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Surface and subsurface products of the interaction of O_2 with Ag under catalytic conditions

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Polycrystalline Ag treated with O_2 at pressures up to 1 bar and at temperatures up to 920 K was examined by TDS. It was found that the peak commonly observed at 595 ± 25 K and assigned to adsorbed atomic oxygen (O_a) is shifted to higher desorption temperatures with rising dosing temperatures. Since saturation of the uptake was not possible either, this peak was identified as dissolved atomic oxygen (O_d). The existence of a maximum for the O_2 uptake after exposure at 820 K was found. Hence, under conditions of formaldehyde synthesis (≈ 920 K) the ability of the catalyst to dissolve oxygen is near its maximum.

Keywords: Silver; oxygen; selective oxidation; thermal desorption; subsurface compounds

1. Introduction

Silver is used as catalyst in two industrially important oxidation syntheses–that of ethylene to ethylene epoxide and that of methanol to formaldehyde [1]. Since the mechanisms of both reactions are not clear up to now the interaction between silver and oxygen under practical conditions is still of interest.

The system was frequently examined with thermal desorption spectroscopy (TDS) [2–10]. In most of these experiments O_2 was dosed at temperatures below 500 K. Subsequently heating caused always a peak at 595 ± 25 K which was assigned to recombination and desorption of adsorbed atomic oxygen (O_a) [2–10]. Besides this peak a further signal was detected at 830 ± 160 K when O_2 was dosed at 473 K, and this signal was assigned to the recombination and desorption of dissolved atomic oxygen (O_d) [2,6–10]. The existence of chemisorbed molecular oxygen (O_2-c) was postulated, as well, and it was assumed that two different species of this kind are formed on Ag: Campbell et

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al. [4] after treating Ag(110) at 135 K with 1900 L O_2 reported the desorption to take place at 187 K whereas Grant et al. [5] and Bao et al. [7] stated 420 ± 40 K.

TDS experiment after dosing O_2 above 500 K have scarcely been performed. Rovida et al. [2] reported exposures in this range, however, the observed peaks were suggested to be not specific for oxygen on Ag and thus the corresponding spectra were not displayed. Bowker et al. [10] treating Ag powder with O_2 observed the disappearence of the peak at 595 ± 25 K raising the dosing temperature from 473 K to 673 K, and they found a new peak at 700 K in this experiment besides the desorption at 830 ± 60 K being assigned to a subsurface species of oxygen.

Our TDS experiments were performed to examine this temperature range and to come close to the real conditions of the catalysed syntheses of CH_2O. Oxygen was dosed at pressures up to 1 bar and at temperatures up to 920 K. Furthermore, since most of the investigations published so far were performed on single crystals with ideal surfaces our examinations were carried out with polycrystalline Ag.

These conditions led to results which indicate that the assignments made in the literature for O_a and O_d are not correct. It was shown that the peak commonly observed at 595 ± 25 K after dosing O_2 at temperatures below 500 K is shifted to higher desorption temperatures with rising dosing temperatures. In addition it was not possible to saturate the uptake which convinced us that this peak is due to dissolved oxygen. On the other hand the high temperature desorption peak being assigned in the literature to O_d could be saturated and its desorption temperature was hardly shifted suggesting that this peak is due to adsorbed atomic oxygen (O_a).

2. Methods

The investigations were carried out in the ultra high vacuum (UHV) system schematically displayed in fig. 1 (base pressure of 10^{-8} mbar). The sample -1-, a trough (length × width × height = 25 mm × 15 mm × 7.5 mm) made of polycrystalline Ag foil (Ventron, 99.999%, thickness = 0.25 mm) was placed in a quartz cell which could be isolated from the pumping system by the gate valve -7- permitting treatments with up to 1 bar O_2. Research grade oxygen was used with a purity better than 99.999% (Linde). Heating was achieved by an oven formed as a tube so that fast removal of the heating source was possible when desired. The temperature was registered with an attached Ni/Cr Ni thermocouple -2- contained in a porcellain tube (∅ = 3 mm) with only the head protruding. The temperature was regulated with a controller of Newtronics (Micro 96) and linear heating at a rate of 1 K/sec over the range 300–1070 K was possible using computer controlled dynamic PID parameters for the controller.

Oxygen was dosed at different temperatures and after each exposure the sample was cooled to 300 K (≈ 2 min) before the chamber was evacuated

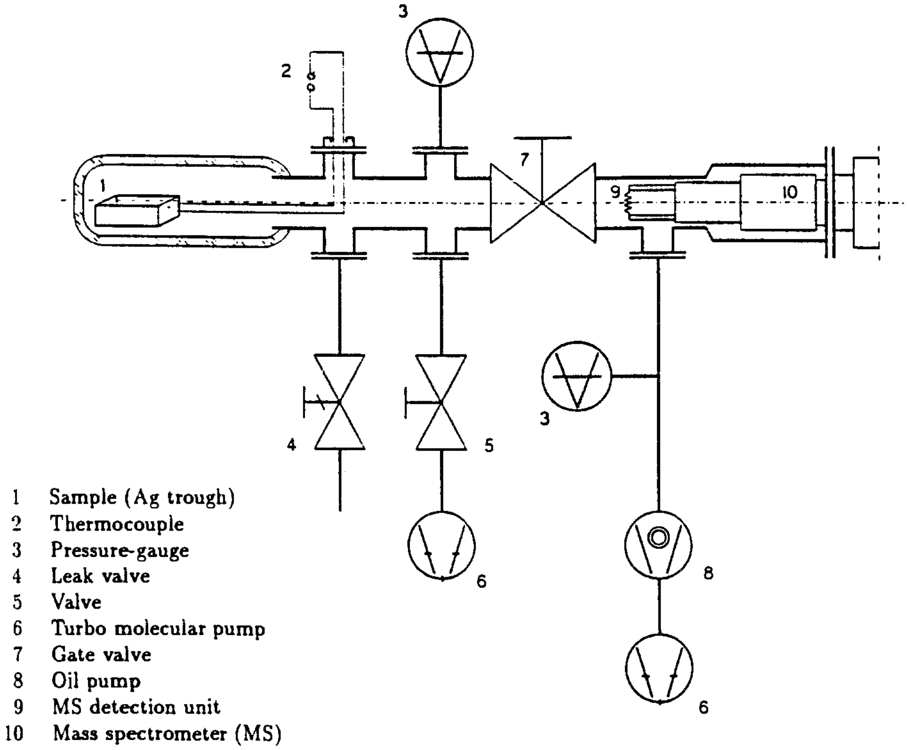


Fig. 1. UHV system and quartz cell used in this TDS investigation.

(+about 2 min). During measurements the sample was heated from 300 K to 1070 K. Desorbing gases were monitored with a Leybold Q100 quadrupole mass spectrometer -10- the sensitivity of which was significantly increased by pumping the analysis gas through the ion source -9- of the spectrometer.

To obtain the absolute amounts of the oxygen uptakes the mass spectrometer was calibrated by dosing a continuous flow of O_2 ($\approx 10^{-6}$ mbar) from a receptical (volume 3 cm^3, initial pressure 900 mbar). The response was registered with MS and after a controlled pressure drop of 20 mbar the O_2 flow was stopped. The area of the registered peak was correlated with the mole number n according to the ideal gas equation. Comparing the TDS peaks with this result allowed to estimate absolute amounts of the oxygen uptake.

3. Results

SUMMARY OF PREVIOUS RESULTS [11]

The investigations presented here were based on experiments previously performed with TDS, X-ray and ultra-violet photoelectron spectroscopy (XPS and UPS) the results of which are summarized as follows.

The TDS results were obtained by treating Ag-foil mounted on a stainless steel holder with 10 mbar oxygen at temperatures up to 770 K. Since blank experiments without sample revealed that the sample holder contributed to the desorptions, subtraction of the corresponding blank data was necessary to obtain the result spectra.

In all experiments research grade oxygen was used with a purity better than 99.999% (Linde). However, since at treatments with 10 mbar O_2 the sum of the partial pressures of the residual gases is not far below 10^{-5} mbar, interactions with Ag and residual gases had to be considered and thus the possible desorptions of H_2, H_2O, and CO_2 were checked besides O_2 in all experiments. This precaution proved to be justified since after exposure at 300 K besides the desorption of O_2 taking place at 580 K the desorption of carbon dioxide was found at 480 K.

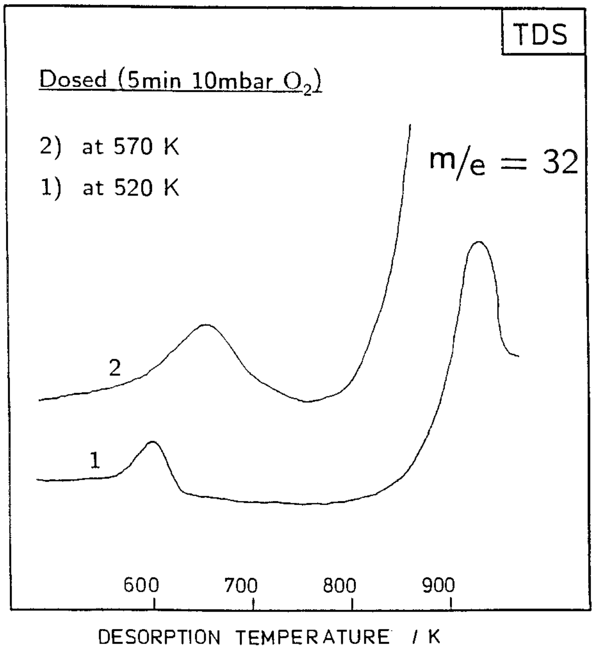
This species was also detected with UPS (peaks at 8.6 eV, 3.4 eV, and 2.0 eV) and comparison with the literature revealed that these emissons had been taken by Grant et al. [5] and Bao et al. [7] to confirm the assignments of the observed desorption peaks at 420 ± 40 K to chemisorbed molecular oxygen. The possibility that they were due to carbonate was discussed by Grant et al. [5], but since with XPS the C_{1s} peak of this species at 287.4 eV was not observed they rejected this option. Our investigations revealed, however, that carbonate is indeed present but that because of the low amount its detection is only possible at high resolution. The above-mentioned TDS peak at 420 ± 40 K was found in our experiments, as well, but blank experiments revealed that it was exclusively due to desorptions from the sample holder. All this proved that chemisorbed molecular oxygen does not exist on silver at temperatures above 300 K.

To avoid carbonate, further experiments were performed above the decomposition temperature of Ag_2CO_3 (480 K) and in these investigations it was found with UPS and XPS that only two different oxygen species do exist on silver (O_a and O_d). In contrast to all TDS results published so far indicating that oxygen is completely desorbed at temperatures below 900 K, these experiments revealed that an oxygen-free sample is not obtained even when heated for hours at 920 K in UHV. It was shown further that O_d is stable even in 1 mbar of H_2 heated for 15 h at 900 K.

All these results motivated us to the present investigations which were made possible with a new TDS cell without any background contributions.

ISOBAR EXPOSURES

In a first sequence the sample for 5 min to 10 mbar O_2 at different temperatures. The corresponding TDS spectra are displayed in fig. 2. After treating Ag at 520 K we observed two desorption peaks at 600 K and 925 K being assigned in the literature O_a citer2,b13,c1,g3,b24,b14,t5,m1,b25 and O_d [2,6–10].



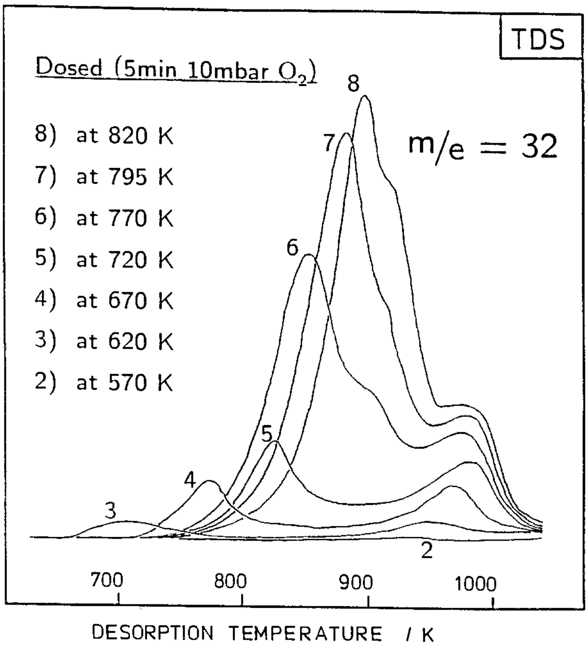


Fig. 2A. Polycrystalline silver after different isobar exposures to oxygen. Curve 2 is also displayed in fig. 2B, allowing comparison of the desorption intensities.

Fig. 2B. Polycrystalline silver after different isobar exposures to oxygen. Curve 8 is also displayed in fig. 2C, allowing comparison of the desorption intensities.

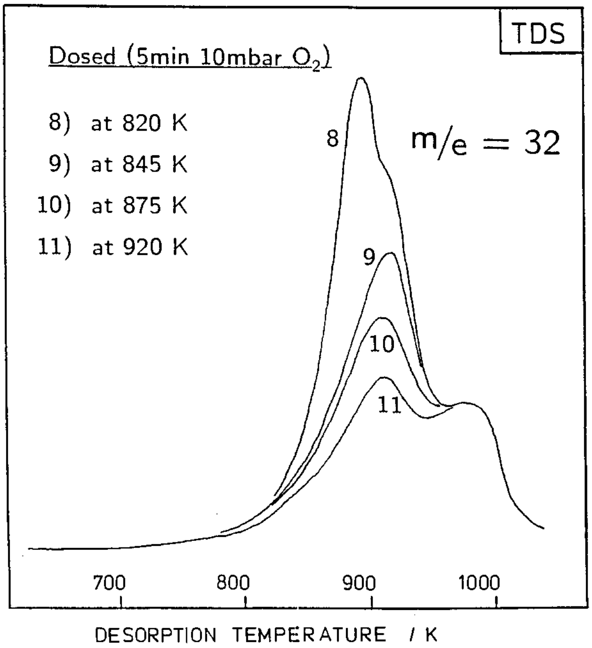


Fig. 2C. Polycrystalline silver after different isobar exposures to oxygen.

The desorption temperature of the first peak continuously increased with raising the dosing temperature, as can be seen from fig. 3. This peak, from now on denoted as α, thus cannot be due to O_a. The second peak being initially observed at 925 K, from now on denoted as β, is also shifted, however, only in the region between 925 K and 980 K. This was one of the reasons convincing us that this species is actually due to O_a.

Returning to fig. 2B after dosing O_2 at about 720 K the desorption of a third species becomes visible at 900 K and this species, denoted as γ, also hardly shifted. Exposures above 820 K led to the complete disappearence of α and to smaller desorption peaks for the β and γ states.

The isobar of this experimental sequence shown in fig. 4 reveals that the oxygen uptake is exponentially increased with raising dosing temperatures and that its maximum is reached after dosing O_2 at 820 K.

EXPOSURE FOR 16 h TO 1 bar O_2 AT 300 K

The desorption of chemisorbed molecular oxygen (O_2-c) was reported by Bao et al. [7] and Grant et al. [5] to take place at 460 K and 380 K when silver is treated with O_2 at 300 K. Similar features were, however, previously identified by us with contributions from the sample holder and further experiments with photoelectron spectroscopy (UPS and XPS) showed that O_2-c does not exist on Ag above 370 K [11].

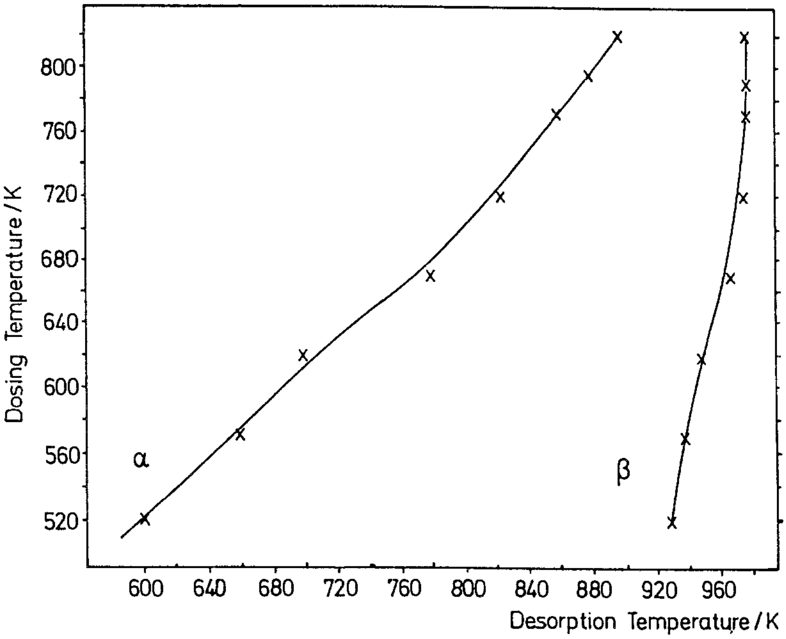


Fig. 3. Polycrystalline silver after different isobar exposures to oxygen. Correlation of peak positions and dosing temperatures.

The sample was extensively treated for 16 h with 1 bar O_2 at 300 K. The corresponding desorption spectrum is displayed in fig. 5 and no evolution of oxygen is visible below 660 K even after this treatment.

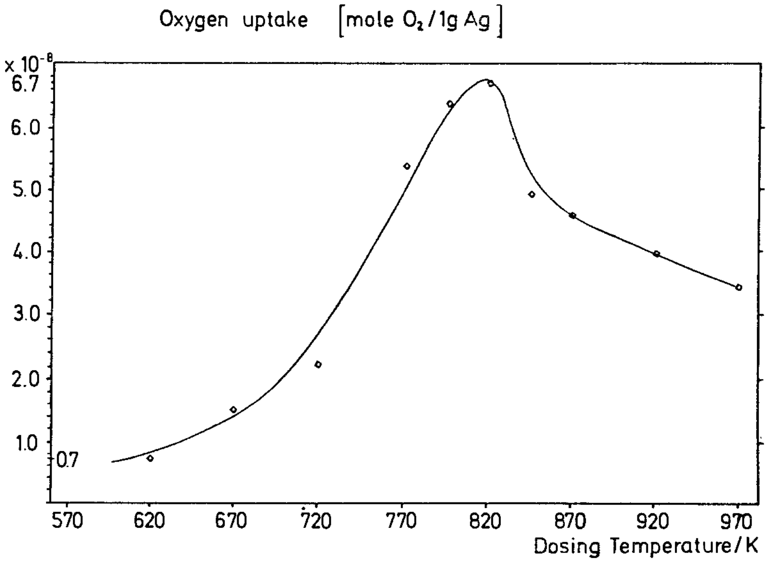


Fig. 4. Polycrystalline silver after different isobar exposures to oxygen (10 mbar 5 min). The uptake reaches a maximum after dosing O_2 at 820 K.

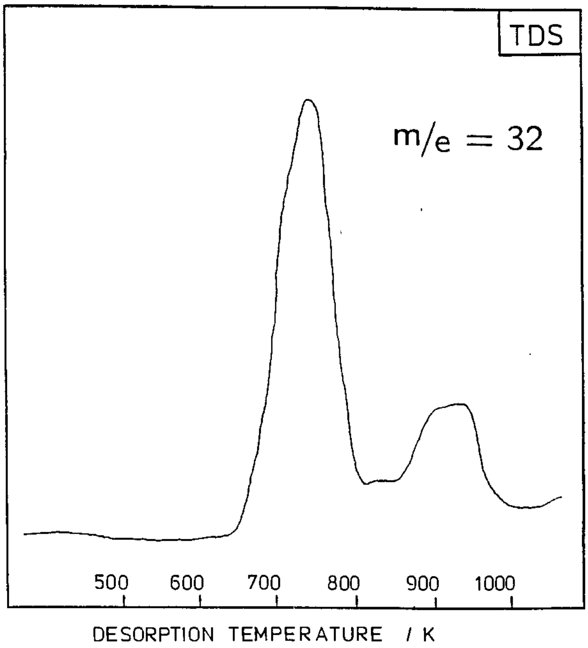


Fig. 5. Polycrystalline silver after exposure for 16 h to 1 bar O_2 at 300 K. No desorption of O_2 is observed at temperatures below 660 K.

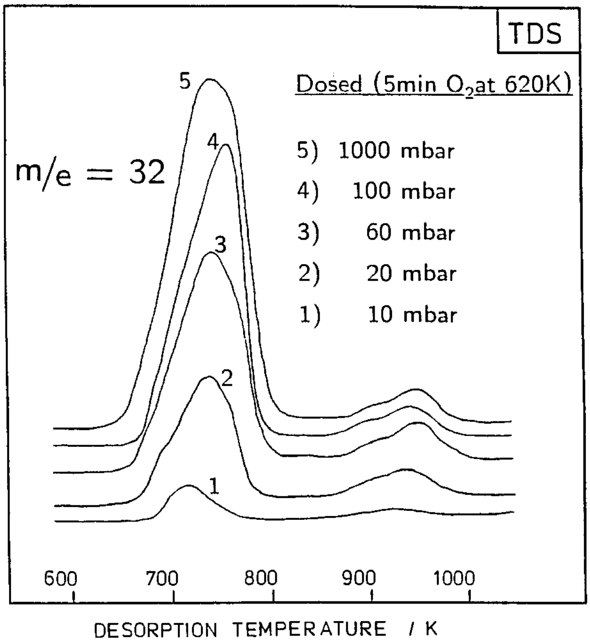


Fig. 6. Polycrystalline silver after different isothermal exposures to oxygen.

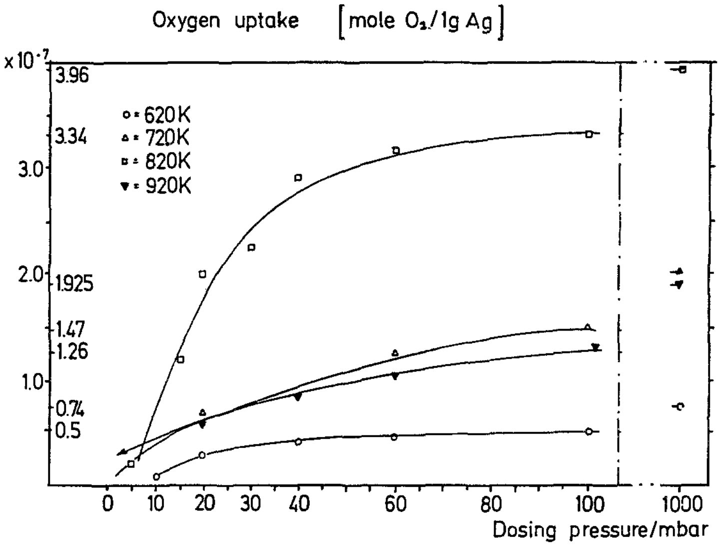


Fig. 7. Polycrystalline silver after different isothermal exposures to oxygen.

ISOTHERMAL EXPOSURES

In a further sequence of experiments the sample was treated with oxygen under isothermal conditions (5 min 620 K). The results, shown in fig. 6, were obtained after dosing 10 mbar, 20 mbar, 60 mbar, 100 mbar, and 1000 mbar O_2. The species α, β, and γ are always observed to desorb at 700 K, 945 K, and 900 K, respectively. Raising of dosing pressures led to an increase of the oxygen uptake, however, only α was enlarged. After exposure to 1 bar O_2 the peak area of this species was found to be about the thirtyfold of β and γ. This indicates once again that α cannot possibly be due to the desorption of O_a and β be due to O_d since then the saturation behavior should be exactly the opposite.

Isothermal sequences in the pressure range 1–1000 mbar were measured at 620 K, 720 K, 820 K, and 920 K. The resulting isotherms are displayed in fig. 7. O_2 was dosed in all cases for 5 min. It is evident from these curves that the oxygen uptakes were relatively high at low pressures and showed saturation at higher pressures and it is once again confirmed that the O_2 uptake reached its maximum when O_2 was dosed at 820 K.

4. Discussion

SPECIES α AND β

After treating Ag with O_2 at temperatures below 500 K the desorption of oxygen was observed by many authors [2–10] to take place at 595 ± 25 K and in all cases this peak was suggested to be due to adsorbed atomic oxygen (O_a). In experiments under isobar conditions we found, however, that this peak, denoted as α, is shifted to higher desorption temperatures with raising the dosing temperature. Since O_a is suggested to be bound on specific adsorption sites (= characteristic binding energy) the desorption of O_a has to take place–according to the Arhenius equation–at one specific temperature. This demonstrates that α is not due to adsorbed atomic oxygen. On the other hand, for β, being assigned in the literature to O_d [2,6–10], a relatively constant desorption temperature was observed (in the range 945 K–980 K) which is not typical for a dissolved species.

Experiments under isothermal conditions showed that α can not be saturated whereas β is saturated. This result indicates that α is due to dissolved oxygen and β is due to adsorbed atomic oxygen.

The maximum oxygen uptake was used to determine the localisation of the adsorbate on or below the surface. An amount of 3.96×10^{-7} [mole O_2/g Ag] was measured to desorb after an exposure for 5 min to 1 bar O_2 at 820 K (see fig. 7). Assuming that only oxygen atoms are adsorbed this value has to be doubled (7.92×10^{-7} [mole O-atoms/g Ag]). About 10^{15} [Ag-atoms/cm^2] are present on a silver surface according to Joyner et al. [12]. Our smooth sample was made out of an Ag foil sized (30 × 40) mm having a surface area of 24 cm^2. About 24×10^{15} Ag-atoms (4×10^{-8} [mole]) were thus present on our silver sample. The normalized oxygen uptake in fig. 7 has to be multiplied with the weight of the sample (3.147 g) to obtain the corresponding oxygen amounts. Assuming each Ag surface atom to adsorb one oxygen atom leads to the following ratios:

Dosing temperature	920 K	820 K	720 K	620 K
Uptake [mole O-atoms]	1.2×10^{-6}	2.5×10^{-6}	1.23×10^{-6}	0.46×10^{-6}
O-atoms/ Ag-surface atoms	30	62.5	30.8	11.6

These values clearly indicate that the desorbed oxygen was mainly dissolved in the silver bulk since otherwise, the unlikely formation of up to 60 layers of oxygen atoms would have to be assumed.

Further, it can easily be calculated from the Ag crystal structure (fcc) that O-atoms fit perfectly in the octahedral holes of the Ag lattice [13]. Taking into account that 9.27×10^{-3} [mole] octahedral holes are contained per gram silver it follows that ≈ 0.01% of the octahedral holes of the Ag lattice are most likely occupied when Ag is treated for 5 min with 1 bar O_2 at 820 K.

SPECIES γ

Besides α and β a third species (γ) was observed when oxygen was dosed above 720 K and its desorption was always found to take place at 910 ± 10 K. In a previously published investigation [11] only two oxygen species were distinguished with photoelectron spectroscopy (O_a and O_d) and thus it has to be assumed that two of the three species possess identical electron configurations. Under isobar conditions the desorption temperature of α was found to converge against the desorption temperature of γ with raising dosing temperatures. Hence it is to assume that γ is due to dissolved oxygen, as well. The difference between the two species is that α originates from the subsurface region of Ag whereas γ from the Ag bulk. Distinguishing between α and γ is possible because of the temperature dependence of the diffusion coefficient M_d of O_d. Johnson et al. [14] examining the permeability of Ag membranes (0.2 mm) to oxygen have found that M_d is exponentially increased with rising the Ag temperature. The following values were measured at an O_2 pressure of 1 bar:

Sample temperature [K]	680	740	780	850	900 K
M_d [cm^3/m^2 h]	7	14	65	180	396

Since in our experiments the sample was heated at a linear rate (of 1 K/sec) α was quickly removed whereas γ desorbed not before a sufficiently high mobility of O_d was reached.

The dependence between oxygen uptake and dosing temperature has also been examined by Eichenauer et al. [15], treating large Ag cylinders (0.5 cm × 30 cm) with O_2, and then estimating the O_2 uptake by evacuating the dosing chamber without cooling the sample until no further oxygen desorbed. A comparison with our results shown in table 1 reveals that the values agree fairly well at dosing temperatures below 820 K. The slightly higher uptakes found by us are explained by the higher ratio between numbers of surface adsorption sites and bulk absorption sites. Our desorbed amounts consisted of surface (β) and

Table 1
Solubility of oxygen in silver at different dosing temperatures. Our results were obtained after treating Ag at different temperatures always for 5 min with 1 bar O_2.

Dosing temperature [K]	Eichenauer et al. [mole O_2 /g Ag]	Our results (see fig. 7) [mole O_2 /g Ag]
570	0.08×10^{-7}	
620		0.74×10^{-7}
670	0.39×10^{-7}	
720		2.00×10^{-7}
770	1.23×10^{-7}	
820		3.96×10^{-7}
870	2.99×10^{-7}	
920		1.92×10^{-7}
970	6.05×10^{-7}	
1070	10.7×10^{-7}	
1170	17.2×10^{-7}	

dissolved species (α and γ) whereas the amounts estimated by Eichenauer et al. [15] have to be assumed to be exclusively due to γ.

Above 820 K Eichenauer et al. [15] observed further increase of O_2 uptake with rising temperatures whereas we detected a maximum at 820 K. This may be explained as follows: The oxygen uptake is correlated on the one hand with temperature dependence of the diffusion coefficient M_d. On the other hand one has to take into account that raising the sample temperature increases also the vibration amplitudes of the Ag-atoms in the silver lattice and this softening decreases the stability of O-atoms contained in octahedral holes. These opposite effects lead to a maximum for the oxygen uptake. The discrepancy to Eichenauer et al. [15] arises therefore from the fact that we measured under steady state conditions–always dosing same O_2 amounts (1 bar 5 min) and always using same desorption procedure (heating from 300 K to 1070 K at a linear rate of 1 K/sec)–whereas Eichenauer et al. [15] trying to measure the thermodynamic equilibrium data used different desorption conditions for each dosing procedure and thus their O_2 amounts are actually not comparable with each other.

5. Conclusion

The experiments showed that oxygen is dissolved in silver even at 300 K and that the amount of O_d is exponentially increased with rising dosing temperature. Two peaks were detected for O_d and assigned to oxygen dissolved in the subsurface region and to O_d from the Ag bulk.

The results show that under conditions of formaldehyde synthesis (performed at about 920 K) the ability of the catalyst to dissolve oxygen is near its maximum. The catalyst bulk acts as a reservoir for oxygen atoms mobile at reaction temperature at which the species O_a is still stable and thus chemically still active. The role of the catalyst in the overall reaction might thus be the supply of mobile oxygen atoms which can either react with the methanol dehydration product hydrogen or directly attached co-adsorbed methanol.

Acknowledgments

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