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Influence of cycle parameters on periodically operated fluidised bed reactor for CH_4 autoreforming

Kingsley Opoku-Gyamfi, Joaquim Vieira-Dias, Adesoji A. Adesina*

Reactor Engineering and Technology Group, School of Chemical Engineering and Industrial Chemistry,
University of New South Wales, Sydney, NSW 2052, Australia

Abstract

Autothermal reforming of CH_4 has been studied under both periodic and steady state conditions. The investigation was conducted over Co–NiO in a fluidised bed reactor at 873 K and 101.32 kPa. Cycle periods of 1–40 min were used whilst the cycle split, S_{ox} (with respect to the O_2-rich cycle) was varied from 0.1 to 0.9. Generally, CH_4 oxidation stimulated CO formation, however, steam reforming yielded predominantly CO_2 and H_2. Although O_2-rich cycling ($S_{ox} \geq 0.5$) was detrimental to H_2 formation, H_2O-rich cycling resulted in a 15% improvement in steady state H_2 formation. Theoretical as well as experimental investigations pointed to a resonant frequency of about 6.7 mHz for CH_4 oxidation to produce super steady state H_2 yields. By periodic operation, it is possible to tune H_2/CO ratios over the range 2.5–7 for the same feed composition. Interestingly, $S_{ox} = 0.1$ yielded the highest ratios, whereas the lowest ratios were attained at $S_{ox} = 0.9$. Periodic composition cycling introduces a more flexible approach to reactor operation — H_2/CO can be easily modulated by varying the cycle parameters — compared to steady state operation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ammonia; Methanol; Reactor

1. Introduction

Autothermal reforming of CH_4 is a well-proven technology and has been used in ammonia and methanol plants, and for the production of pure H_2 and CO [1]. Compared to other competing technologies for syngas generation, autothermal reforming results in compact unit design, low investment, economy of scale, flexible operation and soot-free operation [1]. The main reactions involved in this process are:

$$CH_4 + 2O_2 = CO_2 + 2H_2O, \quad \Delta H = -802.31\,\mathrm{kJ\,mol^{-1}} \qquad (1)$$

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H = 225.4\,\mathrm{kJ\,mol^{-1}} \qquad (2)$$

Despite these advantages, conventional autoreforming often leads to low H_2 yield since H_2 formed may react with O_2 to yield H_2O. To circumvent this problem, we proposed for the first time, a periodically operated autoreforming system with feed composition alternating between CH_4/O_2 and CH_4/H_2O mixtures [2]. It was envisaged that this would promote independent CH_4 oxidation and steam reforming steps and thus minimise the reconversion of H_2. Indeed, periodic operation of reactor systems has been the subject of extensive experimental and theoretical investigations for three decades. Early work by Douglas [3–5] and Bailey [6,7] indicated that operating catalytic reactors by alternately switching between two predetermined feed compositions or temperature settings, it may be

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* Corresponding author. Tel.: +61-2-9385-5268;
fax: +61-2-9385-5966.
E-mail address: a.adesina@unsw.edu.au (A.A. Adesina).

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Nomenclature

TAR	time-average rate (mol g^{-1} s^{-1})
τ	cycle period (s)
N	total number of points within a cycle
r_i	instantaneous rate (mol g^{-1} s^{-1})
Δt_i	time interval between consecutive points (s)
τ_v	characteristic reactor time based on volume (s)
v	effective free volume of reactor (m^3)
Q_o	volumetric flow rate of reactant at operating conditions (m^3 s^{-1})
τ_a	characteristic reactor time based on the surface capacity of the catalyst (s)
a_m	total surface area of supported catalyst (130 m^2 g^{-1})
L_m	adsorption capacity of catalyst surface (1.42×10^{-5} mol m^{-2})
$[I]_o$	time-average concentration of reactant I in feed (mol m^{-3})

possible to achieve large improvements in reaction rate and selectivity. These tremendous gains are often attributed to the non-linear behaviour of the chemical process [8] which offers the opportunity to improve the time-averaged performance of a reaction-conversion, selectivity and yield. Incidentally, most of the studies on periodic operation reported in the literature have involved CO oxidation and hydrogenation.

One of the first investigations of CO oxidation under periodic operation was carried out by Cutlip [9], who found that periodic switching between CO and O_2 in a gradientless reactor resulted in a significant increase in reaction rate. He ascribed this improvement to the shifting reactant coverage of the catalyst surface during periodic operation. Barshad and Gulari [10] extended the study of CO oxidation to Pd/γ-Al_2O_3. They reported a 10-fold increase in CO oxidation rate at a CO/O_2 ratio of 2, 393 K and a split of 0.3 (based on the CO pulse), while at a CO/O_2 ratio of 1, 363 K and a split of 0.3, greater than 15-fold increase was obtained. The authors observed that as the period decreased, the effect of split changed. They therefore proposed that the time of exposure to CO may be a more important variable than split or period. They also concluded that the reaction proceeds via the surface interaction of adsorbed CO and adsorbed oxygen.

Given the intricate interaction of period, split, reaction rate and product selectivity observed in the foregoing studies, it appears feasible to exploit periodic operation to improve the flexibility of reactor operation as well as reactor performance. Since autothermal reforming involves both methane oxidation and steam reforming, an effort to optimise the overall process must take into consideration the individual oxidation and steam reforming steps. While Ni is widely used for steam reforming [11], Pt and Co have shown excellent activities for CH_4 oxidation [12–13]. Thus, by formulating catalysts where oxidation (Co and Pt) and steam reforming (Ni) sites are contiguously located on the same support, autoreforming may be enhanced. In a previous study, we observed excellent CH_4 oxidation and steam reforming activities for Co–NiO [14–15]. This catalyst has been employed for the present study.

2. Experimental

2.1. Catalyst

The bimetallic Co–NiO/δ-Al_2O_3 catalyst composed of 1 Co:10 Ni:100 Al_2O_3 was prepared by multiple impregnation technique from aqueous solutions of $Co(NO_3)_2$ and $Ni(NO_3)_2$ [15].

2.2. Apparatus and reaction conditions

A schematic diagram and detailed description of the experimental system has been provided elsewhere [2,16]. Autothermal reforming was carried out in a quartz (ID = 1 cm) fluidised bed reactor charged with about 4 g of catalyst ($d_p = 180$–250 μm) and operated with an upward flowing gas of 300 ml min^{-1} (293 K and 1 atm) consisting of CH_4, O_2 (or H_2O) and argon (as diluent). This hydrodynamics ensured smooth fluidisation where efficient mixing in the emulsion phase approximates the behaviour in a well-stirred reactor. In the present study, the reaction heat was supplied externally by an electric furnace. All runs were conducted over Co–NiO at 873 K and 101.32 kPa.

For the transient experiments the reactor feed was alternately switched between CH_4–O_2 (2:1) and CH_4–H_2O (1:3) mixtures. Cycle period, τ, between

1 and 40 min was used. Each cycle period was investigated at five cycle split levels ($S_{\mathrm{ox}} = 0.1$–0.9), where cycle split is defined as the fraction of time spent in the O_2-rich region. Using the on-line GC, instantaneous product composition measurements of all species were made at regular intervals during the oxidation and steam reforming partial cycles. However, water was condensed out prior to analysis in an ice/acetone cooled U-tube. The time-average rates (TAR) at each set of cycle parameters were computed after the attainment of cycle invariant state (state at which instantaneous reaction rate profile within a cycle is unchanged in successive cycles), using

$$\mathrm{TAR} = \frac{1}{\tau}\sum_{i=1}^{N} r_i \Delta t_i \tag{3}$$

Instantaneous temperature measurements within the bed showed that the temperature difference between the oxidation and steam reforming sections of the cycle was within ±1 K of the set temperature at 873 K. The steady state rate corresponding to the additive mixture of feed streams in both partial cycles, namely; CH_4:O_2:H_2O = 2:1:6 was also determined and used as a basis for evaluating the performance under periodic operation.

3. Results

3.1. Transient behaviour of reaction system

Fig. 1 displays the instantaneous rate versus time curves for CH_4,, CO, CO_2 and H_2 at $\tau = 20$ min, $S_{\mathrm{ox}} = 0.5$. Interestingly, the H_2, CH_4 and CO_2 curves were in phase with each other. However, the CO plot lagged these curves by about 180°. The highest rates for CH_4, CO_2 and H_2 were observed during the steam

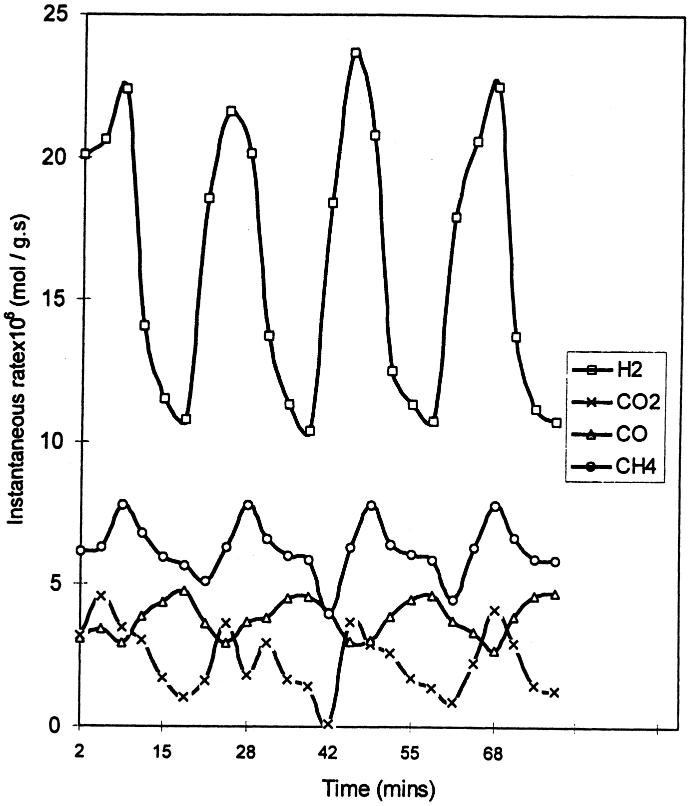

Fig. 1. Instantaneous rate versus time ($\tau = 20$ min, $S_{\mathrm{ox}} = 0.5$).

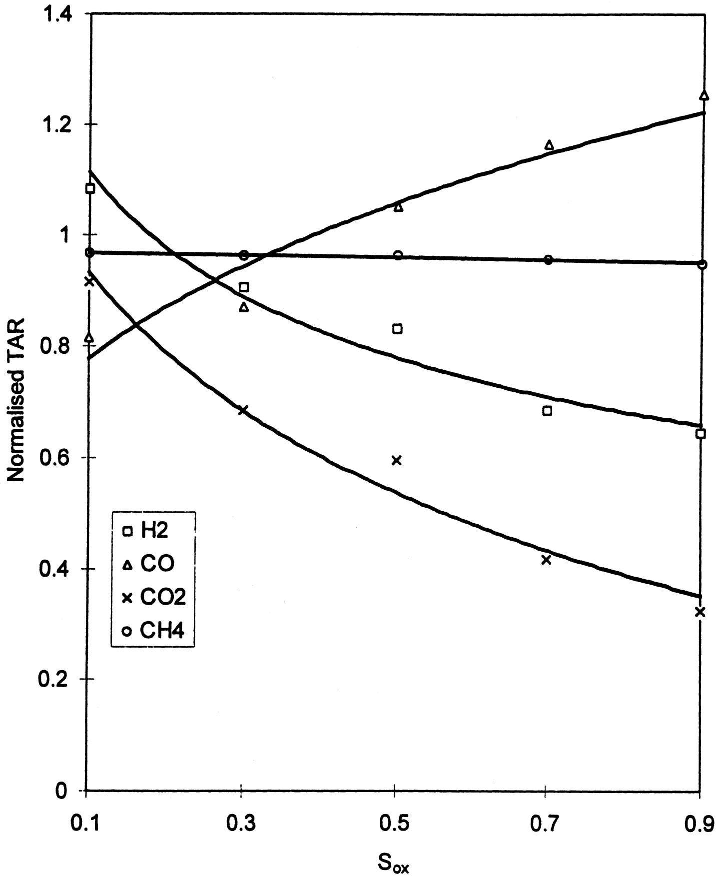

Fig. 2. Influence of cycle split on product distribution ($\tau = 10$ min).

reforming partial cycle (maxima points), whilst the highest CO rates were attained during the oxidation partial cycle. This suggests that during cycling, CH_4 steam reforming leads to the predominant formation of CO_2 and H_2, whilst CH_4 oxidation favours CO formation. The possible O_2 gasification of any deposited carbon during CH_4 reforming may have also contributed to CO formation during the O_2-rich partial cycle.

3.2. Effect of periodic operation on product distribution

The variation of the normalised time-average rates of CH_4, CO, CO_2 and H_2 with S_{ox} (cycle split with respect to the O_2-rich cycle) for cycle periods of 10 and 20 min as depicted in Figs. 2 and 3. It seems that the H_2 and CO_2 formation trends were opposite to that of CO. While H_2 and CO_2 rates decreased, CO rates increased with increasing cycle split. In particular, normalised time-average rates (TAR/rate at S.S) exceeding unity were observed for H_2 and CO at $S_{ox} < 0.3$ and $S_{ox} > 0.3$, respectively. These observations suggest that $S_{ox} < 0.3$ stimulates H_2 and CO_2 formation, whilst $S_{ox} > 0.3$ promotes CO formation and provide further indication that steam reforming and oxidation maximise CO_2/H_2 and CO formation, respectively. Interestingly, the methane depletion curves remained almost flat under the whole range of cycle split.

The effect of period on CO_2 formation is shown in Fig. 4. Generally, CO_2 formation decreased with increasing cycle period. Under all cycling conditions, periodic operation yielded lower CO_2 rates compared to operation at steady state. By contrast, CO formation increased with increasing cycle period, with $S_{ox} = 0.9$

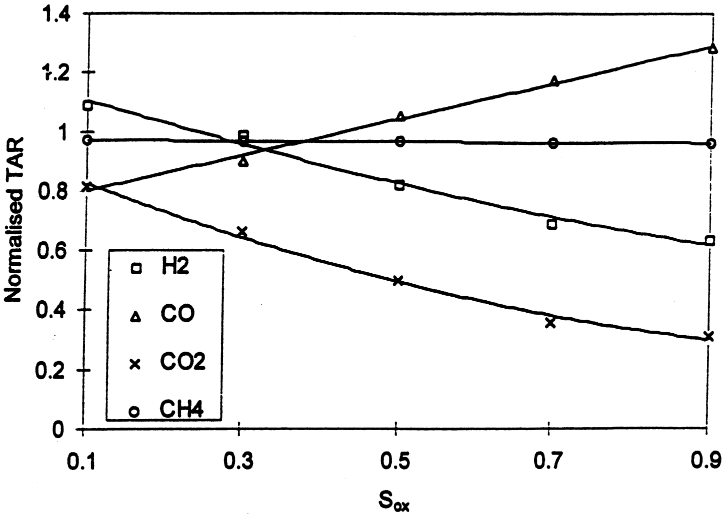

Fig. 3. Influence of cycle split on product distribution ($\tau = 20\,\text{min}$).

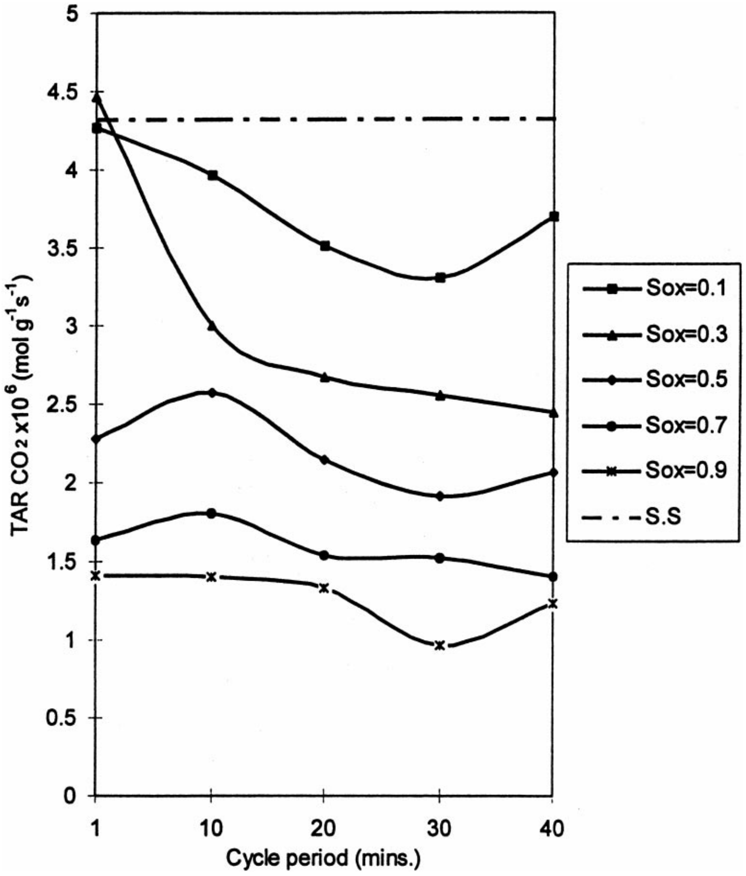

Fig. 4. Effect of period on CO_2 formation.

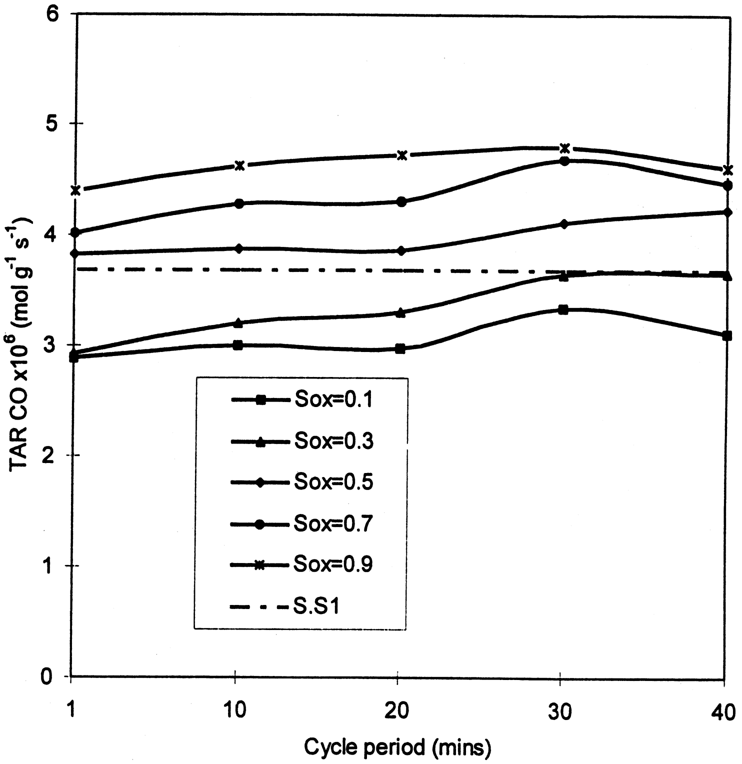

Fig. 5. Effect of period on CO formation.

showing the highest rates (cf. Fig. 5). It is evident that operation with $S_{ox} = 0.5, 0.7$ and 0.9 resulted in higher CO formation rates than the steady state value. This observation suggests that composition modulation may be used to stimulate CO formation. The effect of cycle period on H_2/CO ratio is presented in Fig. 6. While steady state autoreforming corresponding to the mean feed composition gave a value of 5.2, periodic operation yielded values in the range 2.5–7, with $S_{ox} = 0.1$ and $S_{ox} = 0.9$ giving the highest and lowest ratios, respectively.

4. Discussion

4.1. Instantaneous response curves

The sinusoidal wave-forms observed from the instantaneous rate versus time plot (Fig. 1) are typical of chemical systems under square-wave feed composition cycling [15] and signify the variable response of the catalyst to different feed environments during cycling. The fact that the CO_2 and H_2 peaks attained maxima values during the steam reforming partial cycle, whereas the CO peak attained maxima values during the oxidation partial cycle indicates that during cycling, CO_2–H_2 and CO–H_2O are the major steam reforming and oxidation products, respectively.

Interestingly, there was a perfect overlap of the CO_2 and H_2 peaks with the valley of the CO curve at this cycle period. This may suggest that a period of about 20 min is required for the autothermal system to show the characteristics of pure CH_4–O_2 and CH_4–H_2O systems. In other words, the half-cycle times at this period are long enough to permit a period within each cycle where the catalyst surface is composed entirely of entities resulting from the adsorption of only CH_4 and O_2 or CH_4 and H_2O. According to Lynch and Sadhankar [17], for a system under periodic operation, the two characteristic times of the reactor based on

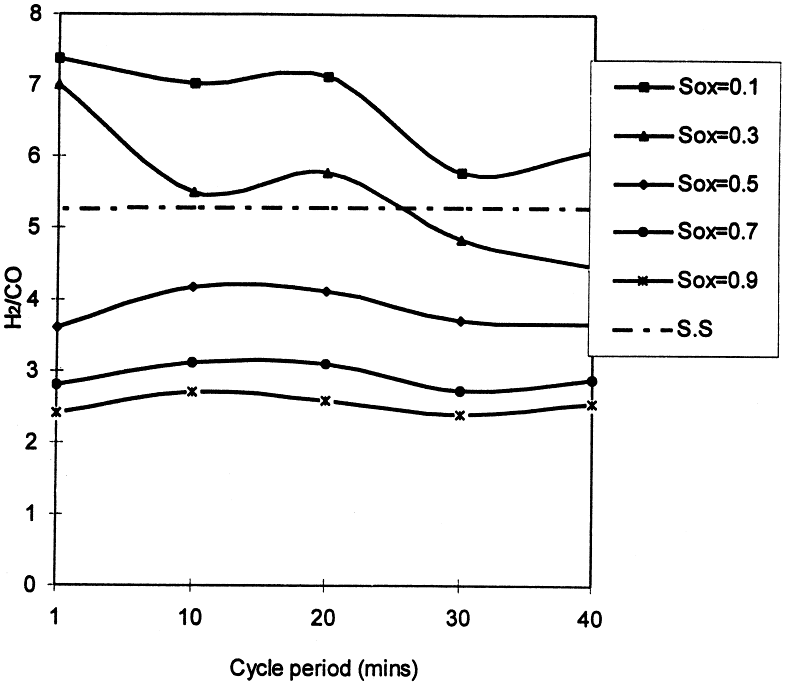

Fig. 6. H_2/CO versus cycle period.

volume (τ_v) and the surface capacity of the catalyst (τ_a) are defined by

$$\tau_v = \frac{v}{Q_o} \tag{4}$$

and

$$\tau_a = \frac{a_m L_m}{Q_o[I]_o} \tag{5}$$

Under the reaction conditions in this study, Eqs. (4) and (5) gave values of 7.3, 24.6 s, and 2.47 min for τ_v, τ_a (H_2O) and τ_a (O_2), respectively. For any species, τ_a is the characteristic response time of the system and resonant frequency (reciprocal of cycle period) would correspond to this period or its multiples. Consequently, cycling at periods greater than 20 min provides an opportunity for total coverage of the catalyst surface with adsorbed reactants during each partial cycle. It is possible that during the steam reforming partial cycle, the catalyst surface becomes saturated with entities derived from the dissociative adsorption of CH_4 and H_2O [15]. These entities may then interact to yield CO_2 and H_2 as shown by the instantaneous rate curves (Fig. 1). At the beginning of the oxidation partial cycle, the catalyst surface is composed of derivatives of CH_4 and H_2O from the previous partial cycle. However, with the introduction of O_2, the H_2O derivatives are progressively replaced with O_2 species. Interaction of the CH_4 and O_2 derivatives then yields CO and H_2O as the predominant products. Although the formation of C_{2+} hydrocarbons may be possible under these conditions, however, they were not observed. This explains why a CO peak was observed in this cycle. The corresponding minima observed for H_2 and CO_2 reflects the relatively low yields of these products during the oxidation partial cycle. As expected, a surge in H_2 and CO_2 formation rate was observed again when the feed was switched from CH_4–O_2 to CH_4–H_2O. The fact that CO and CO_2 rates show similar conversion rates during the oxidation and steam reforming partial cycles suggests that both are directly produced from CH_4 in each section of the cycle. Interestingly, CO peaks lagged H_2 and CO_2 peaks by approximately 180° indicating that H_2 and CO_2 were exclusively produced during steam reforming portion of the cycle.

4.2. *Effect of cycle variables on product distribution*

The influence of cycle split on product composition is presented in Figs. 2 and 3. As may be seen, at the cycle periods of 10 min (Fig. 2) and 20 min (Fig. 3), $S_{ox} = 0.1$ gave H_2 rates above the steady state values. Interestingly, these two cycling conditions ($\tau = 10\,\text{min},\ S_{ox} = 0.1;\ \tau = 20\,\text{min},\ S_{ox} = 0.1$) corresponded to oxidation cycling times of 1 and 2 min. A one-step increment in split from $S_{ox} = 0.1$ resulted in a decline in the H_2 rate below the steady state value (Figs. 2 and 3). Intriguingly, under these cycling conditions ($\tau = 10\,\text{min},\ S_{ox} = 0.3;\ \tau = 20\,\text{min},\ S_{ox} = 0.3$), the oxidation cycles lasted for 3 and 6 min, respectively. Since characteristic response time for O_2 was 2.47 min (resonant frequency of about 6.7 mHz), it is possible that this is the maximum time the catalyst should be exposed to CH_4 oxidation to produce an improvement in H_2 rate beyond the steady state value. Apparently, exposure of the catalyst to CH_4 oxidation for a period longer than this threshold value leads to increased coverage of the catalyst surface with O_2 species, which would survive into the next steam reforming partial cycle and result in a reduction in H_2 formation. This explains the rationale for using a relatively high CH_4:O_2 ratio (2:1) in the oxidation portion of the cycle. As expected this threshold value would vary with change in experimental conditions.

It is seen from Figs. 4 and 5 that CO_2 rates increased with decreasing split whilst CO formation rate improved with split. This is in agreement with our previous observation that steam reforming favours CO_2 and H_2 formation whereas oxidation enhances CO formation. Indeed, it is clear from Fig. 5 that periodic operation can be employed to stimulate CO formation beyond steady state rates. Under cycling, it is possible to induce a shift in reactant coverage of the catalyst surface that will maximise CO formation yet minimise its depletion through the water-gas-shift reaction. However, during steady state operation this may not be possible since CH_4 oxidation and steam reforming take place simultaneously.

The flexibility in reactor operation offered by periodic cycling is evident from Fig. 6. While steady state operation yielded a H_2/CO ratio of 5.2, ratios of 2.5–7 were achieved through periodic operation. This versatility may be attributed to the ability to manipulate the entities on the catalyst surface during cycling. Since CH_4 oxidation and steam reforming promote CO and H_2O and CO_2 and H_2 formation, respectively (Fig. 1), it follows that low cycle splits (O_2-lean cycling) will yield high H_2/CO ratios whilst high cycle splits (O_2-rich cycling) will produce low H_2/CO ratios. The fact that steady state operation gave a H_2/CO ratio of 5.2 — a value greater than the stoichiometric requirement (3 or 4) seem to indicate that other H_2 forming reactions, such as the water-gas-shift reaction occurred.

5. Conclusions

The foregoing results indicate that under periodic cycling, CH_4 steam reforming proceed via the interaction of entities derived from the dissociative adsorption of CH_4 and H_2O leading to the predominant formation of CO_2 and H_2. CH_4 oxidation on the other hand occurs through the reaction of adsorbed CH_4 and O_2 derivatives to form CO and H_2O as the major products. At $\tau = 1\,\text{min},\ S_{ox} = 0.1;\ \tau = 10\,\text{min},\ S_{ox} = 0.1;\ \tau = 20\,\text{min},\ S_{ox} = 0.1$, periodic cycling resulted in higher (15% increase) H_2 formation rates compared to steady state operation. Theoretical and experimental evidence indicate that under the reaction conditions, the oxidation partial cycle time should not exceed 2.47 min if H_2 rates above the steady state value are to be attained. Periodic operation offers a more convenient and flexible approach to modulating H_2/CO ratio during autoreforming than steady state operation.

Acknowledgements

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