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Kinetics of the Carbon Monoxide Oxidation Reaction Under Microwave Heating

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Abstract

915 MHz microwave heating has been used to drive the CO oxidation reaction over Pd/Al₂O₃ without significantly affecting the reaction kinetics. As compared to an identical conventionally heated system, the activation energy, pre-exponential factor, and reaction order with respect to CO were unchanged. Temperature was measured using a thermocouple extrapolation technique. Microwave-induced thermal gradients were found to play a significant role in kinetic observations.

Introduction

Microwave energy is an alternative to conventional heating in catalytic processes and has proved successful in driving the CO oxidation reaction over Pd and Pt on γ -Al₂O₃ without significantly affecting the reaction kinetics. There are many ways the microwave might interact with the catalyst to have an effect on chemical kinetics in this system: 1) space charge effects around the supported metal particles such that an induced surface charge has significant effect on the dipolar CO molecule either on/near the surface; 2) differential heating of the metal versus the ceramic support; 3) the oxidation of the polar CO molecule could be affected both in the gas phase and near the catalyst surface by the electric field. If any of these effects were important, a significant alteration in the kinetics would be observed with respect to conventional heating.

In most of the literature reviewed [1,2,3,4], beneficial effects of microwave heating were shown. However, little has been done to understand the effect of microwaves on the underlying kinetic and mechanistic process due to the difficulties experienced in measuring temperature and the non-isothermal nature of a microwave heated packed-bed. Because of the temperature gradients and lack of temperature data, it is difficult to ascertain the root cause of the beneficial effects. In the research presented, we have taken steps to determine the temperature and temperature gradients so that an accurate comparison of chemical kinetics during microwave and conventional heating can be made.

Experimental

In this paper we will compare the kinetics of the CO oxidation reaction over Pt and Pd/ γ -Al₂O₃ as observed in a specially constructed microwave heated differential [5] reactor. These kinetics were compared to a conventionally heated reactor. To eliminate the effects of temperature gradients, a differential mass of active supported catalyst was sandwiched between two masses of inactive support inside a quartz tube, which was radially insulated with microwave transparent sapphire wool. The geometry located the active material on the maxima of the temperature profile, and the short length of the active material approximated an isothermal bed. A schematic of a typical experimental reactor is shown in Fig. 1.

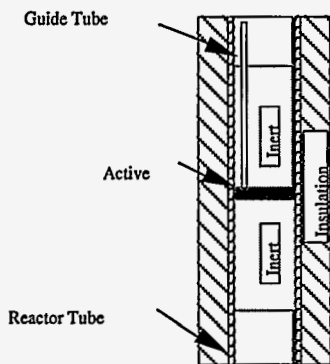


Figure 1. Schematic of reactor configuration used in both the microwave and conventional experiments. "Differential" active catalyst zones were axially thin to minimize thermal gradients, and inert material was also added to minimize gradients. Insulation was provided to minimize radial gradients.

We chose the CO oxidation reaction over a supported metal catalyst because the reaction kinetics are well known, and because of the diverse dielectric properties of the various elements in the system: CO is a polar molecule, O₂ and CO₂ are non-polar, Al₂O₃ is a dielectric, and Pt and Pd are conductors. The literature [6,7] has revealed the conventionally-heated reaction kinetic and mechanistic details, with the desorption of CO being the rate limiting step.

The thermal reactor system was heated by a digitally controlled 1" tube furnace. The microwave reactor was heated by a magnetron based system operated on a continuous basis at 915 MHz. The power to the experiment was 850W to 1000W and was delivered to a resonant applicator via rectangular waveguide in the TE₀₁₀ mode. The reactor tube was inserted through the rectangular resonant applicator parallel to the direction of the electric field. Product analysis was performed using gas chromatography. Reactant ratios were fixed by mass flow controllers, and the pressure was regulated by a bypass valve and monitored with a capacitance manometer.

The catalyst used for the final experiments was 5% (by weight) Palladium supported on γ -Al₂O₃. Preliminary experiments used 1% Pt/ γ -Al₂O₃. To determine the activation energy, E_a, and the pre-exponential, A, factor in the Arrhenius expression temperature versus reaction rates were recorded. The flow rate for CO was 2 cc/s and 1 cc/s for O₂, and the reactor pressure was fixed at 1000 Torr. The dependency on CO partial pressure was found by using an excess of oxygen and the CO partial pressure ranged from 35 - 95 Torr. The reactor pressure was held at 1000 Torr and the temperature was 135 C for these experiments.

Temperature was measured in the microwave system by inserting a thermocouple into the bed after the microwave power was turned off. For the final experiments, the thermocouple was inserted through a "guide tube" (see Figure 1) until it came to rest in the hottest (active) part of the bed. The temperature decay curve was recorded on a x-y recorder. The temperature versus time curve was linearized and coordinates were entered into a curvefitting routine. The routine provided an expression in the form $y=mx+b$ where b was the initial temperature. The thermal mass of the thermocouple was not insignificant with respect to the mass of the bed and a corrective procedure was employed: The digitally controlled tube furnace was allowed to reach a known equilibrium temperature, furnace power was terminated, the furnace was opened, the thermocouple was inserted and the recorder was started. Several data points were recorded and a best fit line expression was then used to correct the temperature measurements.

Results and Discussion

Apparent kinetics. Early experiments were performed using an integral-type reactor [5]. A schematic of this reactor is shown in Figure 2 along with the comparative Arrhenius plot. The experiment used 2 grams of 1% Pt/Al₂O₃. The thermocouple extrapolation technique was employed and the probe was inserted such that it was in contact with the

packed bed as shown in Fig 2. The microwave-heated packed bed was shown by thermal imaging in Figure 3 to be very non-isothermal. The non-isothermal nature of this packed bed precluded accurate temperature measurement and resulted in the apparent rate enhancement , activation energy and pre-exponential .

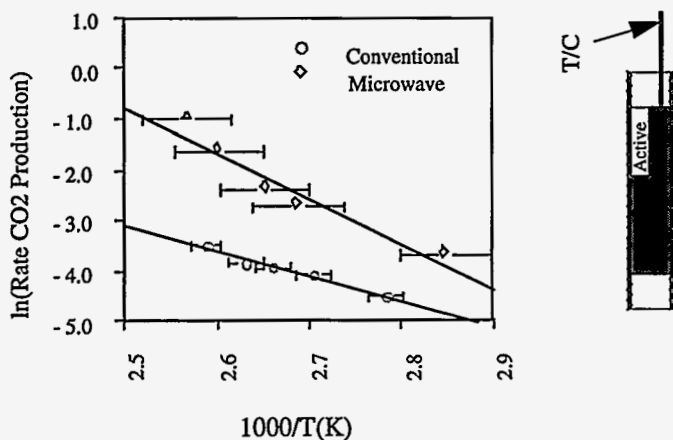


Figure 2. Comparative Arrhenius plot and Schematic of an integral-type packed-bed reactor. Error bars reflect maximum possible error.

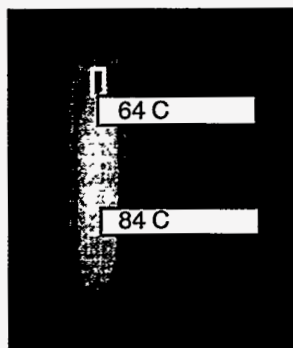


Figure 3. Thermal (infrared) image of microwave heated packed bed. Temperatures shown are the average temperatures of the areas outlined by the boxes.

A subsequent experimental design used $\alpha\text{-Al}_2\text{O}_3$ for the inert insulating material and $\gamma\text{-Al}_2\text{O}_3$ was used to support the active metal (see Fig. 1). Figure 4 shows a comparative Arrhenius plot and the associated thermal profile obtained from this differential configuration. The plot clearly shows an apparent rate enhancement. The probe was inserted into the active portion of the bed as shown in Figure 1. A qualitative experiment was performed, and $\gamma\text{-Al}_2\text{O}_3$ was observed to absorb microwave energy more efficiently than $\alpha\text{-Al}_2\text{O}_3$. Thus, the true reaction temperature was greater than the average, observable temperature as shown in Figure 4.

The true reaction temperature of the $\gamma\text{-Al}_2\text{O}_3$ was not observable with our technique for two reasons: 1) the mass of the active portion of the bed was much less than the inactive portion and the thermocouple will primarily “see” the inactive (cooler) mass; 2) the time required for the isolated $\gamma\text{-Al}_2\text{O}_3$ particles to cool to the temperature of the $\alpha\text{-Al}_2\text{O}_3$ was much less than the time required to insert the thermocouple. This time for cooling can be estimated rigorously by performing a transient heat conduction analysis. Because of the rapid cooling and low mass fraction, the reaction was occurring at a hotter temperature than was observed by the thermocouple and yielded the apparent results shown in Figure 4.

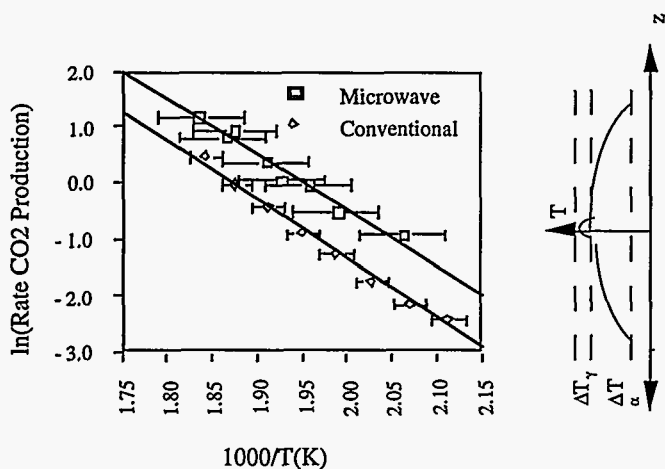


Figure 4. Result for differential type reactor where active catalyst was supported on γ -alumina and insulating alumina was α -type. This material mismatch gave rise to the qualitative temperature profile shown here. The rise at $z=0$ results from more efficient absorption of microwave energy by the γ -alumina. Error bars reflect maximum error.

This experiment illustrates the difficulty in observing the proper temperature when one material absorbs more efficiently than another. The situation is analogous to the case where the supported metal particles absorb energy preferentially to the support. The metal particle temperature would not be observable due to the observability discussed above, and a discrepancy similar to that shown in figure 8 would result if preferential absorption were occurring.

True kinetics. A comparative Arrhenius plot is shown in Figure 5 for CO reaction over $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$. The reaction rates were nearly identical within experimental error. The slightly higher rate observed in the microwave reactor resulted from thermal gradients which cannot be eliminated and the reaction surface was always hotter than the average temperature observable using a thermocouple.

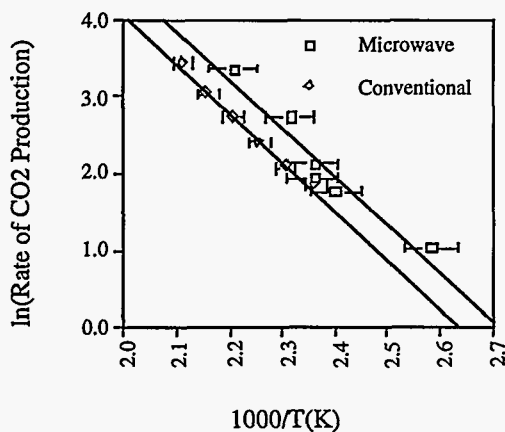


Figure 5. Plot shows comparison of data obtained in the microwave-heated reactor vs. the conventionally heated reactor. The slope of both lines is nearly identical, yielding an activation energy of approximately 13 kcal/mol. The proximity of the data indicates no significant microwave effect. Error bars represent maximum error.

The conductive palladium did not couple effectively with the microwave energy with respect to the alumina support. Had the metal coupled more strongly, the local metal surface temperature would be greater than the support, and the rate would appear faster in the microwave than the conventional furnace. The specific metal temperature was not observable for reasons described above.

The other possible effect considers a specific microwave effect on the desorption rate of CO, the most likely area for a specific microwave effect. A specific effect would appear as a change in CO reaction order. Figure 6 shows the rate dependence as a function

of CO partial pressure, yielding reaction orders (slopes) which are nearly identical. These results support the conclusion that the process is unaffected by the heating mode.

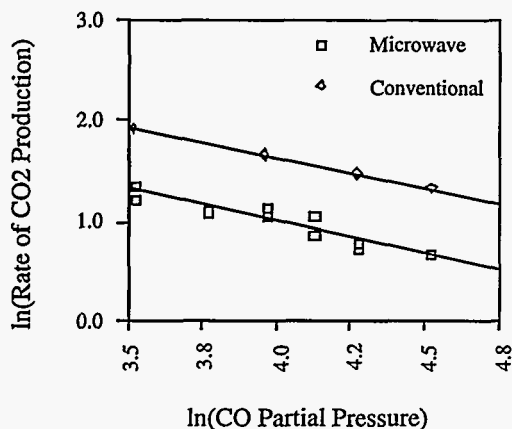


Figure 6. Plot indicates the dependence of the overall rate of reaction on CO partial pressure in both the microwave and conventional reactors. The slopes are -0.59 and -0.64, respectively. The near equality of the slopes indicates that no significant alterations of the reaction pathway occurs in the microwave reactor. The conventional temperature was 135 C; the microwave temperature was not measured. Pressure is in Torr.

Conclusion

The primary conclusion obtained from the data presented is that no alterations in the kinetic behavior of the reaction were observed using the Pd/Al₂O₃ catalyst. This was a significant result considering the potential for direct interaction of microwave energy with both the small Pd catalyst particles and the highly polar CO reactant.

We would like to stress the overriding theme of this research: The highly non-isothermal nature of the microwave heated packed bed can lead to improper conclusions about rate behavior. Taken at face value, early experimental results would have pointed to a significant rate enhancement which was clearly erroneous. Therefore, to correctly observe true chemical kinetics, the unique heat transfer effects that are present in a microwave heated experimental reactor must be carefully considered.

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