

Hydrogen Rich Syngas Oxidative Catalytic Activity of Nickel and Inconel

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1 Introduction

Because of concerns regarding the effect of human activities on climate change, there is considerable interest in finding alternative fuel sources that produce lower fossil carbon emissions. One path is the use of hydrogen rich syngas as proposed for Integrated Coal and/or Biomass Gasification/Combine Cycle (ICGCC) systems. In addition, operating the combustor under lean, premixed conditions with lower temperatures is ideal to reduce the formation of NO_x [1–3].

Syngas is composed primarily of H_2 , CO , and CO_2 and while this seems a simple mixture, the presence of large amounts of gaseous hydrogen complicate matters because of its tendency to be extremely sensitive to preignition under oxidizing conditions. Indeed, at this time there is an unexplained discrepancy between measured and predicted ignition times and flame speeds for hydrogen enriched syngas fuels at the high pressures (10–20 bar) and low temperatures (600–800 K) typical of stationary gas turbine combustor inlets [3]. This discrepancy was highlighted in a paper published by Petersen et al. [2]. The discrepancy in predicted ignition time can be quite large; at 20 bar and 700 K, typical gas turbine combustor inlet conditions, it is about three orders of magnitude. This has a negative impact requiring an overly conservative design to avoid unwanted preignition events.

A number of recent papers speculate about several possibilities for how this difference between the reactor studies and the prediction of gas-phase mechanisms could occur [1, 2, 4–8]. Following their suggestions we explored four possible gas-phase explanations. The first is that one or more rates in existing mechanisms are in error enough to cause the observed differences. The second is that additional species are present at the combustor inlet conditions that have not been found to be important under the more extensively studied low pressure and high temperature conditions. These additional species could potentially undergo chain branching reactions that would accelerate ignition. A third possibility is that sensitizing species such as NO and NO_2 found in ambient air or hydrocarbon impurities found in laboratory gases could explain the discrepancy. A final possibility is that the mechanisms are correct, but that experimental conditions are insufficiently well understood so that at some locations in the flow field the thermodynamic state encourages more rapid reaction. None of these appear to explain the observed behavior at the lower temperatures of interest in turbine inlets. If gas-phase explanations cannot be found, then some other source of the discrepancy must exist. One possibility is catalysis, either due to wall interactions or particulate matter in the gas flow. The purpose of our work was to explore whether high nickel engineering materials of the class used in gas turbine inlets have sufficient catalytic activity to contribute to the experimental observations.

The contribution of surface effects to oxidation kinetics has been discussed throughout the history of scientific exploration of hydrogen chemistry. Lewis and von Elbe [9] showed that different coatings

resulted in different combustion behavior, demonstrating clearly that surface reactions can impact the chemistry. However, they did not have enough information to understand the detailed surface reaction mechanism, and indeed, these mechanisms are still not well understood. The work prior to 1980 was reviewed by Norton [10], and there have been numerous studies since then exploring the effect of surfaces on combustion properties.

There has been much less work that presents detailed reaction mechanisms. Of that body, the most notable is probably the work of Deutschmann et al. [11–13] who developed detailed mechanisms on platinum and palladium for the oxidation of methane, carbon monoxide and hydrogen. There is also the older works of Dadayan et al. [14–16] and more recent work of Zhu [17] on nickel. Of course, none of the experimental apparatuses in the studies reported by Petersen et al. [2] were constructed of these metals that are known for their catalytic properties. Indeed, it is unknown what materials were used in most cases, although the most likely is a stainless steel of some type. Gas turbine inlets are typically manufactured from proprietary high temperature materials like Inconels and Hastelloys.

2 Experimental Methods

Our interest in exploring the activity of engineering materials and desire to infer some kinetic information led us to carry out experiments in a flow reactor. A readily available facility offered the combination of a miniature tubular reactor assembly coupled with matrix isolation/infrared spectroscopy diagnostics (Fig. 1). The advantages of the system were that different reactors could be manufactured from the materials of interest and the diagnostics are very sensitive. The main disadvantages of the system were a short residence time and large uncertainties in the measured conversion rates. (The reactor facility we used was initially designed to produce short-lived organic radicals for further study [18–20].)

In utilizing our flow reactor system, we were limited to operating at relatively low pressure in the reactor, typically about 0.1 bar. Since the application is high pressure gas turbine inlets, one must establish that pressure is not an important parameter. We believe that is the case based on what is known about surface oxidation on nickel. The three body reactions that are so critical in high pressure hydrogen oxidation, are not as likely to change the character of the surface chemistry kinetics [14–16] and this is supported by kinetic calculations using recent mechanisms (i.e. Zhu [17]).

Another important consideration is that of the reactants and products of hydrogen oxidation, only H₂O is detectable by infrared spectroscopy. Unfortunately, it is extremely difficult to remove unwanted water vapor from any experimental system, and in our case the contamination masks water produced by reaction. As a result we decided to replace the molecular hydrogen in our experiments with D₂, molecular deuterium, as is commonly done in similar situations. Deuterium has essentially identical electronic and thus bonding and reaction properties as hydrogen, but the IR spectrum of D₂O is sufficiently shifted from that of H₂O to make spectral identification straight forward.

Matrix isolation infrared spectroscopy is a technique that involves freezing the gas to be analyzed on a cold IR transparent window (CsI) and analyzing the composition with infrared spectroscopy. This technique requires a low pressure (about 10⁻⁵ Torr) to avoid further reactions downstream of the reactor exit and a low temperature (20 K) environment to freeze the gases. Typically one runs an inert carrier gas, argon in this case, and dilute reactants. A major advantage of the method is that one can continue to deposit gas on the window for lengthy periods of time, in that way building up signal level for improved detection.

The reactant mixture is prepared in a glass 1.2 L stagnation reservoir at pressures of about 1 atm and concentrations of about 1:100 to 1:10 in argon. The pulsed valve, operating at 20 Hz, controls the flow through the reactor. The gas is pulsed for two reasons: (1) to protect the pumps, as they are not designed

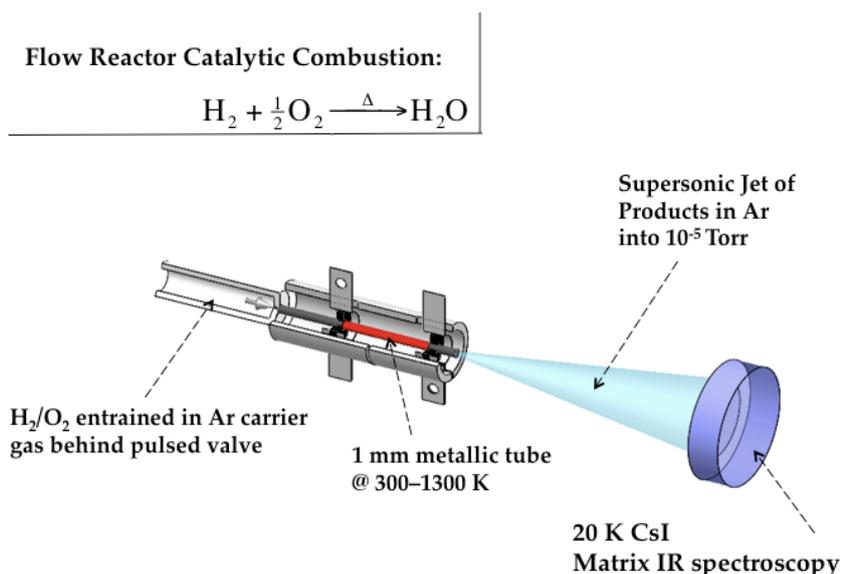


Figure 1: Schematic view of the flow reactor/matrix infrared window arrangement

to handle large gas flows, and (2) to maximize the freezing efficiency to the window. The pressure drop in the reservoir, measured by a capacitance manometer, indicates the amount of gas deposited on the window. Typically the pressure drop in the reservoir is set to about 1-2 Torr/min, which is equivalent to about 5×10^{16} molecules per pulse.

At the reactor exit the free-jet expansion rapidly cools the gas down to about 40 K rotationally, thus quenching thermal reactions. The molecular beam impinges on the cold matrix window and the products, trapped in frozen argon, can be detected through infrared spectroscopy. The vibrational spectra are measured using a Nicolet Magna 550 infrared spectrometer equipped with a liquid N₂ cooled mercury/cadmium/telluride (MCT/A) detector ($4000\text{--}600\text{ cm}^{-1}$) in combination with a KBr beamsplitter. The spectrometer is purged with purified dried air and the spectra are collected with the OMNIC 5.0 software package on a Windows operating system. A more detailed description of the reactor and diagnostic technique is provided elsewhere [19, 20].

3 Results

This section presents the spectral results for the three different metallic reactors, stainless steel, nickel, and Inconel.

3.1 Stainless Steel

Our interest in stainless steel stemmed from the fact that laboratory reactors are most likely fabricated from stainless steel and we wished to see if any catalytic activity could be observed. Several combinations of reactant concentrations and temperatures were tested and no appreciable amount of D₂O was formed by reaction of D₂ and O₂.

3.2 Nickel

Nickel is a transition metal part of Group 10 on the periodic table, the same group as platinum and palladium which are known to be very effective catalysts for hydrocarbon and hydrogen oxidation. Of the metals in this series, nickel is the most abundant, and therefore the most cost-effective material for catalytic applications. Nickel is well-known for its catalytic behavior in reforming hydrocarbons to H₂ and CO [17], but it is less studied as an oxidation catalyst for hydrogen. However, nickel is a very common metal in a number of alloys for engineering applications and for this reason, nickel 200 was chosen as the pure “catalyst” to be tested for this project. Nickel 200 is a commercially pure (99.6%) wrought nickel.

Experiments with the nickel reactor resulted in reaction of D₂ and O₂ to produce D₂O. The results of the nickel experiments show that hydrogen oxidation occurs and is enhanced by the presence of a pure nickel surface. However, the conversion efficiency in the nickel reactor is quite low, with the highest conversion estimated at 1%. Error estimates for %-conversion were carried out. The number of molecules is calculated based on c (concentration of absorbers), z (matrix thickness), and a (matrix area). This uncertainty was determined, rather crudely, based on an estimated 30% error in the integration of the absorbance bands (which is proportional to cz), and another 30% error in the spot size of the matrix. Using these two estimates results in an uncertainty of the calculated %-conversion to be about $\pm 45\%$.

3.3 Inconel

Inconel is a common engineering material for operations at high temperatures and is known for its oxidation and corrosion resistant properties. All alloys have a chemical composition of more than 50% nickel, and the Inconel alloy tested in this research was Inconel 600 (nickel-chromium-iron; approx. 72% Ni). Inconel was tested over a temperature range from room temperature to 1270 K. Experiments were performed with near-stoichiometric mixtures of D₂ and O₂ in concentrations of about 4-11% D₂ and 2-5.5% O₂. An estimate of percent conversion from reactants to products in the Inconel reactor was performed in the same manner as the nickel results. It is estimated that the maximum conversion achieved in the Inconel reactor is 0.3%, which is about a factor of four less than that observed with nickel.

4 Summary and Conclusions

We believe that it can now be concluded that high nickel content materials such as Inconel do have some degree of catalytic activity. This is consistent with the small amount of previous work (Bustamonte et al. [21]) and does seem likely given the high nickel content and known catalytic activity of nickel. However, our experiments are not in quantitative agreement with published mechanisms, our observations indicating overall rates approximately two orders of magnitude less than predicted.

The remaining question is whether the activity is enough to bring about the observed rapid increase in ignition events seen in high pressure experiments where average ignition delays are two to three orders of magnitude faster than predicted using state-of-the-art gas phase reaction mechanisms. As discussed above, none of the various proposed routes to fast ignition, taken alone, would seem to result in the observed behavior. However, it is possible that a combination of events would do the job. For example, turbulence could raise the local temperature, and that combined with a catalytic wall might be enough to cause ignition. For both the Deutschmann et al. [13] and Zhu et al. [17] mechanisms, a 100 K increase in temperature will result in roughly an order of magnitude decrease in ignition delay. Furthermore, in a turbulent flow, even in the best designs, transient regions of low velocity can develop in the flow. The

combination of higher temperature and lower velocity could account for the observations of premature ignition. Indeed, most ignition delay experiments display a high degree of variability.

However, there remains a fairly large uncertainty regarding premature ignition in gas turbine inlets when burning high hydrogen content syngas. We have shown experimentally that at least one engineering material used in gas turbines has some catalytic activity for hydrogen oxidation. To further understand the ignition problem will likely require state of the art large eddy simulation/direct numerical simulations of realistic inlets and combustors coupled with reasonably accurate reduced gas phase and surface reaction mechanisms.

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