

THE OXIDATIVE DEHYDROGENATION OF METHANOL TO FORMALDEHYDE OVER SILVER CATALYSTS
IN RELATION TO THE OXYGEN-SILVER INTERACTION

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ABSTRACT

The properties of silver in the oxidative dehydrogenation of methanol were studied in a flow reactor under near industrial conditions. The influences of temperature, concentration of both reactants, gas velocity, space velocity, the form of the silver catalyst and surface composition of the catalyst were studied. A model for the reaction is proposed which is based on the experimental observations and on the nature of the interaction of silver with oxygen. It is suggested that different oxygen species on the silver surface play different roles in the reactions to CO, CO₂ and H₂CO. Gas phase reactions only contribute to the conversion to CO.

INTRODUCTION

Oxidative dehydrogenation of methanol using silver as a catalyst is a well-known industrial process for the production of formaldehyde. At one atmosphere with temperatures around 600°C, it is possible with an excess of methanol relative to oxygen to reach a selectivity of 90% towards formaldehyde with almost complete conversion of the methanol. The main by-products are CO, CO₂, H₂ and H₂O.

The catalytic behaviour of silver has been reviewed by Clayton and Norval [1]. Much research has been done using as catalyst both pure silver and silver supported on low area-alumina or on alumina-silicates. It is still not clear how the process on the silver surface takes place, especially under industrial conditions.

Gavrillin and Popov [2] have reported that an unstable temperature range exists due to the exothermic nature of the reaction. Above the temperatures corresponding to this instability, conversion of the oxygen of the reaction mixture is complete. Several workers have stated that the process is diffusion controlled above 500°C [3-6]. It has been shown that the presence of oxygen is necessary for reaction to occur [7]; i.e. no further reaction occurs on the silver in that part of the bed in which the oxygen has been exhausted.

Kaliya and his coworkers [6,8,9] have reported that selective oxidation (Equation 1) and dehydrogenation (Equation 2):





both play a role in the process.

In only a few of the studies reported in the literature has attention been paid to the way in which the by-products of the reaction are formed [3,10,11]. The suggestion has been made that total oxidation and selective oxidation take place on different surface sites [9,10].

Ultra-high vacuum (UHV) studies, reviewed by Hedge [12], Barteau and Madix [13] and by Madix [14], have led to a mechanistic model where such a difference is not included; this is not entirely surprising because of the low temperatures used in these investigations. However, it has recently been suggested [15,16] that only one of two oxygen-species present on the surface is involved in the interaction with methanol under these mild conditions of temperature and pressure. Bearing in mind the fact that the conditions of UHV studies are very different from those of industrial use, the results indicate that it is possible that different species may play different roles in the process. Thus, it is important to characterise the silver-oxygen interaction on the catalysts studied in the present work under conditions similar to those used in catalysis. Results of such a study of the different oxygen sites are to be published [17].

There has been no single study covering the influence of temperature, of the concentration of both methanol and oxygen, of the space velocity (SV) and linear gas velocity (v_g) under near industrial conditions. Because of differences in the catalysts and the conditions used in the various reports which have appeared, it is still not clear how the process takes place. We have therefore studied the effects of all these parameters for pure silver materials. A mechanism is proposed for the reaction under our conditions which is consistent with the results and also with the results of our study of the silver-oxygen interaction [17].

EXPERIMENTAL

Catalytic measurements

The equipment used, which is of the fixed-bed flow type, is shown schematically in Figure 1. Technical grade oxygen and helium are first passed through molecular sieve traps to remove water. These gas streams, regulated by pressure and flow controllers, are then mixed and passed through a methanol saturator (1) at room temperature and then through a saturator held at a lower temperature which is regulated by a cryostat (2). The gas is then introduced into a one-way quartz reactor (3), inner diameter 5 mm., supplied with electrical temperature control. A thermocouple, protected from the reaction mixture by a quartz sleeve in order to avoid there being any contribution to the catalytic activity from the thermocouple material, is placed on the top of the bed. A few experiments were performed using a methanol-formaldehyde mixture; an aqueous solution of these compounds containing 30% formaldehyde was used as source of the gaseous mixture.

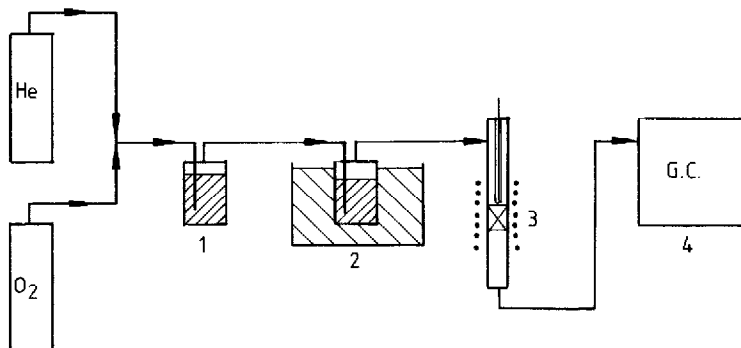


FIGURE 1 Schematic diagram of the catalytic flow equipment.

The composition of the product mixture was determined using a sample valve with a HP 5880 temperature-programmable gas chromatograph (4) fitted with a Carbosieve column and a thermal conductivity detector. This permits quantitative analysis of the molecules H_2 , O_2 , CO , CO_2 , H_2CO and CH_3OH and qualitative analysis of the molecules H_2O and $HCOOCH_3$.

None of the individual samples of the silver catalysts was used for longer than four weeks, during which period of continuous operation no deactivation effects were observed. Nevertheless, it was found that the silver sintered markedly. Experimental reaction conditions in typical experiments were as follows: temperature between 150 and 700°C; total pressure between 1.0 and 1.1 bar; bed height between 3 and 12 mm.; linear gas velocity between 0.01 and 0.1 $m\ s^{-1}$; space velocity between 6×10^3 and $15 \times 10^4\ h^{-1}$; oxygen pressure between 0 and 0.04 bar; and methanol pressure between 0 and 0.10 bar. The reactant concentrations are somewhat lower than used in commercial practice in order to minimise heating of the bed due to the exothermic nature of the reaction.

The conversion to product i is defined by:

$$y_i = [i]_{out} / [CH_3OH]_{in} \times 100\%$$

and the selectivity to formaldehyde is defined by:

$$s = [CH_2O]_{out} / ([CH_3OH]_{in} - [CH_3OH]_{out}) \times 100\%$$

Materials

The silver catalysts studied were industrially used non-porous materials with mean particle sizes of 0.2 or 0.5 mm, these are referred to in the text as Ag0.2 and Ag0.5 respectively. These materials were prepared commercially by an electrolytic method. In addition, another material, also consisting of pure silver but having a less uniform shape, which gives a lower packing density was also examined;

this is referred to in the text as Ag III. The catalyst samples were cleaned before use with diluted nitric acid at room temperature for 10 min. Several samples were also tested without cleaning.

XPS measurements showed, besides silver, the presence of carbon, oxygen and trace amounts of silicon and chlorine as impurities on the surface. The same surface composition was found for all three materials. We thus conclude that there are no appreciable impurities on the catalyst surface. Furthermore it appeared that cleaning Ag III with water or diluted nitric acid lowered the amount of carbon on the surface.

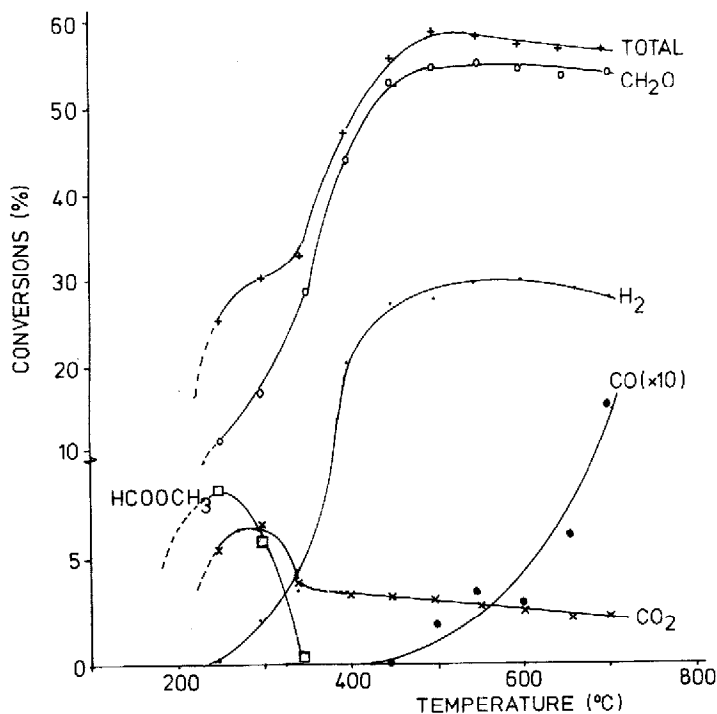


FIGURE 2 The influence of temperature on the conversion of methanol over Ag_{0.2}; $O_{2in} = 2.0\%$; $CH_3OH_{in} = 8.8\%$; $SV = 5 \times 10^4 \text{ h}^{-1}$ and $v_g = 8.2 \text{ cm s}^{-1}$.

RESULTS

Reaction in the empty reactor

The conversion of methanol in the presence of oxygen was found to be negligible in an empty reactor for temperatures up to 600°C under the following standard conditions: $O_{2in} = 2.0\%$, $CH_3OH_{in} = 8.8\%$, balance He, total pressure = 1.1 bar, $SV = 5.10^4 \text{ h}^{-1}$, $v_g = 8.4 \text{ cm s}^{-1}$. Only when the gas velocity was reduced below 2 cm s^{-1} and the temperature was above 550°C did methanol and oxygen react to give

predominantly a mixture of CO and CH₂O, the methanol conversion rising above 5%. When the quartz-shielded thermocouple was removed from the reactor, a decrease in conversion was observed. We therefore conclude that the conversion with the empty reactor is mainly catalysed by the quartz walls rather than being due to a gas phase reaction. Measurements above 600°C showed somewhat greater conversions.

Effect of reaction temperature

The influence of temperature on the conversion of methanol under the standard conditions given above are shown in Figure 2 for the sample Ag0.2. Almost identical results were also obtained for the other two forms of the catalyst. The small differences which were found between Ag0.2, Ag0.5 and Ag III are discussed later. No conversion was observed below 150°C and the system was not stable between 150 and 250°C. Above 250°C, the system was found to be stable and all the oxygen of the reaction mixture was found to have been consumed, there being a concurrent increase in the temperature of the bed by approximately 25°C. The lowest temperature at which this stable system was found is referred to hereafter as the light-off temperature.

Figure 2 also shows the effect of temperature on the product distribution in the reaction. It can be seen that there exists a maximum in the conversion to CO₂ and methylformate at around 300°C. The formation of H₂ and CH₂O increases in the temperature range from 300 to 500°C. Above 500°C, the conversions appear to decrease again very slowly with increasing temperature; however, this is almost certainly an experimental artefact caused by a small increase, with increasing temperature, in the pressure drop over the catalyst bed which in turn causes a slight decrease (<5%) in the oxygen concentration at the input to the bed. In the temperature region above 500°C, only the conversion to CO continues to increase. There thus exists a broad maximum in the yield of CH₂O at around 500°C. Most of the results presented below were, in consequence, obtained at a reaction temperature of 500°C.

Effect of reactant concentrations

Figure 3 shows the effect of increasing the methanol inlet concentration while keeping the oxygen inlet concentration constant at a catalyst temperature of 500°C. The total conversion of the methanol decreases but the proportion of formaldehyde in the products increases. The effect of increasing the oxygen inlet concentration while keeping the methanol inlet concentration constant is shown for two different bed temperatures in Figures 4a (500°C) and 4b (640°C). In both cases, the total conversion increases with oxygen concentration but the proportion of formaldehyde in the products decreases. It should be noted that the conversion scales in these figures are non-linear.

The greatest effect of reactant concentration is seen in the proportion of CO₂ in the products. As is shown in Figure 3, an increase in the methanol concentration causes a drop in the CO₂ concentration from 20% to about 3%. Conversely an increase

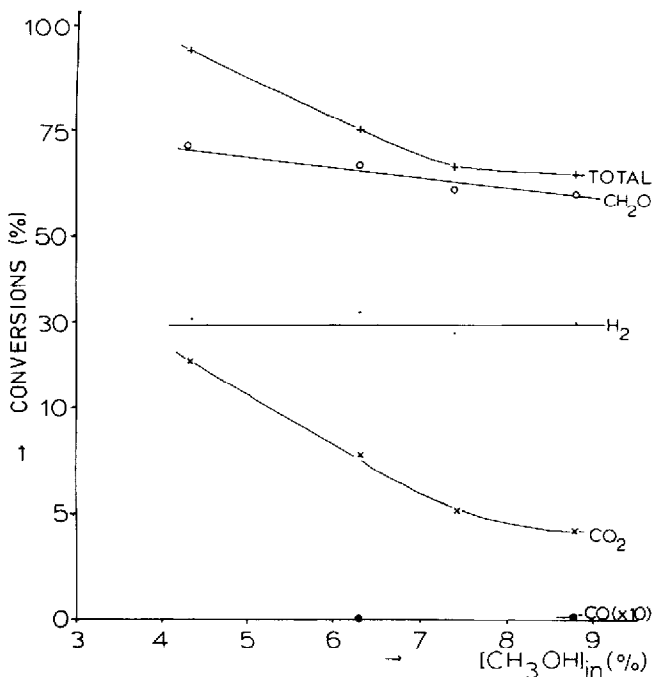


FIGURE 3 The influence of the inlet concentration of CH_3OH on the conversion over $\text{Ag}_{0.2}$; $\text{O}_{2\text{in}} = 2.0\%$; $T = 500^\circ\text{C}$; $\text{SV} = 5.1 \times 10^4 \text{ h}^{-1}$ and $v_g = 8.5 \text{ cm s}^{-1}$.

in the conversion to CO_2 is observed on increasing the oxygen concentration as is shown in Figure 4a. When oxygen is removed from the reaction mixture, the conversion of methanol drops to below 3% after a few hours of operation. The conversion to CO is small, especially at low concentrations of O_2 . However, when the reaction temperature was increased to 640°C (Figure 4b), the conversion to CO , in agreement with the higher temperature results of Figure 2, was much higher and went through a maximum at low oxygen concentration.

Effect of space and gas velocities

The effects of space velocity (SV) and linear gas velocity (v_g) were examined in order to obtain information about diffusion processes and the kinetics of the reaction. SV is defined as the ratio of the gas volume flow rate (in $\text{cm}^3 \text{ s}^{-1}$ at 25°C and 1 bar) and the total volume of the catalyst bed (in cm^3). The quantity v_g is defined as the ratio of the gas volume flow rate and the area of the reactor cross-section in cm^2 . Thus, SV can be varied at constant v_g by altering the height of the bed of catalyst while v_g can be varied at a constant value of SV by altering the gas volume flow rates and the bed height at the same time.

Figure 5 shows the influence of SV on the conversion when v_g is held constant at 4.3 cm s^{-1} . A small decrease in total conversion is observed, the proportion of

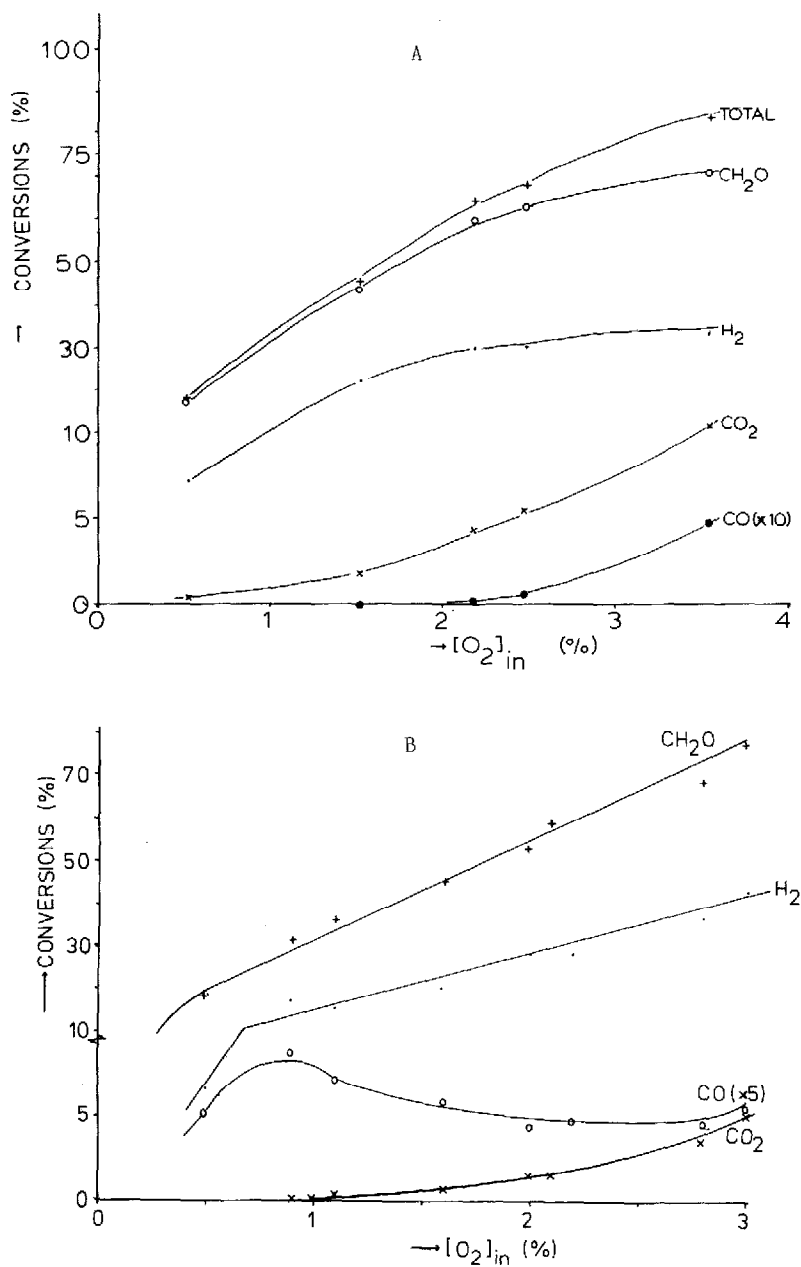


FIGURE 4 The influence of the inlet concentration of oxygen on the conversion over AgO.2; $CH_3OH_{in} = 8.8\%$; $SV = 5.1 \times 10^4 \text{ h}^{-1}$ and $v_g = 8.5 \text{ cm s}^{-1}$, (a) $T = 500^\circ\text{C}$, (b) $T = 640^\circ\text{C}$.

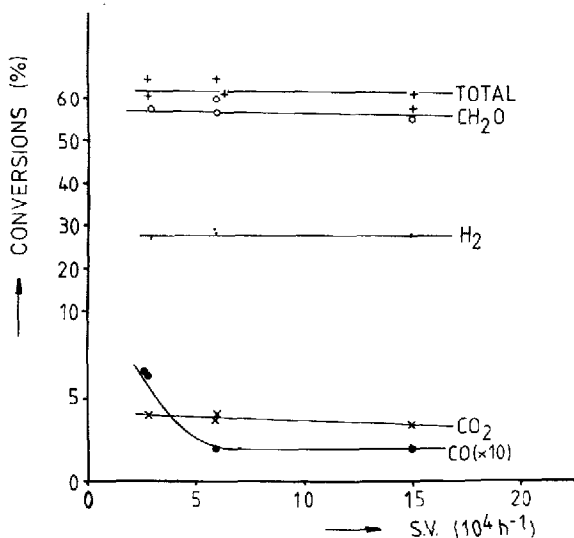


FIGURE 5 The influence of the space velocity on the conversion of methanol over Ag0.2; $O_{2in} = 2.2\%$; $CH_3OH_{in} = 8.8\%$; $T = 500^\circ\text{C}$ and $v_g = 4.3 \text{ cm s}^{-1}$.

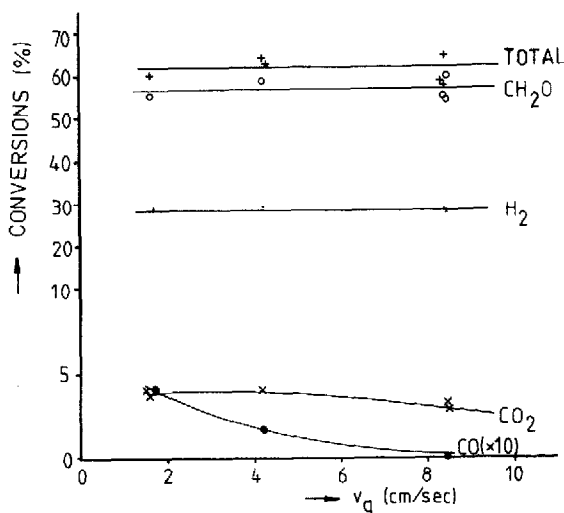


FIGURE 6 The influence of the linear gas velocity on the conversion of methanol over Ag0.2; $O_{2in} = 2.2\%$; $CH_3OH_{in} = 8.8\%$; $T = 500^\circ\text{C}$ and $SV = 6 \times 10^4 \text{ h}^{-1}$.

formaldehyde increasing slightly. There is a marked decrease in the concentration of CO formed, it being found only in significant quantities at low SV at 500°C ; there is also a small decrease in the concentration of CO_2 formed. Because the conversion to CO is very small and the changes in the CO_2 concentration are also

small, the selectivity to formaldehyde is very little affected, as is noted above. Similar results for the effect of SV were found for the other forms of silver. Very similar results were also found for the effect of v_g , as is shown in Figure 6; an increase in v_g at constant SV causes a very small decrease in the total conversion, a slight increase in the proportion of formaldehyde in the products, a decrease in conversion to CO and a very small decrease in the conversion to CO₂. It should be noted that the rather large experimental uncertainty in the total conversion and the conversion to formaldehyde and CO₂ shown in Figures 5 and 6 arise from difficulties in the accurate control of the oxygen partial pressure when changing the total flow rate. Only in the case of CO are the effects clearly significant.

Decomposition of methanol and formaldehyde in an empty reactor

The decomposition reactions of methanol and of a formaldehyde-methanol mixture was measured by leading them through the empty reactor in the absence of oxygen at temperatures between 500 and 700°C, using a low linear gas velocity of less than 2 cm s⁻¹. To distinguish between gas phase reactions and reactions on the walls of the quartz reactor, the experiments were performed with and without the quartz-shielded thermocouple; insertion of the thermocouple decreases the residence time and increases the quartz area.

Using pure methanol, almost no conversion was observed at any temperature in the range studied. However, when formaldehyde was introduced, reaction was observed at higher temperatures with CO as the predominant product. Insertion of the thermocouple decreased this conversion. Thus, we can conclude that the decomposition of formaldehyde takes place predominantly in the gaseous phase. The formaldehyde conversion is about 20% at 650°C; however, quantitative experiments were not possible because there exists a temperature profile over the whole reactor, even though the temperature is constant through that proportion of the reactor normally occupied by the silver catalyst.

Different forms of silver

The best way in which to compare different catalysts has proved to be with the aid of a correlation between total conversion and selectivity, using the oxygen inlet concentration as the variable parameter: small variations in the oxygen concentration have marked effects on both conversion and selectivity. Results of this type are presented in Figure 7, which shows that there exist almost no differences between the samples; the only significant difference is that Ag III gives a lower selectivity at high conversions. Further, it appears that cleaning with dilute nitric acid only effects the behaviour of Ag III. The same effect is observed after cleaning with water only. If the sample is not cleaned, there results a higher conversion to CO₂. This is a temporary effect which is observed only in the first two weeks of operation.

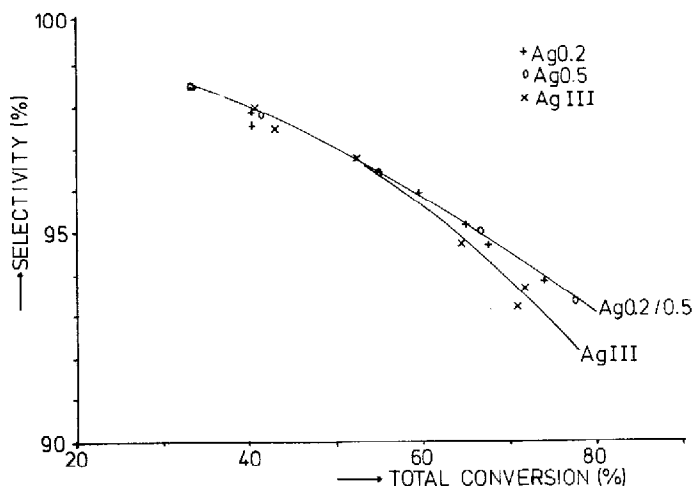


FIGURE 7 Plot of selectivity to formaldehyde versus conversion for a range of oxygen partial pressures over different forms of silver; $\text{CH}_3\text{OH}_{\text{in}} = 8.8\%$; $T = 500^\circ\text{C}$; $\text{SV} = 5.6 \times 10^4 \text{ h}^{-1}$ and $v_g = 9.3 \text{ cm s}^{-1}$.

Figures 8 a and b show the conversions to CO and CO_2 at different total conversion levels for cleaned catalysts. It shows that the main difference between Ag III and the other samples is found in a higher conversion to CO.

DISCUSSION

In the following, the results are first discussed in relation to those appearing in the literature. A mechanism is then proposed which is discussed firstly in relation to the literature data and secondly in relation to the present results.

Oxygen exhaustion

It appears that only the upper part of the silver catalyst bed is active in the methanol oxidation reaction, this being that part where oxygen is present. This conclusion is supported by the facts that the space velocity has almost no influence on the product composition (Figure 5), that oxygen is consumed totally for temperatures above 300°C (Figure 2), and also that the calculated thermodynamic equilibrium composition [18] is not achieved in our measurements.

This conclusion, similar to that reached by Sperber [7], applies only when the reaction is ignited. The occurrence of an unstable temperature region and of the light-off phenomenon has also been reported by Gavrillin and Popov [2] and by Popov [19].

A consequence of the exhaustion of the oxygen is that it is impossible to measure the kinetics of the reactions occurring under the conditions used in this study.

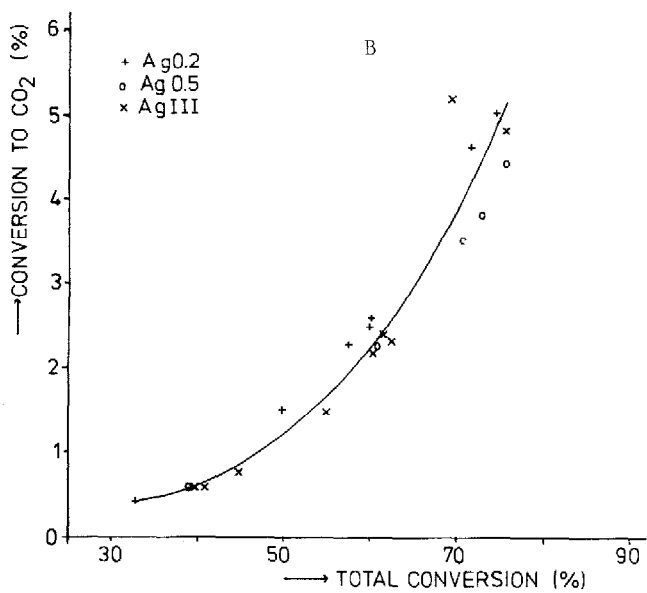
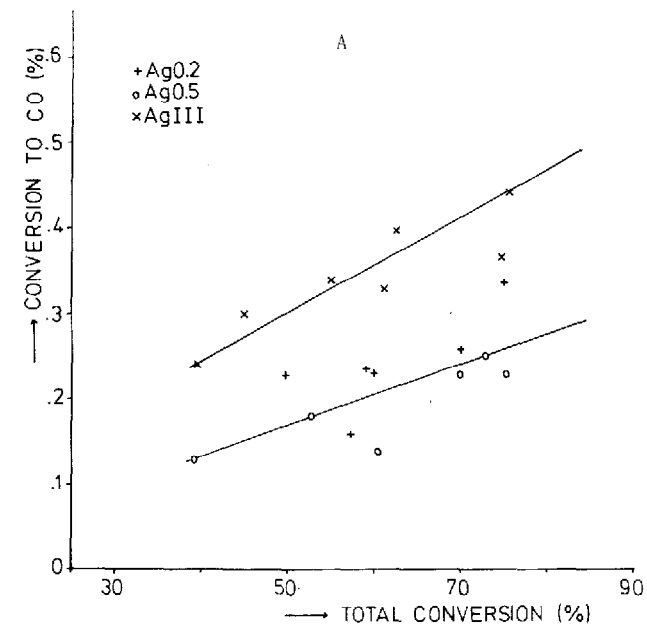


FIGURE 8 Plots of selectivity to CO and CO₂ for a range of oxygen partial pressures over different forms of silver; CH₃OH_{in} = 8.8%; T = 500°C; SV = 5.6 × 10⁴ h⁻¹ and v_g = 9.3 cm s⁻¹.

Reactions in the active layer at temperatures above light-off

Several different reactions can take place in the active layer; these are selective oxidation:



dehydrogenation:



and total oxidation:



The competition between these reactions determines both the selectivity and total conversion because both reactions (3) and (4) use far less oxygen than does reaction (5) and thus the thickness of the active layer is dependent on the extent to which these different reactions occur.

An increase in the reaction temperature causes greater increases in the rates of reactions (3) and (4) relative to the rate of total oxidation (reaction 5), as is illustrated by the decrease in conversion to CO_2 shown in Figure 2. This is in agreement with other studies [2,3,10]. The conversion to methylformate which we have observed at temperatures just above light-off (see Figure 2) has not been reported before.

Formation of carbon monoxide

The formation of CO can proceed in many ways. Our results show that CO is formed both in the gas phase and on the surface of the active layer of the catalyst, as will be discussed below.

The experiments with the empty reactor show that formaldehyde decomposes much faster than does methanol, according to the reaction:



The influence of the space velocity on the conversions in the presence of silver (see Figure 5) shows that the reaction to give CO is influenced by the residence time while the main reaction is not. Thus, while the main reaction takes place only in that part of the bed where oxygen is available (as discussed above), the formation of CO can take place throughout and we can conclude that oxygen is not necessarily involved. It was also shown that formaldehyde decomposition in the empty reactor probably takes place as a gas phase reaction, not on the reactor wall. Hence, a gas phase reaction may contribute to the formation of CO under methanol oxidation conditions.

Experiments on the influence of the linear gas velocity on the conversion to CO (Figure 6) show that the CO concentration decreases with increasing gas velocity while there is no effect on the methanol conversion. Increasing the gas velocity has the effect of decreasing the thickness of the gas film around the catalyst surface and thus of increasing the rate of diffusion of reactants and products away through that film. We thus suggest that the formaldehyde formed in the active part of the layer is desorbed and can then readsorb on another site, probably bare silver, where it decomposes by reaction (6); increased gas velocity increases the rate of diffusion away from the surface and thus, by decreasing the concentration of formaldehyde on the surface, decreases the formation of CO. This suggestion is also in agreement with the results of Figure 4b which shows that there is a maximum in the formation of CO at lower oxygen partial pressure at the higher reaction temperature, suggesting that the decomposition of the formaldehyde occurs predominantly in the active part of the bed on sites which are depleted in oxygen; at higher oxygen partial pressures, the proportion of these sites is decreased. At high oxygen concentration, the conversion to CO increases again because the higher conversion to CH_2O results in more gas phase decomposition.

Mass transfer

Several workers have stated that the methanol oxidation process is mass-transfer limited above a certain temperature. With the help of a circulating flow technique, Obratsov et al. showed that this was the case for temperatures above 350°C [4], but the presence of products in the reaction mixture may have had an influence. Other workers [2,21,22] have concluded from measurements made with about 90% conversion of oxygen that diffusion inhibition occurs at 480°C ; however, a too small amount of a very dilute supported silver catalyst was used in these studies in such a way that break-through or tunnelling is highly likely to have occurred. Kaliya et al. [6] and Lazarov et al. [3] appear to have misinterpreted their measurements on the influence of the total flow through the bed. The total reaction rates, expressed in $\text{mol s}^{-1} (\text{cm}^3 \text{catalyst})^{-1}$, increase because more oxygen is provided and not necessarily because of changes in mass transfer rates. Furthermore, the slow increase of total conversion with temperature above 400°C [3] is also a result of oxygen exhaustion and of the competition between the oxygen-consuming reactions instead of being due to diffusion limitation.

The problem that the existence of diffusion limitation cannot be proven directly is also encountered in this study because of existence of total conversion of the oxygen. Nevertheless, the linear gas velocity clearly influences the conversion to CO as discussed above, indicating that mass-transfer effects do in fact exist.

Different forms of silver and surface composition

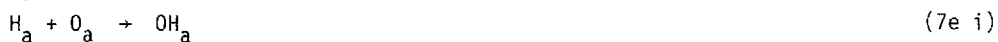
It is shown in Figure 7 that almost the same results are found for all three forms of silver. Only at high conversions does Ag III produce more CO. It is reasonable to assume that this is caused by increased decomposition of formaldehyde in the gas phase because Ag III has a much lower packing density.

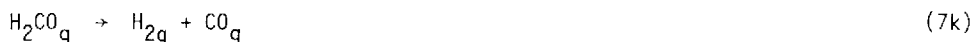
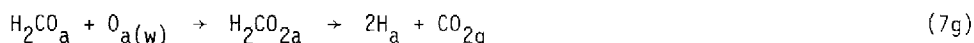
The fact that no other differences are observed is in agreement with the XPS results, which showed no marked differences in the surface composition of all three cleaned forms. A marked lower selectivity, caused by a higher conversion to CO₂, is measured only when Ag III is not cleaned with diluted nitric acid or water. The same treatments also decrease the amount of carbon on the surface as measured with XPS. Thus carbonate species or some sort of water soluble organic molecules are probably responsible for the increase in conversion to CO₂. Because this effect is observed over a period of several days, the increase in conversion to CO₂ is not explainable by removal of the carbon itself; we must therefore conclude that the surface carbon influences the catalytic properties of the silver sample.

Mechanism of the process

Based on the results of this study and also making use of literature data, we propose the reaction scheme presented below. It is based on the concept that two types of oxygen sites are involved in the reaction [17] and it is consistent with the suggestion made by a number of workers that the selective oxidation and dehydrogenation reactions of methanol take place at sites associated with strongly bound surface oxygen whereas the total oxidation reaction proceeds on sites associated with weakly bound oxygen [1,9,22]; however, it differs in a number of respects from these schemes. Following a description of the scheme, the arguments in favour of the various steps proposed will be discussed.

Reaction scheme. We propose that the steps occurring during the oxidation of methanol over unsupported silver catalysts in the temperature range 300 to 700°C are as follows:





Two types of surface oxygen species are formed in step (7a), strongly and weakly adsorbed. The way of formation of these species is open to discussion. Methanol can adsorb only on the oxygenated surface by steps (7b) through interaction of the hydrogen atom of its OH group either with surface oxygen (step 7b i) or with the surface OH groups thus formed (step 7b ii). It is not possible to distinguish clearly between strongly and weakly bound oxygen in this reaction; the weakly bound oxygen is probably more active in methanol adsorption. Step (7b ii) may not be as important as step (7b i) as the OH groups can also react with surface hydrogen in step (7c ii).

The adsorption steps are followed by dehydrogenation of the surface methoxy species on a site associated with the strongly adsorbed oxygen species in step (7c), again with the formation of surface hydrogen species. The hydrogen species formed in the dehydrogenation step can either desorb associatively as in step (7d) or can react with adsorbed oxygen or OH groups as in steps (7e i) and (7e ii), finally desorbing as molecular water in step (7e iii). It is to be expected that weakly bound oxygen is more reactive than strongly bound oxygen. The formaldehyde species formed in step (7c) can either simply desorb in step (7f) or it can react further by step (7g) with weakly adsorbed oxygen to give CO_2 . Finally, the formaldehyde can react to give CO and hydrogen, either without first desorbing (step 7h) or by reaction in the gas phase (step 7k), as discussed above. Step (7l) shows how it is also possible to produce methylformate by reaction of the intermediate formed in step (7g) with a methoxy group.

Adsorption steps. We shall present in a subsequent publication [17] a discussion of the evidence from the literature for the assumption of the existence of several types of oxygen species on the surface as a result of adsorption of oxygen and we shall also present confirmatory experimental results for the different samples studied here. From measurements involving temperature programmed desorption of oxygen, temperature programmed reduction with hydrogen and temperature programmed

reaction with methanol, it appears that strongly bound oxygen is active in methanol dehydrogenation. Furthermore, methanol enhances the removal of oxygen from the surface and this causes the loss of activity of the catalyst when no oxygen is present in the reaction mixture. In steps (7b) of the scheme, we depict the methanol as adsorbed on the surface through the oxygen, as has been shown in ultra-high vacuum studies [13].

Product formation. The model can explain the observations concerning the product distributions made in this study. An increase of the catalyst temperature in the range above 300°C (see Figure 2) will cause a decrease in the concentration of AgO_w . This decrease will have an effect on the adsorption steps but it will also have a major effect on step (7g) which requires a weakly adsorbed oxygen for the reaction to form CO_2 . Thus CO_2 formation is decreased and, because the surface concentration of formaldehyde species is thus increased, the rate of formation of gaseous formaldehyde is also increased. Furthermore less oxygen is now consumed via steps (7e) and (7g), so that oxygen is present in a larger part of the bed, increasing the conversion to CH_2O .

The same argument can be used to explain the effects of oxygen and methanol concentration. An increase in oxygen concentration will increase the concentration of AgO_w more than that of AgO_s , so that step (7g) will produce more CO_2 as can be seen in Figure 4a. This effect becomes less clear at 640°C because the extent of the silver-oxygen interaction is decreased by the increase in temperature. When the methanol concentration is high, steps (7b) cause a smaller AgO_w concentration, thus slowing down step (7g). Hence, the conversion to CO_2 will drop far more sharply than the conversion to CH_2O , as is shown in Figure 3.

In contrast to the above scheme, in which the CO_2 is formed in only one way, Robb and Harriott [10] and Kurina and Morozov [11] proposed a parallel-consecutive mechanism for the formation of CO_2 ; i.e. they argued that CO_2 was formed both directly from methanol and by a consecutive reaction of the formaldehyde. Robb found, in experiments which involved changing the amount of catalyst, that the selectivity remained constant when the oxygen conversion was increased from 5% to 30%, but that it decreased when the oxygen conversion was increased further to 70%. The investigation performed by Robb and Harriott was performed in the unignited region, with a very high oxygen/methanol ratio and, in common with Kurina and Morozov, they used a supported silver catalyst. It is thus possible, for instance, that a second reaction occurs on the oxidic carrier. Ai [23] showed that formaldehyde can decompose easily on oxidic carriers. Hence, such a mechanism would not be usable in the present study. The relationship between selectivity and oxygen conversion reported by Robb cannot be compared with the observed relationship between selectivity and methanol conversion shown in Figure 7 because we measured at oxygen conversions of 100%. In the scheme we propose that the CO_2 is formed via the intermediate involved in the reaction to CH_2O ; this means that it is not possible to say whether the reactions are parallel or consecutive because it is not clear which reactions are rate determining.

The influence of the gas velocity on the conversion to CO indicates that the adsorption steps (7b) and (7c) are not very much slower than the desorption of formaldehyde (7f), resulting in competition between steps (7f) and (7h). From the influence of the oxygen concentration at 640°C it appears that competitive adsorption of oxygen and formaldehyde influences the desorption of formaldehyde. Probably this occurs at specific sites.

The effect of changing the space velocity on the conversion to CO (see Figure 6), is not directly related with the proposed mechanism. As stated before, the CO conversion proceeds partly in the gas phase, step (7k), outside the active layer. This is confirmed by the higher conversion to CO over Ag III, this material having a higher free volume.

CONCLUSIONS

We have shown that the selective oxidative dehydrogenation of methanol over silver catalysts under near industrial conditions is controlled by the silver-oxygen interaction. This is true for the reactions to both CH_2O and CO_2 . The formation of CO is controlled by the desorption of formaldehyde, which may be influenced by the oxygen concentration, but it may also occur by the gas phase decomposition of CH_2O . There is no direct evidence for or against the occurrence of diffusion limitations in the reaction, but there are indications that there is diffusion inhibition in the desorption of formaldehyde. On the basis of these observations, a model is suggested which can explain the influence of reaction conditions such as temperature, reactant concentrations, space velocity, linear gas velocity and the form of silver particles on the product composition.

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