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Knight, EH, Dupont, VAL, Twigg, MV, Ross, AB and Rickett, GL (2008) *Carbon laydown during steam methane reforming start up conditions.* In: Abstracts of Papers of the American Chemical Society. UNSPECIFIED. 235th National Meeting of the American Chemical Society .

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# CARBON LAYDOWN DURING STEAM METHANE REFORMING START UP CONDITIONS

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**Paper accepted and published. Full reference**:

E.H. Knight, V. Dupont., M.V. Twigg, A. B. Ross, G. L. Rickett. Carbon Laydown during Steam Methane Reforming Start up conditions. Preprint paper. and Oral presentation (E. Knight). 228th National meeting of the American Chemical Society, 6-10thApril 2008, New Orleans, USA.

## Introduction

Steam reforming currently accounts for 48% of global hydrogen production with methane being the predominant feedstock.1 The steam methane reforming (SMR) reaction occurs alongside the water shift reaction, whose reverse is active at ‘industrial’ steam reforming temperatures (800°C), limiting the steam conversion to H2. As a result, the theoretical steam to carbon ratio (S:C) of SMR is near 1.7. Commercial SMR catalysts consist in their majority of dispersed nickel on a ceramic support. Ni catalysts tend to promote thermal decomposition of methane however, and as such an excess of steam (S:C up to 3.5) is generally used at steady state using tubular reactors.2 The formation of carbon on the catalyst blocks catalytic sites for steam reforming, gradually reducing the steam conversion, and decreasing the catalyst’s lifetime. Using an excess of steam not only promotes the steam reforming and water shift reactions, decreasing the fuel thermal decomposition, but also eliminates those carbon deposits formed on reduced Ni sites. On the other hand, higher steam reactant feeds require a higher energy and material input to SMR. As such, there is a trade off between reducing carbon lay down and making the process as economic as possible.

The minimization of carbon deposition during start up conditions is particularly important as thermal decomposition of methane is initially prevalent as NiO makes up most of the ‘as-received’ catalyst. NiO has poor activity for SMR, and needs to be chemically reduced to the SMR-active Ni. During start up, a S:C of 7 is recommended to prevent carbon lay-down.3 The reduction phase can then take several hours (up to 10), and represents material and energy costs. Once the catalyst has been reduced, the S:C is gradually lowered to between 1.7 and 3.5. The extent of the reduction of the catalyst is evaluated approximately by monitoring the concentration of methane in the outlet gas.

The purpose of the present experiments was to determine the effect of steam to carbon ratio on carbon lay down using both fresh and pretreated commercial SMR catalysts, with the aim of better understanding the chemistry of start-up and revise the guidelines for catalyst reduction achieving minimum carbon lay-down.

## Experimental

Experiments were carried out on a rig designed to study both steady state and cyclic steam reforming processes such as unmixed steam reforming.4 The catalyst was placed in a tubular stainless steel reactor and heated externally with a heating coil. Flows of nitrogen and methane into the SMR reactor were regulated by MKS mass flow controllers calibrated for the specific flow rate. The flow rate of water was regulated using a peristaltic pump and super heated to 400°C in a pre-heater prior to entering the reactor. The flows of CH4, N2 and water were started using a sequence generator. The product gases were cooled using condenser-ice bath-silica gel sequence. The dry gas volume concentrations of CO, CO2, CH4, H2 and O2 were monitored online using analyzers from ABB. In all experiments a commercial Ni-based catalyst containing 14.1% wt Ni supplied by Johnson Matthey was used, crushed to 1-2 mm diameter size.

For all experiments, 20g of catalyst were packed into the centre of the reactor supported on either side by plugs of alumina. The set temperature was 740˚C and experiments were run at 1 atm. Inlet flows of 300 sccm of N2 and 100 sccm of CH4 were used. Water flows ranged from 0-0.643 ml min-1 for different S:C. Four sets of experiments were performed. The first, termed ‘FR’, was carried out on fresh catalysts for each S:C studied. The second and third termed ‘PT1’ and ‘PT2’ respectively, used the same catalyst for a set of S:Cs (increasing S:C for PT1, decreasing S:C for PT2). As such, the catalyst had a known history of previous runs in the PT1 and PT2 sets. The FR experiments were carried out on S:Cs of 0, 1, 2, 4, 5, 6, 7 and 8. After each FR run, the reduced catalyst was removed from the reactor and divided into six portions for further analysis. The reduction phase was run for 3600 seconds (1 hour). This duration ensured complete reduction of NiO to Ni on the catalyst support. CHN analysis was performed on selected samples of catalyst after removal from the reactor using a Thermo Flash EA 1112 series CHNS-O analyzer. This was to determine the presence of carbon.

In the PT1 and PT2 sets of experiments, steam reforming runs were performed with different S:C alternated with oxidation phases under air flow, in the S:C order 2, 2, 4, 6, 8 and 0 (PT1) and 2, 8, 6, 4 and 2 (PT2) respectively. The order reversal was designed to rule out effects of chronology. At the start of both PT1 and PT2, a fresh, as received catalyst, was used. The initial reduction in each experiment was a pretreatment with a S:C of 2 followed by an oxidation step. The purpose of this step was to homogenize the Ni distribution on the surface of the catalyst for the remaining reduction runs. In the final set of experiments, a nitrogen only feed followed a CH4/N2 feed on the fully oxidized catalyst. Subsequently, a steam/N2 flow was fed in order to investigate which specific reactions of carbon removal occurred during the SMR at start up conditions.

## Results and Discussion

The raw data obtained from the online analyzers were processed via material balances of the N, H, C and O elements, yielding fuel and steam conversions, rate of carbon formation and rate of NiO reduction. The results are discussed below. As can be seen in Fig. 2, for the FR set of experiments, there was little correlation between S:C and rate of carbon formation for S:C between 1 and 8. The S:C of 0 exhibited a steady rate of carbon formation reaching its maximum with 100 % carbon product selectivity once all the NiO had been reduced. The level of carbon was immediately obvious when visually examining the catalyst bed after the run. This result was confirmed with CHN analysis, indicating that in the particular sample tested, 12.84% wt carbon was present. The lay down of carbon across the bed was not uniform, however and further samples will be tested in order to determine quantitative agreement with the elemental balance, which indicated 12wt% C for this run. With S:Cs of 2 to 8, no obvious carbon deposition was observed to the naked eye upon the catalyst following the runs. CHN analysis of samples of catalyst from both ends of the catalyst bed for the two S:C of 2 and 8 revealed that the carbon was below the resolution of 0.3 wt%. This result was consistent with the carbon balances where, for S:C of 2-8, carbon accumulation was calculated to be below 0.005 mol (0.06g) on 20g of catalyst, i.e., 0.3% wt.

Results were compared from the time of the end of methane breakthrough from the reactor to rule out the time error due to reactants flowing from the inlet valves and products reaching the analyzers.

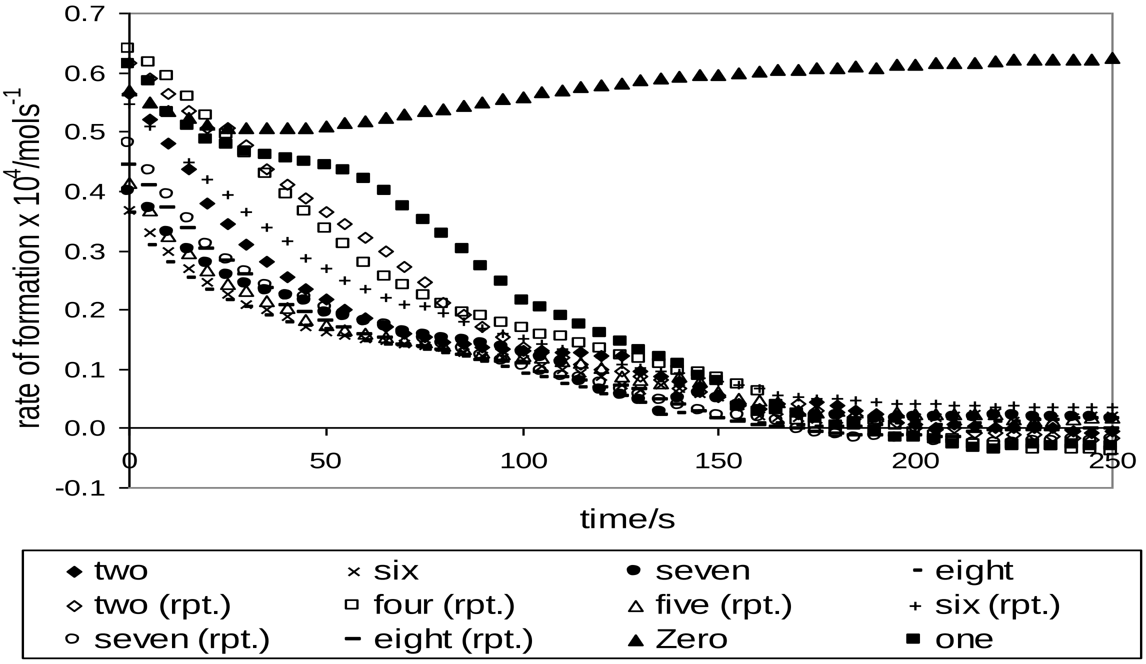

Figure 1. Rate of carbon formation (mol s-1) from the end of breakthrough of methane, for S:C of 0, 2, 4, 5, 6, 7 and 8. Results refer to FR experiments. (rpt) means repeated experiment.

In the FR experiments, higher S:Cs were expected to result in a lower carbon formation, but this was not the case. One explanation was that fresh, ‘as received’ catalysts are not homogeneous, but become so with early usage. To address this, the PT1 and PT2 runs were performed. The oxidation cycle between each S:C run was intended to homogenize the Ni/NiO particles distribution and morphology on the support, as well as burning the carbon, if any, from the previous reduction. The results obtained for PT1 yielded the same trends as those for PT2, shown in Fig. 2. In each case, the rate of carbon formation initially fell with increasing S:C, as expected, but there are no significant differences in the rates of carbon formation obtained. When alternating the different S:C with one oxidation phase, no noticeable carbon burn-off was observed during the oxidation phase, except for the S:C of 0. This result is consistent with the CHN analysis and the elemental balance. The catalyst did not appear to lose significant activity over the course of the experiment.

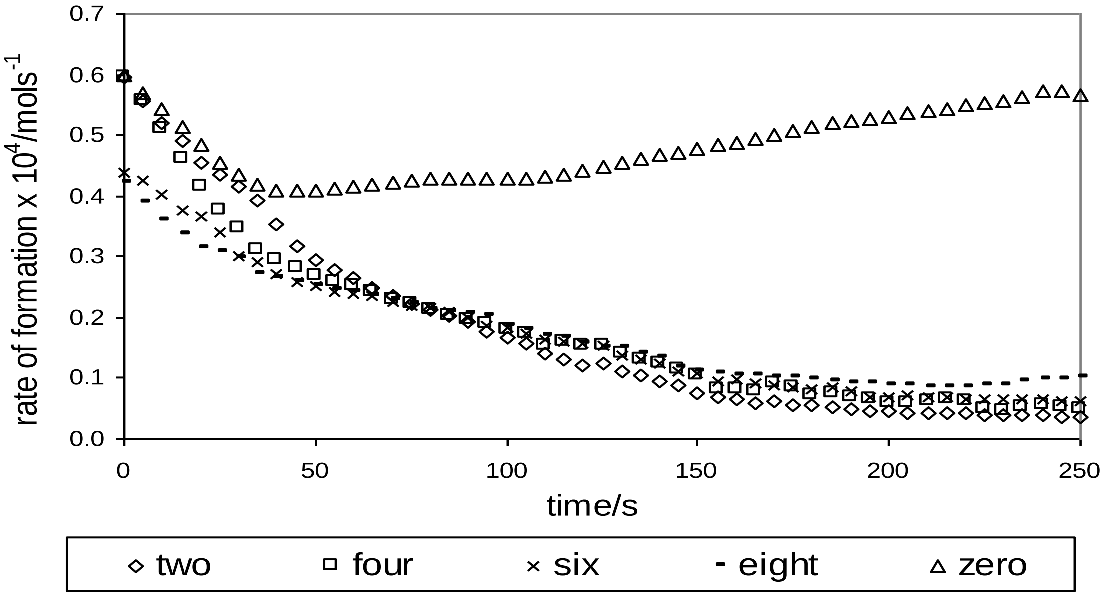

Figure 2. Rate of C formation for different S:C in PT2 set of experiments

For all the S:C ratios (0-8), the initial carbon formation (35 s) follows a similar downward slope, as shown in Fig. 2. Raw data and balance derived data further indicated that C was the main carbon product to begin with, with CO2 increasingly the only other significant C-product. Water is a major product in this period too. At the same time, the NiO reduction rate increases, as shown in Fig. 3. This is consistent with the reduction of NiO by methane and by the H2 from methane thermal decomposition. If steam gasification of carbon had been significant, CO would have been expected to be the second largest C-product, with CO2 the third, unless all the CO of the carbon-steam gasification was subsequently used to reduce NiO producing CO2. We also needed to establish whether carbon could be oxidized by NiO, producing CO2. A methane/N2 feed was used on a fully oxidized catalyst, and then the methane flow was stopped. No CO or CO2 evolution occurred beyond the interruption time, ruling out carbon oxidation by NiO. Furthermore, from the start the water production rate was twice the CH4 conversion, and plateaued there for around 60s. This indicated that the CH4 consumption routes CH4+4NiO⍰CO2+2H2O+4Ni, and CH4⍰C+2H2 followed by 2NiO+2H2⍰2H2O+2Ni, both producing two H2O per consumed CH4, did not occur alongside C+H2O⍰CO+H2. The subsequent experiment, where a CH4/N2 feed, followed by N2, and steam/N2 feeds were used in sequence, indicated that during the steam/N2 feed, all the carbon laid down in the CH4/N2 feed was gasified. This was expected as by then all the NiO had been reduced to Ni by the mechanism described earlier. These experiments indicated that the steam gasification of carbon did not occur on the NiO, and that only when sufficient Ni was reduced did the steam gasification of carbon and the SMR reaction begin. Indeed, beyond the first 35 s, CO began to evolve and eventually, a net positive steam conversion was calculated. This indicated that steam reforming set in, as well as water shift. These reactions decreased further carbon lay down by competing with the NiO reduction reactions described above, hence the changing rates in both Fig. 2 and 3, in addition to the decreasing availability of NiO. By 200s, the NiO was fully reduced according to the balances, and the small residual NiO rate shown is likely due to error accumulation from the rate integration. All the above show that using a S:C above two at atmospheric pressure in this study is of little use throughout the reduction of the NiO to Ni of start up.

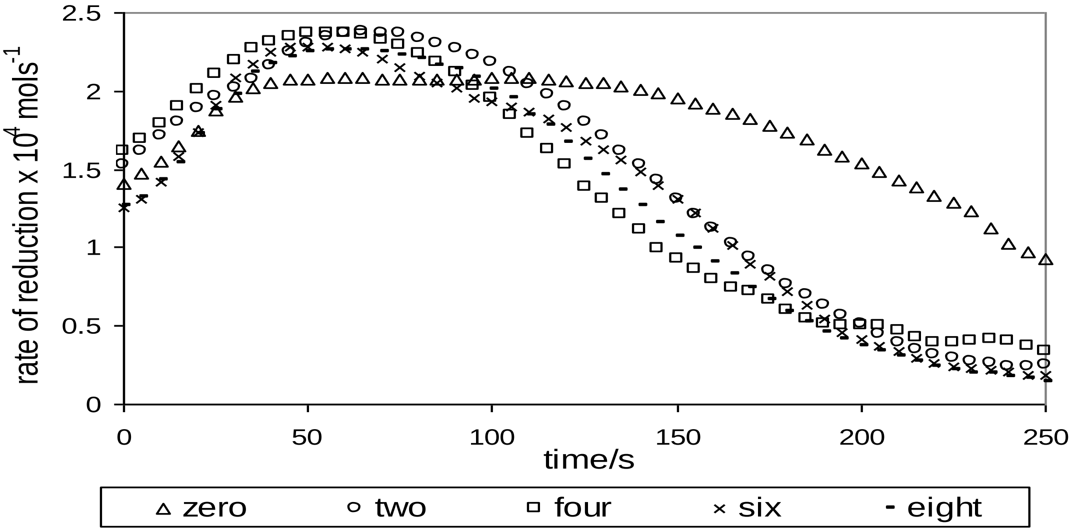

Figure 3. Rate of NiO reduction for different S:C in PT2 set of experiments

## Conclusions

For S:C of 2-8, the difference in rate of carbon formation and NiO reduction is small. This is explained by the methane feed simultaneously reducing the catalyst and decreasing the part of thermal decomposition, as well as a lack of carbon gasification by steam on NiO. Further investigation could determine whether this remains applicable at the elevated pressures of the industrial SMR process and to a wider range of SR catalysts and fuels.

Acknowledgement. The EPSRC and Johnson Matthey are gratefully acknowledged for financial support. Thanks also to Elise Clochette and Diego Scoganmiglio for experimental assistance.

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