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Production and stability of low amount fraction of formaldehyde in hydrogen gas standards

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Abstract

Formaldehyde is an intermediate of the steam methane reforming process for hydrogen production. This molecule is required to be analysed at an amount fraction of 10 nmol/mol in hydrogen to allow its use for fuel cell electrical vehicles (FCEV) according to the international standard ISO14687. The production of formaldehyde gas standards in hydrogen is crucial to validate the analytical results and ensure measurement reliability for FCEV industry. NPL demonstrated that formaldehyde in hydrogen gas standard can be gravimetrically prepared and validated at 10 µmol/mol with 8 weeks shelf-life (stability uncertainty <10%; k=1). Formaldehyde showed instability and degraded into methanol and dimethoxymethane as shown by FTIR spectroscopy, GC-MS and SIFT-MS. The degradation kinetics is more rapid than predicted by thermodynamics and requires a catalyst, which may be linked to the internal cylinder surface. The presence of by-products (methanol and dimethoxymethane) requires further investigation to establish any potential undesirable impacts on FCEV lifetime.

Introduction

The demand for hydrogen fuel cell vehicles is growing across Europe and several countries worldwide have initiated national policies to rapidly introduce hydrogen technologies to the market over the next few decades. In the UK it is expected that there could be 1.6 million fuel cell vehicles on the road by 2030 supported by 1,100 hydrogen refuelling stations [1]. Hydrogen fuel cell vehicles have strict requirements in term of hydrogen purity [2]. Formaldehyde is an intermediate of the steam methane reforming process, which is currently the prevalent method for producing hydrogen. Without appropriate purification steps downstream of the process formaldehyde may end up in the hydrogen product. Formaldehyde is one of the 13 gaseous impurities that has to be monitored according to the international standard ISO 14687-2 [2]: if present in the hydrogen fuel it will reduce the lifetime of fuel cells [3]. It is therefore crucial for users and producers that formaldehyde in hydrogen is measured accurately.

One potential barrier that could prevent the uptake of hydrogen technologies in Europe is European Directive 2014/94/EU on the deployment of an alternative fuels infrastructure [3] which sets out that "The hydrogen purity dispensed by hydrogen refuelling points shall comply with the technical specifications included in the ISO 14687-2 standard." According to this directive it will be the responsibility of the hydrogen supplier or system integrator to obtain the evidence that proves that their hydrogen is of suitable purity to be provided to a fuel cell vehicle. This involves reliable purity testing to show that none of the threshold limits for the 14 impurities specified in ISO 14687-2 [2] are exceeded. The maximum limit for the amount fraction of formaldehyde is set at 10 nmol mol^{-1}, which represents an analytical challenge.

A recent literature review by Murugan and Brown [4] compiled all known gas analysis methods for performing purity analysis of fuel cell hydrogen. According to this review, a variety of analysers have been identified for performing measurement of formaldehyde in hydrogen such as cavity ring-down spectroscopy (CRDS) [5], gas chromatography–mass spectrometry (GC-MS) [6], chromatography with methaniser and flame ionisation detector (GC-methaniser-FID) [7] and Fourier-transform infrared spectroscopy (FTIR) [8]. In addition, other techniques have already demonstrated their capability to measure formaldehyde in air, as in the case of differential optical absorption spectroscopy (DOAS) [9] and tuneable diode-laser absorption spectroscopy (TDLAS) [10]. Recently proton transfer reaction mass spectrometry (PTR-MS) [11] and selected-ion-flow-tube mass spectrometry (SIFT-MS) [12] were used to measure formaldehyde in air. SIFT-MS was considered a promising technique to detect formaldehyde in hydrogen due to the sufficiently high detection sensitivity and its capability to work with a hydrogen gas matrix.

Recent inter-laboratory comparison studies from Hak *et al.* [13] and Wisthaler *et al.* [14] observed disagreements in the analysis of formaldehyde samples in air by different techniques. Panda *et al.* [15] attributed this disagreement to the difficulties encountered in the calibration of the instruments and emphasised the need for reliable and traceable formaldehyde gas standards. However preparing a formaldehyde gas standard is challenging due to the reactivity of the molecule itself and the difficulty to find high purity formaldehyde [15-16]. In general, Primary Reference Materials (PRMs) are prepared from the pure gas components, but formaldehyde is not easily available in pure form as it can polymerise into more stable forms such as trioxane or paraformaldehyde at room temperature [15-17]. A variety of methods have been used to generate calibrated mixtures of formaldehyde including permeation devices, diffusion cells, reaction vessels and static gas cells [16]. There are also several alternative methods, detailed in the literature, that usually require a reaction between stable compounds to form formaldehyde. Examples of these include the reaction between ethane and ozone or depolymerisation of *para*-formaldehyde or *alpha*-polyoxymethylene [15]. NPL has developed a method for producing 10 µmol mol^{-1} formaldehyde in nitrogen PRMs by heating trioxane to high temperatures (230 °C) [17]. At this temperature the solid trioxane decomposes into gaseous formaldehyde which then diffuses into an evacuated gas cylinder; the required matrix gas is then added directly into the cylinder. The key advantage of this method is that the amount of formaldehyde added to the gas cylinder can be accurately determined through a measurement of the mass loss of the trioxane and, unlike dynamic methods, no large flows of diluent gas are required (as is the case with permeation tubes and diffusion cells). Stability tests performed on the PRMs indicate that a loss between 1.6 and 0.07 nmol mol^{-1} per day could be achieved,

implying that for a mixture of 10 µmol mol^{-1} formaldehyde in nitrogen a loss of 26 to 576 nmol mol^{-1} would occur over a year. However the stability of mixtures of formaldehyde in nitrogen and of those in hydrogen are expected to be different; for instance, the reaction of formaldehyde with hydrogen to form methanol is the simple addition of hydrogen across the C=O double bond in formaldehyde. This reaction has been studied in the gas phase, as it is the final step in the formation of methanol from the reaction of hydrogen with carbon monoxide or carbon dioxide. These studies [18,19, 20] are based on high concentrations of hydrogen, carbon monoxide/carbon dioxide and formaldehyde; however the energetics of the system, which control the thermodynamics and kinetics of the reaction, are similar over all ranges of amount fraction.

It is therefore the purpose of this paper to describe the production of formaldehyde in hydrogen PRMs using the approach of Brewer *et al.* [17]. This paper also investigates the stability of these PRMs to underpin traceable purity measurements for quality assurance of fuel cell hydrogen. These mixtures are validated using four analytical methods (GC-MS with pre-concentrator, SIFT-MS, FTIR and GC-methaniser-FID) that have been developed as part of this work.

1. Materials and methods

1.1. Preparation of formaldehyde gas standards

Static reference standards of formaldehyde were prepared from diffusion of the trioxane sublimate followed by its thermal conversion, as detailed in the work by Brewer *et al.* [17]. A pellet of 1,3,5-trioxane (Acros Organics 99.5 %, 4-5mm in length and approximately 0.1 g in mass) was prepared and added to a transfer loop, consisting of a piece of 1/8 inch diameter tubing with Swagelok fittings on each end. A granule of phosphorous pentoxide (P_4O_{10}, Sigma Aldrich Company Ltd) was also placed in the transfer loop, which was then connected to a vacuum pump *via* a three-way valve. The transfer loop and the valve were evacuated to a pressure of 4×10^{-3} mbar to ensure no contaminants or air were present in the system or on the surface of the trioxane pellet. The evacuated transfer loop and valve were then weighed on a balance (Sartorius Research, UK). Following the weighing, a converter unit was connected to the transfer loop *via* the three-way valve. The converter, consisting of a long piece of 1/16 inch Silconert-treated tubing coiled within a thermally insulating jacket, was set to the optimum conversion temperature of (230 ± 1) °C. The output of the converter was connected to a minimised dead volume (MDV) valve developed at NPL on an evacuated cylinder (10 L Spectra-Seal cylinder, BOC, UK). The connection from the cylinder to the transfer loop (including the MDV valve and the converter) was evacuated to a pressure of 3×10^{-5} mbar. The transfer loop was then opened to the converter, followed by the opening of the cylinder valve: this enabled the transfer of trioxane *via* the converter to the cylinder. In order to prepare a mixture containing 10 µmol mol^{-1} formaldehyde in hydrogen, the transfer loop was left open for approximately 3 hours in order to transfer approximately 10 mg of formaldehyde into the cylinder. This was calculated from the vapour pressure of trioxane at 20 °C [17]. When the transfer was complete, the three-way valve on the transfer loop was shut but the cylinder valve was left open for an additional two minutes to allow the transfer of any residual formaldehyde in the capillary tube within the converter into the cylinder. After this, the cylinder valve was closed. The transfer loop and valve were disconnected from the converter and weighed: the mass difference between post- and pre-transfer corresponded to the mass of formaldehyde added to the cylinder. Prior to filling with pure hydrogen, the gas cylinder was weighed on a top-pan balance (Mettler Toledo KA30-3/P, UK). To prevent re- polymerisation of formaldehyde, the cylinder was filled with 10 bar of hydrogen just after the transfer of formaldehyde in the 10 L cylinder and then rolled for 20 minutes. After rolling the cylinder, the remaining 90 bar of hydrogen were added. Then the cylinder was weighed and rolled for a further two hours. A list of the mixtures prepared for this study is shown in Table 1. The reference amount fractions quoted were calculated from the masses of formaldehyde and hydrogen introduced in the cylinder. The purity of formaldehyde in the mixture was assessed by FTIR and GC-MS with a preconcentrator.

Table 1. NPL PRMs of formaldehyde amount fraction in hydrogen and associated uncertainty.

Mixture	Formaldehyde amount fraction and uncertainty (k=1) [µmol mol^{-1}]	Matrix	Date of preparation
A	12.85 ± 0.12	nitrogen	16/10/2013
B	9.88 ± 0.15	hydrogen	24/07/2015
C	10.00 ± 0.12	hydrogen	24/07/2015
D	9.88 ± 0.12	hydrogen	07/04/2016
E	11.11 ± 0.28	hydrogen	17/01/2017

1.2. Stability study of formaldehyde in hydrogen

The stability of mixtures B and C (Table 1) was monitored over 1.5 years. The mixtures were analysed on the day of production and then on days 3, 4, 5, 10, 18, 25, 40, 60, 83, 105, 139, 165, 203, 396 and 545 after preparation using a GC-methaniser-FID set-up. The measurements were made in comparison to mixture A, which was prepared in nitrogen and used as a stable reference [17]. Mixture D was analysed on the day of production, and then 4 and 8 months later using the same GC-methaniser-FID instrument. Mixture E was measured on the day of production at the same time as mixtures A, B, C and D to perform an isochronous stability analysis aimed at minimising the impact of day-to-day analysis variation: for this particular measurement, all mixtures prepared in hydrogen (mixtures B, C, D and E) were analysed under repeatable condition against the reference standard (mixture A). This allowed any variations between the mixtures in hydrogen and the standard caused by instability to be established.

1.3. Analytical methods

1.3.1. Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopic measurements of standards prepared at 10 µmol/mol of formaldehyde in hydrogen were made on a benchtop FTIR spectrometer (Nicolet 6700, Thermo Fisher Scientific, UK) equipped with N_2 purged multi-range optics, a KBr beam splitter and a liquid nitrogen cooled MCT-A detector. The spectrometer was fitted with a "White" type gas cell (Cyclone C5, Specac, UK) , nominal path length: 8 m and volume = 2 L, equipped with a borosilicate glass body and KBr windows. Absorption spectra of the formaldehyde standards and the background single beam spectra of a pure hydrogen gas (Hydrogen BIP®+, Air Products, UK) were made at a temperature of 29 °C, pressure of 1050 mbar with a sample flow rate of 0.5 L min^{-1}. The instrumental spectral resolution was 0.5 cm^{-1} and the spectral window ranged from 4000 to 640 cm^{-1}.

1.3.2. Gas chromatography with methaniser and flame ionisation detector (GC-methaniser-FID)

A GC-methaniser-FID (Peak Laboratories, USA) instrument was used to measure formaldehyde in hydrogen. The measurement routine involved a Hayesep D packed column (Peak Laboratories, USA) to separate the formaldehyde from other compounds. In order to ensure fast elution of the formaldehyde component, the oven temperature was set at 170 °C. Formaldehyde was converted into methane using a methaniser set at 270 ^{o}C, which was then detected using FID. The instrument was calibrated using a standard of formaldehyde in nitrogen (mixture A; National Physical Laboratory, UK). The analyses were performed under the same conditions for the duration of the study, with sample flow rates of 30 mL min^{-1} and the sample loop size of 5 mL. Prior to each run, the injection line was thoroughly purged seven times with high flow (above 100 mL min^{-1}) to remove any trace of contaminants from the previous analysis and any traces of air.

1.3.3. Gas chromatography with mass spectrometry (GC-MS) and preconcentrator

The sampling system employed to analyse the mixtures consisted of an Entech 7200 preconcentrator (Entech Instruments Inc., US) coupled to an Agilent 7890A GC with 5975C inert XL mass spectrometry detector (Agilent, US). This instrument was specially configured to detect dry or humidified samples of volatile organic compounds (VOCs) at amount fractions in the nmol mol^{-1} to µmol mol^{-1} regime.
Aliquots of gas (100 mL) from each gas mixture were introduced through a silanised stainless steel line into the preconcentrator, which contained three traps which were cryogenically cooled with liquid nitrogen to remove water vapour and permanent gases. Initially Trap 1 was cooled to -40 °C to collect the sample, and then was heated to 10 °C. The gas sample was then transferred into trap 2, which contained the sorbent Tenax, maintained at -30 °C. Trap 2 was then heated to 180 °C and the sample was then transferred to trap 3. This trap was cooled to -160 °C and then heated to 60 °C, to introduce the sample into the GC. The analysis of the formaldehyde in nitrogen and formaldehyde in hydrogen samples was carried out in the GC with a column (Agilent J&W) containing a stationary phase of DB-5MS (60m x 0.320 mm x 1.00 µm), which could operate in the oven temperature range -60^{0}C to 325 ^{0}C. In the GC method the oven was initially maintained at 35 ^{0}C for 5 minutes, and then temperature ramped to 85 ^{0}C at 10 ^{0}C min^{-1} for optimum separation of formaldehyde from other potential impurities. An important advantage of this method over direct injection into a GC was that the chromatographic retention times of the various components in the sample were not affected by matrix effects since the output of the preconcentrator in the GC contained little of the hydrogen diluent. The mass spectrometer was useful in conclusively identifying the parent formaldehyde and the presence of any impurities or decomposition products.

1.3.4. SIFT-MS

Analysis of the formaldehyde gas mixtures was carried out on a Syft Technolgies' Voice 200ultra SIFT-MS (Anatune, UK) directly from the gas cylinders. The sample was introduced to the instrument *via* a heated transfer line at 120 °C, using a flow passed configuration. The SIFT-MS instrument passively sampled at approximately 30 mL/min, with the flow controlled by a narrow-bore capillary. The samples were delivered directly from the gas cylinder to the instrument using 1/8 inch stainless steel tubing attached to the transfer line *via* a T-piece union. The

flow from the cylinder was kept above 50 mL/min, with the instrument sampling at the required rate, with any excess sample flow passing across the T-piece to vent. Full mass scans were run for the three positive reagent ions – H_3O^+, NO^+ and O_2^+ – from *m*/*z* 15 to 150 Da. Concentrations were calculated from the full mass scan data, using the reaction rate constants (*k*) available in the instrument library. The validity of these reaction rates have not been confirmed for compounds in hydrogen, therefore the results should be taken as indicative only.

1.3.5. Gas chromatography with pulse discharge helium ionisation detector (GC-PDHID)

A custom-made Agilent 7890A GC-PDHID (AC analytical controls BV, NL) performed accurate measurements of carbon monoxide in mixtures A, B and C. The GC was equipped with a Molsieve 5A PLOT column (30 m × 0.53 mm × 50 µm, Restek, UK) and used helium as carrier gas. The sample loop was 1 mL in volume and the sample flow rate was set at (30 ± 2) mL min^{-1}. The detector used was a pulse discharge helium ionisation detector from VICI (Restek, UK). The carbon monoxide retention time for the method used was 8 min. The instrument was calibrated using gravimetric standards of 0.1 and 1 µmol/mol carbon monoxide in hydrogen produced and validated by the National Physical Laboratory (Teddington, UK). Prior to each run, the injection line was thoroughly purged seven times with high flow (above 100 mL min^{-1}) to remove any trace of contaminants from the previous analysis and any traces of air.

1.4. Data treatment and evaluation

SIFT-MS quantification

Whilst SIFT-MS is inherently quantitative, the quantitation relies on accurate values for the ion-molecule reaction rate constants (*k*) for the reactions taking place in the flow tube. There are numerous literature sources for this data [21], however there is very limited data on reaction rate constants in hydrogen gas matrices. The *k*-values used in the calculations in this paper are derived from analytes in either nitrogen or air and consequently may not be correct. For this reason, the SIFT-MS results should be taken as indicative only.

Three *k*-value were used in this study: $k = 3.4\times10^{-9}$ cm^3 s^{-1} from Helium reaction rate '*k*' coefficients, $k = 1.16\times10^{-9}$ cm^3 s^{-1} derived from SIFT analysis of formaldehyde in nitrogen NPL gas standard (Reference value: 12.2 µmol/mol in nitrogen matrix) and a revised value of the *k* coefficient derived from SIFT analysis of formaldehyde in nitrogen NPL gas standard (decay rate: 1.6 nmol day^{-1}) to consider potential degradation of the standard over time $k = 1.35\times10^{-9}$ cm^3 s^{-1} .

Normalisation

As the response of the detectors coupled with gas chromatography can exhibit significant day-to-day variations, a data normalisation routine was applied to the stability study of formaldehyde in hydrogen by GC-methaniser-FID in order to limit the uncertainty or bias introduced by performing repeat measurements over long periods of time. The normalisation procedure was based on the assumption that mixture A (formaldehyde in nitrogen) was stable over the whole duration of the study. Mixture A was therefore used as the reference standard and the following equation was applied:

$$x_{\mathrm{norm,y,t}} = \frac{x_{y,t}}{x_{ref,t}} \qquad \text{Equation 1}$$

$x_{\mathrm{norm,y,t}}$ normalised formaldehyde amount fraction *y* at time *t*
$x_{\mathrm{y,t}}$ certified formaldehyde amount fraction for mixture *y* at time *t*
$xref_{,\mathrm{t}}$ reference formaldehyde amount fraction for mixture A at time *t*

The uncertainty reported was the combination of the measurement uncertainties of the sample and of the reference standard (mixture A), each estimated as the relative standard deviation of more than three measurements.

Stability

Due to the intrinsic variation of measurement results, no study can rule out the degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, *i.e.* to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is 0 ± x % per unit time".

Uncertainties of stability during dispatch and storage were estimated as described in [22] for each parameter. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contribution u_{sts} and u_{lts} are calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{\mathrm{lts,rel}} = \frac{RSD}{\sqrt{\sum \left(x_i - \bar{x}\right)^2}} \cdot t_{\mathrm{sl}}$$ Equation 2

RSD relative standard deviation of all results of the stability study
x_i result at time point i
$\bar{x}$ mean results for all time points
t_{sl} chosen shelf life (8 weeks at 18 ºC)

The following uncertainties were estimated:

- $u_{\mathrm{lts,rel}}$, the stability during storage. This uncertainty contribution was estimated from the (18 ± 2) °C study. The uncertainty contribution describes the possible degradation during 8 weeks storage at 18 °C.

2. Results and discussion

2.1. Validation of formaldehyde in hydrogen gas mixtures

The gas mixtures produced at 10 µmol mol^{-1} of formaldehyde in hydrogen were validated against a standard of formaldehyde in nitrogen (mixture A). The relative difference between the gravimetric formaldehyde amount fraction and the value obtained from the GC-methaniser-FID measurements was below 9 %. This difference may be due to the analytical method, or to the difference in matrix between the samples and the standard, or to the fast degradation of formaldehyde in hydrogen (Figure 1). FTIR and GC-MS were used to assess the presence of contaminants or by-products in the freshly prepared mixtures. As shown in Figures 2 and 3, the analysis support the fact that only formaldehyde was present in mixtures B and C on the day of production.

2.2. Stability of formaldehyde in hydrogen

2.2.1. Evolution of formaldehyde amount fraction in hydrogen over time

The evolution of the formaldehyde amount fraction in hydrogen was followed over time using the GC-methaniser-FID technique. As described above, this relied on the assumption that the standard in nitrogen (mixture A) was completely stable during testing. The stability of mixture A was assessed by CRDS against a dynamic standard generated by diffusion [17]. The amount fraction of formaldehyde in nitrogen was considered to be stable (decay rate: 1.6 nmol day^{-1}) within measurement uncertainty over the time of this study.

Figure 1 shows the normalised formaldehyde amount fraction in mixtures B and C over the timescale of this study. The first observation is the clear decrease in formaldehyde amount fraction: this appears reasonably linear for the first 300 days, only for the formaldehyde amount fraction to stabilise after this period.

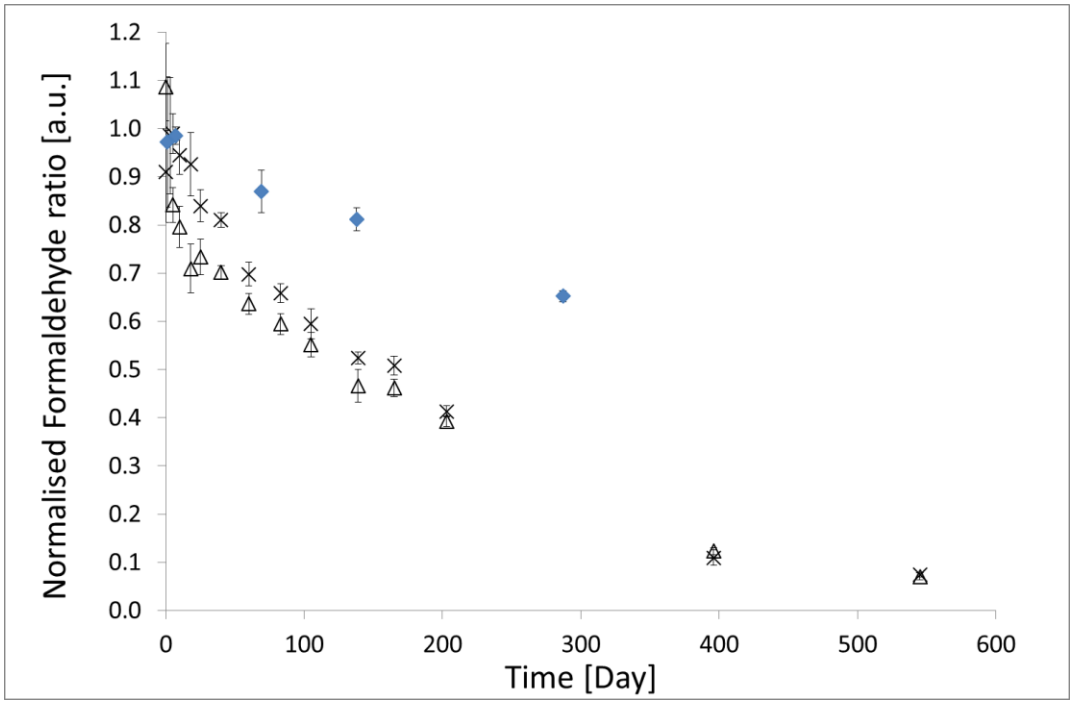


Figure 1. Normalised formaldehyde ratio of mixture B (symbol: x), C (symbol: Δ) and D (symbol: ♦) over time in days. Uncertainty is reported with k=1.

In order to certify gas mixtures, it is important to determine the uncertainty of the stability as defined in ISO Guide 34 [23]. For this reason and to minimise the impact of day-to-day variations, an isochronous study was performed. Standards prepared on different dates (in week 0, 56 and 78 since the beginning of the study) were analysed under repeatable conditions to observe deviations from the nominal amount fraction due to instability. For the isochronous study for formaldehyde, the time 0 (corresponding to mixture E), 56 (corresponding to mixture D) and 78 weeks (corresponding to mixture B) were evaluated. The slope of the linear regression was significant at the 95% confidence level. No outliers were observed using Grubb's test at the 95 and 99% confidence levels. For a given shelf life of 6 weeks, the relative stability uncertainty was estimated at 6.3 % (k=1) including the degradation uncertainty. For a given shelf life of 8 weeks, the relative stability uncertainty was estimated at 8.4 % (k=1) including the degradation uncertainty.

To evaluate the difference between an isochronous and a non-isochronous study, the normalised results of mixture B were used considering the following time points (0, 3.6, 8.6, 15, 23.6, 29, 56 and 78 weeks). The slope of the linear regression was significant at the 95% confidence level and no outliers were observed using Grubb's test at the 95 and 99% confidence levels. For a given shelf life of 6 weeks, the relative stability uncertainty was estimated to 7.1 % (k=1) including the degradation uncertainty. For a given shelf life of 8 weeks, the relative stability uncertainty was estimated to be 9.5 % (k=1) including the degradation uncertainty.

Regarding a shelf life of 8 weeks, the stability uncertainties obtained using the isochronous and non-isochronous analyses are in good agreement. For a formaldehyde standard in hydrogen, following the preparation procedure described in this study, it is recommended to use a stability uncertainty of 9.5 % for a shelf life of 8 weeks.

The degradation rate seems to be different between mixture D and mixture B and C (Fig 1). Cylinders B and C were purchased from the same batch, whilst cylinder D came from a different batch (purchased one year later). Cylinders batch effect could not be ruled out as mixture D appeared more stable than mixtures B and C, indicating that further investigations are required.

2.2.2. Determination of decomposition products

Following the observation of decreasing formaldehyde amount fraction in a hydrogen matrix, three techniques were used on mixtures B and C to identify the formaldehyde degradation products for over 1 year from preparation.

Fourier-transform infrared (FTIR)

The FTIR spectroscopic technique was used to identify the compounds present in the mixture. The first objective was to confirm the purity of formaldehyde. After preparation of the formaldehyde in hydrogen gas standard, the

FTIR spectra (Fig. 2B) clearly matched the reference spectra from the Pacific Northwestern National Laboratory database (PNNL) [24]. The presence of the by-products dimethoxymethane or methanol were absent (Fig. 2A). Comparison of the initial FTIR spectra of the mixtures with those taken more than one year later shows that formaldehyde has degraded with time as shown by the decrease in the principal absorption bands between 1810 – 1690 cm^{-1} (**Error! Reference source not found.**). Furthermore the appearance of new absorption features at 1300 – 900 cm^{-1} implies the presence of new species that were not present when the standards were initially prepared, supporting the idea of formaldehyde undergoing reactions under the reducing atmosphere within the hydrogen cylinder.

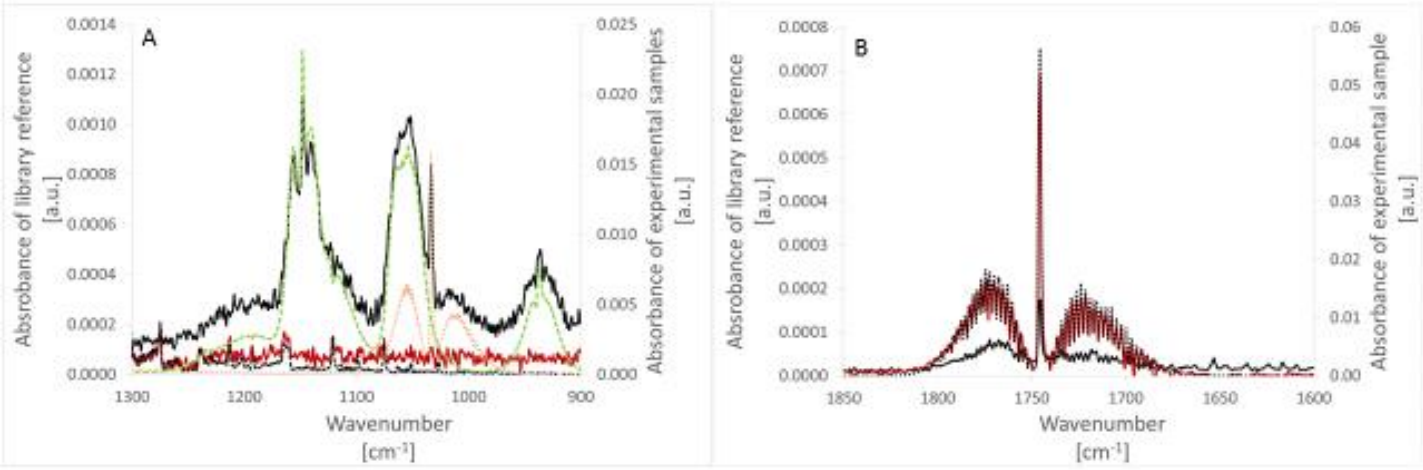


Figure 2. FTIR spectra of a formaldehyde in hydrogen standard after different storage times, held at ambient temperature. Figure **2A** presents the FTIR spectra in wavelength area 1300-900 cm^{-1}. This spectral region presents the characteristic absorptions from the C-O bond in the methanol and dimethoxymethane fingerprint. Figure **2B** presents FTIR spectra in wavelength area 1850-1600 cm^{-1}. This spectra region presents the carbonyl stretch of formaldehyde. The red line correspond to formaldehyde in hydrogen after 1 day of production. The solid black line correspond to formaldehyde in hydrogen after 1 year. The grey dotted line corresponds to the formaldehyde reference spectrum; the green dotted line to the dimethoxymethane reference spectrum and the yellow dotted line to the methanol reference spectrum. All reference spectra are taken from the PNNL database.

By referring to library spectra from the PNNL database [24], the presence of methanol and dimethoxymethane can be identified from the convoluted absorption bands around 1300 – 900 cm^{-1} (Fig 2A) and 3100 – 2500 cm^{-1}. The emergence of these species is the likely result of the reduction of the carbonyl bond within formaldehyde. The decrease of formaldehyde amount fraction over time (shown in figure 2B) is correlated to appearance of methanol and dimethoxymethane, after one year of storage.

SIFT-MS

The SIFT-MS technique was also used to identify the by-products of the formaldehyde degradation in hydrogen gas. The full mass scans were run for the three positive reagent ions – H_3O^+, NO^+ and O_2^+ – from *m/z* 15 to 150 Da for formaldehyde in hydrogen standard aged 3 months (E) and 1.5 years (C). The mass spectra using H_3O^+ clearly showed a strong signal for m/z 31 (CH_2OH^+) [21]. The mass spectra of the standard B using H_3O^+ ions (Fig. 4B) showed additional m/z ratio response at 45 and 75 which were identified as dimethoxymethane and at m/z 33 (CH_5O^+) identified as methanol [25]. The ions NO^+ confirmed the presence of m/z 45 and 75. The ions O_2^+ did not show additional compounds.

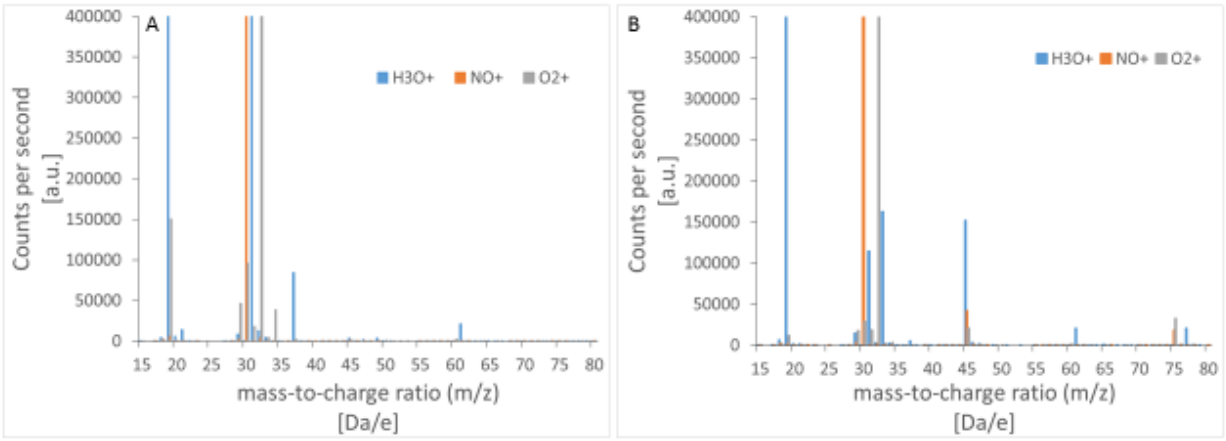


Figure 3. Full mass spectra from 15 - 80 Da/e using H_3O^+, NO^+ and O_2^+ ions of two formaldehyde in hydrogen standard. Figure 4A presents the spectra of standard E, formaldehyde in hydrogen standard only 3 months old, stored at room temperature. Figure 4B presents the spectra of Standard B, formaldehyde in hydrogen standard almost 1.5 year old, stored at room temperature.

The technique was able to measure and estimate the content of three compounds in the formaldehyde in hydrogen gas standard: dimethoxymethane, methanol and formaldehyde (Table 2). The amount fractions were estimated based on the *k* value from SIFT-MS database. The results clearly showed the presence of methanol and dimethoxymethane at amount fractions equivalent or above formaldehyde in mixture C (the oldest one). On the other hand, only formaldehyde is observed in mixture D and E by SIFT-MS. This supports the difference in formaldehyde degradation observed between the cylinders.

Table 2. Quantification of formaldehyde, methanol and dimethoxymethane in three standards of formaldehyde in hydrogen. The amount fractions were estimated based on the *k* value from SIFT-MS database.

Sample number	Number of day after production	Formaldehyde amount fraction [µmol mol^{-1}]	Methanol amount fraction [µmol mol^{-1}]	Dimethoxymethane amount fraction [µmol mol^{-1}]
C	602	0.74	0.99	1.57
D	344	4.63	0.02	0.05
E	59	4.56	0.03	0.04

The SIFT-MS techniques relies on reaction rate '*k*' coefficient in the SIFT database. NPL formaldehyde in nitrogen gas standard was used to determine a reaction rate '*k*' coefficient for formaldehyde in nitrogen. This new reaction rate '*k*' coefficient (k=1.16×10^{-9} cm^3 s^{-1}) was applied to quantify formaldehyde in hydrogen standard. The results of the different reaction rate are compared in Table 3.

Table 3. Quantification of formaldehyde amount fraction in three standard (C, D and E) using different reaction rate '*k*' coefficient (Helium and nitrogen)

Sample number	Quantification of formaldehyde amount fraction using Helium reaction rate '*k*' coefficients (k=3.4×10^{-9} cm^3 s^{-1}) [µmol mol^{-1}]	Quantification of formaldehyde amount fraction using nitrogen reaction rate '*k*' coefficients (k=1.16×10^{-9} cm^3 s^{-1}) [µmol mol^{-1}]	Quantification of formaldehyde amount fraction using nitrogen reaction rate '*k*' coefficient corrected for stability (k=1.35×10^{-9} cm^3 s^{-1}) [µmol mol^{-1}]
C	0.74	2.17	1.86
D	4.63	13.6	11.6
E	4.56	13.4	11.5

The quantification using the helium reaction and the nitrogen reaction rate provided completely different results. The use of the gravimetric value for formaldehyde in nitrogen required a slight correction to consider the potential degradation of formaldehyde over time using the decay rate of 1.6 nmol day^{-1} [17]. The standard E and D were quantified around 9.3 and 6.7 µmol mol^{-1}. It clearly showed that none of the reaction rate coefficient are entirely accurate for quantifying formaldehyde in hydrogen. The use of helium reaction rate led to a relative underestimation

of 28 - 51 %. The use of the corrected nitrogen reaction rate (k=1.35×10^{-9} cm^3 s^{-1}) led to a relative overestimation of 23 - 79%.

Matrix effect should be considered regarding the use of reaction rate coefficient. Moreover a clear need of traceability and robust reaction rate determination in hydrogen matrix is recommended to allow SIFT-MS to provide reliable quantitative value in hydrogen matrix.

Gas chromatography with mass spectrometer

The GC-MS with preconcentrator was used to perform analysis of mixtures A, B and C several times during the first 6 months (see Figure 4). The presence of formaldehyde was demonstrated by the mass spectra (most abundant m/z: 29). The presence of CH_3OH and $CH_2(OCH_3)$ were identified at 3.3 and 4.9 min respectively by the mass spectra. The mass spectra of the peak at 3.3 min showed strong abundance of the following mass over charge ratio 31, 44 and 60 Da/e which matched methanol. The mass spectra of the peak at 4.9 min should strong abundance of the following mass over charge ratio 29, 45 and 75 Da/e which matched dimethoxymethane.

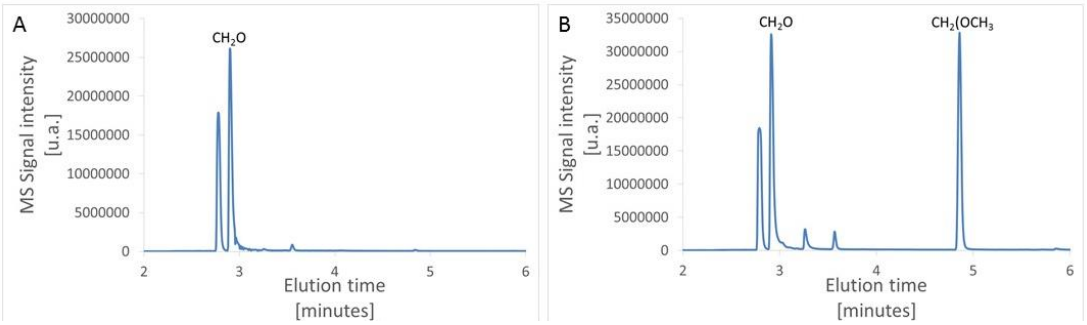


Figure 4. GC-MS with preconcentrator chromatograms for mixture B. The Figure 3A presents the chromatogram of mixture B after preparation (aged 1 day). Only one compound is present, CH_2O. The Figure 3B presents the chromatogram of mixture B after 80 days of storage at room temperature. Three species were identified using the mass spectra: CH_2O, CH_3OH and $CH_2(OCH_3)$.

The results clearly demonstrate the increase in methanol and dimethoxymethane peak area and the decrease in formaldehyde. The evolution of the ratio between dimethoxymethane and methanol was difficult to follow as the experiments were performed at different times.

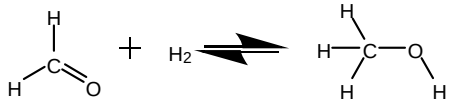
By-products results

The three techniques identified similar by-products of formaldehyde decomposition in hydrogen: methanol and dimethoxymethane. The ratio between methanol and dimethoxymethane was difficult to establish as no gas standards were available in a hydrogen matrix however they became the preponderant compounds in the formaldehyde in hydrogen mixture after several months.

For the purpose of hydrogen purity for fuel cell vehicles, the presence of carbon monoxide which has severe impact on the fuel cells and is a potential final by-product of formaldehyde decomposition, was investigated. Using the GC-PDHID instrument and gas standard of low amount fraction carbon monoxide in hydrogen, no carbon monoxide was observed above the limit of detection of our method (0.1 µmol mol^{-1}), which represents less than 1% of the original formaldehyde amount fraction. For this reason, carbon monoxide was not considered a significant by-product of formaldehyde in hydrogen as prepared in this study.

2.2.3. Thermodynamic stability of formaldehyde in hydrogen

The reaction of formaldehyde with hydrogen gas to form methanol as observed above is the simple addition of the hydrogen (hydrogenation) across the C=O double bond in formaldehyde (Equation 3). This reaction has been studied in the gas phase, as it is the final step in the formation of methanol between hydrogen and either carbon monoxide [18, 19] or carbon dioxide [20]. These studies were performed at high concentrations of hydrogen, and carbon monoxide/carbon dioxide or formaldehyde; but the thermodynamics are equally valid for this dilute system.



Equation 3. Methanol formation

Direct measurements [19], thermodynamic calculations [26], and *ab initio* calculations [27] all give that gaseous methanol is approximately 88 kJ mol^{-1} more stable than a hydrogen/formaldehyde gas mixture (see Table 4). This large enthalpy change indicates that formaldehyde should convert to methanol at equilibrium. Using the data from NIST, as presented in Table 6, the Gibbs free energy for the formation of methanol from formaldehyde was calculated at various temperatures as listed in Table 5. The calculated ΔG for the reaction is -56 kJ mol^{-1} at room

temperature (298 K) which is large and negative agreeing with the observed result that formaldehyde is unstable in hydrogen.

Table 4 Enthalpy and entropy change for the reactions

	ΔH_R [kJ mol^{-1}]	ΔS_R [J K^{-1} mol^{-1}]
$CH_2O + H_2 \Rightarrow CH_3OH$ (Table 6)	-89.1	-109.73
$CH_2O + H_2 \Rightarrow CH_3OH$ [19]	-88	-123
$CH_2O + H_2 \Rightarrow CH_3OH$ [27]	-84	-
$CH_2O + 2(CH_3OH) \Rightarrow CH_2(OCH_3)_2 + H_2O$	-63.93	-173.91

The equilibrium constant (*K*) was also calculated from the Gibbs free energy using Equation 2 (results in Table 5). Assuming that the concentration of formaldehyde and methanol is low (<< 1 %) and the balance is hydrogen at 1 bar then we can assume that the partial pressure of hydrogen, p_{H2}, is approximately 1. This simplifies Equation 5 so that *K* is effectively the equilibrium ratio of methanol to formaldehyde for these dilute systems.

$$\Delta G = \Delta H - T\Delta S = -RT \ln K \qquad \text{Equation 4}$$

$$K = \frac{pCH_3OH}{pH_2\ pCH_2O} \approx \frac{pCH_3OH}{ptot\ pCH_2O} = \frac{x_{CH_3OH}}{x_{CH_2O}} \quad \text{if } p_{H2} = 1 \text{ bar} \qquad \text{Equation 5}$$

This means that for a formaldehyde mixture at equilibrium, at room temperature and 1 bar, there should be 1x10^8 times less formaldehyde than methanol and there would still be about 200 times less formaldehyde at 300 ˚C. So for any volume of gas stored at room temperature, practically all the formaldehyde would be converted to methanol at equilibrium, assuming low initial amount fraction of formaldehyde. Table 5 also shows that temperatures need to be in the order of 500 ˚C or higher to make formaldehyde stable in hydrogen at reasonable concentrations at one bar, which would not be feasible for storing gas standards. As the pressure in the cylinder increases (p_{H2}) the amount of formaldehyde will decrease proportionally, so in the 100 bar test cylinders, there would be 100 times less formaldehyde at equilibrium. This is much lower than the measured amounts of formaldehyde, showing that the samples had not reached equilibrium over the course of the experiments.

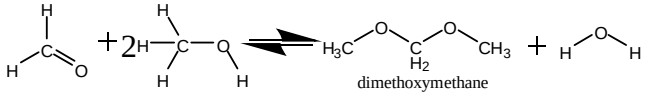
Table 5 Gibbs free energy and Equilibrium constants for the hydrogenation of formaldehyde at various temperatures based on thermochemical data from Table 6.

Temperature [K]	Temperature [˚C]	ΔG_R [kJ mol^{-1}]	Equilibrium constant [K]
298	25	-56.4	7.70 x 10^9
373	100	-45.2	5.57 x 10^6
573	300	-23.3	245
773	500	-1.3	1.95
973	700	+20.6	0.11

Thermodynamic stability: Dimethoxymethane formation

The other species observed in the gas mixtures was Dimethoxymethane (DMM, Methylal) which forms from the reaction of two methanol molecules with one formaldehyde molecule as shown in Equation 4. As with methanol formation, the formation of DMM (and water) is exothermic (64 kJ mol^{-1}), with equilibrium position favouring DMM formation up to 367 K (94 ˚C) (data from Table 6). This equation suggests there should be water formation as well that was observed after 1 year storage. Water amount fraction was measured using cavity ring down spectrometer after 1 year in mixture B and C. The amount fraction in both mixture was between 2.0 - 2.4 µmol/mol. which is coherent with the equation.

The thermodynamics clearly agrees with the observed data that a mixture of dilute formaldehyde in hydrogen is unstable when stored below 300 ˚C, and will completely convert to methanol or methanol and DMM at equilibrium. The timescale of this process is clearly on the scales of weeks to months, but it is useful to look at the kinetics to understand the process better and to understand why the species formed were different in the two samples.



Equation 6

Methanol formation Kinetics

Ab initio studies of this system [27;28] provide an estimate of the activation barrier for the conversion of formaldehyde to methanol, and which can be used to give an indication of its reaction kinetics. The activation energy barrier (ΔE_a) for the gas phase reaction of formaldehyde and hydrogen is estimated in the range between 250 kJ mol^{-1} [28] and 290 kJ mol^{-1} [27]. This is a very large energy barrier and will result in very slow kinetics at low temperatures. Assuming Arrhenius kinetics, with reaction rate constant k defined as $k = Ae^{-\Delta E_a/RT}$, and with the pre-exponential factor (A) of 10^{-11} and ΔE_a = 292 kJ mol^{-1} from Jasper *et al* [27], the rate formation of methanol at 25 ˚C would be approximately 4.2 × 10^{-40} Pa s^{-1}. This is extremely slow, and implies that formaldehyde in the mixture would be kinetically stable with respect to the gas-phase reaction with hydrogen for considerable periods of time at ambient temperature.

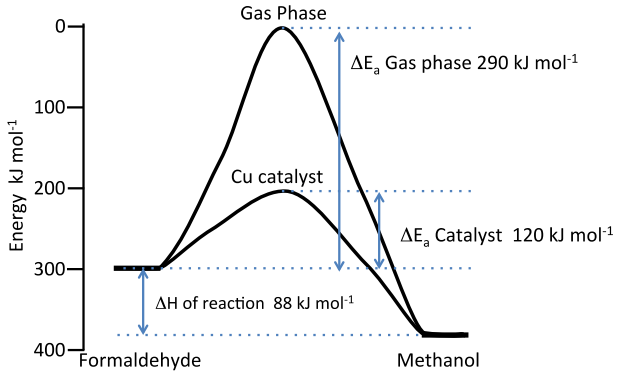
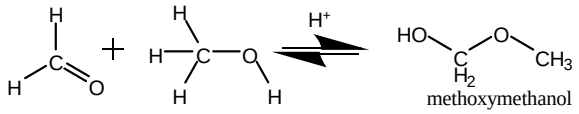


Figure 5 Reaction pathway based on data from Jasper at al. [28] and Studt et al. [32].

However formaldehyde adsorbs strongly onto surfaces (one of the reasons why it is a poison to fuel cell catalysts [29]). This adsorption is thought to facilitate the hydrogenation reaction. There have been several studies on the kinetics of hydrogenation on various catalytic surfaces such as platinum, nickel, palladium, ruthenium, cobalt, rhodium, osmium, iridium, and iron [30-31], copper [32], iron carbides [33], copper-zinc [34], etc. All surfaces show significant catalytic activity with the activation barrier dropping, for example, to 107 kJ mol^{-1} on copper [32] or to 125 kJ mol^{-1} on nickel(111) [31]. The various energy levels are depicted in **Error! Reference source not found.**. This much lower barrier, along with the enhanced surface concentration resulting from formaldehyde adsorption, would give a significant turnover of formaldehyde in a reasonable at even room temperature. With the low levels of formaldehyde and the still lengthy time scales observed above, it would only require a small amount of catalyst in a cylinder, such as exposed iron or nickel inclusions in the stainless steel or any metal fragments/dust on the cylinder internal surface to produce the observed reaction rate.

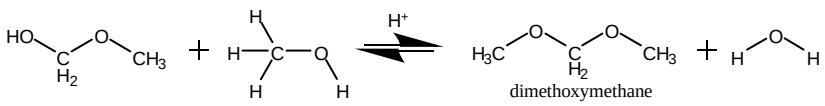
DMM kinetics

The mechanism to form DMM is a two-step process with the reaction of one formaldehyde with one methanol to form the hemicetal methoxymethanol, (**Error! Reference source not found.**), then the addition of another methanol to the hemiacetal to form the stable acetal, DMM, (**Error! Reference source not found.**) [35].



Equation 7

$CH_2O + CH_3OH \Leftrightarrow CH_2OH\text{-}OCH_3$



Equation 8

$CH_2OH\text{-}OCH_3 + CH_3OH \Leftrightarrow H_3CO\text{-}CH_2\text{-}OCH_3 + H_2O$

Both these steps need an external source of H^+ to occur [36] therefore this reaction cannot happen in a purely gaseous system, unlike methanol formation. It requires either an acidic solution or a solid acid catalyst to occur. However any catalyst that could adsorb formaldehyde and aid its conversion to methanol, is also probably capable of catalysing this reaction. The presence of DMM in only one cylinder suggests that it has a slightly different catalytic

impurity than the other cylinder. This also means the amount of the two species will depend on the type and amount of catalyst present.

The thermodynamic data agrees with the observed results, that the dilute formaldehyde in hydrogen will hydrogenate to form methanol and/or dimethoxymethane. However both these species require a catalyst to form at the rate observed. The rate of conversion and the species formed will entirely depend on the adventitious materials in the cylinder that act as the catalyst, which will vary from cylinder to cylinder as seen between similar cylinders B and C and later cylinder D.

Table 6. Thermochemical data of species, data from NIST [26]

	ΔH_f [kJ mol^{-1}]	S [J K^{-1} mol^{-1}]
CH_3OH	-205	239.9
CH_2O	-115.9	218.95
H_2	0	130.68
$CH_2(OCH_3)_2$	-348	336
H_2O	-241.83	188.84

Table 7. Kinetic related Data used for the calculation

Variable	Initial unit	SI unit
Partial Pressure H_2	100 Bar	1 x 10^7 Pa
Partial Pressure CH_2O	1 ppm	10 Pa
Pre-exponential A [27]	2.285 × 10^{-11} cm^3 molecule^{-1} s^{-1}	5.55 x 10^3 Pa^{-1} s^{-1}
ΔE_A Gas phase [27]	35080 K	292 kJ mol^{-1}
ΔE_A Cu surface	1.11 eV	107 kJ mol^{-1}

2.3. Recommendations to the hydrogen industry

This study has demonstrated that formaldehyde is unstable in hydrogen. The observed degradation kinetics is quicker than that calculated from the thermodynamic data and may be linked to a catalytic conversion. Reactive surfaces in the cylinder and, by extension, the piping material used in the hydrogen industry may act as catalyst for the hydrogenation of formaldehyde. Therefore the absence of formaldehyde in a hydrogen sample may be linked to similar reactivity. If that was the case, the by-products observed in this study (methanol and dimethoxymethane) may be present in a real hydrogen sample. During this study, a real sample of hydrogen from the electrolysis process was analysed for methanol and dimethoxymethane by GC-MS with preconcentrator, which was the most sensitive technique available. No formaldehyde, methanol or dimethoxymethane were observed; which was expected as the electrolysis process would never form formaldehyde during operation. Further studies are required to investigate the presence of the formaldehyde by-products in real samples from the steam-methane reforming process, which are more likely to contain formaldehyde impurities. Moreover, as the formaldehyde would immediately convert to methanol and dimethoxymethane by-products, the impact of these impurities to fuel cells should be studied as they could contribute to degradation.

Summary

NPL successfully prepared gas standards of formaldehyde in hydrogen. The mixtures prepared were stable for 8 weeks to within a 10 % uncertainty, mainly due to formaldehyde degradation. The main degradation products were identified as methanol and dimethoxymethane by means of FTIR, GC-MS and SIFT-MS. Thermodynamic calculations confirmed that formaldehyde is unstable in hydrogen and reacts to form methanol, which can go on to form dimethoxymethane (as well as other possible compounds). These reactions however do need some form of catalyst to occur at reasonable rates at room temperature (which could be cylinder walls or the metallic inner surface of the hydrogen refueling station). The catalytic nature of formaldehyde instability indicates that the cylinder or vessel used is crucial to determine the mixture stability. For the purpose of this study, aluminum cylinders with a surface passivation treatment (Spectraseal, BOC, UK) were used as the current state-of-the-art. Primary reference Material of formaldehyde in hydrogen can be indeed prepared bearing in mind that a short shelf life should be provided (8 weeks for stability uncertainty of 10 %). The mixture uncertainty will be strongly linked to the stability uncertainty and the validity of the certified value. Further studies are required to determine if new cylinder types or surface passivation techniques can reduce the catalytic degradation of formaldehyde.

The study has also directly called into question the very presence of formaldehyde in hydrogen produced in industrial processes (electrolysis, steam methane reforming or chlor-alkali) as the gas lines used may provide sufficient catalytic surface area to ensure transformation of formaldehyde into methanol or dimethoxymethane (if formaldehyde would have been present in the first place). The presence of methanol or dimethoxymethane may

therefore be a marker for formaldehyde impurities. This study did not observe any degradation of formaldehyde into carbon monoxide providing that this is unlikely to happen during hydrogen production.

Further studies are required to investigate other preparation methods of mixtures of formaldehyde in hydrogen (i.e. dynamics methods) as well as to establish the presence of formaldehyde by-products in real samples of hydrogen coming from hydrogen refueling stations. If these findings prove that there is very little risk of formaldehyde being present in hydrogen provided to fuel cell vehicles, it would be sound evidence for removing this impurity from the ISO 14687 specifications.

Acknowledgements

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Production and stability of low amount fraction of formaldehyde in hydrogen gas standards

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