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Catalyst instabilities during the liquid phase partial oxidation of methane

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Abstract

A promising catalytic system for the low temperature oxidation of methane to a methanol derivative has been investigated under both batch and semi-continuous operation in two different reactor types. The system comprises of a bimetallic palladium and copper(II) chloride catalyst contained in a trifluoroacetic acid (TFA) and an aqueous phase. Methane, oxygen and a co-reductant carbon monoxide constitute the gas phase. Typical operating conditions were a temperature of 85 °C and a pressure of 83 bar.

The yields of the methyl trifluoroacetate product observed in this present work were less than those obtained in other batch autoclave works, which employed only 4 ml of liquid phase, compared with 50 ml in this study. Furthermore, an encouraging initial product formation rate of ca. 40 mol/m^3 h, quickly decreased after the first hour, and came to an apparent end after only 2 h. This observation had not been reported previously.

Work performed in a semi-continuous porous tube reactor (300 ml of re-circulating liquid phase) also showed the same reaction characteristics as in the batch reactor. Thus, the deteriorating product formation rate cannot be attributed to gaseous reactant depletion (batch operation). The results suggest problems associated with catalyst instabilities, e.g. with the previously elucidated Wacker chemistry.

Keywords: Methane; Partial oxidation; Methanol; Palladium and copper catalysts; Wacker oxidation; Catalyst instabilities

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1. Introduction

The economic conversion of natural gas to liquid fuels represents a favourable alternative to the environmentally detrimental venting and/or flaring of the gas at the well head. In some regions the amount of gas vented or flared constitutes a significant fraction of the gross production, e.g. Africa. Furthermore, the transport of liquid fuels would be facilitated by the vast distribution infrastructure that is already in operation for crude oil [1]. In comparison, the transport of natural gas (mainly methane) either under pressure or liquefied (requires pressure and refrigeration) is a costly process. Methanol is an example of a high-energy liquid fuel, being the primary oxygenate of methane. It is produced on an industrial scale by an energy intensive, two-step process, with the generation of a synthesis gas intermediate. A direct one-step process would be highly desirable if the process economics and engineering aspects were favourable [2–5]. Also, a “simpler” process would be more easily fabricated on-site for the natural gas reserves found in remote locations.

A significant amount of research has been conducted on the subject of methane (the main component of natural gas) conversion to methanol or a

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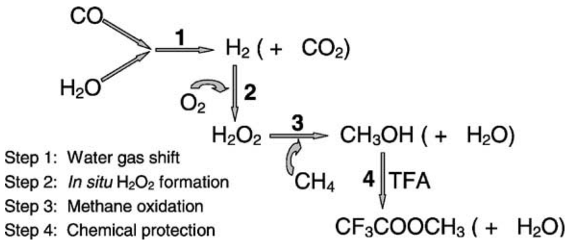
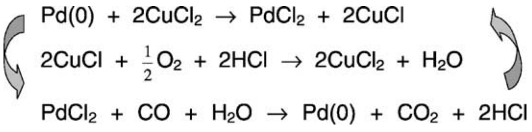
methanol derivative. The works can be broadly classified as being carried out either in the gas phase [6–10] or in a liquid phase medium [11–27]. The latter often incorporates activation of the methane substrate via organometallic complexes [28–31], with electrophilic-type mechanisms being prevalent [32] at relatively low temperatures. The selectivities here are often higher than in the corresponding gas phase whereby indiscriminate radical mechanisms lead to the formation of deep oxidation products (e.g. CO, CO_2).

Many of the more recent liquid phase systems for methane functionalisation have been carried out in protic media. The reasons are twofold; firstly the conjugate bases of strong acids are poorly co-ordinating, thereby enhancing the electrophilicity of the catalyst metal ion and secondly the acid serves to chemically protect the methanol from further oxidation by in situ esterification [31–33]. Trifluoroacetic acid (TFA) is an exemplary solvent for such reaction chemistry [17,20,23,25]. A downside to this protection system is the requirement to hydrolyse the methyl trifluoroacetate product back to the desired methanol as illustrated by Álvarez et al. [34].

To date the most promising liquid phase catalytic system for the conversion of methane to a methanol derivative is that discovered by Periana et al. [15]. The authors employed a medium of 100% sulphuric acid and mercury(II) ions giving an unprecedented methane conversion of 50%, with a methyl bisulphate product selectivity of 85% and a 43% yield. The catalyst was later superseded by a bipyrimidine complex of platinum(II) generating even more impressive results [16]. However, the possible use of mercury presents a disposal hazard and the long-term stability of the platinum(II) catalyst has been questioned [35]. Furthermore, the use of concentrated sulphuric acid as the stoichiometric oxidant could be costly, although it was envisaged that molecular oxygen could possibly be incorporated into the system to regenerate the sulphuric acid, although no experimental results for this have yet been published. Indeed, economic and environmental viewpoints suggest that molecular oxygen is the preferred terminal oxidant for the conversion process [31,32,36], although some earlier catalyst systems were incompatible (i.e. deactivated) in the presence of oxygen [37]. One promising system utilising molecular oxygen was developed by Lin et al. [13]. It employs a mixture of metallic palladium and copper(II) chloride in a solvent mixture of TFA and water. An unprecedented property of this system is its ability to effect C–C cleavage as well as C–H cleavage. Thus, methanol could be obtained from C_{2+} substrates, e.g. ethane, in a “one-pot” system, which has obvious implications for a variable natural gas feedstock. The chemistry bears an analogue with methane monooxygenase (MMO), the natural enzyme for the conversion of methane to methanol [32]. The synthetic system necessitates the use of carbon monoxide as a co-reductant for the generation of hydrogen from water, which ultimately reacts to form in situ hydrogen peroxide (H_2O_2). The proposed reaction pathway is shown in Scheme 1. In situ formed H_2O_2 is also a desirable route for the requirements of “green chemistry” [38] with its reduced form being simply water, and less expensive and safer than the direct use of this oxidant [36]. Additional work on the reaction mechanism by Park et al. [14] has indicated the involvement of Wacker chemistry for the oxidation of CO by the palladium and copper catalysts (Scheme 2). They proposed that while the Pd(0) was responsible for catalysing the formation of hydrogen peroxide, it was the oxidised Pd(II) that was used for the subsequent methane oxidation to methanol. Thus, the presence of both Pd(0) and Pd(II) was deemed necessary for an efficient system. One practical aspect of the aforementioned studies on this system is the use of only a small liquid phase volume of 4 ml together with a batch autoclave, which is



Scheme 1.



Scheme 2.

the classical reactor-type for this kind of study. However, no on-line liquid sampling or semi-continuous operation was mentioned in that study.

The present work applies the same catalytic system, but with larger liquid volumes in two different reactor types, one being a commercial batch autoclave and the other an "in-house" built semi-continuous (or semi-batch) porous tube reactor, which uses a ceramic porous tube as a gas–liquid distributor. This latter reactor accommodated 300 ml or more of a re-circulated liquid phase, and with on-line sampling facilities enabled a time-course behaviour of reaction to be established, not evident in the earlier works.

2. Experimental section

2.1. Experimental set-up and procedure

The liquid inventory comprised of a mixture of TFA and water in a 3:1 v/v ratio, which had previously been shown to be the most efficient composition for the oxidation reaction [13,14]. The use of a less expensive solvent, acetic acid, was briefly examined in this current study and although it displayed similar reaction credentials, e.g. batch reaction pressure drop and methane functionalisation, the corresponding methyl acetate product yield was less than that for the ester obtained using TFA. Therefore, further work involving this solvent was not pursued at this stage.

Copper(II) chloride (99.999%) was first dissolved in the water with a concentration range of 5–20 mol/m^3 depending on the experiment. Then the 5 wt.% Pd/C (catalyst loading = 0.25–1.4 kg/m^3) or the homogeneous $Pd(CH_3COO)_2$ was added ($[Pd^{2+}]$ = 0.12–0.66 mol/m^3). Finally, the TFA was added. The volume of the liquid mixture used in the experiments was 50 ml for the batch autoclave and 300 ml for the semi-continuous porous tube reactor.

The TFA (99.9%) was obtained from Apollo Scientific (UK), and the palladium and copper(II) chloride catalysts from Sigma–Aldrich Chemical. SEM analysis of the 5 wt.% Pd/C catalyst revealed a particle size range between 50 and 100 μm. The gases methane (99.5%), carbon monoxide (99.9%) and oxygen (99.5%) were supplied by BOC Gases Ltd. All chemicals were used as received, without any further purification.

(a) *Batch operation*: a 175 ml glass-lined 316 stainless steel autoclave was used, supplied by Baskerville Reactors and Autoclaves Ltd. (Fig. 1). A PTFE-covered magnetic-drive stirrer and thermocouple pocket were used to minimise contact of the reactants with the stainless steel walls. The effective volume of the vessel was ca. 125 ml for the gas and liquid together. The 50 ml liquid mixture, containing the catalysts, was added

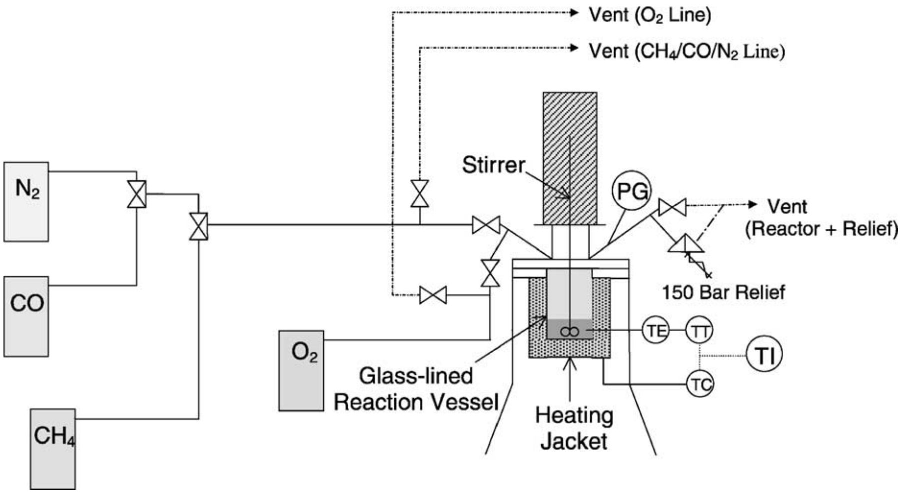


Fig. 1. Batch autoclave reactor set-up.

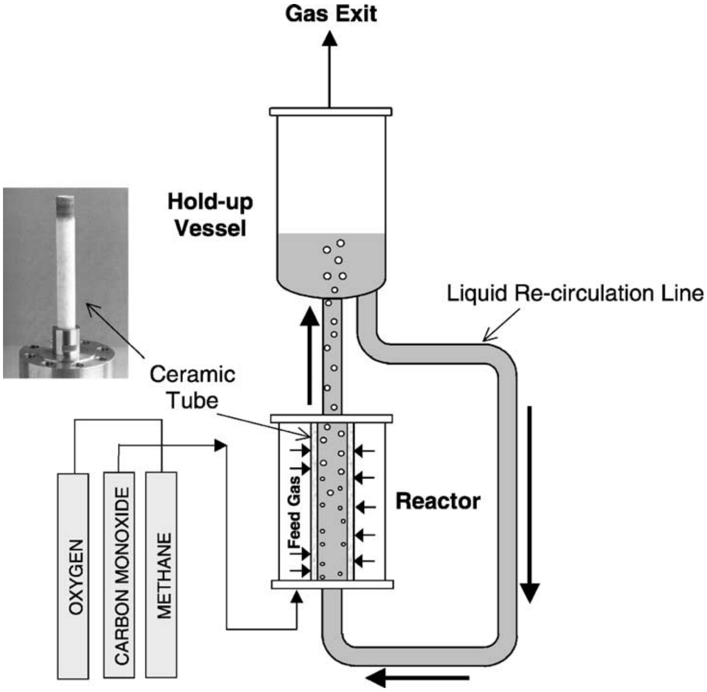


Fig. 2. Porous tube reactor simplified schematic.

to the glass-liner and placed inside the reaction vessel. The reactor was first pressure tested with nitrogen for two hours, vented and then purged with methane. The vessel was then preheated with 10 bar of methane to the desired operating temperature (no reaction occurred in the absence of oxygen). When a stable temperature had been reached, the methane pressure was adjusted to its required partial pressure (nominally 62 bar), followed by careful addition of carbon monoxide (14 bar) and then oxygen (7 bar). As the experiments were generally conducted below 100 °C, the contribution of the liquid phase vapour pressure was estimated to be of the order of 1 bar and so was neglected. The stirrer speed was then selected and the timing started with regular monitoring of the reactor pressure change and also the liquid temperature to ensure effective isothermal conditions. A stirring rate of 500 rpm or more was selected based on an experimental assessment of varying this parameter and observing that the external mass transfer was not limiting. Intraparticle diffusion in the small catalyst particles was estimated to be insignificant based on the Weisz-Prater criterion [39]. At the end of the experiment the heater unit was removed and the vessel was cooled quickly to ambient conditions using iced-water. The gases were slowly vented and the liquid contents removed for analysis.

(b) *Semi-continuous operation*: an “in-house” built porous tube reactor was used as shown in Fig. 2. The 316 stainless steel reactor allowed for a continuous supply of the three reactant gases (CH_4, CO and O_2) via thermal mass flow controllers (Brooks 5850S), with re-circulation of an initial 300 ml of liquid phase by the passive “air-lift” effect. The reactor pressure was controlled by two manual needle valves (Swagelok) positioned in the gas exit line and indicated by a Borden gauge (0–100 bar) supplied by S.M. Gauge Co. A differential pressure transducer (Ashdown Process Control Ltd.) was installed to measure the pressure difference between the reactor gas inlet and gas outlet from which inference of tube fouling/plugging could also be obtained. Gas–liquid contacting was achieved via a porous ceramic tube sealed with viton O-rings (James Walker) in a stainless steel flange. The alumina-based tube had the trade name Sillimantin 65 and was supplied by Multilab Ltd., with an approximate pore size of 1 μm. To reduce losses of the ester product, a concentric tube water-cooled condenser was connected in the gas exit line together with a smaller version in the liquid sample line, the latter which was operated prior to sampling. As with the autoclave, the liquid mixture (300 ml) was added to the reactor and preheated using 10 bar of methane gas, continuously flowing to induce the natural circulation of the liquid. Uniform heating of the liquid and hence the presence of liquid circulation was inferred by the onset of similar temperature readings from thermocouples (hastelloy, type K) located at various points circumventing the main reactor. When a stable temperature was reached an initial liquid sample was taken. The methane pressure inside the reactor and corresponding flow were then adjusted to the desired value, followed by a similar process for addition of carbon monoxide and then oxygen. The individual flowrates were selected based on the ratio of their batch partial pressures to obtain a total gaseous flowrate for all the gases of 2 l/min (0 °C, 1.013 bar), e.g. if the partial pressures for CH_4:CO:O_2 were 62:14:7 bar, the corresponding flowrates were 1.49:0.34:0.17 l/min. After the addition of oxygen, the timing was started. Every 30 min a liquid sample was taken and kept in ice prior to analysis. At the end of the experimental run, the heaters were turned-off and the reactor allowed to cool-down. The gas flows were then stopped and the reactor vented with the final liquid sample collected. The reactor was then thoroughly cleaned before its use for subsequent experiments.

2.2. *Analysis*

The liquid samples were analysed for the methyl trifluoroacetate product using a gas chromatograph (GC, HP 5890 Series II), equipped with an FI detector and using a helium carrier gas. A capillary column (BP20, SGE Europe) was installed for the analysis. Further verification of the product was performed via a gas chromatograph mass spectrometer (GCMS, Perkin Elmer Q-Mass 910). To avoid “plugging” of the column, the samples were completely distilled prior to analysis at 45–50 °C under vacuum, with a liquid nitrogen cold-trap.

Analysis for the presence of Pd^{2+} was performed using atomic absorption spectrometry (AAS, Varian AA-275 Series) calibrated with authentic standards (Sigma–Aldrich). The absorption wavelength selected for the palladium lamp was 244.8 nm, with acetylene and air being used for the oxidising flame. All samples were filtered prior to AAS analysis to avoid the presence of solid Pd(0) particles.

An attempt to measure the concentration of hydrogen peroxide in the reaction mixture was undertaken using titration with potassium permanganate. These results, however, showed only qualitatively the presence of hydrogen peroxide. The presence of a blue copper solution prevented a quantitative assessment from being obtained. A Philips X-ray diffraction (XRD) unit was also used to identify the existence of metallic palladium.

3. Results and discussion

3.1. *Batch autoclave reactor*

Experiments were carried out in the batch autoclave using similar base conditions (catalyst concentrations, etc.) as in [13], but with an increased liquid phase volume of 50 ml. The results are shown in Fig. 3 for both the methyl trifluoroacetate concentration and the reaction induced pressure drop. A change in reactor pressure had not been previously noted, probably because of the much higher gas:liquid volume ratio therein employed (in this present work a gas:liquid ratio of ca. 1.6 was used, compared with the earlier studies incorporating ca. 31 or greater). The first point to note was that less ester product was obtained in this work. For example, in 20 h at 85 °C, a concentration of 51 mol/m^3 was obtained in this work compared with 120 mol/m^3 at 85–95 °C [13]. This represents a product yield of only 1.5% (here yield = (concentration of ester product)/(initial charge of methane gas), with ideal gas behaviour assumed). However, the main point of interest here is the apparent end of reaction after only 2 h, although the product formation rate based on the first hour was an

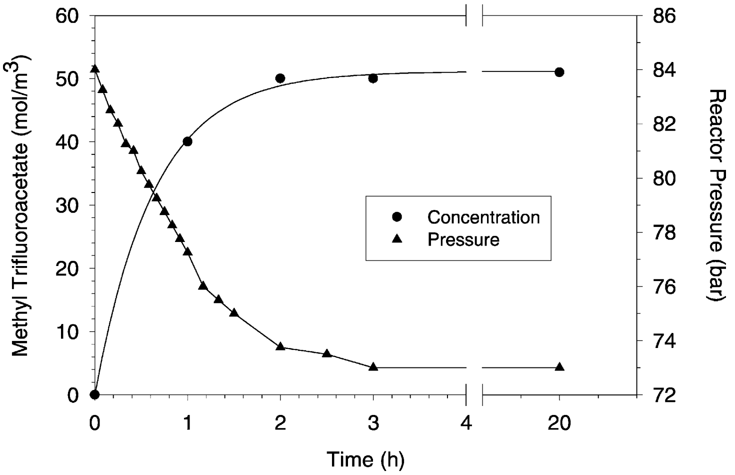


Fig. 3. Time course of methanol-based product (batch autoclave). Conditions: $P_{CH_4(i)} = 62$ bar, $P_{CO(i)} = 14$ bar, $P_{O_2(i)} = 7$ bar, 5 wt.% Pd/C = 12.5 mg, $[CuCl_2] = 20$ mol/m^3, TFA:H_2O = 3:1 (50 ml), $T = 85$ °C, $N = 500$ rpm.

encouraging 40 mol/m^3 h. To the contrary, Lin et al. [13] observed an increase in product formation over a time period of 90 h. In this current study, the decrease in reactor pressure also effectively ended after ca. 2 h. As the reactor was set-up for non-continuous experiments, one explanation to the observed behaviour was due to depletion of the reactant gases. This was later shown to be not the cause from semi-continuous experiments carried out in the porous tube reactor.

In this batch study, the observation of the change in reactor pressure during the time course of reaction could be linked with the overall gas consuming reactions depicted in Schemes 1 and 2. Additional experiments were also performed in the absence of the methane substrate, i.e. using only carbon monoxide, oxygen and a balance of nitrogen (Fig. 4). It can be seen that the pressure drop behaviour is similar to that obtained from using methane, with around 80% of the complete system pressure drop occurring without the use of this substrate gas. Applying the ideal gas law and including the stoichiometry of the process (Scheme 1) it was possible to calculate the pressure drop for the final amount of methyl trifluoroacetate (for $t = 3$ h, results shown in Fig. 3). A calculated pressure drop, $\Delta p = 2.02$ bar, was in good agreement with the experimental data presented in Fig. 4. This is represented as the difference between the final pressure drop for methane oxidation and that for the reaction without the presence of methane (Steps 1–4, and Steps 1 and 2, respectively, Scheme 1). The formation of hydrogen peroxide (see Reaction 1) was observed in both cases, however, as already explained in Section 2, due to the presence of coloured solution of copper salt, it was not possible to quantify the amount of hydrogen peroxide. Assuming quantitative conversion to hydrogen peroxide according to Scheme 1, it looks like that only ca. 20% of in-situ formed oxidant was used to produce methanol. Either part of the hydrogen peroxide underwent a decomposition reaction

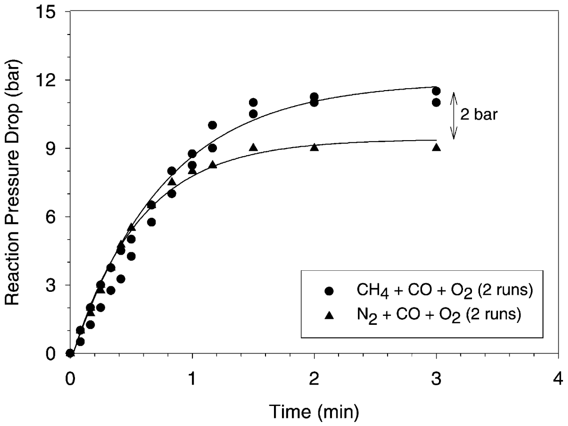


Fig. 4. Influence of methane presence on reaction pressure drop. Conditions: $P_{CH_4(i)}/P_{N_2} = 0$ or 62 bar, $P_{CO(i)} = 14$ bar, $P_{O_2(i)} = 7$ bar, 5 wt.% Pd/C = 12.5 mg, $[CuCl_2] = 20$ mol/m^3, TFA:H_2O = 3:1 (50 ml), $T = 85$ °C, $N = 700$ rpm.

(but its presence after 3 h was qualitatively illustrated) or the catalytic system for the final methane oxidation step was unstable. This aspect needs further experimental work. It might be also possible that the Wacker oxidation of carbon monoxide (Reaction 2) contributes to the total pressure drop.

$$H_2 + O_2 \rightarrow H_2O_2 \quad (1)$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \quad (2)$$

The batch reactor was also used to test the influence of stainless steel on the reaction performance using a sample of 316 stainless steel affixed to the stirrer (Table 1). This aspect had direct relevance for the porous tube reactor which, unlike the batch, incorporated no glass insert. The impact of the reactor wall material has been demonstrated in both gas phase methane partial oxidation studies [9] and those carried out in a liquid medium [21], with changes in the observed product selectivity and yield observed from using either the original stainless steel reactor material or a glass-lining. In both these aforementioned studies, radical-based chemistry was proposed, with any relatively unstable compounds being either oxidised or decomposed with this process being facilitated by the stainless steel walls [21]. The results for this current work, although by no means exhaustive, indicated no significant influence of stainless steel under the employed reaction conditions, with the same apparent end of product formation occurring after the first 2 h.

Table 1
Effect of 316 stainless steel on base reaction[a]

Batch time (h)	316 Stainless steel (Y)es/(N)o	Reaction ΔP (bar)	[Methyl trifluoroacetate] (mol/m^3)
1	Y	8	38
	N	7	40
2	Y	10	49
	N	9.5	50
20	Y	11	54
	N	11	51

[a] Conditions: $P_{CH_4(i)} = 62$ bar, $P_{CO(i)} = 14$ bar, $P_{O_2(i)} = 7$ bar, 5 wt.% Pd/C = 12.5 mg, $[CuCl_2] = 20$ mol/m^3, TFA:H_2O = 3:1 (50 ml), $T = 85\,^\circ$C, $N = 700$ rpm.

3.2. Semi-continuous porous tube reactor

The advantage of this reactor over the batch autoclave used in this work was that it accommodated larger liquid volumes and incorporated liquid sampling facilities. Furthermore, it allowed for the continuous supply of the gaseous reactants eliminating the effect of gaseous reactant depletion on product formation as may have been influencing the performance in the batch reactor. Lastly, the use of this type of reactor is somewhat of a novelty in this field of research.

The ceramic porous tube was primarily used as a gas–liquid contactor, but also lent itself as a catalyst support, as was previously demonstrated in another study involving the hydrogenation of α-methyl styrene [40]. An attempt was made to coat the inside of the tube with palladium, with prior addition of a γ-alumina washcoat, although on considering the redox chemistry between the palladium and copper catalysts (Scheme 2), this was proven futile with the metallic palladium leaching into solution (indicated by AAS analysis). The use of homogeneous palladium for this reaction was disclosed in a previous study [14] and shown to be as active as starting with bulk supported palladium, in accordance with the Wacker redox chemistry. Evidence of the presence of both oxidation states of palladium (Pd(0) and Pd^{2+}) in the final product mixture was also shown by AAS (Pd^{2+}) and XRD (metallic palladium). Therefore, palladium(II) acetate was used for experiments in the porous tube reactor, eliminating possible problems of valve blockages or maldistribution with the use of a bulk solid catalyst. The results are shown in Fig. 5. Similar product concentrations were obtained as in the corresponding batch work, even with five times the equivalent initial amount of homogeneous palladium catalyst being used. Interestingly, the effective end of product formation was again observed after ca. 2 h.

The effect of the amount of copper(II) chloride co-catalyst used was explored (Fig. 6) displaying a similarly reported trend [14] that both too much and too little copper(II) chloride was deleterious to reaction performance. According to Park et al. [14], the copper(II) chloride co-catalyst was involved not only in the redox chemistry of the Wacker oxidation of CO, but also as a provider of chloride ions which stabilise the palladium(II) oxidation state necessary for effective methane functionalisation (in this case

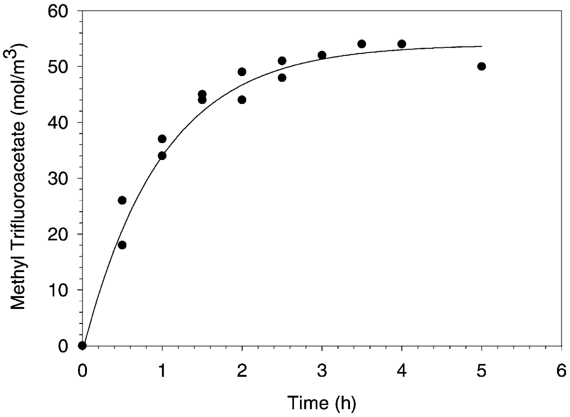


Fig. 5. Time course of methanol-based product (semi-continuous porous tube reactor). Conditions: $P_{CH_4(i)} = 62$ bar, $P_{CO(i)} =$ 14 bar, $P_{O_2(i)} = 7$ bar, total flow = 2 l/min, $[Pd^{2+}] = 0.66\,mol/m^3$, $[CuCl_2] = 4.9\,mol/m^3$, TFA:H_2O = 3:1 (300 ml), $T = 85\,°C$.

oxidation). However, if this Pd(II) oxidation state was prevalent in the reaction mixture, because it was also shown to catalyse the oxidation of CO then less of this co-reductant was available for the generation of the in situ oxidant (Scheme 1) and hence less product would be subsequently formed. This could explain why an excess of copper(II) chloride had a detrimental effect on the methyl trifluoroacetate product formation. It should also be noted that in the absence of chloride ions, no reaction pressure drop (batch autoclave) or methane functionalisation was observed in the present study. In the case of low $CuCl_2/Pd^{2+}$ ratio (=8) the reacting system did not come to an apparent end during the course of experiment. However, because of the low product formation rate (8 mol/m³ h) during the third hour of the experiment (comparing to standard 35–40 mol/m³ h for first hour), the experiment was not continued beyond a 3 h limit. The same was applied in the case of experimental data shown in Fig. 10 for heterogeneously catalysed methane formation.

The effect of the amount of palladium catalyst (Pd/C) had been previously reported in the original work [13] to have not been significant and was also verified in this study for the homogenous palladium. Increasing the amount of both the palladium and copper(II) catalysts had little impact on the reaction performance (Fig. 7). At this stage of investigation it is difficult to discuss the effect of individual components in the catalytic system (Pd^{2+}, Cu^{2+}, or Cl^-) on the overall performance of the reactor and the effect on the mechanism of the overall reaction. Further studies are necessary.

The influence of the partial pressures of both methane and carbon monoxide on the reaction is shown in Figs. 8 and 9, respectively. Although an increase in methyl trifluoroacetate product concentration was observed on using an increased partial pressure of methane or carbon monoxide, with an approximate first-order dependence being exhibited for methane, this had no impact on the characteristic

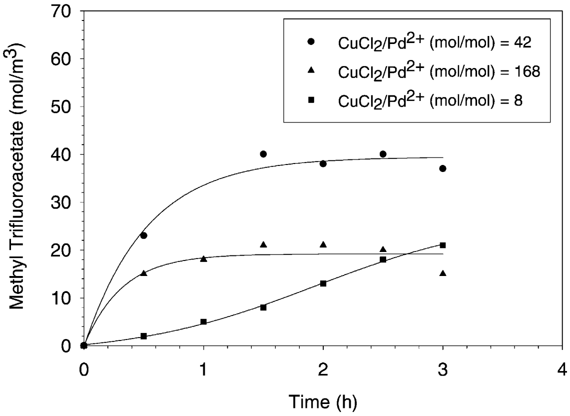


Fig. 6. Effect of $CuCl_2$ on product concentration. Conditions: $P_{CH_4(i)} = 62$ bar, $P_{CO(i)} = 14$ bar, $P_{O_2(i)} = 7$ bar, total flow = 2 l/min, $[Pd^{2+}] = 0.12\,mol/m^3$, TFA:$H_2O$ = 3:1 (300 ml), $T = 85\,°C$.

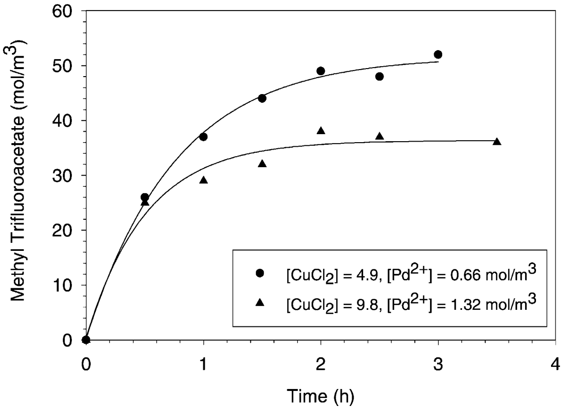


Fig. 7. Effect of doubling catalyst concentrations on product formation. Conditions: $P_{CH_4(i)} = 62$ bar, $P_{CO(i)} = 14$ bar, $P_{O_2(i)} = 7$ bar, total flow = 2 l/min, TFA:H_2O = 3:1 (300 ml), $T = 85\,°C$.

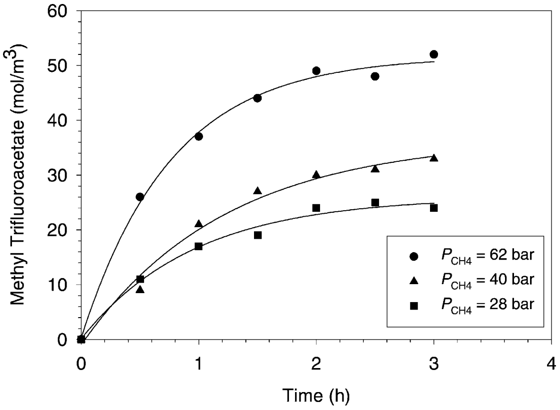


Fig. 8. Influence of methane partial pressure on product formation. Conditions: $P_{\mathrm{CO}(i)} = 14$ bar, $P_{\mathrm{O_2}(i)} = 7$ bar, total flow $= 2$ l/min, $[\mathrm{Pd}^{2+}] = 0.66\,\mathrm{mol/m^3}$, $[\mathrm{CuCl_2}] = 4.9\,\mathrm{mol/m^3}$, TFA:$H_2O$ = 3:1 (300 ml), $T = 85\,^{\circ}\mathrm{C}$.

behaviour of the product formation as the system “deactivation” was still apparent.

To ascertain whether the nature of the palladium catalyst starting material was relevant for the stability of this system, although not apparent from this current batch work, the supported Pd/C was briefly examined in the porous tube reactor (Fig. 10). Although less product was formed compared with the use of the homogeneous Pd^{2+}, the important point to note is still the occurrence of the apparent end of reaction.

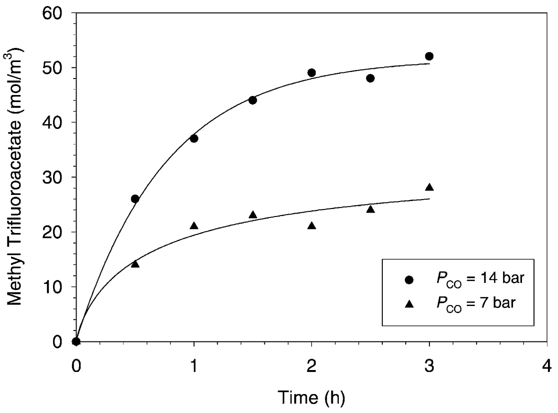


Fig. 9. Influence of carbon monoxide partial pressure on product formation. Conditions: $P_{\mathrm{CH_4}(i)} = 62$ bar, $P_{\mathrm{O_2}(i)} = 7$ bar, total flow $= 2$ l/min, $[\mathrm{Pd}^{2+}] = 0.66\,\mathrm{mol/m^3}$, $[\mathrm{CuCl_2}] = 4.9\,\mathrm{mol/m^3}$, TFA:$H_2O$ = 3:1 (300 ml), $T = 85\,^{\circ}\mathrm{C}$.

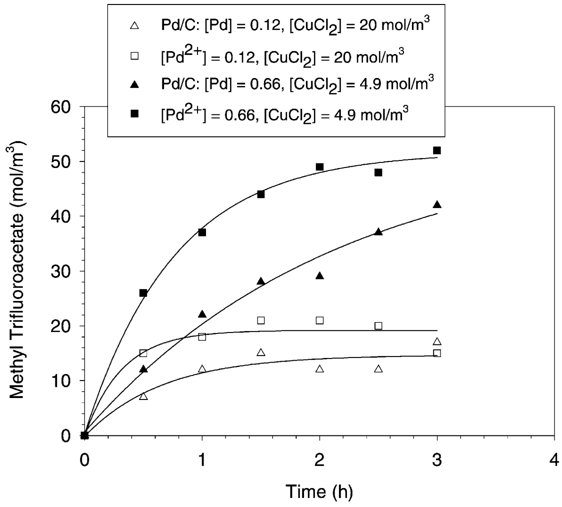


Fig. 10. Heterogeneous palladium versus homogeneous palladium catalysis. Conditions: $P_{\mathrm{CH_4}(i)} = 62$ bar, $P_{\mathrm{CO}(i)} = 14$ bar, $P_{\mathrm{O_2}(i)} = 7$ bar, total flow $= 2$ l/min, TFA:H_2O = 3:1 (300 ml), $T = 85\,^{\circ}\mathrm{C}$.

Being oxidative in nature, the reaction is unlikely to be limited by thermodynamic equilibrium. Also, additional experiments incorporating the ester product in the liquid feedstock showed that the reaction was not inhibited in some way by the ester itself. Therefore, from this study incorporating the use of both a batch autoclave and a semi-continuous porous tube reactor, it appears that instabilities in the catalyst system may be an explanation as to why the product formation was limited, although further work is undoubtedly necessary to verify the exact cause.

4. Conclusions

In this study, a previously discovered catalytic system for the conversion of methane to a methanol derivative has been applied in two different reactor types, employing an increased liquid inventory. In both cases, the results differ from those obtained in the original work [13] in that both the amount of product obtained was less and, more interestingly, the effective end of product formation was observed in this work after a relatively short time. The use of the two reactor types incorporating both batch and semi-continuous modes of operation, has indicated the likely presence of catalyst deactivation in this system limiting the achievable product yield. Although the observed initial reaction rate appears promising, in this system, "deactivation" limits the obtainable yield to less than 2%. This value is far removed from that required for a competitive industrial process, which has previously been estimated to be greater than 20% [33]. More work is necessary to identify the exact cause of this system bottleneck, which may be linked with the intricacies of the synergistic behaviour between the palladium and copper catalysts involved in the Wacker chemistry. Furthermore, difficulties in re-oxidation of the palladium(0) species, especially if allowed to aggregate, have been previously observed in other catalyst systems involving the Pd(II)/(0)/(II) cycle [41,42]. Once this understanding has been established, further studies on ameliorating the productivity can continue.

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