



## ON-LINE MEASUREMENTS OF OXIDATION OF CARBON USING VISIBLE SPECTROSCOPY

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### ABSTRACT

*We have identified four different band heads belonging to the  $B^1\Sigma-A^1\Pi$  bands of the Angstrom system of the CO spectrum in the visible region at  $\lambda = 561.0, 519.8, 451.1$  and  $439.3$  nm, for on-line monitoring of conversion of carbon to carbon monoxide in the 'de-coking' process of a 'coked' catalyst. A low-power glow discharge in oxygen gas was used as a source for oxidizing carbon from a 'coked' zeolite catalyst. Evolution of CO as a function of time was systematically monitored using the  $451.1$  nm band head since there is no overlap with any possible impurities including oxygen, nitrogen or water vapor. An interesting observation is an exponential increase in the evolution of CO typically after about 10 minutes from the initiation of the discharge. The results may be of particular interest in monitoring catalyst regeneration on-line as well as environmental monitoring of CO.*

**Keywords:** CO Monitoring, Visible Region, Catalyst Regeneration, Oxidation of Coke, Glow Discharge

## B $\Sigma$ - A $\Pi$

### 1. INTRODUCTION

Absorption and emission of radiation from atoms and molecules provide a simple and effective mechanism for unambiguously identifying particular species in a complex mixture of gases or materials [Svanberg, 2001]. It is noted that most molecules exhibit strong emissions in the infrared (IR) or ultraviolet (UV) region [Pearse and Gaydon, 1976; Hollas, 1992]. However, because of the problems associated with the optics as well as detectors in the IR and UV regions, it is easier to work in the visible region for spectroscopically monitoring radiative transitions of atoms and molecules [Hollas, 1992; Svanberg, 2001].

In our experiments, a low-power glow discharge in oxygen was used for oxidizing carbon from a 'coked' zeolite catalyst [Hollahan and Bell, 1974; Dadashova et al, 1992]. Reactions of atomic oxygen created in the discharge with layers of 'coke' on the catalyst generated the CO and CO<sub>2</sub> gases [Hollahan and Bell, 1974; Hutchings et al, 1987; Dadashova et al, 1992; Pieck et al, 1997; Sweeney et al, 1997]. We have identified four different band heads belonging to the B<sup>1</sup> $\Sigma$ -A<sup>1</sup> $\Pi$  bands of the Angstrom system of the CO spectrum in the visible region at  $\lambda = 561.0, 519.8, 451.1$  and  $439.3$  nm [Pearse and Gaydon, 1976] for on-line monitoring of oxidation of carbon. However, no suitable transitions of CO<sub>2</sub> gas in the visible region could be identified for use in on-line monitoring even though it is clear that CO<sub>2</sub> is also created in the same process.

Evolution of CO as a function of time was systematically monitored using the 451.1 nm band head since there was no overlap with any possible impurities including oxygen, nitrogen, and water vapor. An interesting observation is an exponential growth in the evolution of CO typically about 10 minutes after the initiation of the discharge. Important applications of these findings are envisaged in on-line monitoring of catalyst regeneration. Furthermore, these visible transitions can also be used for environmental monitoring of CO [Dolan, 1985].

## 2. EXPERIMENTAL CONSIDERATIONS

A schematic diagram of the experimental set up is presented in figure 1. The discharge cell consisted of a 25 cm long and 3.75 cm diameter Pyrex tube having two electrodes to apply the DC voltage. The cell had optical windows for some diagnostic applications. One of the windows was demountable. This allowed the catalyst to be placed inside the discharge tube. A side port was also available for collecting fluorescence from various atomic and molecular species present in the discharge, for the purpose of monitoring and analysis. It was also possible to collect fluorescence in the axial direction. The cell was first evacuated to pressures of the order of  $10^{-3}$  mbar and then filled to the appropriate pressure of the desired gas or gas mixture under carefully controlled conditions.

The regeneration process yields gases such as CO, CO<sub>2</sub> as well as other gaseous products. Our set-up allows the possibilities of static experiments, continuous and controlled gas-flow, as well as an on-line purge and refill facility for prompt removal of CO and CO<sub>2</sub> etc. created as a result of oxidation reactions. These are important considerations because while sufficient time is needed for the reaction to proceed, the reverse reactions have to be avoided. At the same time sufficient amount of oxygen should remain available for the oxidation reactions. Thus, a system with only a small amount of the gas actually flowing at any particular time, or a periodic purge with fresh oxygen after controllable periods have to be used.

It is noted that with time, the discharge generates a considerable amount of heat especially if the current drawn is not restricted. In particular, the electrodes have to be cooled to contain this build up of heat. Furthermore, the oxidation of carbon is exo-thermic in nature [Hutchings et al, 1987]. This also contributes to the build up of heat. We monitored the temperature of the cell walls externally to get some idea of the heat generated. For this, we wrapped a heating tape around the cell for thermal insulation, but no current was passed through this tape. A thermocouple was inserted between the tape and the body of the cell to monitor the temperature of the outside wall. We observed a steady increase in the temperature up to about 150<sup>0</sup>C under our experimental conditions.

While the high temperature increases thermal velocities of the gas molecules thus increasing the collision probability and facilitating deeper penetrations thereby enhancing the reactions of atomic oxygen with coke, excess heat can have some harmful effects. In our experiments, this led to cracks appearing in the cell particularly in the region where the electrodes were fused into the cell. Therefore, arrangements had to be made to maintain a certain temperature level and to remove the excess heat beyond that point. We used a cooling fan and an insulating tape around the central parts of the cell to accomplish this.

To calibrate the system, the cell was filled with different gases or gas mixtures (air, nitrogen, oxygen, oxygen + nitrogen, oxygen + helium, oxygen + argon, or CO<sub>2</sub> gases) at different pressures. A discharge was excited in the selected gas or gas mixture. The population

densities of various atomic and molecular species were monitored using spectroscopic emission. For this purpose, a monochromator coupled to a thermoelectrically cooled photomultiplier was used to record the spectrally resolved light emitted by the discharge. Composition of the gas mixture, gas pressure and the discharge current were varied to observe possible enhancements in the emission from particular species for the purpose of unambiguous identification and correlation. Further checks were made to insure mutual- and self-consistency of results.

For experiments on removal of coke in an O<sub>2</sub> discharge, a small amount of ‘coked’ catalyst (i.e., sample) was spread evenly inside a ceramic boat essentially as a single layer and placed in the discharge tube before evacuating the cell and then filling it with oxygen or oxygen-containing gas mixture. This was exposed to the discharge for known times and the sample was subsequently analyzed to record changes in the carbon content of the catalyst. The influence of exposure time on the degree of ‘de-coking’ was investigated. Our measurements using surface science techniques for quantifying residual carbon content as compared to the carbon present in the original ‘coked’ sample clearly confirmed the process of oxidation and removal of coke [Khan et al, 2002].

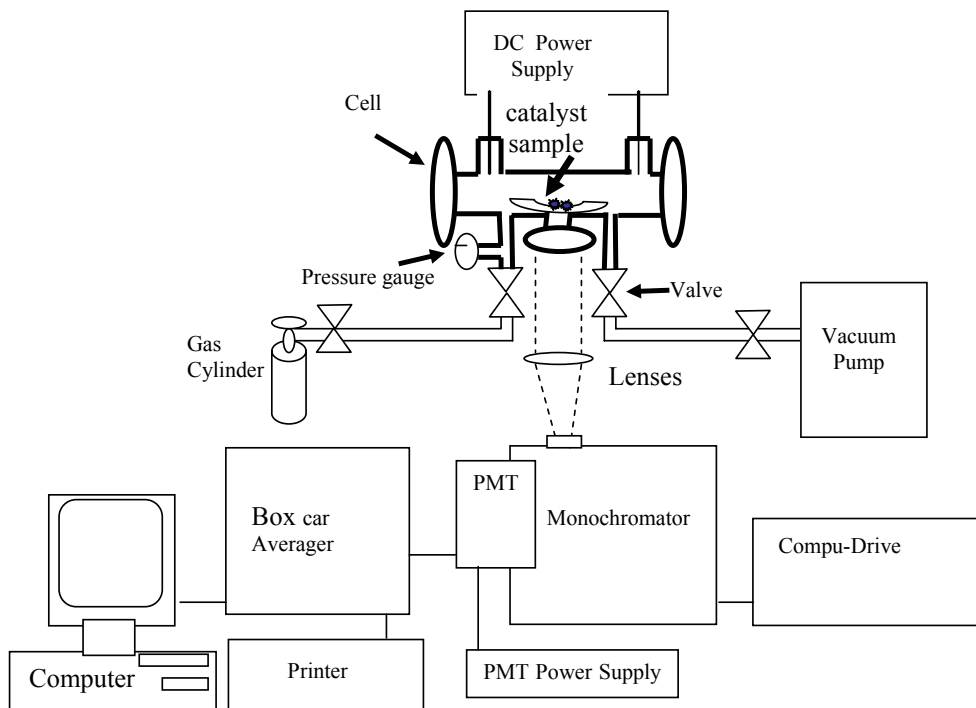


Figure 1: Experimental set-up

### 3. RESULTS AND DISCUSSION

In the course of developing the experimental facility, several preliminary tests were necessary. These included spectral data analysis for identification of the species present and correlating their relative abundance. In particular, it was necessary to insure that no ambiguity existed with respect to a given transition belonging to a specific atom or molecule. In this context, spectral regions and transitions having possible overlaps from different species were avoided. Furthermore, considering the enhanced reactivity of atomic oxygen, a major step in the oxidation of 'coke' was the actual atomization of oxygen. Additional experiments involved the study of behavior of the observed species under different experimental conditions.

#### 3.1. Atomization of O<sub>2</sub>

Dissociation of the O<sub>2</sub> molecule in the electric discharge yielding two oxygen atoms [Hollahan and Bell, 1974] was monitored through a detailed study of the radiated emission on several transitions of oxygen atom. The 3s <sup>5</sup>S– 3p <sup>5</sup>P transitions around 777.2 - 777.5 nm [Striganov and Sventitski, 1968] were finally selected for monitoring this process on-line. Fig. 2 shows a typical record of spectral emission from these transitions as a function of wavelength. Here, the discharge was in pure O<sub>2</sub> at a pressure of 6 mbar while the discharge current was 60 mA. Spectral records in this particular region were also obtained for emissions from discharges in air, nitrogen, oxygen, oxygen + nitrogen, oxygen + helium, oxygen + argon, or CO<sub>2</sub> gases under similar conditions. It was established beyond any shade of doubt that only the transitions from atomic oxygen were present here.

#### 3.2. Discharge in CO<sub>2</sub>

Electric discharge in CO<sub>2</sub> gas was of particular interest to us. More specifically, we wanted to find suitable transitions of CO<sub>2</sub> and CO primarily in the visible region that could be used for on-line monitoring of these gases. After several experiments and subsequent analyses of the spectral data, we identified four different band heads at 561.0, 519.8, 451.1 and 439.3 nm belonging to the B<sup>1</sup>Σ-A<sup>1</sup>Π bands of the Angstrom system of the CO spectrum in the visible region [Pearse and Gaydon, 1976] for monitoring carbon monoxide. Furthermore, the absence of these transitions from discharges in pure O<sub>2</sub> gas or pure N<sub>2</sub> gas established beyond any doubt that the identified transitions indeed belonged to CO. However, we did not succeed in finding any suitable transitions of CO<sub>2</sub> in the *visible region* for their use in on-line monitoring. Indeed, the IR and UV spectral regions contain a large number of CO<sub>2</sub> transitions and any UV or IR spectrometer should accomplish on-line monitoring quite easily, but we did not use these in the present study.

We selected the CO band head at 451.1 nm for our experiments (see figure 3) since there was no overlap with any possible impurities.

### 3.3. Oxidation of 'coke' in O<sub>2</sub> discharge

A low-power glow discharge in oxygen gas was used as a source for oxidizing carbon from a 'coked' zeolite catalyst. In addition to the electrons and various ionic species, the discharge also created sufficient amount of atomic oxygen, as noted earlier. Subsequent reactions of atomic oxygen with layers of carbon on the catalyst generated the CO and CO<sub>2</sub> gases.

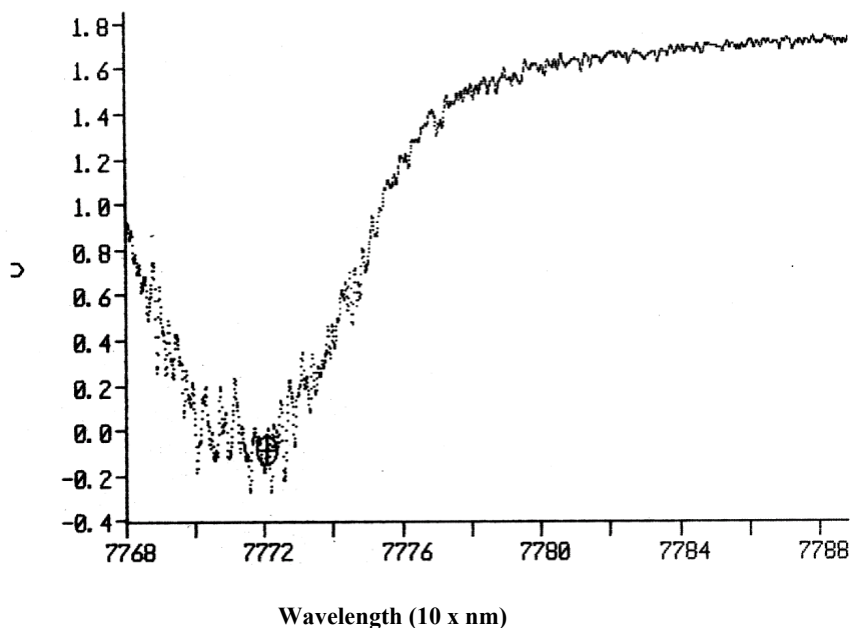


Fig. 2: A typical record of spectral emission from  $3s\ ^5S-3p\ ^5P$  transitions of atomic oxygen.

Figure 4 shows an example of the spectral emission from CO when atomic oxygen reacted with the coke resulting in the generation of CO<sub>2</sub> and CO gases in our experiments. The pressure of oxygen was again 6 mbar and the discharge current was 60 mA.

### 3.4. Time-History of Evolution of CO

In our experiments, the evolution of CO in time was monitored using the band head of CO at 451.1 nm, as mentioned earlier. The monochromator was fixed at 451.1 nm corresponding to the peak of this transition. One particularly noteworthy point is that in addition to the heat generated by the discharge, the oxidation reaction itself is exo-thermic. So, heat builds up rapidly inside the cell, with time. While this has some useful influence on the reaction yield, it also caused some undesirable effects. Accordingly some arrangements had to be made to remove the excess heat beyond a certain point.

Figure 5 shows the evolution of CO in time for the first 10 minutes when most of the excess heat was effectively removed by the cooling fan, without using any thermal insulation. Note that the time scale marked along the horizontal axis is in arbitrary units. We notice that the amount of CO increases steadily but also decreases quite quickly. This could be understood from the consideration that the amount of oxygen available has been consumed or that the reverse reactions convert CO back to CO<sub>2</sub> or even coke and other gaseous products. The presence of O atoms in the discharge can indeed facilitate the formation of CO<sub>2</sub> from CO. We need further experiments to determine the rates of back conversion of CO to CO<sub>2</sub> and that could be reported in a future publication.

When thermal insulation was used to contain a good part of the generated heat within the gas volume, an interesting observation was a marked increase in the evolution of CO as a function of exposure time/temperature typically about 10 minutes from the start of the discharge (figure 6 a, b). This is a truly remarkable result and we were able to reproduce this several times. The actual rate of growth of CO varies considerably with the experimental conditions (figure 6 a, b). However, the rates of forward reactions seem to far exceed any reverse reactions.

The build up of heat inside the cell did lead to a breakdown of our cell at least on two occasions. This prompted us to completely re-design the discharge cell keeping in view the need for controlled yet adequate outflow of heat.

It is also important to note that the regeneration of the ‘coked’ catalyst discussed here is accomplished essentially at room temperature without any additional /external heating [Khan et al, 2002].

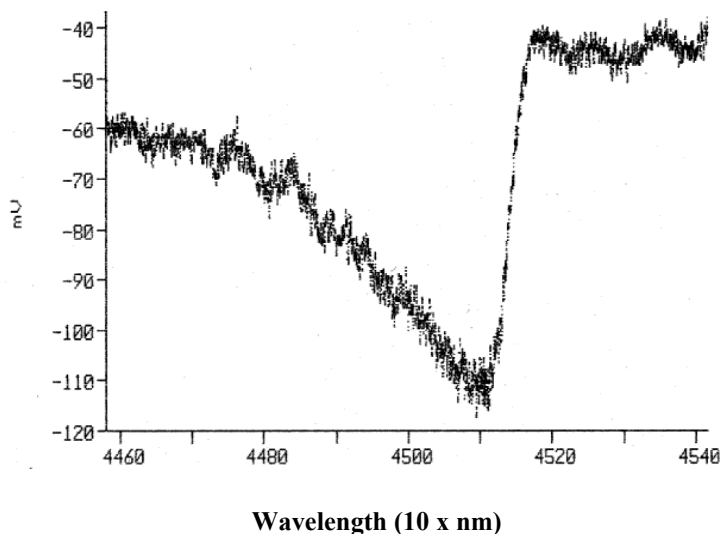


Fig. 3: A typical record of spectral emission from a transition at 451.1 nm of the B<sup>1</sup>Σ-A<sup>1</sup>Π band of CO originating from a glow discharge in CO<sub>2</sub>

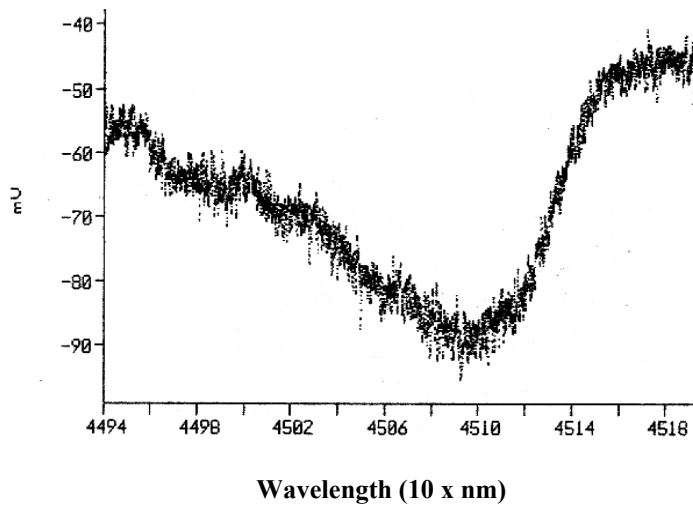


Figure 4: A typical record of spectral emission from the transition at 451.1 nm of CO originating from oxidation of 'coke' in O<sub>2</sub> discharge.

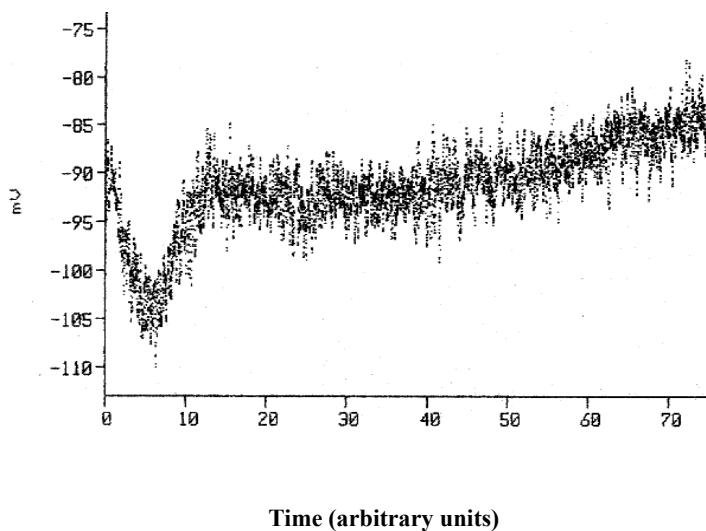


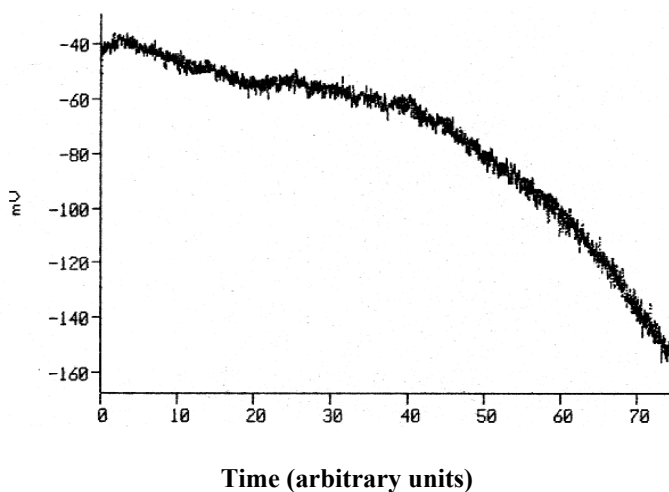
Fig. 5: Time history of evolution of CO during the oxidation of 'coke' in O<sub>2</sub> discharge. No thermal insulation was used in this case.



#### 4. CONCLUSIONS

On-line monitoring of oxidation of 'coke, in an  $O_2$  discharge using the 451.1 nm band head of the  $B^1\Sigma-A^1\Pi$  bands of the Angstrom system of CO in the visible region is demonstrated. A low-power glow discharge in oxygen gas was used as a source for oxidizing carbon from a 'coked' zeolite catalyst. A particularly interesting observation is an exponential increase in the evolution of CO as a function of exposure time / temperature. Since no additional heating

(a)



(b)

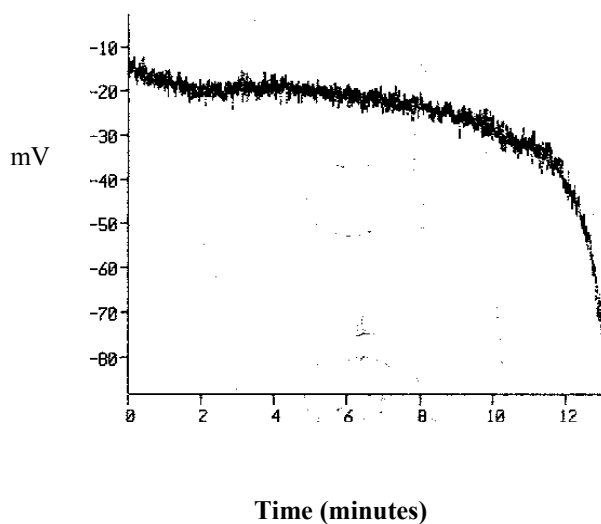


Figure 6(a, b): Time history of evolution of CO during the oxidation of 'coke' in  $O_2$  discharge. Different parts of the discharge tube were thermally insulated in these two cases.

was used, this temperature is considerably less than the range hitherto employed. Important applications of these findings are envisaged in monitoring catalyst regeneration on-line as well as environmental monitoring of CO.

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