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Temperature-staged methanation: An alternative method to purify hydrogen-rich fuel gas for PEFC

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Abstract

The preferential CO oxidation (PROX) is considered to be the only reliable technology for purifying hydrogen-rich fuel gases applied to the polymer electrolyte fuel cells (PEFCs), but the technology demands a close control of its oxidant supply. In this article we devised an oxidant-free technology called the temperature-staged methanation. Over a 0.5%Ru/Al_2O_3 catalyst we found that the complete selective CO methanation without CO_2 methanation is possible for hydrogen-rich gases containing CO of up to 1.0 mol%, provided the reaction temperature is controlled to be lower than a critical value. This critical temperature decreased with decreasing the initial CO content in the gas. Consequently, with methanation high-selective CO removal from CO_2-rich hydrogenous gases can be realized through dividing the required catalyst bed into more than one reaction zones that run at gradually lower temperatures. While at least one upstream zone at a higher reaction temperature performs to methanate most CO present in the treated gas under selectivity close to 1.0, the last zone at a lower temperature is conditioned to assure the desired outlet CO levels of lower than 100 ppm under selectivity above 0.5. The overall selectivity to methanate CO of the multi-staged reaction system depended on the number of the adopted reaction stages, which was shown to be possibly 0.95 in a three-stage system treating a simulated reformate consisting of (in volume) 69% H_2, 30% CO_2 and 1.0% CO and with water steam of 55% of the dry gas.

Keywords: Selective CO methanation; PROX; Fuel cell; Hydrogen purification; Ru catalyst

1. Introduction

Power generation with the polymer electrolyte fuel cell (PEFC) requires necessarily a fuel gas cleanup unit to reduce the residual CO present in the hydrogen-rich fuel gas, which comes usually from an upstream water-gas-shift (WGS, Eq. (1)) reactor, to the PEFC-anode tolerable levels. The tolerable CO levels of PEFC have long been considered to be below 10 ppm when only pure-Pt anode catalyst was available [1]. By applying several advanced anode technologies this stringent tolerance has recently been greatly relaxed. The state-of-the-art anode catalysts are steadily tolerant to CO contents of up to 100 ppm, even possibly to a few hundreds of ppm [1–4]:

$$\text{CO water-gas-shift}: \quad CO + H_2O \leftrightarrow H_2 + CO_2, \quad \Delta H^0_{298} = -41\ \text{kJ/mol} \qquad (1)$$

Theoretically, there are several methods that can be used to remove CO from hydrogen-rich gases [5–8]. As for the applications of PEFCs to transportation vehicles, residential co-generators and portable devices, however, the feasible choice may be only between the preferential CO oxidation (PROX) and selective CO methanation (SMET) because of the limited available spaces and low operating pressures in such application systems. The PROX has so far been extensively tested [9–11] since it is somehow reliable to remove CO down to 10 ppm by raising the oxygen consumption unlimitedly. Nonetheless, the technology requires a closely controlled low O_2 supply to keep the possibly lowest H_2 oxidation and a generally narrow window of suitable working temperatures. This, while making the method costly and complicated, obviously hinders its application to low-power PEFCs where very small oxidant flows have to be provided by use of well-refined expensive flow meters, such as mass flow meters. On the other hand, the fuel cells with power of tens of watts to a few kilowatts (<1.0–2.0 kW usually) constitute the major promising market of PEFCs [12–14]. Con-

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sequently, it should be challenging to apply the PROX to the on-commercializing small PEFCs for residential and portable uses.

Without any additional reactant required, the SMET can avoid the above-mentioned shortcomings of PROX. Furthermore, the CO and CO_2 methanations (Eqs. (2) and (3)) are less exothermic than the CO and H_2 oxidations (Eqs. (4) and (5)). Thus, the SMET is inherently easier controllable than PROX. Eq. (2) shows that the removal of one mole CO via methanation requires three moles of H_2. Of these two moles are restored in the CH_4 product, which can be reused after PEFC reactions through re-circulating the cell's off-gas into the reformer as a feedstock or as a fuel burnt for heating. A PEFC system, in general, has to be equipped with an off-gas re-circulation line to recover the unreacted H_2 that may reach 10–20% of its original feed [15]. Hence, for SMET the actual H_2 loss into water should be one mole for one-mole CO removal, if the methanation selectivity toward CO is 1.0 or 100%. For PROX there is theoretically no H_2 loss at 100% selectivity (based on Eq. (4)). This theoretical efficiency, however, is certainly impossible in practice. Not only does the technique itself hardly reach such an efficiency over commercial catalysts [10,16,17], but also none is willing to risk the system safety to adopt an oxygen supply at O/CO = 1.0 (v/v), even if the catalyst allows. Furthermore, an actual PEFC system fluctuates inherently, which requires oxygen supplies responding to the maximal inlet CO content appearing in the fluctuations [5]. Therefore, hydrogen loss, via Eq. (5), surely exists in practical PROX reactors. This loss, based on literature reports [10,16,17], should be at least one to two moles of H_2 for one-mole CO removal because actual PROX reactors run generally at O/CO ratios of 2.0–3.0 (v/v):

$$\text{CO methanation}: \quad CO + 3H_2 \leftrightarrow CH_4 + H_2O, \quad \Delta H^0_{298} = -206\,\text{kJ/mol} \tag{2}$$

$$CO_2\ \text{methanation}: \quad CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O, \quad \Delta H^0_{298} = -165\,\text{kJ/mol} \tag{3}$$

$$\text{CO oxidation}: \quad CO + (1/2)O_2 \leftrightarrow CO_2, \quad \Delta H^0_{298} = -284\,\text{kJ/mol} \tag{4}$$

$$H_2\ \text{oxidation}: \quad H_2 + (1/2)O_2 \leftrightarrow H_2O, \quad \Delta H^0_{298} = -244\,\text{kJ/mol} \tag{5}$$

Despite the preceding merits of SMET, no efforts have been made for its use with PEFC fuel gases. The available prolific reports about CO and CO_2 methanations [18] are mostly under other different gaseous atmospheres. For PEFC fuel gases containing CO and CO_2, it is widely suggested that the simultaneous CO_2 methanation (Eq. (3)) makes it almost impossible to remove their CO selectively [5,6,9,19]. Some previous work [7,19] adopted the CO methanation method to develop PEFC systems, but their treated gases were free of CO_2 (i.e. CO_2 being removed in advance).

Since 2002 we have started to challenge the use of the SMET method to purify the PEFC fuel gases rich in H_2, CO_2 and steam under acceptably high selectivity to CO methanation. This resulted in our proposal of the thermally differential methanation (TDM) method, which was first published in the 94th Meeting of Catalysis Society of Japan in 2004 [20]. Theoretically, the TDM is capable of 100% selective CO methanation (i.e. without CO_2 methanated) until the gas' CO content is below 100 ppm. On the other hand, a Japanese company, Osaka Gas Co. Ltd., had been engaged in the investigation of the methanation method as well [21]. With full understanding of the dependences of methanated CO on various operating parameters, the so-called multi-stage methanation method was proposed in 2004 to remove reformate's CO to 10 ppm from 0.54 mol% at selectivity of 0.79 (selectivity definition being the same as that shown in Eq. (6)). Consequently, both of these quoted works opened a new way, as an alternative technology of PROX, to purify the hydrogen-rich fuel gases for PEFC applications. More than this, these successes in the SMET method make also the design of PEFC systems flexible. For instance, one can have the technical choice to abate most CO in a gas with a PROX reactor at oxidation selectivity (to CO) close to 100% and then to remove the left CO with a SMET reactor to make the CO content meet the PEFC-acceptable levels, say, <100 ppm. This combination of PROX and SMET results in low CH_4 formation and H_2 consumption so that high overall selectivity to the reactions with CO, i.e. both oxidation and methanation, becomes possible. Furthermore, the combination solves a problem faced when applying the PROX only. That is, at the PEFC-tolerable CO concentrations, say, tens to hundreds of ppm, the oxidation reaction is in favor of H_2 such that high oxidation selectivity towards CO is commonly hardly achievable [5,6].

Succeeding our last report [20], the present article is devoted to providing more details about the TDM method. From the viewpoint of actual application, it is considered that the TDM may have to appear in the temperature-staged form studied in this article. Thus, the article will clarify, for the first time, the principle and necessary challenging problem of temperature-staged methanation based on the data taken both in an integral-flow reactor and a temperature-programmed reaction (TPR) facility.

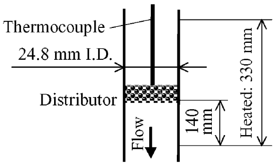
2. Experimental

All data reported herein were obtained from tests over a commercial 0.5%Ru/Al_2O_3 catalyst in either a metallic integral-flow reactor or a temperature-programmed-reaction (TPR) facility coupled with a micro quartz reactor. While the metallic integral-flow reactor was used to acquire the performances close to practical conditions (for steam-containing gases), the tests in TPR were conducted to demonstrate further the chemical behavior occurring in the integral-flow reactor by using steam-free hydrogenous gases. Table 1 specifies the involved catalyst, reaction facilities and major operating parameters. The original catalyst was commercially available from N.E. Chemcat Co., which had a cylindric pellet shape in size of Ø3.2 mm × 3.5 mm. Its average bulk density and BET surface area were 950 kg/m^3 and 92.9 m^2/g, respectively. The catalyst contained mesopores in sizes of 3.2–38.5 nm, with a mean pore size of about 6.8 nm.

Table 1
Adopted catalyst, reaction facilities and major operating parameters

Catalyst (commercially available from N.E. Chemcat. Corp.)
Composition: 0.5%Ru/Al_2O_3; size: Ø3.2 mm × 3.5 mm; BET surface: 92.9 m^2/g; shape: cylindric pellet; bulk density: 950 kg/m^3; mesopore sizes: 3.2–38.5 nm; Ru dispersion (from CO adsorption): about 60%

Reaction facilities
Integral-flow reactor (fixed bed made of stainless steel, as illustrated)
Reactant gas: from gas cylinders; flow control: mass flow meters; steam generation: pump + evaporator; composition measure: Micro TDC; thermocouple was 15 mm above the distributor



Temperature-programmed-reaction facility (TPR, detailed in context)

Operating conditions
For integral-flow reactor
Catalyst load: 20 g non-smashed (40 mm high in the reactor); dry-gas flow rate: 355 ml/min, giving a space velocity of 1060 ml/(g h) at 273 K and 1.0 atm; steam-to-gas ratio S/G: 0.55 v/v (wet-base percentage: 36 mol%)
For TPR (no steam was involved in the test)
Catalyst load: 300 mg smashed (500–800 μm); dry-gas flow rate: 100 ml/min, giving a much higher space velocity than that in the integral-flow reactor

Via CO adsorption the Ru dispersion of the original catalyst was shown to be about 60%.

2.1. Test in integral-flow reactor

The used integral-flow reactor was made of stainless steel and had an I.D. of 24.8 mm. As illustrated in Table 1, the reactor was electrically heated in a 330 mm long section, and a sintered-plate at 140 mm above the lower-end of the heated section supported the catalyst. A K-type thermocouple measured the reaction temperature at 15 mm above the distributor, and the temperature was further controlled with a PID controller. Twenty grams (but 10 g for the test in Fig. 5) of non-smashed catalyst was packed into the reactor, which created a catalyst bed of about 40 mm high. The reactant gases, i.e. simulated reformates, were obtained by mixing H_2, CO_2, CO and steam generated in a water evaporator. The evaporator was a stainless steel pipe of 14.9 mm I.D. packed with steel balls. The flows of all dry gases were controlled using mass flow meters. The dry inlet CO concentration of the simulated reformates varied between 0.2 and 1.0 mol%, and their initial H_2 and CO_2 concentrations were determined based on a molar ratio of 70/30 v/v. Steam added to the dry-gas feed was fixed at 55% of the dry-gas volume. This steam ratio was assumed to be typical for the gas streams after WGS because the steam-to-CH_4 volume ratio in the upstream reformer is usually less than 5.0. By passing through the water evaporator, the H_2 stream was used to carry steam to the exit of the evaporator, whereat H_2 and steam were further mixed with CO_2 and CO. Running temperature of the evaporator was usually 473 K, and warming up the flow pipes between the evaporator and reactor to about 373 K prevented steam from condensation. A high-pressure liquid pump (L-7110, Hitachi) controlled the water amount sent to the evaporator and, in turn, the steam amount generated. The molar compositions of reactant and reacted gases were measured in a micro TCD gas chromatograph (P200H, Micro Technology), which allowed a few ppm of CO and CH_4 to be detected. All experiments in the metallic integral-flow reactor were carried out at a dry-base gas flow rate of 355 ml/min, which led to a space velocity of 1060 ml/(g h) under 20 g catalyst load inside the reactor (the quoted gas volumes and velocities being estimated at 273 K and 1.0 atm).

Before test, the catalyst was reduced in a hydrogen–argon (H_2: 10 vol.%) stream of 60 ml/min via a temperature program that first increased the temperature to 673 K at rates less than 100 K/h and then kept it at 673 K for 30 min. Decreasing the catalyst temperature from 673 K to experimental ones was realized by naturally cooling the reactor in the same hydrogen–argon stream. The flow switch from H_2–Ar to the gas mixture of H_2, CO and CO_2 then started the test. Steam feed was started later at a temperature that initiated obvious CH_4 release (see Fig. 1). A blank test without catalyst load in the reactor demonstrated that the materials (mainly metals) of the experimental system had negligible catalytic effect on the methanation reactions under the tested temperatures.

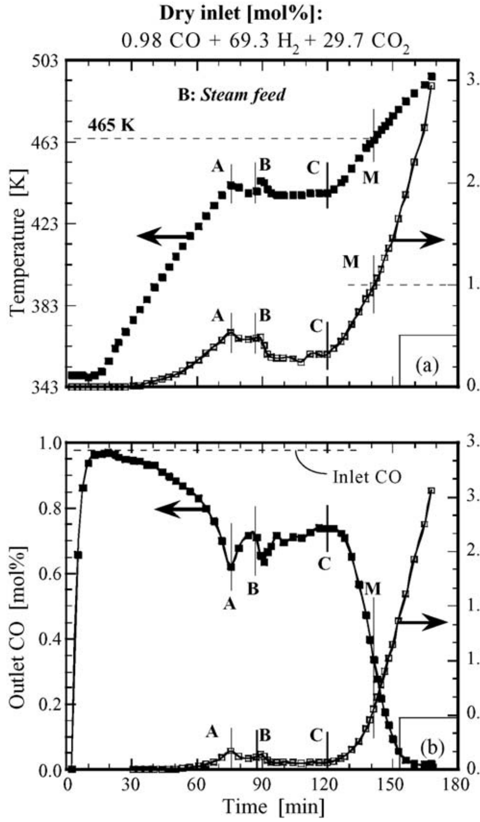


Fig. 1. Methanation performance for a steam-containing simulated reformate under controlled reaction temperatures in the metallic integral-flow reactor.

2.2. *Test in TPR facility*

The used TPR facility had a cylindrical micro quartz reactor of 10 mm I.D. (details in Ref. [22]), and the tests were conducted via passing a gas flow of 100 ml/min through 300 mg smashed 0.5%Ru/Al_2O_3 catalyst (20–35 mesh). The catalyst in the reactor was first reduced in a He–H_2 (H_2: 10 mol%) gas by heating the reactor to 673 K at a rate of 10 K/min and subsequently keeping the temperature for 30 min. Then, in the same He–H_2 flow the catalyst was naturally cooled down to 313 K. The formal test and data acquisition were started with flow switching from He–H_2 to a hydrogenous gas, either He-based or reformate-simulated (free of steam). The He-base hydrogenous gases contained only 20 mol% H_2 and no more than 0.5 mol% CO and CO_2 (see Fig. 7) so that any small changes in CO and CO_2 concentrations could be detectable. In contrast to this, the simulated reformates consisting of much more CO_2 (22 mol%), up to 1.0 mol% CO and balanced H_2 (see Figs. 2 and 8) were used to validate or to further demonstrate the findings from the tests in the integral-flow reactor. The molar compositions of the reactant and reacted gases were analyzed either in a quadrupole mass chromatograph coupled to the TPR, when a He-base gas was tested (Fig. 7), or in a micro TCD gas chromatograph (P200H, Micro Technology) when a simulated reformate was examined. The analysis for the reacted gas was started generally 30 min before the reactant gas was supplied and ended 20 min after the gas supply was stopped.

In all these tests with the TPR facility the dry volume flow rate of reacted gas was measured using a digital gas meter to determine the precise amounts (moles or volumes) of removed CO and produced CH_4. This, in turn, allowed the selectivity to be accurately estimated according to:

$$\text{Selectivity} = \frac{\text{Moles of removed CO}}{\text{Moles of produced CH}_4} \qquad (6)$$

This selectivity calculation equation was applicable also to the tests in the aforementioned integral-flow reactor (their reacted gas volumes being measured with the same gas meter used here). In addition, the spent catalyst from each methanation test in the TPR, which was first cooled down to room temperature in the conditions without any gas flowing over the catalyst, were purged with either a He–O_2 or a He–H_2 stream under a programmed temperature rise of up to 673 K to confirm if C was really deposited on the catalyst during methanation reactions. The confirmation was based on if CO_2 or CH_4 evolution was detected with the TPR's quadrupole mass chromatograph during the purge procedure.

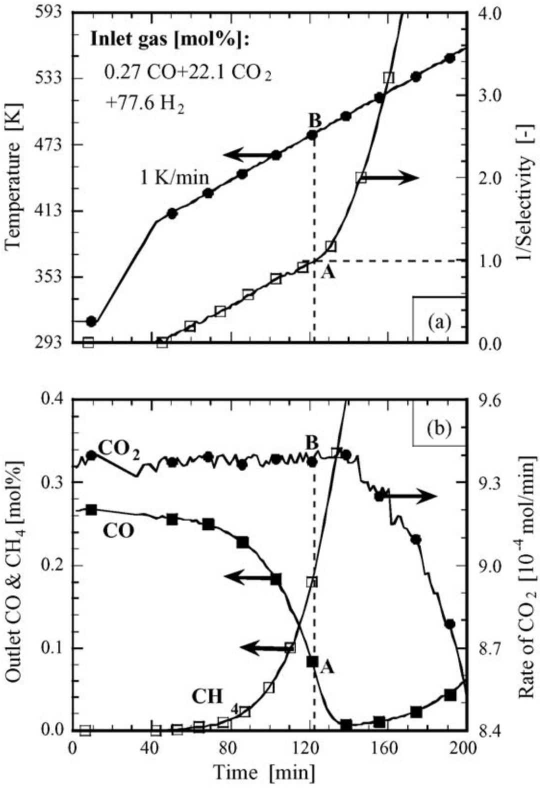


Fig. 2. Demonstration (in the TPR facility) of the complete priority of methanation of CO over CO_2 in a CO–CO_2 coexisting hydrogen-rich gas.

3. Results

3.1. *Priority of CO methanation*

It has long been recognized that in CO–CO_2 coexisting gases CO can be methanated in prior to CO_2 [23–25], but there are very few examinations made for gases rich in steam. To verify the methanation priority of CO over CO_2 for steam-containing gases is thus the preliminary purpose of this section. The section discusses also whether complete priority is possible and how to maintain this priority.

Fig. 1 shows the result of a methanation test on a steam-containing simulated reformate under programmed reaction temperatures in the integral-flow reactor. The reformate gas, free of steam at this stage, was fed into the reactor at time zero. In about 20 min (temperature being 360 K) the outlet CO concentration quickly reached the inlet concentration value of 0.98 mol% (Fig. 1b), indicating that the physical adsorption of CO onto the catalyst should have little contribution to the successive CO removal at other higher temperatures. The temperature diagram in Fig. 1a shows that there were two periods of temperature increase, say, before annotation A and after C (realized by adjusting the heating intensity). The temperature-rise rate was about 1.5 K/min. Steam feed was started at annotation B. Through a successive transition period from B to C (about 30 min) the steam thus could develop its full actions on the relevant reactions.

The outlet concentrations of CO and CH_4 in Fig. 1b demonstrate that increasing the reaction temperature progressively decreased CO release and increased CH_4 production. The produced CH_4 became detectable at 375 K or about 30 min. Until annotation A (433 K) the occurrence degree of methanation was mild so that the outlet CH_4 concentration was hardly above 0.2 mol%.

Steam feed at annotation B led to an instantly higher temperature (Fig. 1a), as a result of the instantly larger heat input with the steam. This led to some slightly lower outlet CO concentrations soon after B, but the released CH_4 amount did not show much increase. Instead, The outlet CH_4 concentration remained basically decreasing until it stabilized itself at some obviously lower values (about 0.1 mol%). Thus, the presence of steam would inhibit the methanation reactions, as was similarly observed for the methanation reactions involved in PROX over the same catalyst [26].

The temperature increase after annotation C from 438 K rapidly decreased the outlet CO content and increased the CH_4 production. For the tested inlet CO concentration of 0.98 mol% the lowest outlet CO concentration reached a few hundred ppm at about 483 K (i.e. at 160 min), resulting in a corresponding CH_4 content in the reacted gas higher than 3.0 mol%. Further increasing the reaction temperature (>483 K) decreased the outlet CO content very slightly but kept the similar quick increase in CH_4 production, indicating substantial methanation of CO_2 at those high temperatures.

With the obtained outlet CO and CH_4 concentrations the selectivity of methanation towards CO was calculated according to Eq. (6) and shown in Fig. 1a. Noting that the produced CH_4 is zero at low temperatures, the reciprocal of the selectivity, i.e. 1/selectivity, is plotted. The result demonstrates that the selectivity decreased, or its reciprocal increased on increasing the reaction temperature. From annotations A to C the reaction temperature was basically constant, causing the selectivity to vary little as well. Overall, the selectivity's reciprocal ranged from 0 to 3.0, indicative of a corresponding variation of the selectivity from values above 1.0 to about 0.35 (annotation M referring to the selectivity 1.0). A selectivity value lower than 1.0 means that the moles of methanated CO are less than that of the produced CH_4, which is surely due to the simultaneous CO_2 methanation. Then, Fig. 1a demonstrates that only at certainly high reaction temperatures, typically over 465 K (after M), the CO_2 methanation can be pronounced to cause the CH_4 production to exceed the CO removal. At the other lower temperatures until M, the removed CO and produced CH_4 varied correspondingly (see Fig. 1b), implicating a predominant methanation of CO. In this case, we expected a selectivity of 1.0, as theoretically indicated in reaction (2). The actual selectivity in Fig. 1a, however, was higher than 1.0 (its reciprocal <1.0), showing consequently a CO removal in excess of the CH_4 production. In the coming section, the CO chemisorption:

$$CO + M \rightarrow M\text{–}CO \tag{7}$$

and CO decomposition

$$2M\text{–}CO \rightarrow M\text{–}C + M\text{–}CO_2 \rightarrow M\text{–}C + CO_2 \tag{8}$$

will be identified to be responsible for the result. What we like to stress here is that for the examined steam-rich reformate the preferential CO methanation is still evident (before the annotation M). Although the reactions (7) and (8) may influence more or less the catalyst's performance, it would never violate the priority of CO methanation.

Fig. 1 does not clarify if there was really no CO_2 methanation before annotation M. In order to gain an insight into this, a temperature-controlled methanation shown in Fig. 2 was conducted in the TPR facility to measure simultaneously the outlet CO concentration (Fig. 2b) and CO_2 release rate (Fig. 2b) during methanation. The CO_2 release rate was determined according to the measured outlet CO_2 concentration and dry volume of reacted gas. We believed that the differential-reaction nature of the TPR reactor, compared to the metallic integral-flow reactor, would make the demonstration more reliable. The release rate of CO_2, instead of outlet CO_2 concentration, was used for the reason that with methanation the dry volume of reacted gas slightly decreases, which would increase the CO_2 concentration, even if the CO_2 amount in the gas remained the same. The temperature-rise rate was 1 K/min for the plotted test (●, Fig. 2a). Using an initially higher heating rate until 40 min was just for shortening the testing time. As in Fig. 1, the selectivity of methanation towards CO is presented with 1/selectivity in Fig. 2a (□), as a function of temperature. One can see from Fig. 2b that until the dotted-line AB corresponding to the selectivity 1.0 the outlet CO concentration (■) decreased, whereas the CO_2 release rate (●) was unchanged. Hence, until AB the methanation reaction had a complete priority towards CO, which allows CO to be methanated without any CO_2 methanation involved. Nonetheless, this 100% selective CO methanation can be achievable only when the reaction temperature does not exceed a critical value, such as 483 K at line AB for Fig. 2 and 465 K at annotation M for Fig. 1.

The estimated selectivity in Fig. 2a (□) was higher than 1.0 until line AB (reciprocal <1.0). In the entire temperature range tested the selectivity gradually decreased (its reciprocal increased) with increasing reaction temperature. All of these demonstrate the same features as those clarified in Fig. 1 for the selectivity of CO methanation. Thus, the existence of selectivity values higher than 1.0 at some low temperatures is definite and unavoidable for methanation of CO-containing gases over Ru/Al_2O_3 catalyst. Indeed, reactions (7) and (8), which are responsible for the phenomenon (see further clarification in Section 4), truly contribute to CO removal, causing the estimated selectivity to be above 1.0. In practice, however, these reactions, especially reaction (8), should be avoided because the resultant M–C (C deposition) may deactivate the catalyst, as will be shown in Fig. 8.

3.2. Temperature-staged methanation

At the highest possible temperature allowing the selectivity 1.0, say, corresponding to annotation M in Fig. 1 and line AB in Fig. 2, the achievable lowest outlet CO level was about 0.33 mol% and 750 ppm in Figs. 1 and 2, respectively. These CO concentrations are much higher than the PEFC-tolerable levels below 100 ppm. Meanwhile, it is noteworthy that in Fig. 2 the inlet CO was only 0.27 mol%, which represents the possibly lowest CO content present in the actual reformates. Consequently, we believe that with the conventional methanation method, which runs the reactor at a uniform temperature, it must be difficult to achieve outlet CO levels lower than 100 ppm and 100% selectivity of CO methanation at the same rime. This leads to our proposal of the so-called thermally differential methanation (TDM) method to assure both simultaneously (being first publicly reported in 2004 [20]). In a sense of practical application the

TDM may appear most possibly in the temperature-staged form studied in this article. This form represents a simplified TDM such that it looks like the multi-stage methanation provided by Osaka Gas Co. Ltd., in 2004 [21].

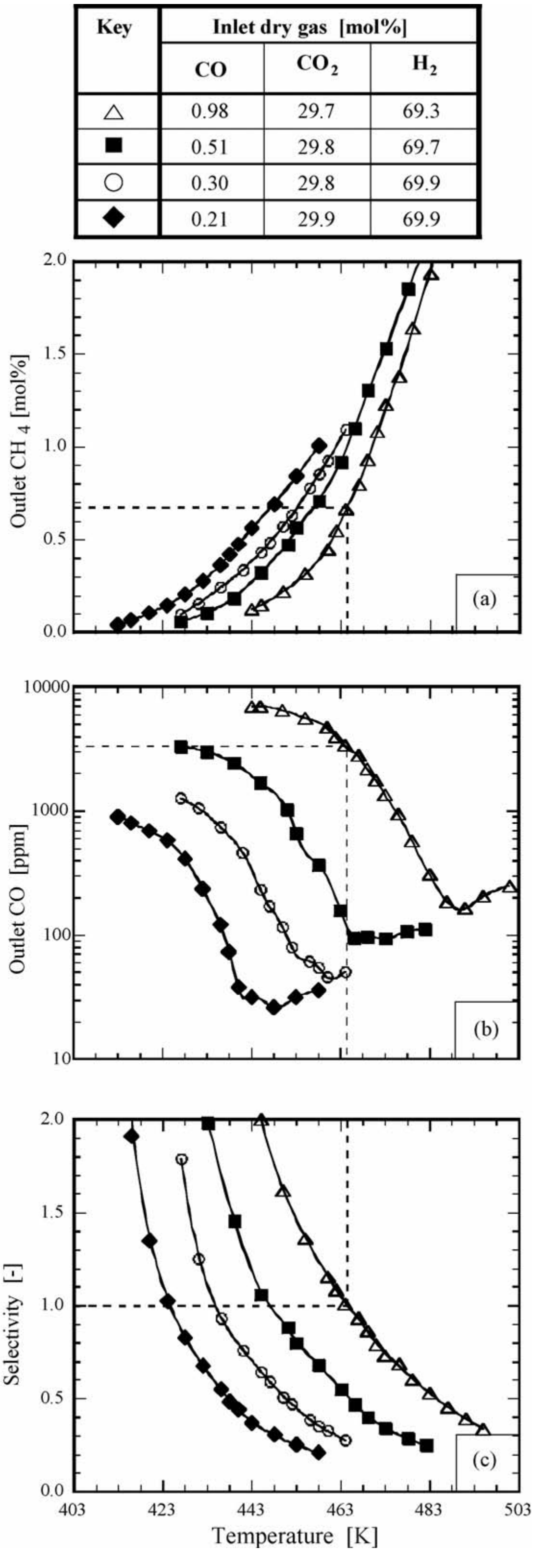
The concept of TDM or temperature-staged methanation are based on the following fundamentals: (a) the highest reaction temperature allowing the same selectivity towards CO methanation (including 1.0) decreases with decreasing the initial CO concentration; (b) the outlet CO concentration at the same selectivity is lower at an initially lower CO content; (c) the desired outlet CO levels lower than 100 ppm are definitely achievable at reasonable selectivity values, provided the gas' initial CO content is appropriately low. In order to demonstrate all of these fundamentals, the temperature-controlled methanation following the test procedure illustrated in Fig. 1 was extended to a few other steam-rich simulated reformates with CO contents of up to 1.0 mol%. Fig. 3 shows the resulting outlet CH_4 (Fig. 3a) and CO (Fig. 3b) concentrations and the estimated selectivity (Fig. 3c) as functions of reaction temperature (the plotted data being only for the period after annotation C exemplified in Fig. 1).

From Fig. 3 we can see first some characteristic variations of all the quoted parameters. With increasing temperature the outlet CH_4 concentration (Fig. 3a) gradually increased, whereas the outlet CO concentration (Fig. 3b) first rapidly decreased and then slightly increased. These align with Fig. 1b (the data after annotation C). Fig. 3a clarifies also that at the same reaction temperature less CH_4 was produced when the inlet CO content was higher. The competitive adsorption/dissociation of H_2 and CO on the active catalyst sites is considered to be responsible for the result [26]. That is, the higher the inlet CO concentration, the more CO molecules are in the catalyst bed. This causes more active sites to be occupied by CO so that fewer sites are available to hydrogen adsorption/disassociation that is indispensable to methanations of CO and CO_2 according to the following reaction chain [26,27]:

$$\mathrm{M} + \mathrm{CO_2} \xrightarrow{\mathrm{M{-}H/H_2}} \mathrm{M{-}CO} \xrightarrow{\mathrm{M{-}H/H_2}} \mathrm{M{-}C} \xrightarrow{\mathrm{+M{-}H}} \mathrm{M{-}CH} \xrightarrow{\mathrm{+M{-}H}} \cdots \xrightarrow{\mathrm{+M{-}H}} \mathrm{CH_4} \tag{9}$$

Hence, under a given reaction temperature the fewer available H radials for the gas with a higher initial CO concentration has to cause a lower CH_4 production.

The outlet CO content diagrams in Fig. 3b are subject basically to the gas' inlet CO concentration so that the diagram for lower inlet CO concentration shifted to the lower left to give a lower outlet CO content under a specified reaction temperature. As in Fig. 1a (□), the selectivity to CO methanation in Fig. 3c exhibited values above 1.0 and it gradually decreased (down to 0.2) with raising the temperature, irrespective of the initial CO concentration. When the temperature is given, the selectivity is higher for higher inlet CO content, implying that a gas with more CO has to be treated at a higher reaction temperature in order to maintain the same selectivity of CO methanation. This result just responds to Fig. 3a and b where for the same CH_4 production (Fig. 3a) or CO reduction (Fig. 3b) a gas with a higher initial CO concentration requires a higher temperature.



Key	Inlet dry gas [mol%]		
	CO	CO_2	H_2
△	0.98	29.7	69.3
■	0.51	29.8	69.7
○	0.30	29.8	69.9
◆	0.21	29.9	69.9

Fig. 3. Methanation performance for steam-containing simulated reformates with different initial CO concentrations under gradually raised temperature at about 1.5 K/min (see Fig. 1 for test method).

The preceding three fundamentals leading to the temperature-staged methanation (i.e. TDM) method are clarified in Fig. 4. There, the reaction temperatures and corresponding outlet concentrations of CO and CH_4 for three peculiarly selected selec-

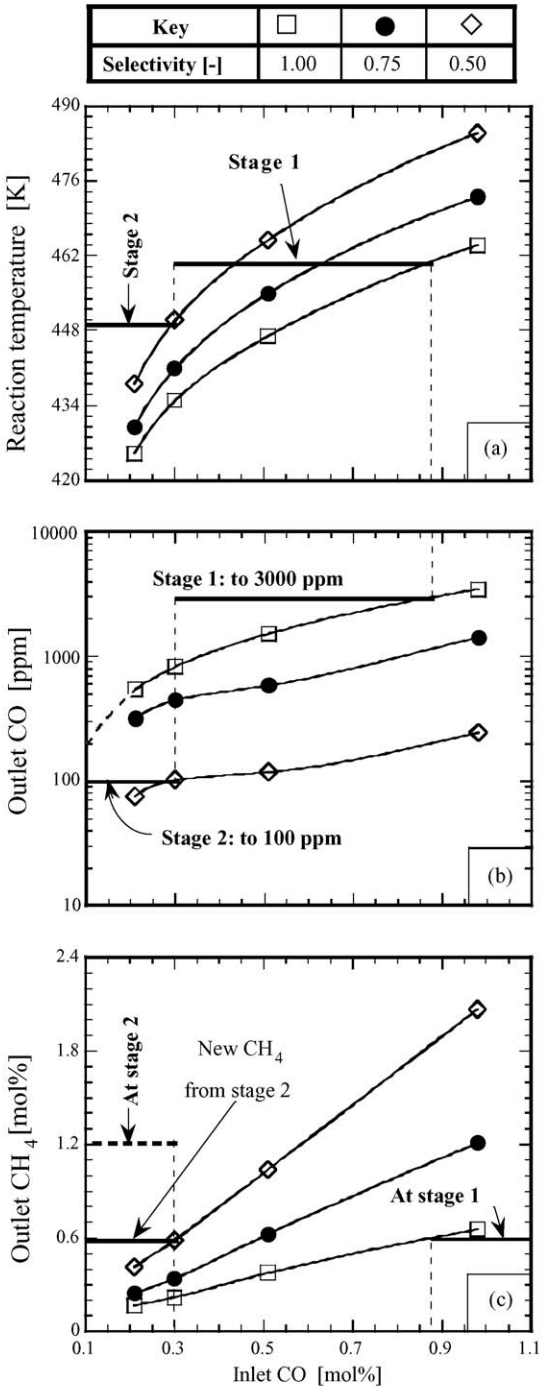


Fig. 4. Outlet CO and CH_4 concentrations and the required reaction temperatures of single-stage methanation reaction corresponding to a few specified selectivity values of CO methanation for gases with different initial CO concentrations (data being derived from Fig. 3).

tivity values, namely, 0.5, 0.75 and 1.0, determined from Fig. 3 are plotted as functions of initial CO concentration. The dotted lines in Fig. 3 illustrate the determination method. While the horizontal line in Fig. 3c specifies the selectivity selected, such as 1.0 for the illustration, the vertical line passing through the point where the horizontal line and selectivity curve intersect defines the corresponding reaction temperature. Further extending the vertical line to Fig. 3b and a determines then the outlet CO and CH_4 concentrations, respectively. Fig. 4a shows the resulting reaction temperatures, indicating an obvious decrease with decreasing initial CO concentration for each of the chosen selectivity values. This demonstrates actually the fundamental (a) for temperature-staged methanation. Under specified selectivity, the outlet CO concentration in Fig. 4b decreases with decreasing the inlet CO concentration, showing just the above-mentioned fundamental (b). Fig. 4b shows also that under a given inlet CO content the outlet CO concentration was lower at lower selectivity (but one should not run the reactions at too low selectivity in order to reduce H_2 loss). As for the plotted cases, the outlet CO content became lower than 100 ppm only at selectivity 0.5 for inlet CO concentrations of about 0.3 mol%. Notwithstanding, Fig. 4b indicates the trend that the outlet CO levels below 100 ppm could be achieved also at other higher selectivity values, if the inlet CO concentration is rather lower. For example, the selectivity can be 1.0 if the inlet CO concentration does not exceed 500 ppm (see the extrapolated dotted line). This verifies actually the aforementioned fundamental (c).

The temperature-staged methanation works to assure simultaneously the final outlet CO levels below 100 ppm and the overall CO methanation selectivity close to 1.0. It runs with a few successive stages at gradually lower reaction temperatures. For each stage its temperature is subject to a desired selectivity and the inlet CO concentration of its treated gas. Generally, one or more upstream stages are required to run under 100% selectivity to abate most CO in the original gas, and then in a final stage at selectivity not lower than 0.5 the remaining CO is reduced to levels below 100 ppm. To achieve this the inlet CO content for the last stage must be lower than 0.3 mol% according to Fig. 4b. Thus, only for the fuel gases with inlet CO below 0.3 mol% a single-stage methanator running at a uniform reaction temperature can fulfill the CO reduction to tens of ppm at selectivity above 0.5. Otherwise (initial CO >0.3 mol%), the temperature-staged methanation is required. Fig. 4b conceptualizes a two-stage reaction system by assuming an initial CO content of 0.87 mol%. While the original CO is reduced to 0.3 mol% in a previous stage under selectivity 1.0, the left CO is further reduced to 100 ppm in a successive stage under 50% selectivity. Certainly, one can run the last stage at any even lower selectivity, but this would not much improve the outlet CO level while it substantially decreases the overall selectivity.

Table 2 summarizes the performances of a few temperature-staged methanation systems determined from Fig. 4 (thus valid for the gases and conditions tested in this article). Generally, more stages are required for higher initial CO content, but the resulting overall selectivity of CO methanation is also higher. By keeping the last stage at selectivity 0.5, Table 2 indicates that the overall selectivity for the exemplified three-stage system can be up to 0.95, and that of the two-stage system is about 0.75. Corresponding to these the single-stage system for a gas containing 0.2 vol.% CO has to work at selectivity below 0.5 in order to assure its outlet CO to be not over 100 ppm. Furthermore, Table 2 verifies that the reaction temperature in the multi-stage systems is gradually lower from the first to last stages. This makes the desired temperature gradient between neighboring stages be eas-

Table 2

A few typical examples of temperature-staged methanation reactions for purifying steam-containing simulated PEFC fuel gases (based on the tests in the metallic integral-flow reactor and the treated gases consisted of 30 mol% CO_2, 70 mol% H_2 and CO of up to 1.0 mol% in dry base)

Inlet CO (mol%)	Parameter	Stage 1	Stage 2	Stage 3	Overall
1.00	Outlet CO (ppm)	3500	1000	~50	~50
	Temperature (K)	465	438	~420	–
	Formed CH_4 (mol%)	0.65	~0.25	~0.2	1.10
	Selectivity (−)	1.0	1.0	0.5	0.93
0.50	Outlet CO (ppm)	1500	~60	–	~60
	Temperature (K)	446	~425	–	–
	Formed CH_4 (mol%)	0.37	~0.30	–	0.67
	Selectivity (−)	1.0	0.5	–	0.75
0.20	Outlet CO (ppm)	75	–	–	75
	Temperature (K)	424	–	–	–
	Formed CH_4 (mol%)	0.40	–	–	0.40
	Selectivity (−)	0.5	–	–	0.5

"Formed CH_4" refers to the increase in outlet CH_4 concentration. "~" means that the value involved extrapolation from Fig. 4. "Overall selectivity" was based on the overall removed CO and formed CH_4.

ily formable because along the stages the released reaction heat responding to the methanated CO is gradually lower.

Comparing to the multi-stage methanation results reported in Ref. [21], the selectivity and efficiency achieved here are higher. While the inlet CO of 1.0 mol% can be lowered to 100 ppm with selectivity of 0.95, the literature case shows somewhat lower selectivity of 0.79 for removing 0.54 mol% CO down to 10 ppm. For this literature work, its less optimal conditions for individual reaction stages should be the cause for its lower selectivity and efficiency. In fact, the literature proposal was based on empirically demonstrated dependences of removed CO on methanation selectivity [21]. Thus, it did not and could also be difficult to clarify how to condition each reaction stage to optimize the overall efficiency and selectivity. In our case, the proposal was started with fundamental demonstration, showing obviously that all the upstream stages should be at methanation selectivity close to 1.0, even though the last stage can run at other lower selectivity to maintain the desired outlet CO levels below 100 ppm. On this basis, the temperature-staged methanation could allow overall selectivity of 100% in principle, given that each stage works under the 100% selective CO methanation conditions.

Consequently, the method shown here provides an alternative way to purify PEFC fuel gases efficiently. Compared to PROX, it is not only inherently easier controllable but also competitive in the achievable selectivity, efficiency and H_2 loss. This hopefully initiates a new challenge to the technical development of PEFC systems, especially of the low-power systems for residential and portable uses to which only PROX is now considered to be applicable. To such systems the temperature-staged methanation would be particularly adaptive by taking account into its good controllability, no need of oxidant supply, and competitive efficiency and H_2 loss against PROX.

4. Discussion

This section is devoted to giving an insight into the selectivity values larger than 1.0, which occur at low temperatures (see Figs. 1–3) and shows essentially that the moles of produced CH_4 are less than that of the reacted CO. Fig. 5 examines if the quoted phenomenon occurs in long-time reaction because the reported tests in Figs. 1–3 are all for raising temperature conditions. The test in Fig. 5 was conducted in the integral-flow reactor over 10 g catalyst for a simulated reformate containing 0.98 mol% CO and steam according to the specification in Table 1. The plotted time zero indicates the onset of CO feed at a reactor temperature of 423 K, which was after the catalyst was reduced according to the procedure explained in the Section 2 and switched to the gas stream containing H_2, CO_2 and steam. At this temperature a CH_4 release was detected but the resulting concentration was lower than 0.02 mol%. The figure shows that the outlet CO content first rapidly increased (in response to the feeding) and then stopped at about 0.8 mol%. In the succeeding 2 h of keeping the reaction at 423 K the outlet CO only slightly elevated, say, to 0.82 mol% at annotation A. Compared to the inlet CO of 0.98 mol%, the removed CO was about 0.16 mol%, much higher than the released CH_4 of about 0.02 mol%. Hence, the adsorp-

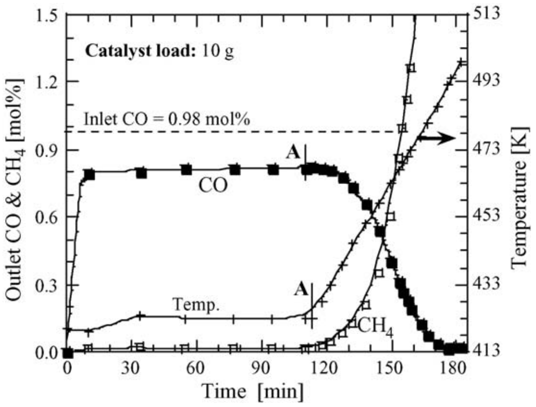


Fig. 5. The lower CH_4 production than CO removal in a long-time reaction in the integral-flow reactor under a given temperature (until A). This temperature is lower than the highest temperature leading to the estimated explicit selectivity of 1.0 of CO methanation.

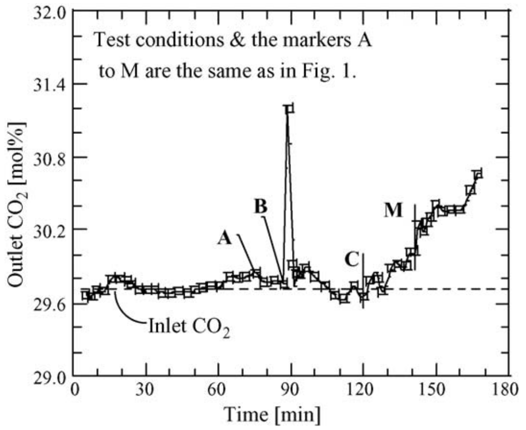


Fig. 6. Outlet CO_2 concentration corresponding to the outlet CO and CH_4 concentrations shown in Fig. 1.

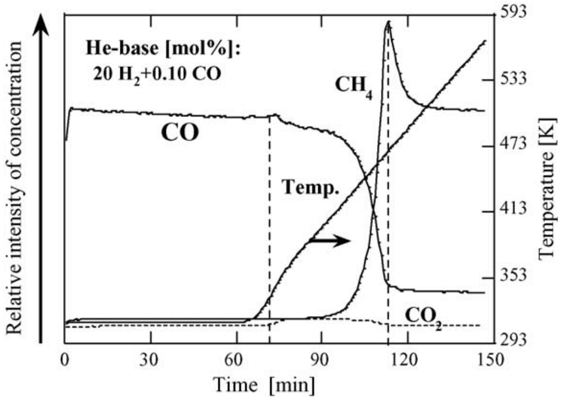


Fig. 7. Methanating a CO_2-free gas in the TPR facility and demonstrating how the carbon deposition reaction $2CO \rightarrow CO_2 + C$ varies with reaction temperature.

tion of formed CH_4 on the catalyst should not be the reason for the observed CH_4 production lower than the accompanied CO removal.

On the other hand, one may argue that some high-C species are formed to make the C output via outlet CO and CH_4 lower than the C supply from inlet CO. Our GC data, however, indicated that this was not the fact. Another possible reason for the unbalanced CH_4 production and CO removal is that the WGS reaction (1) occurred to facilitate the CO removal without CH_4 formation. This concern, however, cannot explain the H_2O balance of Fig. 5 where the only H_2O source for WGS was from the simultaneous methanation reaction (2), which was at most 0.02 mol% in response to the CH_4 production shown in the same figure. Corresponding to Fig. 1, Fig. 6 shows the time-series variation of outlet CO_2 concentration measured in that test. After steam feed at annotation B the outlet CO_2 content did not increase steadily, demonstrating also a weak WGS. Otherwise, the added steam should enhance WGS to raise considerably the outlet CO_2 concentration. Immediately after B, there was an instantly high CO_2 release, which should be due to the instantly quick CO_2 desorption resulting from the presence of steam.

In addition, the approach of outlet CO concentration to inlet CO content at very low temperatures, say, within the first 20 min in Fig. 1b, clarified that the physi-adsorption of CO must not be the reason for retaining C in the reactor. Consequently, we believe that the plausible cause for the observed CH_4 production lower than CO removal is the simultaneous occurrence of CO chemical adsorption according to Eqs. (7) and (8). Fig. 7 shows this with a methanation test in the TPR facility for a gas containing 0.10 mol% CO, 20.0 mol% H_2 and balanced He (free of CO_2). In the first 60 min, the reactor temperature was kept at 313 K such that there were no CO_2 and CH_4 releases and no evident variation in the outlet CO concentration (the concentrations were shown with the signal intensity from the mass chromatograph of the TPR facility). The result verifies thus the approach of outlet CO concentration to inlet CO content at very low temperatures. Then, when the temperature got over 333 K (to the right of the first dotted-line), there appeared an obvious CO_2 release along with a detectable CO concentration decrease. Nonetheless, there was no simultaneous increase in CH_4 concentration until 403 K at 90 min. From 90 min the released CH_4 quickly increased in response to a rapid decrease in the outlet CO concentration. The released trace CO_2 remained till 113 min or 412 K (the second dotted-line), whereat the outlet CH_4 concentration reached a peak and the outlet CO concentration dropped to its possible bottom value. Further increase of the temperature caused CH_4 to move back to a lower stable concentration that appeared equivalent to the inlet CO content of 0.1 mol%. Correspondingly, the outlet CO content remained at its minimal value, while the accompanying CO_2 release decreased to zero.

The detected CO_2 release in Fig. 7 is due to the occurrence of reaction (8), which causes the formed C to deposit on the catalyst. Meanwhile, the chemisorption of CO according to reaction (7) also retains CO on the catalyst, if the formed M–CO cannot be converted into M–C according to Eq. (8) or into CH_4 according to Eq. (9). Consequently, when reaction temperature is raised to increase the hydrogenation speed for M–CO and M–C, the retained C species can be hydrogenated into CH_4 at sufficiently high temperatures, such as above 473 K in Fig. 7. This is why a peak CH_4 production above the inlet CO content was observed in Fig. 7. By comparing the areas covered by the CH_4 peak (relative to the steady CH_4 line) and CO_2 release curve (relative to its base line) shown in Fig. 7 we can see that the former is larger than the latter. This indicates probably a M–CO retainment, in addition to M–C deposition, on the catalyst.

Although it is difficult to distinguish the retained C species of CO chemisorption by reaction (7) from that of CO decomposition through reaction (8), we should recognize that the former has to be involved in the chemical procedure of CO methanation (see Eq. (9)). At temperatures below 473 K (see Fig. 7) the CO chemisorption is quicker than the M–CO dissociation into M–C and its successive hydrogenation of M–C into CH_4, which has to lead M–CO to be retained on the catalyst. The deposited C from reaction (8), on the other hand, may deactivate the catalyst. Thus, a methanation test lasting more than 6 h was conducted to clarify if this is true in the TPR facility on a gas containing 0.5 mol% CO, 22.0 mol% CO_2 and balanced H_2. Fig. 8 shows the acquired result and the test procedure.

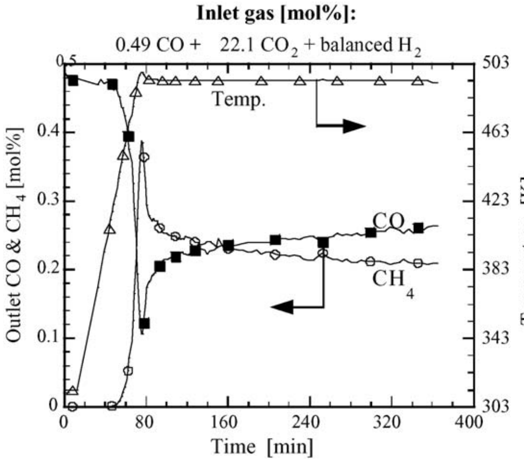


Fig. 8. Demonstration of catalyst deactivation due to carbon deposition in long-time methanation under a temperature for 100% selective CO methanation.

The reaction proceeded first at gradually increased reaction temperatures (3 K/min, until 80 min) and then under a particularly selected constant temperature. This temperature was decided according to the outlet CO and CH$_4$ concentrations measured during temperature increase period so that the selectivity of CO methanation at the temperature is preliminarily close to 1.0. As for the illustrated case in Fig. 8 the selected temperature was 493 K, and the corresponding selectivity was just about 1.0 (not mentioned in Fig. 8). As expected, during temperature increase the outlet CO content gradually decreased, whereas the outlet CH$_4$ concentration correspondingly increased. Stopping the temperature rise to stabilize the temperature at 493 K took about at about 80 min, which caused sharp variations in both the outlet CO (decreased) and CH$_4$ (increased) concentrations. Overheating of the catalyst was considered to be the cause. Since 110 min the variations in the outlet CO and CH$_4$ concentrations became much moderate, indicating possibly the final stabilization of the catalyst temperature at the preset value of 493 K. Then, we see that the outlet CO concentration still gradually elevated in response to a gradual decrease in CH$_4$ production. Within the tested period of about 4 h (at 493 K), the concentration increase in the outlet CO, equivalently the decrease in the outlet CH$_4$ reached about 0.05 mol%. This reveals obviously a catalyst deactivation, which should be relative to the C deposition on the catalyst via reaction (8). Through purging the spent catalyst of this test with a He–H$_2$ (10 mol%) gas we found obvious evolutions of CH$_4$, confirming actually the existence of C species on the catalyst. This, however, cannot identify the forms of the deposited C, entailing thus further works to clarify the problem.

On the other hand, both the above-mentioned CO chemisorption and M–CO deposition, which retain part of the supplied CO on the catalyst, would never violate the principle of the temperature-staged methanation method clarified in Section 3. They indicate just a catalyst deactivation problem for the method so that the development of the catalysts that can quickly hydrogenate M–CO and M–C species on the catalyst becomes highly necessary.

5. Conclusions

Over a 0.5%Ru/Al$_2$O$_3$ catalyst the article found that (a) in any CO–CO$_2$ coexisting hydrogenous gas the complete prior methanation of CO is possible, provided the reaction temperature is certainly low; (b) under a given reaction temperature the CO methanation selectivity estimated as the molar ratio of removed CO over produced CH$_4$, is higher at higher inlet CO concentration; (c) for realizing the same high selectivity of CO methanation, the highest allowable reaction temperature as well as its corresponding outlet CO concentration decreases with decreasing the gas' initial CO content; (d) the desired outlet CO levels below 100 ppm for PEFC applications are surely achievable under 100% selective CO methanation, given that the inlet CO content is appropriately low. Based on all of these findings, the article devised the so-called temperature-staged methanation method to purify the PEFC fuel gases at high selectivity to CO methanation. The method divides the required catalyst bed into more than one reaction zone that run at gradually lower reaction temperatures. While at least one upstream zone runs at a higher reaction temperature to abate most CO in the treated gas under CO methanation selectivity of about 1.0, the last zone at a lower temperature is conditioned to assure the desired outlet CO levels of lower than 100 ppm at selectivity not below 0.5. The overall selectivity of the multi-stage reaction system depends on the number of the adopted reaction stages (zones). Under the tested conditions (in a metallic integral-flow reactor, space velocity being 1100 ml/(g h) at 273 K and 1.0 atm), it could reach 0.95 in a three-stage system for a simulated reformate containing (in mole) 69% H$_2$, 30% CO$_2$ and 1.0% CO and with 55 vol.% steam of dry gas. In the view of purifying PEFC fuel gases this efficiency is competitive to that of the selective CO oxidation (PROX), but the temperature-staged methanation appears more attractive and practical to the small-scale low-power PEFC systems for residential and portable uses because the methanation method is free of oxygen addition and less exothermic so that it is easily controllable.

It was clarified also that the low-temperature methanation condition involved in temperature-staged methanation over Ru catalyst likely retains part of the supplied CO on the catalyst through quick CO chemisorption and CO decomposition. At high enough temperatures the retained all C species on the catalyst can be methanated, but the deposited C from CO decomposition likely deactivates the catalyst at the temperatures for 100% selective CO methanation. This shows in fact that the proposed temperature-staged methanation method requires necessarily newly developed catalyst to quickly dissociate chemisorbed CO and further to hydrogenate the activated C into CH$_4$ at the temperatures assuring 100% selective CO methanation.

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