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Oxidative dehydrogenation of methanol in a microstructured reactor

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Abstract

Microstructured reactors were fabricated on silicon by deep reactive ion etching and were used to study the catalytic oxidative dehydrogenation of methanol to formaldehyde on silver catalyst at temperature up to 823 K. The reaction was carried out with higher oxygen concentration than that typically used in conventional lab-scale or larger reactors. Even when the reaction was performed with undiluted oxygen, conversion of methanol 60–75% with selectivity ~90% was obtained. The reaction was carried out safely at conditions within the flammability limits. Effect of temperature, methanol concentration and residence time was also studied. The results show that the reaction was ca. 0.5 order with respect to methanol. Conversion increased with temperature almost linearly within the temperature range studied, with a slight decrease in selectivity to formaldehyde. The benefits of using microreactors for studying highly exothermic reactions were demonstrated, by comparing the silicon microreactor performance with that of a small quartz tube reactor.

Keywords: Catalysis; Microreaction technology; Oxidative dehydrogenation; Silver; Methanol; Formaldehyde

1. Introduction

The synthesis of formaldehyde from methanol over silver catalyst is a well-known industrial process [1–3]. The production technology is based on the selective oxidation of methanol over a thin layer of electrolytic silver catalyst adiabatically by feeding a mixture of methanol and air (approximately 1:1 molar ratio) in the temperature range of 850–923 K at atmospheric pressure. Provided that steam is added and reaction products are quenched rapidly, yields of 91–92% are possible [4]. Traditionally the overall process is regarded as a combination of partial oxidation and dehydrogenation of methanol:

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O, \quad -159\,kJ\,mol^{-1} \tag{1}$$

$$CH_3OH \rightarrow CH_2O + H_2, \quad +84\,kJ\,mol^{-1} \tag{2}$$

The total reaction is highly exothermic and fast, requiring very short contact time (0.01 s or less) [3]. The main by-products are CO_2, CO, H_2, water and methyl formate/formic acid [2] and the selectivity to formaldehyde is limited by the following reactions [3,5]:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O, \quad -674\,kJ\,mol^{-1} \tag{3}$$

$$CH_2O + 1/2O_2 \rightarrow CO_2 + H_2, \quad -271\,kJ\,mol^{-1} \tag{4}$$

$$CH_2O + O_2 \rightarrow CO_2 + H_2O, \quad -519\,kJ\,mol^{-1} \tag{5}$$

$$CH_2O \rightarrow CO + H_2, \quad +12\,kJ\,mol^{-1} \tag{6}$$

Due to the importance of formaldehyde in organic synthetic industry, numerous research efforts focused onto understanding the catalytic behaviour of silver and the reaction mechanism. It has been long recognised that the catalytic activity of silver is strongly related to the presence of oxygen. However, different opinions exist on the function and importance of different oxygen species. Wachs and Madix [6] studied the oxidation of methanol on a silver (1 1 0) crystal surface by temperature programmed reaction spectroscopy (TPRS) under UHV conditions. They found that there was very little methanol chemisorbed on Ag(1 1 0) in the absence of oxygen and the amount of chemisorbed methanol increased as a function of oxygen exposure. The activity of the partially oxidised silver surface was enhanced by the interaction of the hydroxyl end of

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methanol molecules with the adsorbed surface oxygen atoms to form adsorbed CH_3O (methoxide). The methoxy surface species then decomposed to form formaldehyde and hydrogen, or recombined with surface hydrogen to form methanol or interacted with surface formaldehyde to yield methyl formate. CO_2 could be formed through further oxidation of formaldehyde through a formate intermediate [6]. Schemes similar to those developed by Wachs and Madix were also reported for the oxidation of methanol on Ag(1 1 1) and polycrystalline silver surface under UHV conditions [7,8].

A lot of research focused on the identification and characterization of the oxygen species formed on silver surfaces during the reaction. Lefferts et al. [9] suggested that the selective oxidation of methanol over silver catalysts under near industrial conditions was controlled by the silver–oxygen interaction. Different surface oxygen species were observed [10] which played different roles in the reaction. The selective oxidation active sites were silver atoms modified by 'strongly bound' subsurface oxygen species at the vicinity of grain boundaries and surface defects, while combustion took place at sites occupied by 'weakly bound' atomic oxygen species. Millar et al. [11,12] concluded that the methanol reacted with subsurface oxygen species located in the uppermost layer to produce adsorbed methoxy species and subsurface hydroxyl species which subsequently formed water. However, it is generally accepted that the interaction of oxygen with silver at different temperatures leads to the formation of different oxygen species [11,13–24]. Three species, which were considered to be closely related to the oxidation of methanol under industrial conditions, were proposed as O_α, O_β and O_γ. O_α was weakly chemisorbed surface-bound atomic oxygen species which was formed by the dissociative chemisorption of molecular oxygen on the silver and desorbed at temperature around 600 K in the absence of gas-phase oxygen. O_β derived from the oxygen dissolved in the silver lattice. The strongly bound oxygen species O_γ formed from O_β when the latter segregated from the bulk to the surface and was accompanied by a significant restructuring of the surface at temperatures >900 K. O_γ might also form at lower temperature by the dissociative chemisorption of oxygen on reconstructed Ag(1 1 1) planes located on grain boundaries [25]. The population of these species was a strong function of operating parameters and pre-treatment. The three oxygen species were stable at different temperature regions. Formation of O_γ was favoured through a high-temperature bulk diffusion process. In addition, heating either in oxygen, water or oxygen-methanol atmospheres leads to pronounced morphological changes in the catalyst [26,27]. Much debate has been ongoing in the literature about the function of these oxygen species. However, it is accepted that O_α is dominant at low temperature (<600 K) and participates in both the oxidative dehydrogenation of methanol to formaldehyde and the non-selective oxidation of methanol and formaldehyde to CO_2. O_α also benefits the formation of HCOOH [21]. It is generally believed that O_β cannot participate directly in reaction, as it is located in the bulk. O_γ is the most controversial oxygen species regarding its role in methanol oxidation. Schubert et al. [22,28], Nagy et al. [17,18] and Qian et al. [21] suggested that O_γ was the active agent for dehydrogenation of methanol, with the continuous segregation of O_β to O_γ sites during reaction being important for catalyst function. van Veen et al. [23] and Waterhouse et al. [25] argued that water was a primary gas-phase product of the selective oxidation of methanol with O_γ. During TAP experiments formaldehyde and water showed almost parallel responses to methanol pulses, implying a highly selective oxidative pathway to CH_2O and H_2O, rather than the direct dehydrogenation route. Andreasen et al. [29] reported a microkinetic model based on the reaction mechanism derived by Wachs and Madix [6]. The model was used to simulate the experiments from Robb and Harriott [30], Lefferts et al. [9] and Nagy et al. [17] and they concluded that the mechanism of Wachs and Madix with only one kind of oxygen species O_α could explain industrial formaldehyde synthesis and O_γ was not necessary to be invoked at industrial steady-state conditions.

Despite the numerous mechanistic studies, the kinetics of the reaction at industrially relevant reaction temperature is not available. Bhattacharyya et al. [31] studied the oxidation of methanol over a reduced silver catalyst at a low conversion level and in the temperature range 537–563 K. A reaction rate equation was proposed by applying a modified Hinshelwood mechanism and assuming that formaldehyde was formed by the oxidation of methanol with adsorbed oxygen, whereas CO_2 was formed by the complete oxidation of methanol with adsorbed oxygen or by the oxidation of formaldehyde with adsorbed or gaseous oxygen. At low oxygen concentration the reaction was zero order with respect to methanol and 0.5 order with respect to oxygen. Robb and Harriott [30] investigated the kinetics using a porous alumina supported silver catalyst at an intermediate temperature 693 K. They observed an almost zero-order dependence on oxygen (except at very low pressures), less than first-order dependence on methanol and a relative total rate expression was proposed based on the Langmuir–Hinshelwood model. At high temperatures exceptionally high conversion of oxygen makes it impossible to determine kinetics of the reaction [9,17]. Lack of high quality steady-state kinetic experiments is also due to difficulties in avoiding mass transfer limitations, non-isothermicity, deactivation and aging of silver catalyst in conventional reactors.

To overcome such problems, annular reactors [32,33] and catalytic wall reactors [34,35] have been proposed for highly exothermic and endothermic reactions. Even further improvements in terms of mass and heat transfer can be achieved by microstructured reactors [36]. Microstructured reactors, or microreactors, have reaction channels with features of few microns to hundreds of microns. Due to the reduced scale in dimensions, they can offer clear advantages such as enhanced heat and mass transfer, precise control of reaction temperature and small safety risks over conventional reactors [37]. This makes microreaction systems particularly suitable for highly exothermic reactions, mass transfer limited reactions and for on-demand and safe production of toxic and hazardous chemicals. Microreactors have been used safely within flammable regions [38–44]. Good residence time control, down to the milisecond level, has led to significant improvements in selectivity for various reaction systems such as hydrogenation of c,t,t-1,5,9-cyclododecatriene [45], catalytic dehydration of isopropanol [46] and selective direct fluorination of aromatics [47]. Greatly improved heat and mass transfer can result in the reduction of hot-spot formation thus extending catalyst life while improving conversion [48–50]. In this paper we present a microreactor system for studying the catalytic selective oxidation of methanol to formaldehyde on silver catalyst. A wide range of oxygen concentration and temperature were investigated and the potential in using microreactors for the study of reaction kinetics was explored.

2. Experimental

2.1. Microreactors: design, microfabrication and assembly

A typical microreactor used in this work is shown in Fig. 1 and has been described in more detail previously [51]. It consists of four zones: pre-heating, mixing, reaction and quench. Two reactants can be fed separately into the pre-heating zone, which has a serpentine channel design, where they can be evaporated (if necessary) and brought to the required reaction temperature. Following the mixing T-junction there is a short section without catalyst for complete mixing of reactants (this short mixing zone can be eliminated if the reactants are pre-mixed before entering the reactor). The length of reaction zone can be varied from 20 to 200 mm using a straight short channel design (as shown in Fig. 1) or a serpentine channel design (not shown). After the reaction zone, another short section is left without catalyst and heating to allow the reaction mixture to quench.

Fabrication involves a series of steps: photolithography, etching, catalyst deposition and anodic bonding. The reactor patterns are firstly transferred to silicon(1 0 0) wafers by photolithography using a positive photoresist (AZ4562). The wafers are then etched using deep reactive ion etching (STS multiplex ICP). The reaction channel is 600 μm wide and the desired channel depth is obtained by controlling etching time. After etching, the photoresist is stripped and the wafers are cleaned thoroughly using oxygen plasma and piranha solution (H_2SO_4:H_2O_2 = 1:1).

Silver catalyst can be introduced in this stage or after anodic bonding. Various methods can be used to incorporate catalyst into microchannels such as thin film technology [38], anodisation and impregnation [52], sol–gel washcoating and impregnation [53,54]. In this work, several methods have been tried, including vacuum evaporation with lift-off and shadow mask, electrodeposition with lift-off [55], deposition with silver mirror reaction (in which Tollen's reagent is used as oxidant [56]) after bonding, etc. It was found that the deposition with lift-off was not always successful as the film deposited by vacuum evaporation or electroplating would come off during photoresist stripping. Silver could be deposited in the channel through the silver mirror reaction and showed good reactivity to methanol oxidation. However, the thickness and uniformity was poor and there was also the possibility of channel blockage. Finally, vacuum sputtering or vacuum evaporation of high purity silver (99.99%, Goodfellow) directly on the etched channel with the help of a shadow mask was employed.

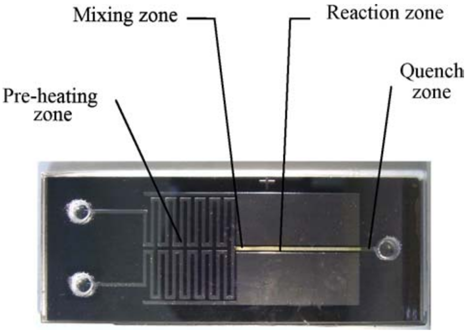


Fig. 1. Silicon–glass microreactor with silver catalyst (25 mm (W) × 63 mm (L)).

After the incorporation of silver catalyst, a Pyrex 7740 glass plate (3 mm thick) with feedthrough holes was anodically bonded to the silicon wafer. Two anodic bonders were used in this study: a commercial anodic bonder (AML, UK) and a home-made bonder at 723 K and 1 kV. The former was operated under vacuum and the latter in air. It is worth noting that silver surface morphology changed after exposure to bonding conditions as shown in Fig. 2.

The silicon–glass microreactors were mounted on a heating block, which contained four cartridge heaters (1/8 in. o.d., Watlow). Five K-type thermocouples (0.5 mm o.d., RS) were located on the back of the block and just 0.5 mm beneath the surface to measure and control the block temperature. Two pairs of cartridges were controlled separately so that a maximum temperature difference of 2 K was obtained in the reaction zone in the experimental temperatures (up to 823 K). Due to the reaction temperature required, graphite was used as sealing material. A stainless steel clamp was initially used to compress a graphite sheet gasket against the reactor to seal the inlet and outlet. However, the catalyst showed strong deactivation with this assembly, associated with the direct contact of reaction gas with the graphite. To avoid such direct contact of reaction gas with the sealing material, a new structure for connecting inlet and outlet tubing to microreactor was designed. The holes on the glass cover were re-shaped using a diamond tapered drill to form a V-type hole. The clamp was modified so that a Swagelok nut could be used to squeeze a graphite ferrule into the V-shaped hole to seal the tube. This sealing structure was satisfactory for reaction temperatures up to 823 K.

2.2. Reaction in microreactors

The reactants (methanol and oxygen/helium) were initially fed into the reactor directly through a syringe pump and mass flow controllers (Brooks 5850TR). Difficulties were encountered in delivering ca. 1 μl/min liquid stably and accurately. Instead of using syringe pumps, methanol was eventually added into the reactor by passing the feed gas through a glass methanol saturator equipped with a frit. Due to the fact that the reactants were pre-mixed before entering the microreactor, a mixing

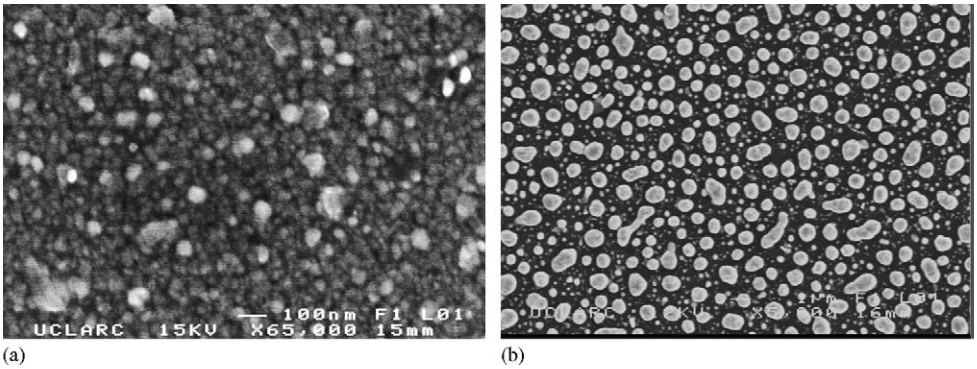


Fig. 2. SEM images of silver film: (a) as prepared by sputtering; (b) heated to 723 °C in air for 1 h.

zone was not needed and the reaction area was extended over the mixing section, as shown in Fig. 1. The reaction mixture was analysed online by a TCD-equipped GC (ThermoQuest Trace GC) with a Carboxen 1006 column (Supelco) and appropriate temperature programming for the determination of CO_2, water, methanol and formaldehyde. The later was calibrated by evaporating paraformaldehyde (95%, Aldrich) in carrier gas. The reactor effluent was cooled and the condensable portion was removed in a separator. The non-condensable gas was analysed using a second GC (Shimadzu GC-14B) with a Carboxen 1000 column for CO and H_2. All the gas lines after the microreactor were heated to prevent condensation of products. The conversion of methanol and selectivity to products were defined as follows:

$$\text{conversion}(\%) = \frac{\text{mol}(\text{MeOH, in}) - \text{mol}(\text{MeOH, out})}{\text{mol}(\text{MeOH, in})} \times 100$$

$$\text{selectivity}(\%) = \frac{\text{mol}(\text{product})}{\text{mol}(\text{MeOH, in}) - \text{mol}(\text{MeOH, out})} \times 100$$

Microreactors with channel depth of 70, 120 and 200 μm were used and are noted as MR70, MR120 and MR200 correspondingly. Contact times ranged from 4 to 25 ms at reaction temperature. Operation pressure was slightly above atmospheric pressure. The concentration of methanol in the feed was 8.5–8.6 vol.% with oxygen or oxygen/helium mixture as balance. Reaction temperature was varied from 723 to 823 K.

The activation of silver catalyst was carried out by repeated oxidation and reaction cycles at 783 K at a residence time of ~10 ms. Oxygen was firstly passed through the microreactor for 1 h (oxidation) and then the reactant mixture (methanol 8.5–8.6 vol.% with oxygen as balance) for 1–2 h (reaction). The procedure was repeated until a stable activity (conversion of methanol) was obtained. Between experiments (i.e. overnight), the microreactor system was kept at 523 K in 10% oxygen flow. A standard run was carried out each day at 783 K, residence time 10 ms and methanol concentration ~8.6% with oxygen as balance to check the reaction activity. Deactivation of silver was sometimes observed, but the activity could be restored by repeating the oxidation-reaction cycle. However, once a microreactor was cooled down and dismounted from the system, re-activation took much longer. It took about 3–4 days to activate the catalyst, and the recovered activity level was about 10–15% lower.

2.3. Reaction in a small quartz tube reactor

To make a comparison of the reaction in microreactors with conventional ones, a tube reactor system was also constructed. It consisted of a quartz tube reactor (2 mm i.d., 4 mm o.d., 22 cm long) and a furnace (Carbolite MFT 10/25/130). 0.005 g silver powder (Alfa Aesar, 99.9995%, 90–125 μm) diluted with 0.01 g quartz of same particle size was packed in the centre of the reactor to form a 2 mm long catalyst bed. The rest of the reactor was filled with segments of quartz powder (125–250 μm) and quartz wool. A thermocouple (K-type) was attached at the outside wall of the quartz tube and located at the middle of the catalyst bed.

Methanol was delivered using a syringe pump (Cole-Parmer 74900-00) into the evaporator where methanol vapour was mixed with and carried by a helium–oxygen gas mixture to the reactor. All the gas lines were heated to prevent condensation and the reaction mixture was analysed online by the GC as described above.

The silver powder catalyst was activated by heating the catalyst in 7.2% oxygen (helium as balance) at 473 K for 1 h. The catalyst was then aged [17] in a reaction mixture (methanol 8.1%, oxygen 2.8%) with a furnace temperature cycle rising from 523 to 723 K and then decreasing to 523 K at a rate of 2 K/min. A lower oxygen concentration was employed in order to avoid temperature increase in the catalyst bed. Temperatures of the furnace and the tube wall were recorded. Initially, a hysteresis behaviour was observed. The temperature cycling was repeated 2–3 times until the initial hysteresis behaviour was eliminated.

3. Results and discussion

3.1. Methanol oxidation in the quartz tube reactor

3.1.1. Reactor thermal effects

In the experiment, a mixture of 8.1% methanol and 2.8% oxygen was introduced into the reactor. The furnace setting temperature (T_F) was then increased/decreased to a desired

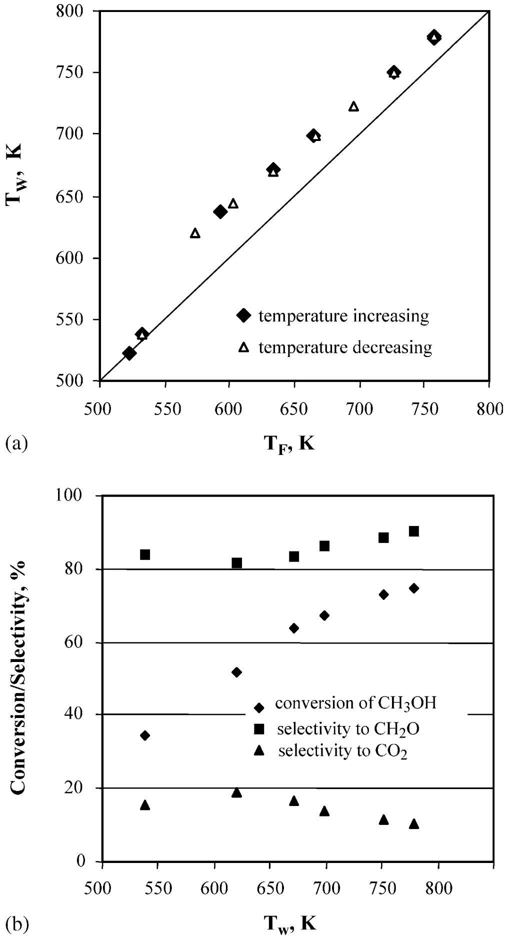


Fig. 3. (a) Quartz tube reactor wall temperature T_W vs. furnace temperature T_F. (b) Conversion/selectivity vs. T_W in temperature cycle 523–758–523 K (CH_3OH 8.06%, O_2 2.8%, He as balance. Space velocity 6.0×10^5 h^{-1}, $P = 1.52$ bar).

value and the reaction mixture was analysed after the reactor wall temperature (T_W) was stable for 30 min. Fig. 3a is a plot of T_W versus T_F in a temperature cycle 523–758–523 K. In the up-cycle, at $T_F = 523$ K, the reactor wall temperature T_W was equal to T_F and there was no reaction product detected. With increasing T_F to ~533K, T_W increased to 538 K and formaldehyde was detected. The reaction rate increased significantly upon increasing T_F to 573 K and a maximum temperature difference $T_W - T_F$ of 47 K was observed. Oxygen was almost completely consumed at this stage. With further increasing T_F, T_W was always higher than T_F, however the difference $T_W - T_F$ decreased. In the down-cycle, the same profile was obtained. Fig. 3b shows plots of conversion and selectivity versus the reactor wall temperature T_W, corresponding to Fig. 3a. Conversion of methanol increased with temperature, while at ca. 620 K a weak maximum in CO_2 selectivity and a minimum in formaldehyde selectivity were observed.

The results in Fig. 3 agree with those from similar experiments [9,17,25]. A reaction initiation temperature of ~540 K was observed within the range of 500–550 K reported in the above papers. The temperature rise of catalyst bed was also observed by Nagy et al. [17] (ca. 50 K rise in the reactor wall temperature) and Lefferts et al. [9] (ca. 25 K rise in the catalyst bed temperature). In our experiment where a smaller quartz reactor (2 mm o.d.) and less silver catalyst were employed, we still observed a maximum 47 K increase in the tube wall temperature. Similar behaviour of formaldehyde selectivity with temperature was also observed by the same investigators.

Increased CO_2 concentration in the exit stream with increasing temperature at $T_W < 620$ K would suggest that the highly exothermic oxidation reaction pathway might be dominant due to a high coverage of weakly adsorbed oxygen species (or O_α) [9,17] which is responsible for oxidative dehydrogenation to formaldehyde and water and complete oxidation of methanol and formaldehyde to CO_2 and water. At elevated temperatures ($T_W > 620$ K), selectivity to formaldehyde increased. Since the desorption temperature of O_α is about 600 K, Lefferts et al. [9] and Nagy et al. [17] suggested that strongly bound atomic surface oxygen (or O_γ) would be dominant at $T > 600$ K, which benefits the direct dehydrogenation pathway and results in a decrease in complete oxidation of methanol. However, Waterhouse et al. [25] and van Veen et al. [23] recently argued that O_γ is not involved in pure dehydrogenation pathway but the highly selective oxidative dehydrogenation of methanol to formaldehyde and water is performed on O_γ sites. Waterhouse et al. [25,57] suggest that products of methanol oxidation on O_α sites are CH_2O, CO_2, H_2O and H_2. O_α is also responsible for the non-selective oxidation of CH_2O to $CO_2 + H_2O$ or H_2. On O_γ sites, only CH_2O and H_2O are formed. The selectivity to CH_2O is closely related to the relative population of the O_α and O_γ sites on silver surface during reaction. They further suggest that the increased selectivity to formaldehyde with reaction temperature is due to the increase of the O_γ/O_α ratio. Andreasen et al. [29] on the contrary, suggest that a reaction in serial mode where CO_2 is formed by formaldehyde oxidation, would also explain the selectivity behaviour. Using microkinetic modelling, they showed that the activation enthalpy for oxidation of methanol to formaldehyde was always larger than that for CO_2 formation, hence the rate of formaldehyde formation increased more rapidly than formaldehyde combustion at increasing temperature. They further argued that the selectivity is determined by kinetics not by thermodynamics and at high temperature, oxygen is rapidly consumed in the methanol to formaldehyde reaction, inhibiting further oxidation of formaldehyde.

It is noteworthy that CO was not detectable in our experiments. Lefferts et al. [9] suggested that the formation of CO was controlled by desorption of formaldehyde but it might also occur by the gas phase decomposition of formaldehyde whose extent would depend on residence time and reaction temperature. They observed ca. 20% of formaldehyde decomposed at 923 K. In our experiments, a very short residence time (6 ms) and relative low reaction temperature (773 K) could be the reason that the formation of CO was negligible.

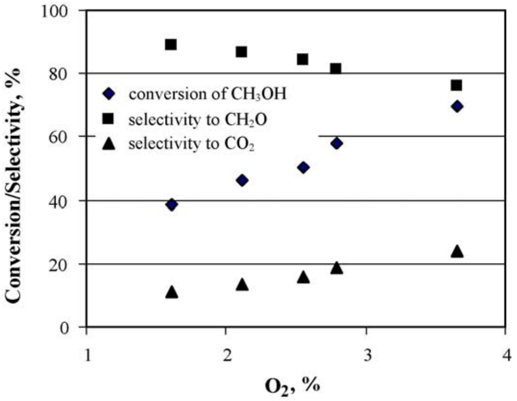


Fig. 4. Effect of oxygen concentration on conversion and selectivity in the quartz tube reactor (CH_3OH 8.1%, He as balance. Space velocity $6.0 \times 10^5\ h^{-1}$, $P = 1.52$ bar, $T_W = 620$ K).

3.1.2. *Effect of oxygen concentration on conversion, selectivity and reactor temperature*

The effect of oxygen on methanol oxidation to formaldehyde was examined by changing the concentration of oxygen in reaction mixture while keeping the methanol concentration (8.1%) and space velocity (total volumetric flow rate at reaction conditions/volume of catalyst bed) constant. Oxygen concentration was changed from 1.6 to 3.68%, corresponding to the ratio of methanol to oxygen (CH_3OH/O_2) changing from 5 to 2.2. It was observed that the reactor wall temperature T_W increased with oxygen concentration. However, in the experiment T_W was kept constant (620 K) by adjusting the furnace temperature setting at each oxygen concentration.

Fig. 4 shows the effect of oxygen concentration on conversion and selectivity in the quartz tube reactor. Methanol conversion increases with increasing oxygen concentration (i.e. decreasing CH_3OH/O_2). Selectivity of formaldehyde decreases with increasing oxygen concentration while that of CO_2 increases. Due to methanol conversion increasing with oxygen, more heat is released and hence lower furnace temperature is required to keep the reactor wall temperature constant (620 K), as can be seen in Fig. 5.

The profile of conversion/selectivity against oxygen concentration (Fig. 4) is similar with that observed by other researchers [9,58] but does not agree with that reported by Robb and Harriott [30] who found that methanol conversion was independent of oxygen concentration above ca. 1%. The latter investigators used supported silver catalyst in a differential reactor (low conversion) and low CH_3OH/O_2 ratio. The increase of CO_2 concentration and decrease of furnace temperature with oxygen concentration indicate that lean oxygen conditions have to be applied in conventional fixed bed reactor in order to minimise local overheating, which could further promote the highly exothermic complete oxidation reactions that are favoured at higher oxygen partial pressure [9,25,30]. Waterhouse et al. [25] obtained complete conversion of methanol when the ratio CH_3OH/O_2 decreased from 4 to 1.5 at a reaction temperature of 923 K. In their experiments, selectivity to formaldehyde showed a slight increase with decreasing CH_3OH/O_2 ratio up to a value of 2.25 and then a sharp decrease followed. This formaldehyde selectivity decrease was accompanied by a dramatic CO_2 yield increase and a modest CO yield increase. The observed behaviour was attributed to the surface concentration of the weakly adsorbed oxygen species O_α increasing with oxygen feed concentration and the reaction involving O_α becoming dominant at low CH_3OH/O_2 ratio. Lefferts et al. [9] similarly suggested that an increase of weakly adsorbed atomic oxygen species in increasing oxygen concentration, resulted to higher CO_2 selectivity. An investigation carried out under industrial reaction conditions by Kaszonyi et al. [59] showed that the reaction approached an unstable state by decreasing the molar ratio of CH_3OH/O_2 below 5. Reaction temperature and conversion increased immediately after increasing oxygen concentration and subsequently decreased rapidly after some oscillations of reaction temperature and product composition. The authors attributed this to partial deactivation of the catalyst, possibly due to overheating and sintering of the most active catalyst particles. Gavrillin and Popov [60] also observed catalyst instability in an intermediate temperature range (570–650 K).

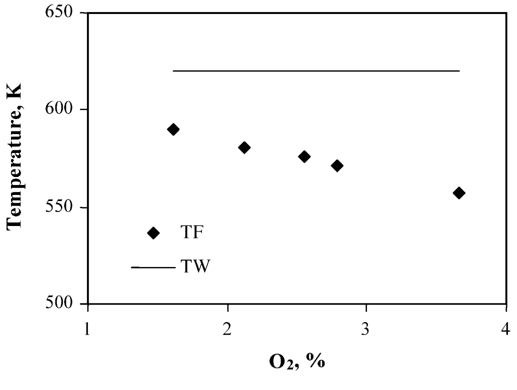


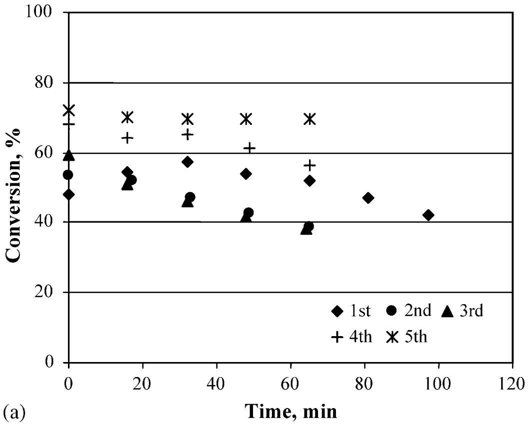
Fig. 5. Effect of oxygen concentration on the quartz tube reactor temperature (CH_3OH 8.06%, He as balance. Space velocity $6.0 \times 10^5\ h^{-1}$, $P = 1.52$ bar).

Silver powder catalyst showed good reactivity in converting methanol to formaldehyde in our experiments. However, the silver powder deactivated quickly after a few days use. By examining the discharged mixture of catalyst and quartz particles, coagulated silver particles were found. Millar et al. [61] observed coalescence of small silver particles into more extended structures as the temperature was elevated to 783 K, which is above the Tammann temperature for silver (643 K). Under reaction conditions, additional structural modification (pinhole formation) is induced by catalytic etching [12,62].

3.2. *Methanol oxidation in microreactors*

3.2.1. *Effect of bonding procedure on catalyst activation*

Fig. 6 shows the activation behaviour for two microreactors: MR200-1 was bonded in the AML anodic bonder under vacuum and MR200-2 in the home-made bonder in air. These activation curves are essentially conversion/time profiles for each reaction step of the oxidation/reaction cycles described earlier. It can be seen that in the case of MR200-1 (bonded in vacuum), the activity of silver built up slowly after each cycle.



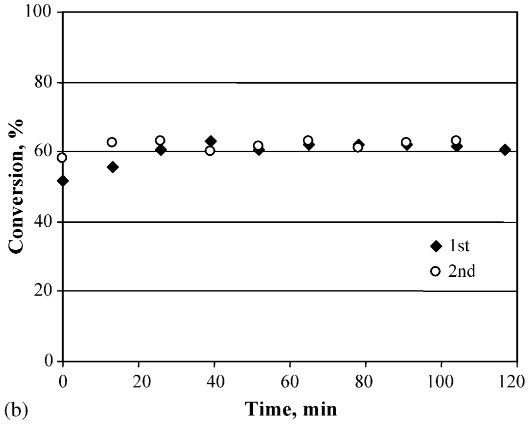


Fig. 6. (a) Activation behaviour of MR200-1 which was bonded in vacuum. (b) Activation behaviour of MR200-2 which was bonded in air (CH_3OH 8.6%, O_2 as balance, $\tau = 10$ ms, $T = 783.15$ K).

Stable conversion was reached after five oxidation-reaction cycles. However, activation of silver catalyst in MR200-2 was more straightforward. Stable and reproducible reaction activity was achieved after only two oxidation-reaction cycles.

Maréchal et al. [63] and Je et al. [64] prepared silver films by dc or rf sputter coating on single crystal silicon wafers. Fine columnar structures, epitaxial films and islands were observed depending on the sputtering conditions. Upon annealing, small islands conglomerated into bigger islands and thin epitaxial films were recrystallised. Millar et al. [65] and Bao et al. [13] suggested that oxidation at 773 K facilitated the reconstruction of silver planes due to formation of subsurface oxygen species. Prolong oxygen treatment caused particle fragmentation as a consequence of excessive oxygen penetration of the silver catalyst at defect sites which allowed the rapid diffusion of oxygen into subsurface positions of the silver lattice [11]. In contrast, high temperature treatment in vacuum induced significant sintering of the silver catalyst. The in situ Raman studies of Millar et al. [11] demonstrated that sub-surface hydroxyl species were formed by the interaction of methanol and sub-surface oxygen, very rapidly on a defected sample, whereas hydroxyl formation was extremely slow on large grained, smooth silver sample. Millar et al. [27] and Waterhouse et al. [57] further suggested that the morphology of silver catalyst (in particular pinhole formation) strongly influenced the 'start up' performance. The above observations can explain the different activation behaviour of the two microreactors. In the case of MR200-2, silver was exposed in air for a few hours during bonding at 723 K. A reconstructed silver surface possibly formed which was easy to activate. However, for MR200-1 which was bonded in vacuum, silver sintering may have occurred and many oxidation/reaction cycles were needed to reconstruct the silver so that it was active and stable for formaldehyde synthesis.

3.2.2. *Effect of oxygen concentration*

Most of the studies on methanol oxidative dehydrogenation considered low oxygen concentration. Since microreactors offer the opportunity of carrying out highly exothermic reactions safely, the effect of oxygen concentration was studied next. Oxygen concentration was varied from 3 to 91.4% while methanol was kept at 8.6%, corresponding to CH_3OH/O_2 ratio from 2.9 to 0.094. Results obtained from reactor MR120 are plotted in Fig. 7. It can be seen that conversion of methanol increases with increasing oxygen concentration at low oxygen level and reaches a maximum at oxygen concentration of ca. 12.5%. Further increasing oxygen concentration leads to a slight decrease of the conversion from 75 to 70%, when oxygen increases from 12.5 to 91.4%. Selectivity to formaldehyde decreases while selectivity to CO_2 increases up to oxygen concentration 12.5%. At higher oxygen concentrations (>12.5%), both selectivity to formaldehyde and carbon dioxide remain approximately constant. It is interesting to note that even when the reaction is carried out with undiluted oxygen, the selectivity to formaldehyde is kept at 90% at a conversion of methanol ~70% which is comparable with industrial practice [2].

In the low oxygen concentration range, increase in conversion of methanol and decrease in formaldehyde selectivity with oxygen were also observed in the experiments using the quartz tube reactor (see Fig. 4), in spite of the fact that the two reactors operated under different conditions (space

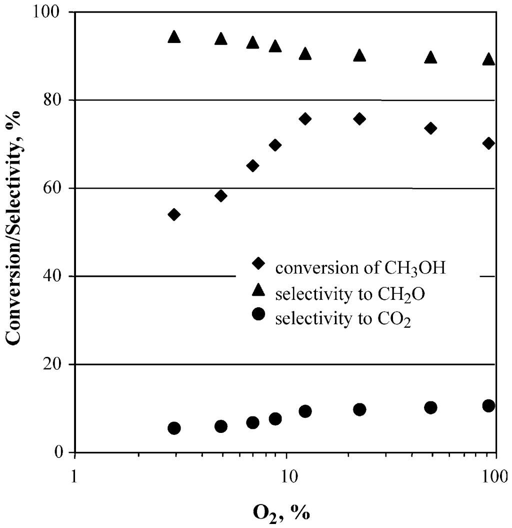


Fig. 7. Effect of oxygen concentration on methanol oxidative dehydrogenation (reactor MR120, CH_3OH 8.6% with He as balance, $T = 783$ K, $\tau = 10$ ms).

velocity (SV) 390 mmol $CH_3OH/cm^2Ag/min$ and $T = 620$ K in the quartz reactor, 95 mmol $CH_3OH/cm^2Ag/min$ and $T = 783$ K in the microreactor). The insensitivity of conversion at high oxygen concentration range agrees with the results of Robb and Harriott [30] at low CH_3OH/O_2 ratios. These investigators showed that at high oxygen concentrations the reaction is zero order with respect to oxygen. The selectivity behaviour with oxygen concentration is rather surprising. It is usually accepted that keeping oxygen concentration low is important in order to avoid formaldehyde combustion [6,9,29]. For example, Wang et al. [58] obtained 69.1% selectivity to formaldehyde at $CH_3OH/O_2 = 0.95$ (conversion was 98.9%). In our work, selectivity appears not to be affected at high oxygen concentration, and remains always above 90%. If H_2 is produced during reaction, it can react with oxygen to give water, which has been shown to improve selectivity [21,66], and this may explain the observed behaviour. Furthermore, if one considers the reaction mechanisms where CO_2 is formed from reaction of absorbed formaldehyde with surface atomic oxygen species [6,9,29,67], then the results at high oxygen concentration can be explained only if the concentration of these species reaches a saturation point and does not increase with further gas phase oxygen increase. In fact, Li et al. [68] demonstrated with density-function theory (DFT) calculations that a strong repulsion between surface oxygen species develops above a certain coverage forcing further oxygen adsorbing from the gas phase to subsurface sites. Similar postulations are applicable also for the reaction mechanisms where CO_2 is formed by O_α and adsorbed methanol or methanol/formaldehyde [13,15,18]. Due to the large surface to volume ratio and excellent heat conductivity of silicon, isothermal condition in the microreactor was easily maintained which may result in a stable surface morphology at reaction temperature hindering the change of O_α and O_γ concentration.

It is worth noting that some experiments were within the explosive limits of methanol/oxygen but were carried out safely. This is due to the smaller channel dimensions than the quenching distance for methanol (viz the critical distance below which no flame can propagate). The quenching distance for methanol by a cold wall has been reported to be 1500 μm [69], more than two times larger than the largest dimension of the microchannels used.

It is worth noting that CO_2 did not increase substantially at high oxygen concentrations, reflecting the absence of homogeneous combustion at 783 K. The lower CO_2 concentrations observed in the microreactor compared to the fixed bed reactor, may be related to different intrinsic catalytic reactivity. CO was not detected in the microreactor possibly due to the short residence time, low reaction temperature (783 K) and high oxygen concentration.

3.2.3. *Effect of reaction temperature*

Methanol conversion and selectivity to formaldehyde as a function of reactor temperature were studied in MR120 by varying reaction temperature from 723 to 829 K at a rate of 0.5 K/min while sampling and analysing with GC at 13 min intervals. The inlet flow contained 8.6% methanol and 94.6% oxygen. The reaction was carried out with both temperature ramping up and down. The results are shown in Fig. 8. A small hysteresis is observed at temperature between 723 and 773 K. Above 773 K, the results are almost identical in up- and down temperature cycles. This indicates that the catalyst had stabilized and physicochemical and morphological changes that had taken place during the activation period, had finished. Nagy et al. [17] observed hysteresis behaviour in fresh silver catalyst but it disappeared after treatment in excess of 873 K. Conversion of methanol increases almost linearly, while a slight decrease of selectivity to formaldehyde and a minor increase of selectivity to CO_2 are observed. The increase of methanol conversion with reaction temperature was observed in fixed-bed reactors in a similar reaction temperature range [9,17,25], with selectivity to CH_2O showing an increase and the selectivity to CO_2 decrease with temperature. In our microreactor the opposite behaviour is observed and this may be connected to the rich oxygen conditions employed. This result indicates that the mechanisms proposed by Nagy et al. [17], Lefferts et al. [9], Waterhouse et al. [25], and Andreasen et al. [29] under low oxygen concentration may not be directly applicable at high oxygen concentrations, since the unselective reaction routes seem to be suppressed. Homogeneous oxidation of methanol and formaldehyde was likely not involved since no significant increase in CO_2 conversion was observed in pure oxygen atmosphere.

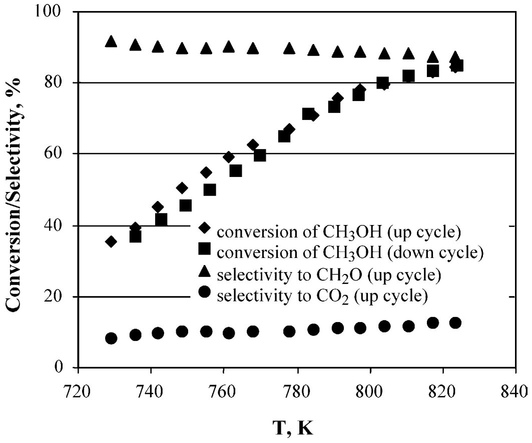


Fig. 8. Effect of reaction temperature on methanol oxidative dehydrogenation (reactor MR120, CH_3OH 8.6%, O_2 as balance, $T = 783$ K, $\tau = 10$ ms).

3.2.4. *Effect of methanol concentration*

Fig. 9 shows conversion and selectivity in MR120 at 783 K with methanol concentration varying from 6.8 to 13.5% (oxygen as balance). It can be seen that the conversion decreases with methanol concentration. The result shows that the reaction is ca. 0.5 order with respect to methanol. Similarly Bhattacharyya et al. [31], Robb and Harriott [30] and Lefferts et al. [9] obtained less than first-order dependence of reaction rate on methanol concentration. In Fig. 9, the selectivity to formaldehyde is shown to increase while to CO_2 to decrease slightly with methanol concentration. Similar trends of selectivity change with methanol have also been observed by Lefferts et al. [9] and Bhattacharyya et al. [31]. This behaviour

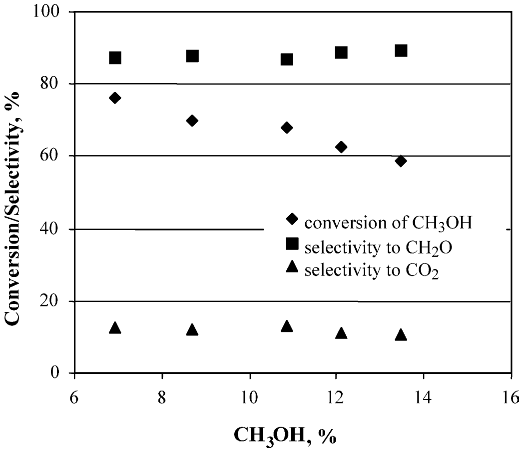


Fig. 9. Effect of methanol concentration on methanol oxidative dehydrogenation (reactor MR120, O_2 as balance, $T = 783$ K, $\tau = 10$ ms).

is consistent with most reaction mechanisms suggested, where a lower CH_3OH/O_2 ratio would promote complete oxidation of intermediates (see also Fig. 4).

3.2.5. Effect of residence time and microchannel depth

Effect of residence time on the reaction was examined in three microreactors with channel depth of 70, 120 and 200 μm respectively by varying the inlet flow and keeping the reactant concentration constant (Fig. 10). The residence time is defined as the ratio of reactor volume containing catalyst to gas volumetric flow rate (at reaction temperature). Conversion of methanol increases with residence time while selectivity to formaldehyde shows a corresponding decrease for all three reactors. The selectivity to CO_2 shows an exact reverse trend (not shown).

Methanol conversion increases with decrease of channel depth. Selectivity profiles show the exact reversed patterns. Since silver is deposited on the bottom surface of reaction channel, the catalyst surface areas in the three reactors are the same as long as the width and length of the reaction channel are kept the same. Even though decreasing channel size improves mass transfer, this is not expected to have any effect on the reactor performance since characteristic diffusion time (d^2/D_{diff}) is 4.0×10^{-5}, 1.6×10^{-5}, and 44×10^{-5} s for channel depth of 70, 120 and 200 μm, respectively. Reducing the channel depth leads to an increase in the ratio of catalyst surface area to reaction channel volume. The conversion in a shallow microreactor is then expected to be higher than that in a deep channel reactor if the residence time is the same and lower selectivity is related to the corresponding high conversion. If one plots Fig. 10 using a modified residence time (defined as catalyst surface area/total flow rate) the conversion curves for MR120 and MR200 almost overlap while the curve for MR70 is higher, possibly due to higher intrinsic catalyst activity (see Fig. 11).

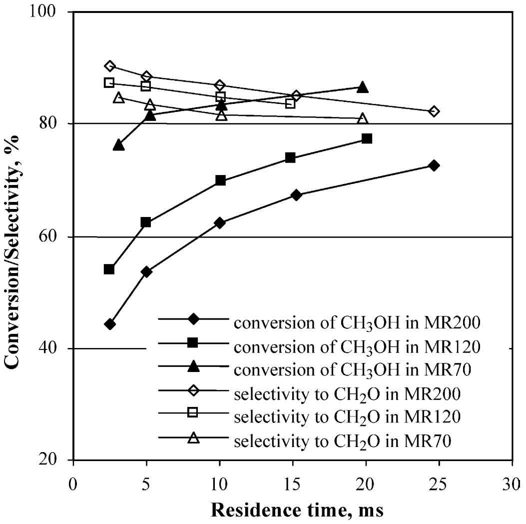


Fig. 10. Effect of residence time on methanol oxidative dehydrogenation in three microreactors (CH_3OH 8.6%, O_2 as balance, $T = 783$ K).

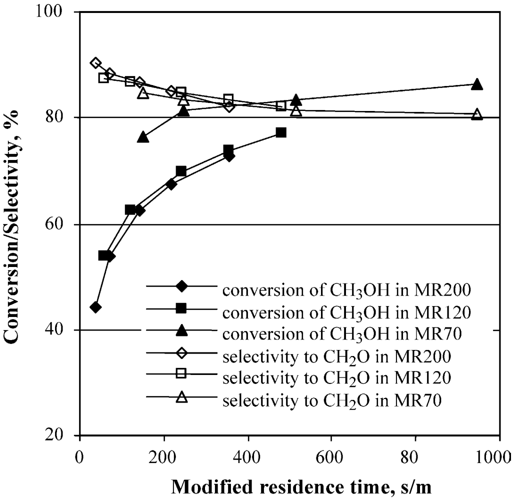


Fig. 11. Effect of modified residence time on methanol oxidative dehydrogenation in three microreactors (CH_3OH 8.6%, O_2 as balance, $T = 783$ K).

4. Conclusions

Microreactors fabricated on silicon were successfully used for the catalytic oxidative dehydrogenation of methanol. High conversion (~75%) and selectivity of 85% were obtained at a temperature of 783 K and residence time 3 ms for the MR70 microreactor. Selectivities remained high (above 90%) even when very high oxygen concentrations were used. Conversion decreased with increasing methanol concentration, indicating a ca. 0.5 order with respect to methanol. When the reaction was carried out in a small fixed bed reactor, significant transverse temperature differences were observed. Overall, the results showed the benefits of using microreactors in the study of highly exothermic reactions. Isothermal reaction conditions can be easily achieved even at high oxygen concentrations due to the high surface to volume ratio and a small amount of reaction mixture involved. The feasibility of varying oxygen concentration in a wide range makes it possible to use microreactors as a powerful tool for kinetic studies which are not achievable in conventional fixed-bed reactors even in laboratory scale.

Acknowledgment

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