J. Vac. Sci. Technol. 10 (1992) 1497.
[19] I.E. Wachs and R.J. Madix, Appl. Surf. Sci. 1 (1978) 303.
[20] M.A. Barteau, M. Bowker and R.J. Madix, Surf. Sci. 94 (1980) 303.
[21] U. Tegtmeyer, Thesis, Frankfurt, Germany (1994).
[22] X. Bao, J.V. Barth, G. Lehmpfuhl, R. Schuster, Y. Uchida, R. Schlögl and G. Ertl, Surf. Sci. 284 (1993) 14.
[23] Gmelin, *Handbuch der Anorganischen Chemie*, Oxygen, Vol. 3, part 3, 8th Ed. (Verlag Chemie, Weinheim, 1958).
[24] X. Bao, B. Pettinger, G. Ertl and R. Schlögl, Ber. Bunsenges. Phys. Chem. 97 (1993) 322.
[25] L. Lefferts, Thesis, University of Twente, The Netherlands (1987).