FUEL PROCESSING FOR PRODUCTION OF HIGH QUALITY REFORMATE FOR PEM FUEL CELLS

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Fuel processing to produce contaminant-free hydrogen is a key enabler among the many technological challenges, which must be met in order for PEM fuel cell systems to gain a foothold in power generation. Foremost among the stringent requirements for reformate quality, is hydrogen purity and the virtual absence of CO which severely poisons the fuel cell anode. Many approaches to attaining high reformate quality have been discussed in the open scientific and patent literature including adsorption, methanation and electrochemical oxidation and catalytic selective oxidation. The latter appears to be the most widely practiced. However, key technical challenges related to catalyst activity, stability and response to variations in reactor environment and reformate composition must be addressed before commercialization of the technology.

As part of our effort to devise a reliable solution to the problem of reformate purity, a fundamental investigation was undertaken to better understand the molecular-scale mechanism of the selective oxidation chemistry. The work described here encompassed use of in-situ characterization tools and laboratory pilot plant testing under realistic process conditions in an effort to determine the type and distribution of adsorbed CO species, other reaction intermediates and reaction products on the working catalyst. The influence of oxygen and water on the nature of reaction intermediates and, indirectly, on the electronic state of the catalytic metal at the surface will be discussed. Adjustment of catalyst composition and preparation conditions in order to change the disposition of the active sites at the catalyst surface was found to have a profound impact on performance.

The paper will illustrate the benefits derived from implementation of fundamental scientific understanding to this challenging technological area. Insights gained from this work have been incorporated in design elements and have resulted in production of low CO (<10 ppmv) reformate for thousands of hours in UOP's fuel processor prototypes.

Introduction

Large advances have been made in PEM fuel cell technologies bringing them close to commercialization. These fuel cells offer many advantages including ease of manufacture, high power densities, and stability of operation and low cost of manufacture. However, the cost and impracticality of transport and storage of hydrogen have made the development of a fuel processor an attractive alternative for hydrogen supply. The most promising approach to accomplishing this objective is reforming of natural gas or liquids to generated hydrogen and carbon oxides. A typical fuel processor consists of a series of catalytic reactors beginning with a synthesis gas generation step followed by water gas shift converters to reduce the CO content of the reformer effluent below the thermodynamic limits prevalent in the reformer and extract more hydrogen. A key process configuration commonly discussed is the autothermal reforming (ATR) process whereby a portion of the natural gas feed is combusted to provide heat to drive the endothermic reforming reactions. The reactions taking place in the fuel processor are shown in the following equations:

$$CH_4 + H_2O = CO + 3\ H_2 \qquad \Delta H = 210\ \text{kJ/mole} \quad (1)$$
$$CO + H_2O = CO_2 + H_2 \qquad \Delta H = -42\ \text{kJ/mole} \quad (2)$$
$$CH_4 + 1/2\ O_2 = CO_2 + 2\ H_2 \qquad \Delta H = -71\ \text{kJ/mole} \quad (3)$$

Reaction (2) is first carried out in the high temperature shift reactor with a typical effluent composition of containing ~3-5% CO limited by thermodynamic constraints. Due to favorable thermodynamics, a second low temperature shift (LTS) step may be carried out at lower temperature in the temperature range of 250 – 350°C over a copper-zinc-alumina or more, recently, noble metal on rare-earth promoted zirconium oxide catalyst systems. The composition of the LTS effluent typically contains 40-50% hydrogen with the balance of CO2, methane, nitrogen and 0.1-1% CO, depending on process conditions and unit design. This level of CO severely poisons the fuel cell anode and must be reduced to levels of less than 50 ppm to achieve stable fuel cell operation. The most widely discussed approaches to this problem, and also the closest to practical application, are catalytic solutions including selective oxidation. Selective methanation of CO has been suggested on occasion but is typically ruled out due to the inherent safety issues. Thus discovery of catalyst compositions able to sustain stable and selective CO combustion in the reformate stream at low temperatures is critical to success of these efforts. The optimum catalytic system should operate at LTS effluent or PEM fuel cell inlet temperatures to minimize the number of heating and cooling operations of the reformate stream. The system must also be able to selectively catalyze CO conversion under a wide range of process conditions resulting from turn up and turndown and from the presence of high water partial pressure and feed contaminants.

UOP's approach to CO clean up in its fuel processor program has been selective oxidation of the residual CO using a proprietary catalyst designed for optimal performance in this environment. Open literature reports teach that catalysts consisting of noble metals such as platinum, palladium, ruthenium, rhenium and gold supported on a variety of supports are suitable for CO oxidation. As part of our own development program for a preferential CO oxidation catalyst, we undertook a large number of studies aimed at developing a deeper fundamental understanding of the working catalyst. This paper will focus on communicating the key results of this effort, especially where they relate to a better definition of the nature of the reactive intermediates involved.

Experimental

Catalysts were prepared by impregnation of alumina spheres possessing specifically selected porosity and surface characteristics with Ru salts as discussed in US patent 6,299,995**[1].** The impregnated supports were subjected to a series of heat treatments under air and hydrogen atmospheres in order to decompose the metal salts and to fix the active metal to the support surface in a well-dispersed form. A typical heat treatment program is shown in **Figure 1.** The oxidation temperature, reduction temperature and duration of treatment were systematically varied to identify processing which provides optimal catalyst performance. In some experiments, the distribution of ruthenium across the catalyst spheres was altered from a standard flat profile to a skewed one in order to

investigate the impact of this parameter on catalyst performance. Resulting catalysts displayed "eggshell" profiles of varying shell thicknesses as shown in **Figure 2.**

Catalyst evaluation for CO conversion was conducted in a laboratory test unit using feed compositions representing expected low temperature shift (LTS) effluent compositions. Conditions employed in catalyst testing as well as the feed composition are summarized in **Table 1.** Temperature, space velocity, water content and air-to-fuel ratios were varied depending on the desired objective of specific experiments. CO and CO_2 analysis of the reactor effluent were carried out using an infrared analyzer and O_2 analysis was carried out using a paramagnetic analyzer. Feed and air flow rates were metered with Brooks mass flow controllers and water was introduced using an Isco pump and entered the reactor after passing through a vaporization zone. The total reactor effluent passed through a dry ice-propylene glycol trap for water removal and subsequently sent to the analyzers.

The catalyst sample to be tested is introduced into the reactor after mixing with an inert diluent in a 3:1 diluent to catalyst ratio in an attempt to maintain an as close to an isothermal bed temperature profile as possible. The degree to which this succeeded varied with catalyst sample activity and a descending temperature profile from top to bottom of the bed was almost always observed. Thermocouples were placed at the reactor inlet and outlets as well as at the top, middle and bottom of the 9-inch catalyst bed.

Catalyst characterization was carried out employing a variety of specialized techniques such as XPS, XANES, and Fourier-transform infrared (FTIR). Experiments were occasionally carried under in-situ or near-in-situ conditions as described below. The XPS analysis was performed in a Quantum 2000 Scanning ESCA Microprobe. The catalyst spheres were ground to a powder and lightly pressed onto Scotch tape held with a Mo sample holder. The spectra were charge referenced by setting the binding energy of the Al 2p = 74.0 eV. The XANES experiments were conducted at beamline X19A at NSLS. The Ru L_3-edge XANES were collected in fluorescence yield mode using a cell designed for in situ x-ray absorption spectroscopy measurements.

Infrared experiments were carried out using a Nicolet 60 SXB spectrometer equipped with a cell designed to permit flow of feed gases over a self-supporting catalyst wafer at temperatures ranging up to 800°C. A specially constructed manifold was employed to flow the dry feed gas shown in **Table 1**. Air was metered in at the desired ratio and the total gas flow was humidified by flowing it through a water saturator. All spectra were normalized to constant catalyst weight.

Results and Discussion

Results of experiment carried out to investigate the impact of catalyst preparation variables on performance are illustrated in **Figure 3**. In a typical run of this type the catalyst is brought on stream at inlet temperature T_1 and a GHSV of 5000 hr^{-1} and feed flow rate is adjusted in steps up to a nominal value of 15,000 hr^{-1} while holding the temperature constant. In some experiments, the space velocity is reduced to the starting value again to determine whether the observed loss of conversion reversible. The data presented in this figure illustrate the very important role the support and the metal distribution profile play in determining catalyst CO conversion activity. Traces 1 & 2 show CO conversion results from standard preparations on two different alumina supports illustrating the profound impact of support properties on performance.

However, adjustment of the ruthenium profile, to give the distribution shown in **Figure 2,** yields significant improvements in performance seen by comparing traces 2, 3 and 4. These variables are exploited to in our program to achieve optimal performance.

Figure 4 presents a plot of CO conversion as a function of gas hourly space velocity and O_2/CO ratio collected over an experimental catalyst early in our program. These results are consistent with expectation of diminished conversion at high space velocity and low O_2/CO ratio except for the apparent drop in conversion on raising the O_2/CO from 3 to 4.

A plausible explanation for this unexpected behavior may be the oxidation of ruthenium at the surface in the presence of excessively high levels of oxygen.

In attempting to define the behavior of the system at high temperatures, we encountered an interesting observation shown in **Figure 5.** This figure shows a plot of CO and CO_2 in the reactor effluent as a function of reactor inlet temperature in the presence of high (30%) and low (1%) water content in the feed. As a temperature of about 200°C is reached, a trend of rising CO and falling CO_2 were observed. This trend accelerated as an inlet temperature of ~300°C was reached. A decreasing CO_2 trend under these conditions may be interpreted in terms of the onset of reverse water-gas shift reaction whereby CO_2 reacts with hydrogen to form CO and water according to the following reaction

$$CO_2 + H_2 = CO + H_2O \qquad \Delta H = +42 \text{ kJ/mole} \quad (4)$$

This reaction may be considered an intermediate reaction along the pathway of CO_2 methanation, which takes place at higher temperatures. Here CO_2 and CO, react with hydrogen to form methane in a reversal of the steam reforming reaction (1). However, the observed effect of water in accelerating the evolution of CO at these high temperatures is not, consistent with the reverse WGS hypothesis. Another reaction pathway must be invoked to explain the role of water. Water might indeed act as a poison to inhibit the CO oxidation reaction. However, it is difficult to reconcile the increase in this inhibition effect would increase at higher temperature where water adsorption is expected to diminish in strength. Of course, the influence of water in modifying the catalyst surface through surface reconstruction or oxidation of Ru sites must be considered in explaining this observation as well as others. Thus, understanding of the molecular-scale events underlying this behavior is, of course, critical to proper design of the catalyst and process combination for optimum performance in CO clean up in fuel processors. To this end we undertook basic characterization work in order to probe the specific changes taking place in the catalyst or at the catalyst surface after exposure to a variety of environments it is likely to encounter in service.

XPS and XANES

As part of the effort to determine the optimum reduction temperature of the catalysts XANES-TPR experiments were carried out to follow the evolution of the Ru oxidation states with temperature in flowing hydrogen. This work was based on an

observation made earlier in a standard TPR experiment of a maximum uptake of hydrogen around 250°C. **Figure 6** shows the evolution of the Ru-L_3 edge band position as a function of temperature. The shift in this band to lower energy indicates reduction to lower oxidation state. This shift is well illustrated in **Figure 7**, which shows a plot of the peak maximum energy as a function of temperature. These data clearly indicate that complete reduction of ruthenium takes place at temperatures exceeding 300°C.

A comparison of the "eggshell" preparation described above (see F**igure 2),** to the standard preparation was carried out by XPS. One can expect significant differences in the intimacy of interaction of the Ru with the support between catalysts possessing such differences in Ru profiles and, consequently, in the electronic nature of the surface ruthenium. A cursory consideration of the impact of such differences in spatial Ru distribution suggests that the "eggshell" catalysts should be prone to less intimate interaction with the surface and, consequently, to being more metallic in nature. It is well established in the literature that the electronic nature of supported metals is strongly influenced by the intimacy of interaction with the support surface.

Thus, it is expected that a comparison of the ruthenium 3d binding energies in XPS spectra of flat and "eggshell" preparations should reveal some key differences between them. These XPS spectra of the two catalysts are shown in **Figure 8**. The binding energies of the sample with a Ru "eggshell" profile are clearly shifted to lower energy than are those of the sample with the flat profile. These shifts are consistent with the ruthenium having a significantly more metallic character in the "eggshell" catalyst than in the sample with the more highly dispersed ruthenium. Thus, the superior performance of the "eggshell" catalysts may in part be attributable to factors related to the electron density at the active metal sites. The strong correlation to performance along with the ease of transformation of Ru^{0} to Ru^{n+} illustrated in this work suggest a need for characterization in-situ or under conditions closely mimicking those of the process.

A proposed model of the working catalyst consistent with these observations is shown schematically in **Figure 9**. Clearly, the presence of and need for an underlying reservoir of reduced Ru metal is suggested by the better performance of the "eggshell" catalysts and by the strong influence of catalyst reduction conditions on performance. However, the presence of oxygen under normal conditions of use, coupled with apparent ease of inter-conversion between Ru oxidation states, suggests an important role for Ru^{n+} species in the catalysis. It further reinforces the need to investigate the exact nature of the surface layers, or islands, containing Ru^{n+} sites in the working catalyst in-situ. For example, RuOx sites have been previously proposed as active sites for CO conversion on model Ru catalysts [2].

Fourier Transform Infrared

Fourier-Transform infrared spectroscopy (FT-IR) is ideally suited for this purpose as it allows the monitoring of adsorbed CO which is frequently employed to probe the dispersion, electronic nature and coordination of supported metals at catalyst surfaces. The fact that it is also a reactant in selective oxidation chemistry presented a unique opportunity to probe the reaction in-situ. The nature of the adsorbed CO on a reduced catalyst was initially investigated by introducing CO in a stream of flowing hydrogen at various temperatures. **Figure 10** shows infrared spectra of samples treated in hydrogen at 108°C and subsequently exposed to CO at 30 and 108°C and after subsequent CO desorption at 100 and 125°C. A strong band at ~ 2040 cm^{-1} and a shoulder around 1970 cm^{-1} can be seen in the spectra after CO adsorption which have been assigned to CO at Ru (0) and Ru^{x+}, respectively [3] . A slight coverage dependence of the frequency of the 2040 band is observed as it shifted to ~ 2025 cm^{-1} in the desorption spectra. Variations in catalyst preparation to effect various levels of Ru dispersion led to large changes in spectral intensity of these bands consistent with expectations of lower intensity for less dispersed samples.

The impact of the reaction environment on the CO spectrum can be seen in **Figure 11** displaying a spectrum of the catalyst after exposure to flowing feed at 108°C. Here, a spectral envelope of at least four CO bands can be seen which we attributed to CO- Ru^{n+} species where $0<n<1$ based on literature assignments summarized by Che *et. al.* [3]. Spectra collected upon flowing feed gas with the composition shown in **Table 1** shows a shift of the 2040 cm^{-1} to around 2060 cm^{-1} and of the 1970 cm^{-1} to around 1990 cm^{-1} along with the appearance of a band around 1580 cm^{-1} . Such shifts to higher energies are consistent with depletion of the adsorption sites of electron density and are strongly indicative of some ruthenium oxidation in the presence of feed. The 1580 cm^{-1} band is consistent with a formate-type species present at the surface. A weak band in this location could be observed albeit with much weaker intensity on exposure of the catalyst to CO and hydrogen only. However, its intensity increases upon exposure to the oxygen- containing feed. Treatment of the catalyst with the wet feed on the other hand, results in significantly lower intensity for this band.

Figure 12 shows a comparison of the infrared spectra of the catalyst in flowing feed at 150°C with and without oxygen present. The spectrum measured in the absence of oxygen shows the influence of higher temperature on the CO spectral profile with a broad band in the lower frequency range of the envelope becoming the most prominent than it had been in the 110°C spectra. A shoulder around 2040 cm^{-1} can also be discerned in this spectrum. The dramatic effect of oxygen introduction on this spectral envelope can be clearly seen in this figure where the spectrum is completely transformed into one primarily displaying the 2040 cm^{-1} and 1990 cm^{-1} bands observed in the 110°C spectra. Introduction of oxygen also results in a loss of intensity of the 1580 cm^{-1} band and the appearance of a weak band around 1850 cm^{-1} . This effect appears reversible as demonstrated in **Figure 13** where the impact of cycling oxygen in and out of the feed mixture on the IR spectrum can be seen. In addition to the reproducible changes in the CO stretching region, the inverse relationship between the formate band and oxygen can also be seen in these spectra.

The loss of intensity of in the lower energy band of the spectral envelop and the position of the remaining bands indicate that CO-Ru species formed at reduced, electron rich, Ru sites are most reactive. This interpretation relies on the assumption that the lower frequency CO bands can be assigned to species adsorbed at reduced metal sites. Many alternative and conflicting literature assignments of some of the CO bands observed on ruthenium catalysts have been proposed [3]. Some of these assignments are consistent with our observations. For example, bands observed in the 2060 – 2100 cm^{-1} have been assigned to di or multi-carbonyl species coordinated to partially oxidized Ru. Their assignment to positively charged ruthenium is of course

consistent with our observation of a shift of the 2040 cm^{-1} band to around 2060 cm^{-1} upon introduction of oxygen to the feed mixture. Other assignments have appeared in the literature supporting coordination to crystallographically specific sites [4-7]**.** Thus, changes in the spectral envelope observed in our studies may also be reflecting surface reconstruction in response to changes in the reaction atmosphere in addition to Ru electronic environment variations.

Whether the formate species observed is a spectator species or an actual participant in the CO oxidation mechanism is not easy to distinguish. A hypothesis involving formate as a reactive intermediate derives support from the observed impact of water and oxygen on its spectrum. We rationalize the decrease in intensity of the formate spectrum in the presence of water in terms of a competitive adsorption model. This, coupled with the observation of the inhibitive role of water for the selective oxidation chemistry, lends support to the hypothesis that formate is indeed a reactive intermediate. At first consideration it is not intuitively obvious why oxygen would diminish, rather than enhance, formate concentration at the catalyst surface. Reactions 5 and 6 below represent routes to its formation and removal from the surface. The source of hydrogen can be the reformate or surface OH groups which eventually are replenished.

$$CO+O2 + H2 \rightarrow HCOO^{-} - ads \quad (5)$$

$$HCOO^{-} - ads + O2 \rightarrow CO2 + H2O \quad (6)$$

Conclusions

The current paper illustrates the complex nature of the working preferential oxidation catalysts. Significant gains in understanding the fundamental processes taking place at the surface of such catalysts under reaction conditions have been achieved through the work summarized here. However, much remains to be done to achieve a detailed understanding of the nature of selective oxidation catalysts and in determining the key variables, which will lead to improvements in the catalyst and process. It is hoped that this illustration of the strong link between catalyst preparation, conditioning variables and performance will spur further work in the catalysis community to help gain better understanding of this important emerging area of catalysis.

Acknowledgment

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TABLE 1. CONDITIONS FOR CATALYST EVALUATION		
Catalyst handling Procedures *Reactor loaded under N_2 purge	Gas Composition (dry basis)	
Reaction Conditions *Reactor Pressure: 3.5 psig *GHSV: 5,000 hr/1-20,000 hr/1 *Evaluated temp range: 60ºC – 350ºC *Duration of test: 75min – 800min *Catalyst to Diluent ratio of 1:3	16.36% 0.64% 3.99% 6.66% 65.34% 5.55% 1.46% 27.62% 02/CO	CO_2 CO CH_4 Ne H_2 N_2 O_2 H2O 2.2
Target Carbon Monoxide Level:<10ppm		

TABLE 2. EXPERIMENTAL CONDITIONS	
Product Analysis	
Carbon Monoxide Detectors Low Range *Infrared *Detection range: 0-1000ppm High Range *Infrared *Detection range 0-10,000ppm	Carbon Dioxide Detectors *Infrared *Detection Range: 0-20%
Oxygen Detector *Paramagnetic *Detection Range: 0-25%	

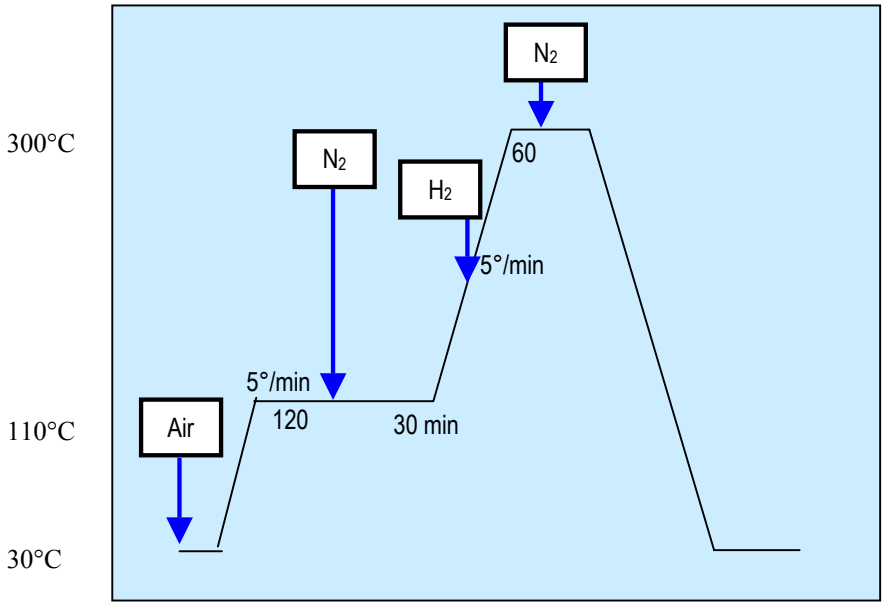

Figure 1. Typical Catalyst Activation Procedure

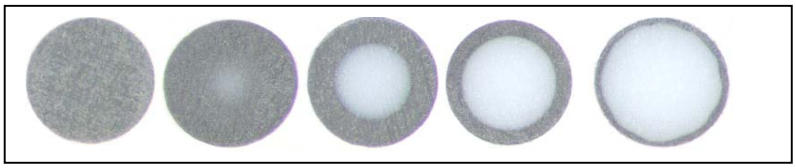

Figure 2. Micrographs of various eggshell profiles

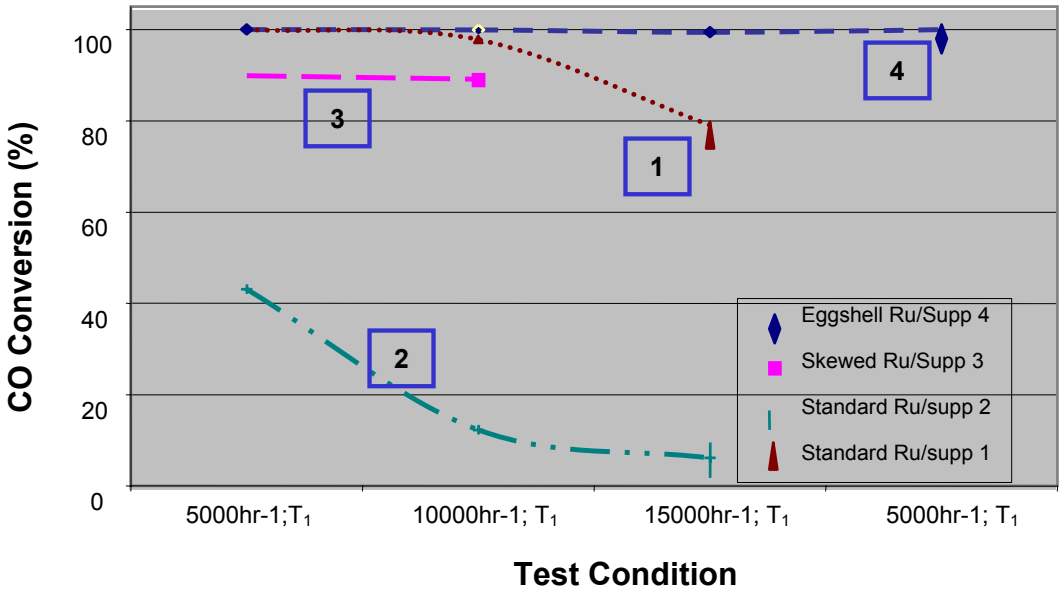

Figure 3. Impact of Support and Ruthenium Profile on CO Conversion, Inlet Temperature T_1

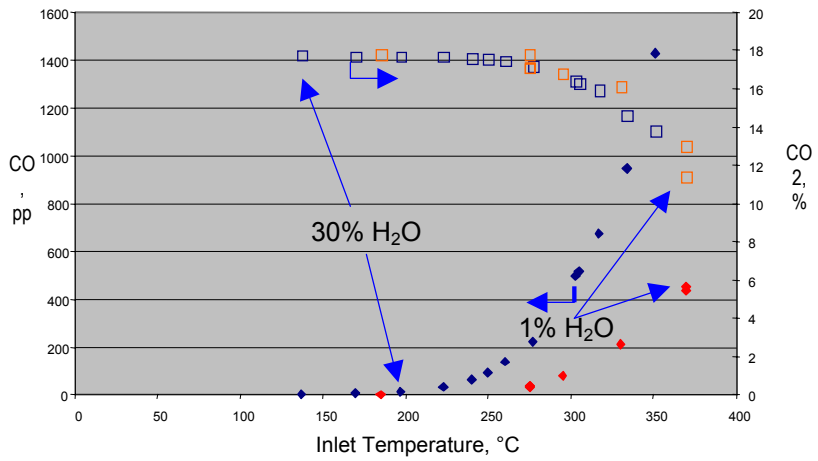

Figure 4. Impact of O_2/CO Ratio on CO Conversion
Inlet Temperature = T_1

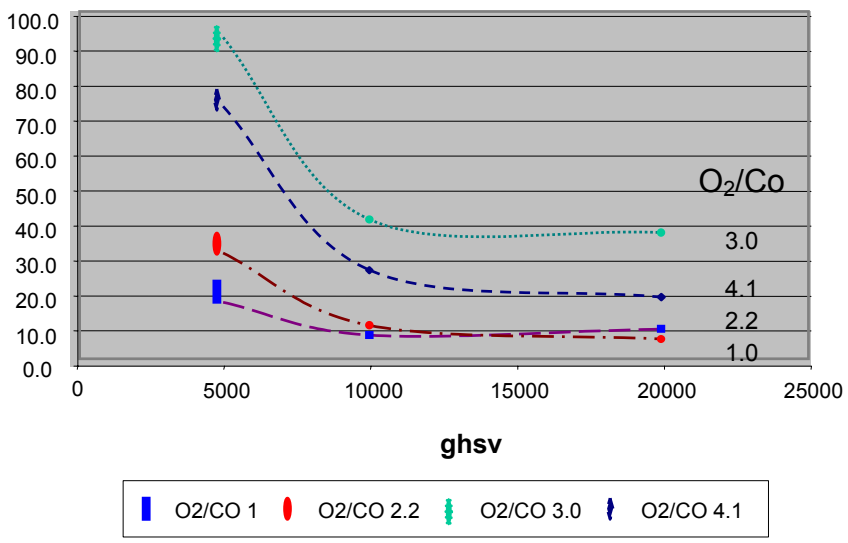

Figure 5. CO Conversion at High Temperature

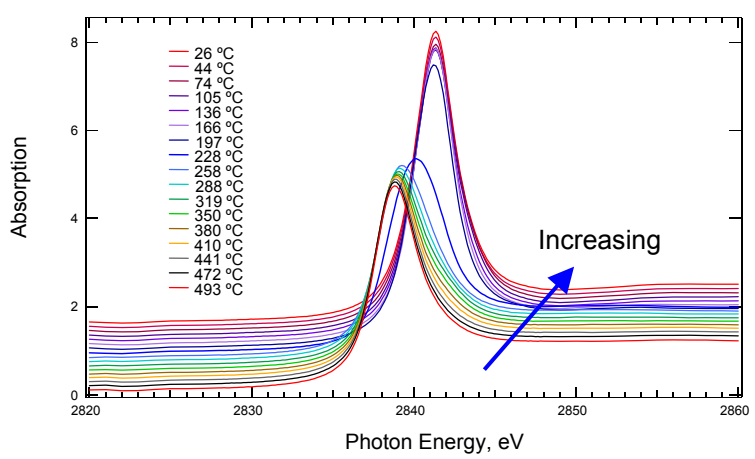

Figure 6. XANES: In-Situ Reduction of Ru
Ru L_3-edge TRP-XANES

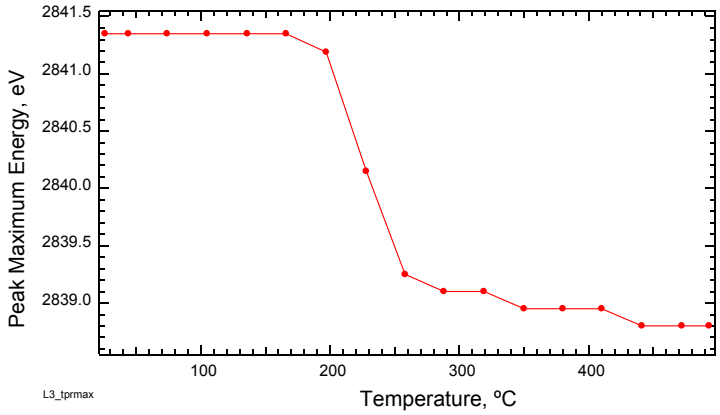

Figure 7. XANES: In-Situ Reduction of Ru

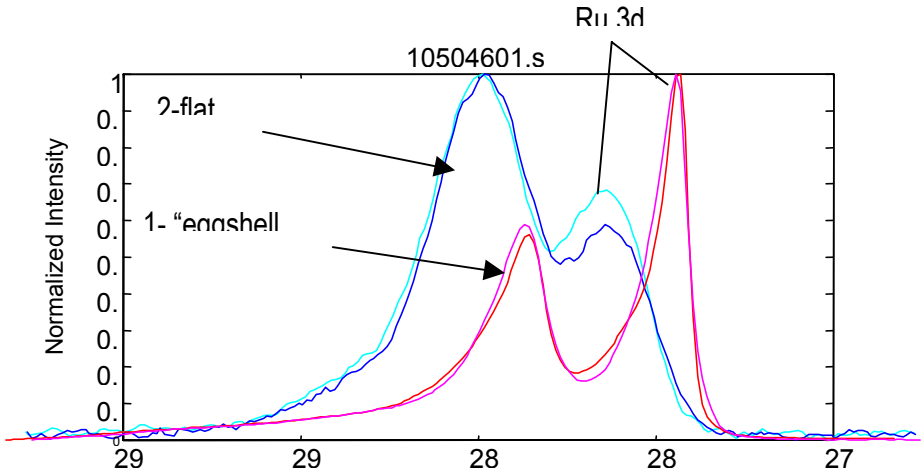

Figure 8. XPS Comparison of Exterior of "Eggshell" and Flat Catalyst Preparations

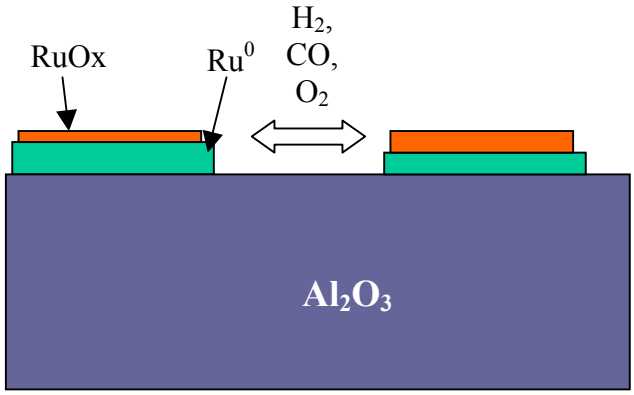

Figure 9. Model of Selective Oxidation Catalyst

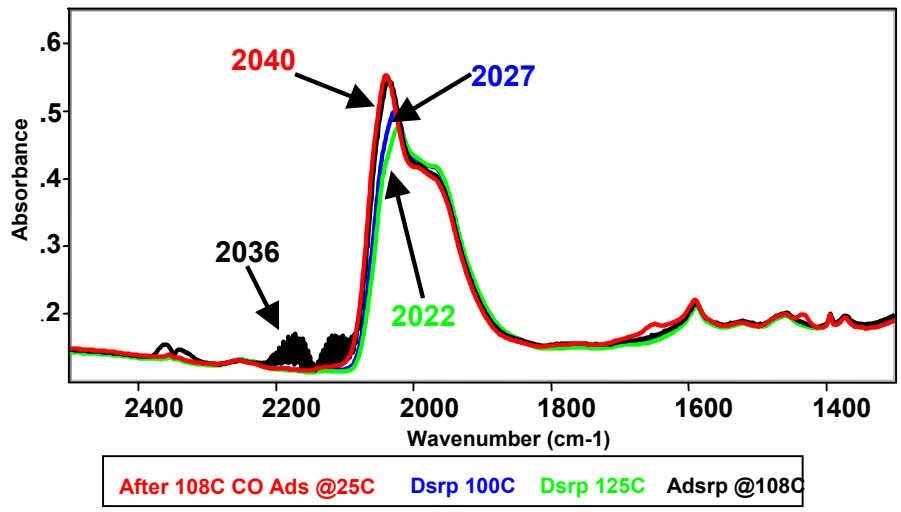

Figure 10. Effect of CO Coverage and Temperature On Carbonyl Frequencies

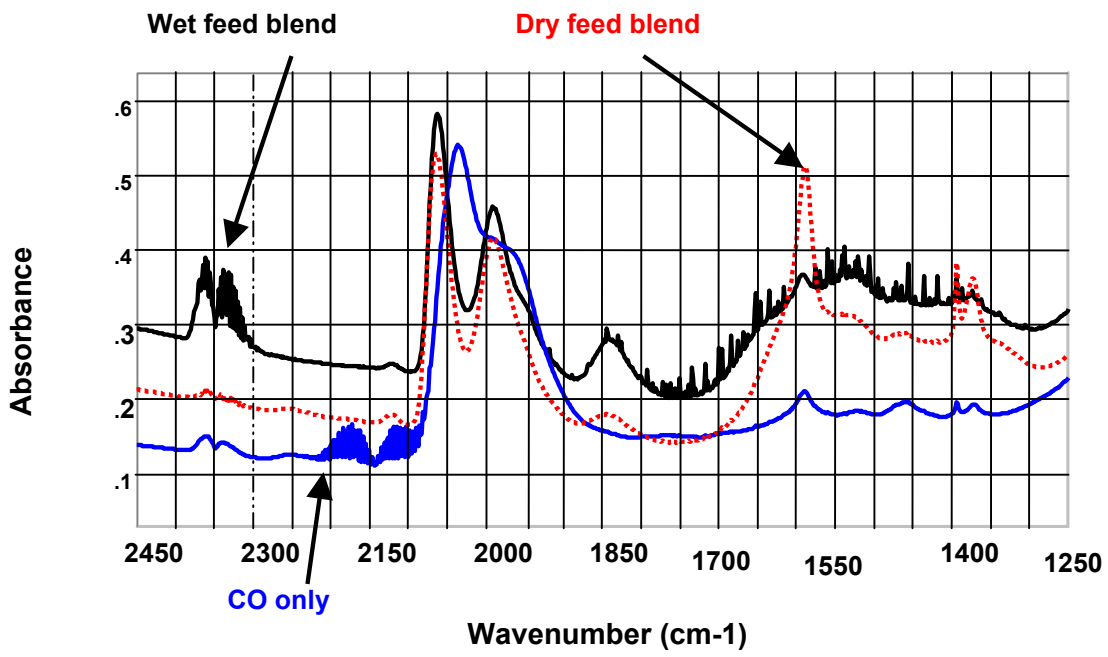

Figure 11. FTIR Spectra of Selective Oxidation Catalyst Exposed to Dry and Wet Feed at 110ºC

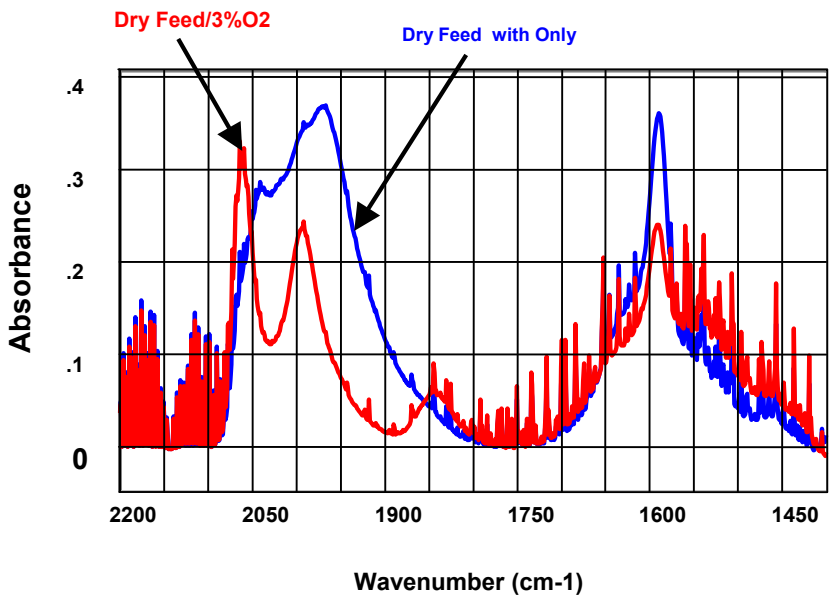

Figure 12. Effect of Oxygen on IR Spectrum of Selective Oxidation Catalyst @ 150ºC

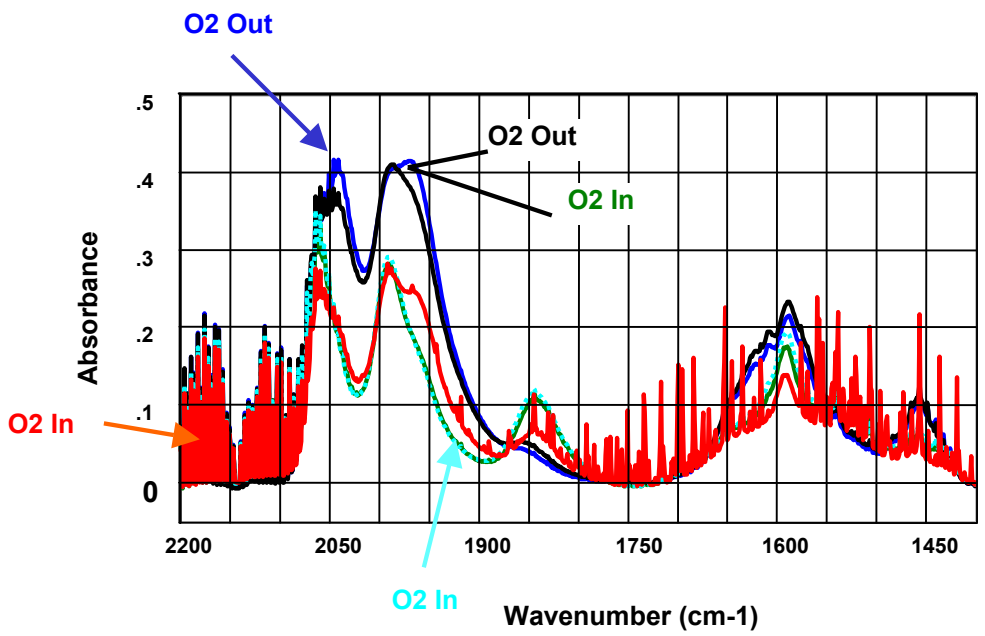

Figure 13. Effect of Oxygen Cycling on IR Spectrum of Selective Oxidation Catalyst @ 150ºC