

Effects of fuel cell anode recycle on catalytic fuel reforming

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Abstract

The presence of steam in the reactant gas of a catalytic fuel reformer decreases the formation of carbon, minimizing catalyst deactivation. However, the operation of the reformer without supplemental water reduces the size, weight, cost, and overall complexity of the system. The work presented here examines experimentally two options for adding steam to the reformer inlet: (I) recycle of a simulated fuel cell anode exit gas (comprised of mainly CO₂, H₂O, and N₂ and some H₂ and CO) and (II) recycle of the reformat from the reformer exit back to the reformer inlet (mainly comprised of H₂, CO, and N₂ and some H₂O and CO₂). As expected, anode gas recycle reduced the carbon formation and increased the hydrogen concentration in the reformat. However, reformer recycle was not as effective due principally to the lower water content in the reformat compared to the anode gas. In fact, reformat recycle showed slightly increased carbon formation compared to no recycle. In an attempt to understand the effects of individual gases in these recycle streams (H₂, CO, CO₂, N₂, and H₂O), individual gas species were independently introduced to the reformer feed.

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1. Introduction

Solid oxide fuel cells are among the most efficient energy conversion devices available [1–3]. They rely on a supply of reformat gas which can be produced by the catalytic reforming of liquid fuels [4], such as diesel fuel, in a fuel processor. Although some reforming processes are based on the addition of steam to reduce the formation of carbon, there are a number of applications where this is not feasible because a supply of water/steam is not readily available. These include mobile applications, remote power supplies in a military environment, and auxiliary power units (APUs) for long-haul diesel trucks.

In these applications, catalytic partial oxidation (CPOX) of the fuel, in which the fuel reacts with substoichiometric air to produce a gas consisting primarily of hydrogen and carbon monoxide, is the preferred reforming process. However, the lack of steam in the reactant gas stream can lead to more rapid deactivation of the catalyst than if steam is present, due primarily to carbon formation. One way to provide at least some steam to the CPOX process is to recycle a portion of the steam-containing anode off-gas, which primarily contains water, carbon dioxide, and nitrogen (Fig. 1). This also has the potential to improve the overall thermal integration of the overall process (and therefore the overall efficiency), and to inhibit the temperature rise in the CPOX reactor, which can limit deactivation due to catalyst sintering.

One of the reactions that helps limit carbon accumulation is the reaction of steam with carbon to form carbon monoxide and hydrogen (Reaction (1)):



$$\Delta H_{298}^{\circ} = +131.3 \text{ kJ/mol}$$

$$\Delta G_{298}^{\circ} = +91.4 \text{ kJ/mol}$$

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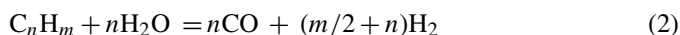
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For carbon-containing “coke” deposits that are thought to be condensed, polynuclear aromatic-type compounds, Reaction (1) can be more generally represented as:



where $n \sim m$ in most “coke” deposits. For the polynuclear aromatics of interest here, this reaction is endothermic and thermodynamically favorable at elevated temperatures (For example, anthracene $C_{14}H_{10}$, it is favorable at $>500^\circ\text{C}$ (1 atm)).

The anode off-gas also contains carbon dioxide. If the anode off-gas is to be recycled to the inlet of the fuel processor, the effect of this component of the gas must be examined as well. Carbon dioxide can be beneficial in reducing the carbon formation by the Boudouard reaction:



$$\Delta H_{298}^\circ = +172.4 \text{ kJ/mol}$$

$$\Delta G_{298}^\circ = +120.0 \text{ kJ/mol}$$

Reactions (1) and (3) become thermodynamically favorable ($\Delta G^\circ < 0$) at temperature of above 675 and 700°C , respectively. In addition to coke inhibition, carbon dioxide and water can react with the fuel directly in the steam and dry reforming reactions [Reactions (4) and (5), respectively]:



These reactions can increase the overall fuel conversion of the reformer, provided there is sufficient heat to drive these endothermic reactions. By recycling the anode off-gas, it is also possible that a lower air/fuel in the feed to the reformer can be used. Overall, water can help suppress carbon formation, allow for better thermal integration and system efficiency, and possibly inhibit temperature rise and catalyst sintering.

Another option to improve the overall efficiency of the process is to recycle a portion of the reformat produced by the fuel processor itself back to the reactor inlet (Fig. 1). This reformat contains primarily carbon monoxide and hydrogen, but also significant concentrations of steam and carbon dioxide. [The

Table 1
Composition (vol%) of simulated anode and reformat recycle streams

Recycle gas component	Composition (%) in simulated anode gas stream	Composition (%) in simulated reformat recycle stream
H ₂	3	22
CO	3	24
CO ₂	24	1
H ₂ O	18	5
N ₂	52	48

essential difference between the composition of this stream and the anode off-gas is the higher concentrations of carbon dioxide and steam in anode off-gas stream.] Among other potential benefits, the hydrogen in this gas stream may limit the dehydrogenation of the hydrocarbons in the fuel, which is one of the primary steps leading to coke formation on the catalyst.

Here, we explore two process configurations designed to provide steam and carbon dioxide to the reformer inlet: (1) recycle of the anode off-gas to the reformer inlet and (2) recycle from the reformer exit (see Fig. 1). These options are compared in terms of the yields and composition of the reformat, hydrocarbon conversion, and carbon formation over a rhodium/ γ -alumina catalyst. The effects of recycle each individual compound in these recycle gases (H₂, CO, CO₂, N₂, and H₂O) on reforming properties are also reported.

2. Experimental

2.1. Activity measurements

A mixture of 40 wt% *n*-tetradecane, 20 wt% *t*-butylbenzene, 18 wt% *t*-butylcyclohexane, and 22 wt% decalin was used as a simulated diesel fuel for this study. The compositions of the simulated anode and reformat recycle streams used here are given in Table 1. The anode recycle gas is much richer in carbon dioxide and steam than the reformat recycle gas, making it a more oxidizing gas. Note that a somewhat higher water composition than expected in actual reformer recycle stream was used for the reformer recycle stream since it was not possible to pump the water accurately at low flow rates. Gases of these compositions were blended with the oxygen-containing feed gas to the reformer to simulate the recycle of the anode off-gas and reformer outlet. When the simulated recycle gases are combined with the hydrocarbon/oxygen feed, the resulting mixture is the actual feed to the catalytic reactor. For each of the two recycle gases, five separate recycle ratios were used to calculate the simulated gas mixture; where recycle ratio is defined as the ratio of the exhaust gas flow from the reformer or anode recycled to the total exhaust flow from the reformer or anode. In addition, the effect of each individual gas (H₂, CO, CO₂, N₂, and H₂O) in the recycle streams was evaluated by adding them individually to the hydrocarbon/oxygen feed. The actual gas compositions resulting from these blends was then fed to the reactor in fifteen separate experiments, shown in Table 2 (one experiment for each of the six the anode gas recycle ratios, one for each of

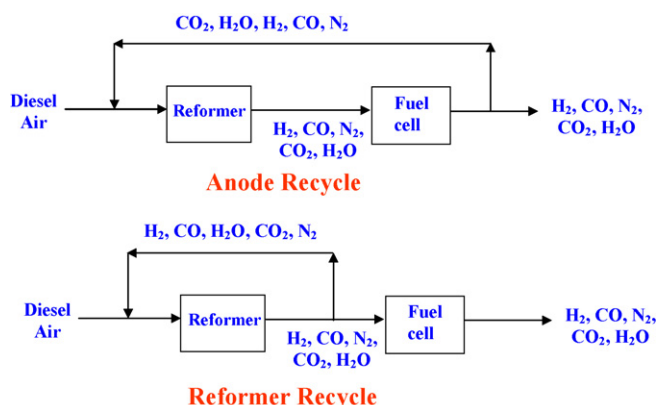


Fig. 1. Recycle configurations.

Table 2

Composition (mol%) of feed for experiments to study the effects of anode off-gas, reformer outlet, and individual components

Comp	Anode-off simulated stream						Reformer-off simulated stream					Individual gases				
	0.0	0.1	0.2	0.3	0.4	0.5	0.0	0.2	0.3	0.4	0.5	N ₂	H ₂	H ₂ O	CO	CO ₂
TD	1.0	1.0	0.8	0.7	0.6	0.5	1.0	0.8	0.7	0.6	0.5	0.6	0.6	0.6	0.6	0.6
TBB	0.7	0.7	0.6	0.5	0.4	0.3	0.7	0.6	0.5	0.4	0.3	0.4	0.4	0.4	0.4	0.4
TBCH	0.6	0.6	0.5	0.4	0.4	0.3	0.6	0.5	0.4	0.4	0.3	0.4	0.4	0.4	0.4	0.4
DL	0.8	0.8	0.7	0.5	0.4	0.4	0.8	0.7	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4
N ₂	79.6	72.6	69.3	66.4	63.7	61.2	79.6	68.5	65.2	62.2	59.4	88.2	75.8	75.8	75.8	75.8
O ₂	17.3	17.3	14.6	12.2	10.0	8.0	17.3	14.6	12.2	10.0	8.0	10.0	10.0	10.0	10.0	10.0
H ₂	–	0.5	0.9	1.3	1.7	2.0	–	6.0	8.6	11.0	13.1	–	12.4	–	–	–
H ₂ O	–	2.5	4.8	6.9	8.7	10.5	–	1.3	1.9	2.4	2.9	–	–	12.4	–	–
CO ₂	–	3.6	6.8	9.7	12.4	14.8	–	0.3	0.4	0.5	0.6	–	–	–	–	12.4
CO	–	0.5	0.9	1.3	1.7	2.1	–	6.7	9.6	12.2	14.6	–	–	–	12.4	–

the four the reformate recycle ratios, and one for each of the five individual gases).

The experimental system used for this study as well as its detailed description is documented elsewhere [5]. Briefly, these runs were carried out in a fixed bed continuous-flow reactor. The catalyst was diluted with quartz sand (5/1 by weight) to avoid channeling and to minimize temperature gradients. The bed was placed in a tubular reactor (8 mm i.d.) with a coaxially centered thermocouple at the center of the bed. Simulated recycle stream and air were delivered by mass flow controllers and the liquid feeds were delivered by a high accuracy HPLC dual pump. A recycle ratio range of 0–0.5 was studied for both configurations.

Experiments were conducted at an O/C ratio of 1.0 (calculated based only on molecular diatomic oxygen in the inlet gas and carbon from hydrocarbons only), a gas hourly space velocity (GHSV = total volumetric flow rate to the reactor at standard temperature and pressure divided by the catalyst bed volume) = 50,000 h⁻¹ and 850 °C. Overall O/C (which includes oxygen contained in CO₂, CO and H₂O and carbon contained in CO₂ and CO) and S/C (steam-to-carbon) ratios are given in Table 3. The catalysts was a 0.5% Rh/γ-alumina (Alfa Aesar 42507, lot D04N26; surface area 100 m² g⁻¹). The fresh feed flow rate was kept constant while the amount of catalyst taken was increased as recycle ratio increased to maintain a constant GHSV. Temperature programmed oxidation (TPO) of the spent catalyst was used to determine the amount of carbon deposited during the reforming reaction. A mixture of 3.5% oxygen balance nitrogen was passed over the used catalyst while

Table 3

Overall O/C and S/C (steam-to-carbon) ratios for both feed configurations used in this study

Recycle ratio	Anode-off stream		Reformer-off stream	
	O/C	S/C	O/C	S/C
0.0	1.00	0.00	1.00	0.00
0.1	1.16	0.07	1.02	0.02
0.2	1.31	0.16	1.04	0.05
0.3	1.47	0.28	1.07	0.08
0.4	1.62	0.44	1.09	0.12
0.5	1.77	0.65	1.11	0.18

it was ramped from 200 °C at 1 °C min⁻¹. An on-line mass spectrometer was used to monitor the carbon dioxide concentrations continuously during TPO. The total carbon accumulated on the catalysts was determined from the area under the TPO curve.

2.2. Product analysis

The gases (N₂, O₂, CO, CO₂, and H₂) were analyzed using a Thermo Onix mass spectrometer (Model no. Prima 8b, a 200 amu scanning magnetic sector mass spectrometer). The gaseous hydrocarbon products (C₁–C₆ paraffins, C₂–C₆ olefins, and benzene) were analyzed using a HP5890 gas chromatograph equipped with a flame ionization detector. The term ‘unsaturates’ refers to ‘olefins + aromatics’. Oxygen conversion was always complete during these experiments. Although, water was produced in the reaction, it was not quantitatively analyzed. Overall carbon balances were typically 100 ± 5%.

Yield of product A (H₂, CO, and CO₂) is defined as:

Yield of A (%)

$$= \frac{(\text{moles of A in reactor effluent} - \text{moles of A in feed}) \times 100}{N \times \text{moles of hydrocarbon fed to the reactor}}$$

where N is the number of moles of hydrogen/mole of hydrocarbon for hydrogen yields and is the number of carbons in hydrocarbon fuel for yields of carbon monoxide and carbon dioxide. In some cases, hydrogen yields may be higher than 100% since steam reforming and water gas shift reaction also contribute in hydrogen production apart from hydrocarbons. Similarly, carbon monoxide yields maybe higher than 100% due to contribution from dry reforming or Boudouard reaction.

Yield of hydrocarbons (olefins, paraffins, and benzene) is defined as:

Hydrocarbon yield (%)

$$= \frac{m \times \text{moles of hydrocarbon produced} \times 100}{N \times \text{moles of hydrocarbon fed to the reactor}}$$

where m is the number of carbons in the hydrocarbon product.

The conversion of hydrocarbons is defined as:

$$\text{Conv (\%)} = \frac{(\text{CO} + \text{CO}_2 + \sum_{i=1-6} i\text{C}_i\text{H}_r) \times 100}{N \times \text{moles of hydrocarbon fed to the reactor}}$$

Carbon formation is defined as

Carbon selectivity(% of C fed)

$$= \frac{\text{moles of carbon formed on the catalyst} \times 100}{\text{moles of carbon fed to the reactor}}$$

where moles of carbon fed to the reactor includes only carbon fed in the form of hydrocarbon feed, not from carbon monoxide and carbon dioxide.

3. Results and discussion

3.1. Effects of anode recycle stream

Yields of hydrogen, carbon monoxide, carbon dioxide, lower paraffins, and unsaturates for anode recycle ratios 0–0.5 are given in Table 4, which also shows how the actual measured gas yields compare to the equilibrium yields at each recycle ratio.

Conversion of the liquid hydrocarbons (diesel simulates) to gaseous products was always close to 100%, as was oxygen conversion. Hydrogen and carbon monoxide yields increased with increasing anode recycle ratio. However, yields of carbon dioxide, paraffins, and unsaturates (C_2 – C_6 olefins + benzene) generally decreased with increasing anode recycle ratio. Negative carbon dioxide yields (or carbon dioxide conversion) and >100% carbon monoxide yields at anode recycle ratio of 0.2 and above suggest that high concentrations of carbon dioxide present in the system at higher recycle ratios facilitate the reverse of water gas shift reaction ($\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$). This is consistent with the equilibrium results, suggesting that the product gas composition is approaching equilibrium at each experimental condition. However, contrary to equilibrium prediction, hydrogen yields increased at higher recycle ratios because the lower hydrocarbons (which were observed at lower recycle ratios) were reformed by carbon dioxide and steam via Reactions (4) and (5) into hydrogen and carbon monoxide, increasing the hydrogen and carbon monoxide yields as well as lowering yields of lower hydrocarbons.

Table 4
Comparison of measured outlet gas yields^a to equilibrium for anode gas recycle experiments

Component	0.0		0.1		0.2		0.3		0.4		0.5	
	Equil	Actual	Equil	Actual	Equil	Actual	Equil	Actual	Equil	Actual	Equil	Actual
CO	96.5	86.2	101.1	92.3	103.0	95.7	104.6	100.9	106.3	101.5	109.1	100.4
H ₂	93.4	82.6	97.3	82.6	96.1	89.4	93.4	89.4	92.0	96.0	90.5	95.4
CO ₂	1.2	7.3	–1.5	3.2	–3.2	1.7	–4.6	–4.4	–7.0	–4.4	–9.5	–4.3
Paraffins	2.6	3.6	0.4	3.0	0.2	2.0	0.1	1.7	0.04	1.2	0.02	2.0
Unsaturation	0.0	3.9	0.0	4.0	0.0	3.1	0.0	1.8	0.0	1.6	0.0	1.9

^a In some cases, hydrogen yields may be higher than 100% since steam reforming and water gas shift reaction also contribute in hydrogen production apart from hydrocarbons. Similarly, carbon monoxide yields may be higher than 100% due to contribution from dry reforming or Boudouard reaction.

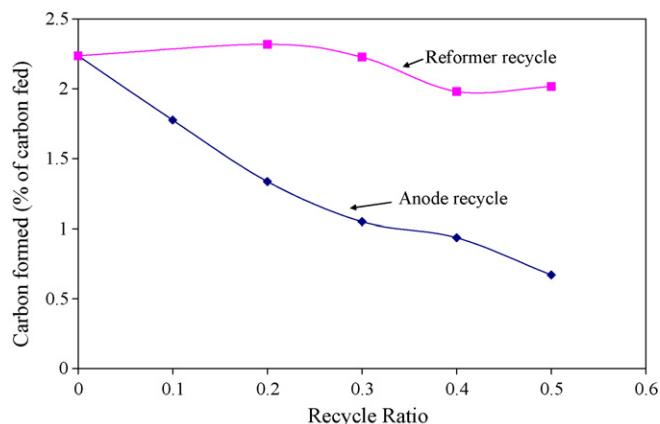


Fig. 2. Effect of recycle on carbon formation (0.5 wt% Rh/ γ -alumina, 850 °C, 50,000 h^{–1}).

Carbon formation, as measured by TPO, decreased significantly with increasing recycle ratio for anode-off recycle streams (Fig. 2). However, reformer recycle was not as effective in reducing carbon formation due principally to the lower water content in the reformat (containing 5% H₂O and 1% CO₂) compared to the anode gas (containing 24% CO₂ + 18% H₂O). In fact, reformat recycle showed slightly increased carbon formation compared to no recycle. Interestingly, the carbon formation is directly related to unsaturates yields—both decreased with increasing anode recycle ratio (Table 4). This is consistent with the generally accepted mechanism for carbon formation, involving dehydrogenation of the hydrocarbon feed as a first step [6–7].

The TPOs of carbon deposited on the catalyst at different anode gas recycle ratios are shown in Fig. 3. Three main peaks were observed in the TPOs of the catalyst used for different recycle ratios. The low-temperature peaks (~580 °C) can be assigned to carbon deposition on rhodium metal sites, which can be oxidized easily at low temperatures [8–11]. The intermediate-temperature peaks (~650 °C) can be assigned to the carbon deposited near the metal–support interface [9,11]. The more refractory carbon corresponding to the high-temperature peaks (~800 °C) can be attributed to the carbon deposited on the alumina support [5,8–10]. The carbon deposition corresponding to the low-temperature peaks decreased significantly with simulated recycle streams. These low-temperature peaks became shoulders to the intermediate-temperature peaks for the catalysts with the recycle streams. The low-temperature peak for the recy-

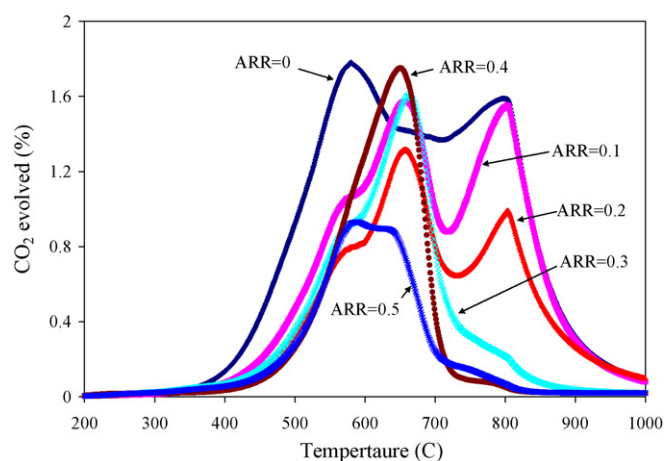


Fig. 3. Effect of recycle on carbon formation type: anode recycle (0.5 wt% Rh/ γ -alumina, 850 °C, 50,000 h⁻¹) (ARR = anode recycle ratio).

cle ratio of 0.4 is not distinct from the intermediate-temperature peak in Fig. 3; most likely both of these peaks overlap in this case. There is no consistent trend for the intermediate-temperature peaks with recycle ratio. However, the carbon deposition corresponding to the high-temperature peak decreases monotonically with increasing recycle ratio, becoming negligible at a recycle ratio of 0.4 and higher. This suggests that the amount of carbon deposited on the support which is more refractory in nature can be reduced in the presence of a recycle stream.

The overall O/C ratio increases at the higher recycle values, although the proportion of O atoms coming from O₂ (versus those in CO₂ + H₂O) decreases (Tables 2 and 3). It might be expected that as the concentration of the more reactive O₂ decreases, more of the refractory carbon, corresponding to the ~800 °C TPO peak in Fig. 3, would be formed even as the overall O/C ratio increases. However, the opposite trend is shown in Fig. 3—the amount of refractory carbon (~800 °C TPO peak)

decreases with decreasing O₂ concentration (and with increasing CO₂ + H₂O concentration). Note also that at the highest recycle ratio (0.5), very little refractory carbon is present, but significant amounts of the more reactive (~580 °C TPO peak) carbon are still present. It appears that the refractory carbon is (a) more reactive with steam and carbon dioxide than the low-temperature carbon and (b) less reactive with oxygen than with carbon dioxide and steam.

3.2. Effects of reformer recycle stream

Yields of hydrogen, carbon monoxide, carbon dioxide, lower paraffins, and unsaturates, and liquid hydrocarbon conversion for reformer recycle ratios 0–0.5 are given in Table 5. Effects of reformer recycle were significantly different than the anode-off recycle. The primary effect is that the yields of hydrogen and carbon monoxide decreased significantly with increased recycle for all levels of recycle. Also contrary to anode recycle, liquid hydrocarbon conversion (i.e., conversion of the simulated diesel fuel) decreased considerably upon the introduction of reformer recycle while the yields of lower paraffins, unsaturates, and carbon dioxide increased. The lower hydrocarbon conversions, along with lower syngas yields of the catalyst may be due to the presence of carbon monoxide, which likely poisons the active sites if it is present in higher concentrations and, thus, decreases the overall conversion as well as syngas formation (Table 6).

Carbon formation/selectivity (moles of carbon formed \times 100/moles of carbon fed to the reactor) was not affected significantly by introducing a reformer recycle stream (Fig. 2). However, the carbon formed per mole of carbon converted in the reactor increased significantly since the overall hydrocarbon conversion was in the range of 80–85% in the presence of reformer recycle streams. For anode-off recycle streams, carbon formed normalized to overall carbon fed and to carbon converted

Table 5
Comparison of measured outlet gas yields and hydrocarbon (HC) conversion to equilibrium for reformer gas recycle experiments

Component	0.0		0.2		0.3		0.4		0.5	
	Equil	Actual	Equil	Actual	Equil	Actual	Equil	Actual	Equil	Actual
CO	96.5	86.2	95.7	61.1	93.8	57.7	92.9	63.5	91.4	49.3
H ₂	93.4	82.6	97.3	66.5	98.3	64.4	100.5	69.1	103.8	64.2
CO ₂	1.2	7.3	2.6	13.2	4.0	11.8	5.3	8.4	7.2	17.2
Paraffins	2.6	3.6	1.7	6.4	1.3	5.4	1.3	5.6	1.3	5.8
Unsaturates	0.0	3.9	0.0	5.9	0.0	10.1	0.0	8.3	0.0	8.6
HC Conv	100	100	100	86.6	100	85.0	100	85.3	100	80.8

Table 6
Comparison of measured outlet gas yields to equilibrium for individual recycle experiments

Component	N ₂		H ₂		H ₂ O		CO		CO ₂	
	Equil	Actual	Equil	Actual	Equil	Actual	Equil	Actual	Equil	Actual
CO	97.2	82.2	94.5	87.0	76.3	82.9	93.9	55.6	123.0	121.3
H ₂	95.7	86.1	88.9	75.6	124.4	114.8	93.1	73.5	75.7	78.7
CO ₂	0.9	5.6	2.3	5.0	25.0	16.6	2.9	14.9	-22.6	-19.6
Paraffins	1.5	2.6	5.2	7.7	0.2	0.9	4.0	4.7	0.1	1.0
Unsaturates	0.0	2.5	0.0	2.1	0.0	0.6	0.0	8.8	0.0	1.6

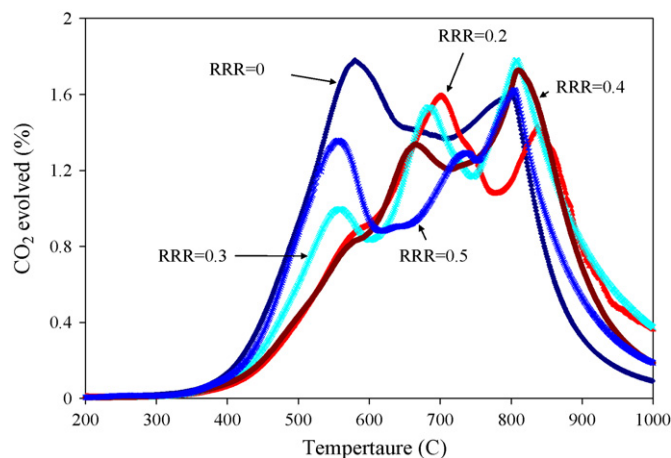


Fig. 4. Effect of individual recycle components on carbon formation (0.5 wt% Rh/ γ -alumina, 850 °C, 50,000 h⁻¹).

was almost the same since the overall hydrocarbon was always close to 100%.

The TPOs of carbon deposited on the catalyst at different reformer gas recycle ratios are shown in Fig. 4. Similar to the TPOs from the anode-off recycle stream (Fig. 3), three main peaks were observed in the TPOs (at roughly the same temperatures) of the catalyst used at different reformer recycle ratios. However, the high-temperature peaks (assigned to the carbon deposited on the support) were not affected by introducing the simulated reformer recycle stream as they were in the presence of the anode-off recycle stream.

3.3. Effects of individual recycle components on carbon formation

Components present in both recycle schemes were the same (H₂, CO, CO₂, H₂O, and N₂), but with completely different concentrations. Therefore, some of those components may have detrimental effects on the yields and carbon formation while others may have positive effects. To delineate the effects of each recycle component, experiments were conducted to examine the effect of five individual components (H₂, CO, CO₂, H₂O, and N₂) on the performance of the reforming catalyst. These runs with individual components were conducted using a flow rate equivalent to a recycle ratio of 0.4. The simulated recycle stream for these runs was consisted of 21 vol% of individual components balanced by nitrogen (see Table 2 for overall feed compositions). In the case of nitrogen only in recycle stream, the whole stream was comprised of only nitrogen and this inert stream was used as a baseline for comparison purposes.

The effect of individual components on carbon formation is shown in Fig. 5. Carbon formation decreases significantly in the presence of either carbon dioxide or steam in the recycle stream, compared to nitrogen or hydrogen. As mentioned earlier, the presence of carbon dioxide in the reactant gas helps in reducing carbon formation by the Boudouard reaction ($C + CO_2 = 2CO$). In addition, carbon can be gasified by steam ($C + H_2O = H_2 + CO$). The lower levels of carbon formed in the

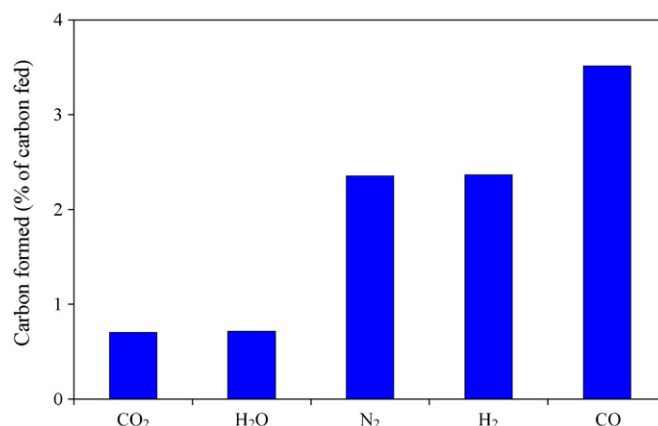


Fig. 5. Effect of recycle on carbon formation type: reformer recycle (0.5 wt% Rh/ γ -alumina, 850 °C, 50,000 h⁻¹) (RRR = reformer recycle ratio).

presence of carbon dioxide and steam recycles are consistent with Fig. 2, which shows that significantly less carbon is formed in the presence of higher levels of carbon dioxide and steam in the simulated anode off-gas than higher levels of carbon monoxide and hydrogen in the simulated reformer recycle gas. The presence of carbon monoxide only in the recycle stream considerably increased the amount of carbon formed compared to nitrogen only in the recycle stream. As discussed earlier, higher carbon monoxide concentrations may drive the formation of Boudouard carbon. The presence of carbon monoxide may also deactivate the active metal sites and, hence, produce higher amounts of unsaturates due to enhanced gas phase chemistry which results in higher amounts of carbon on the catalyst surface. If we assume that nitrogen has no effect on carbon formation, Fig. 5 shows that hydrogen in the recycle stream has no effects on carbon formation.

4. Conclusions

- Recycle of a simulated anode off-gas, which adds high levels of carbon dioxide and steam to the reformer inlet gas, increases carbon monoxide and hydrogen yields and greatly reduces carbon deposition compared to recycle of a simulated reformer product gas.
- The total quantity of carbon formed decreases monotonically with anode gas recycle ratio, probably due to the higher levels of carbon dioxide and steam that oxidize the carbon. However, the reactivity of the carbon shows unusual behavior. The more reactive carbon (as measured by TPO) decreases much less with increasing levels of carbon dioxide and steam than the less reactive carbon. The reasons for this carbon being more reactive with carbon dioxide and steam than with oxygen are not clear.
- The separate effects of five individual components of the recycle gas (H₂, CO, CO₂, H₂O, and N₂) shows that carbon dioxide and water decrease carbon formation while hydrogen has the same effect as the presumably unreactive nitrogen. Carbon monoxide actually increases carbon formation compared to nitrogen. The decrease in carbon formation due to carbon dioxide is believed to be due to the Boudouard reac-

tion, and for water to the gasification of carbon to carbon monoxide + hydrogen.

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