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THE OXIDATION OF CARBON MONOXIDE USING A TIN OXIDE CATALYST

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SUMMARY

This paper outlines some of the steps involved in the development by the United Kingdom Atomic Energy Authority (UKAEA) of a catalytic device for the recombination of carbon monoxide and oxygen in a CO_2 laser system.

It contrasts the differences between CO oxidation for air purification and for laser environmental control, but indicates that there are similarities between the physical specifications. The principal features of catalytic devices are outlined and some experimental work described. This includes measurements concerning the structure and mechanical properties of the artifact, the preparation of the catalyst coating and its interaction with the gaseous environment. The paper concludes with some speculation about the method by which the reaction actually occurs.

INTRODUCTION

During the late 1970's, the United Kingdom Atomic Energy Authority at Harwell became involved in sol-gel technology as a result of oxide fuel development. The sol-gel method was found to be suitable for the preparation of catalytic materials which eventually led to their use in car exhaust catalytic converters and for air purification catalysts. Such catalysts were usually in the form of coatings applied to supporting artifacts such as monoliths, formed from either cordierite or from a corrosion resistant metal such as Fecralloy steel (R). The UKAEA has experience in the use of sol-gel catalysts for CO removal from air and so has a technological link to a system intended to recombine O_2 and CO formed in sealed CO_2 lasers.

Table 1 gives typical specifications for CO oxidation in breathing gear and in a laser recombination system. The main difference lies in the gas composition; the air purifier will be exposed to CO and O_2 concentrations considerably higher than those seen by the recombination catalyst, but will only encounter a fraction of the CO_2. In a laser environment, the CO_2 concentration might be as much as 40% by volume, whereas the CO_2 content of air is $< 1\%$. The operating requirements are very similar, however. Carbon monoxide oxidation is an exothermic process, but both catalytic systems must have a low exhaust temperature. The production of hot air by a breathing appliance can cause respiratory difficulties (catalysts sometimes have very human failings), whereas heated gases within the laser could result in optical distortion. Similarly, mechanical integrity is important to prevent dust and debris from the catalyst becoming inhaled or obscuring the optical system.

(R) Fecralloy steel is a registered trademark of the UKAEA.

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CATALYST TEST RIG

The catalyst device had to be designed to fit within the case of a recycle laser system without impeding the circulation of the laser gas, yet providing sufficient catalytic activity to effect the recombination. To achieve these goals, several types of catalyst artifacts were considered, the final choice being a ceramic monolith coated with a strongly adherent catalyst. An example is shown in figure 1.

The laser test rig is shown in figure 2. The laser cavity, which normally contains the electrode assembly, is at the top, and gas circulation is provided by a tangential fan situated at the left hand side. The gas mixture flows clockwise through the electrode assembly, through the catalyst artifact and may be cooled, if necessary, before returning to the fan. A typical gas velocity through the laser cavity is 7 m/s, which is sufficient to pass three laser volumes per laser pulse. The monolith typically had dimensions of 10 cm long by 5 cm wide by 2 cm deep.

CATALYST PREPARATION AND PERFORMANCE

The initial stages of catalyst development concerned the production of a tin sol. Of the catalyst formulations tried, tin oxide with two precious metal coatings was found to be the best. Several factors had to be considered:

1. The viscosity of the sol must be low enough that there is adequate penetration of the material into the pores of the substrate.
2. The concentration of the sol must be high so that enough catalyst is deposited in a practical number of coating steps.
3. The sol must form a catalyst with a high surface area.
4. The final catalyst coating must adhere to the ceramic substrate.
5. The precious metal should be uniformly distributed over the surface of the catalyst.

Some of these requirements are incompatible, and so a compromise must be sought, for example between concentration and viscosity. It is not just the physical properties which may be altered, one may influence the properties of the catalyst by chemical means. Viscosity, for instance, depends on the concentration of the sol but may be influenced by adjusting the pH of the mixture.

Once the coating has been deposited, the physical and chemical structure of the catalyst control the way in which the reactor behaves. Figure 3 shows the three main processes occurring in a chemical reactor.

Firstly, reactants must pass from the flowing gas stream to the surface of the artifact, in this case the walls of the monolith channel. Such mass transfer is controlled by the linear velocity of the gas, and the channel diameter (hence channel density.) However, these factors also determine the pressure drop required across the monolith in order to maintain the required flow rate. It is apparent that one must compromise between rapid mass transfer and low flow resistance.

The second step involves the diffusion of reactant molecules through the pores of the catalyst until they encounter a catalytic active site. Generally, a high surface area support will give more active sites per unit volume of catalyst. Unfortunately, high surface areas are normally associated with pores of small diameter which restrict diffusion more than would large pores. Again, a balance must be attained. The structural stability of the coating may also be effected by the pore structure.

Finally, the recombination reaction occurs at the active site. Chemical factors are very important; impurities may poison the reaction, the form of the precious metal may be influenced by the precious metal salt used for deposition, the purity and structure of the tin oxide may effect both the dispersion of the precious metal and the reaction itself.

The removal of products may also play a part, especially if the products can react with the catalyst. If product molecules remain attached to the catalyst surface, they may impede the reaction by blocking the diffusion of reagents or by changing the chemical properties of the catalyst.

EXAMPLES OF CATALYST OPTIMIZATION AND TESTING

Surface Area

Figure 4 shows the results of an experiment which measured the effect of sol concentration on the BET surface area of the catalyst coating. These results have been corrected for the surface area of the cordierite support (ca. $3m^2/g$). The graph shows that the highest surface areas were obtained from the lowest concentration sols. After optimization, an improved sol was prepared. This had a concentration of 200 g/l and gave a coating with a surface area between 150 and 200 m^2/g.

Effect Of High Concentrations Of CO_2

It was not known whether the large partial pressure of CO_2 would have any effect on the activity of the catalyst. The rate of recombination was measured for a stoichiometric mixture of 1% CO, 0.5% O_2 in various He/CO_2 mixtures. The results in figure 5 show the rate at a given CO_2 concentration relative to the rate of recombination in a CO_2-free atmosphere. Carbon dioxide has little inhibiting effect at concentrations below 50 vol%. Even above 90 vol% CO_2, the rate was only reduced to 70% of the CO_2-free value.

Reduction Of The Support By CO

The presence of CO in the gas mixture could have modified the surface of the tin oxide. Mossbauer spectroscopy can distinguish between Sn(IV) and Sn(II), so an experiment was undertaken to observe the effect of CO on a catalyst at room temperature. Significant reduction of the catalyst would have introduced a Sn(II) peak in addition to the Sn(IV). The spectra in figure 6 show that no Sn(II) could be observed. This suggests that either CO did not reduce the catalyst, or that the catalyst had reverted to its original form because of oxygen in the environment.

Catalyst Distribution

The catalytically active material (precious metal on tin oxide) was coated on a porous cordierite monolith. For maximum activity, one must ensure that the device supports the maximum amount of catalyst, ie. ensure that all the pores of the cordierite have been coated with catalyst. If this condition has been fulfilled, then the precious metals will be uniformly distributed throughout the wall of the monolith. Figure 7 shows an electron microprobe trace across the thickness of a finished monolith wall. The tin signal shows that the tin oxide profile is matched closely by the precious metal, and decreases slightly towards the center of the wall. Although the profiles are not uniform, they do show that the substrate is porous and that the catalytic materials have penetrated well within the substrate.

Mechanical Properties

The inclusion of a catalyst in the laser device may effect the stability of the instrument by creating dust or obstructing the flow of gas. To study the latter, pressure drop measurements were made by measuring the differential pressure across the catalyst artifact as shown in figure 8. Measuring ports were located before and after the monolith holder in the laser case, and the gas velocity measured using a pitot tube fitted into the laser cavity. Figure 9 shows two curves of pressure drop versus cell density for monoliths of different depth. The gas linear velocity was kept constant throughout. For both monolith depths, the pressure drop for the higher cell densities was approximately twice that of the lower densities.

Mechanical strength and resistance to dusting of the applied coating are very important because of potential damage to the optical system. Shock and vibration tests were carried out by weighing the catalyst artifacts before and after various treatments. The shock test used a 981 m/s^2 half-sine 6 ms pulse applied three times along three mutually perpendicular planes. The vibration test used a 20-500 Hz, 19.8 m/s^2 acceleration for two hours, again along three mutually perpendicular planes. No loss of weight was detected in either test.

MECHANISTIC STUDIES

The mechanism of a catalytic reaction can often indicate how the catalyst works, and so indicate which aspects if its formulation will most benefit its performance. Figure 10 shows the rate of formation of CO_2 for different concentrations of CO in air. The solid curve is from a catalyst reduced in hydrogen before use; the dashed curve is from an unreduced catalyst. Both curves show that there is a maximum rate of reaction which occurs between 1.0 and 1.5 vol% of CO, and that higher concentrations of CO do not cause an increase in the rate as would be expected from a simple (pseudo) first-order process (i.e., in air, the oxygen is always in stoichiometric excess. This is simply explained in terms of strong adsorption of CO. At low CO pressures, the rate of oxidation of CO is high enough to keep the surface of the catalyst fairly free of adsorbed CO. At high pressures, the surface becomes covered with unreacted CO which blocks the supply of oxygen and so causes a reduction in the overall rate even though there is plenty of CO available.

To observe the effect of CO and O_2 partial pressures, two experiments were conducted using powdered samples of catalyst held at 30°C in a differential reactor. The test gas contained CO and O_2 in a helium carrier. Figures 11a and 11b show the rates of CO_2 production as functions of CO and O_2 partial pressures, respectively. In either case, the other reagent concentration was held constant. The reaction appears to be zero order with respect to CO, but first order with respect to O_2. This indicates that under laser recombination conditions, the surface always holds its maximum amount of CO and the rate limiting step is the supply of oxygen (either atoms or molecules) to combine with the CO.

Prof. Bond (ref. 1) has studied the reaction of CO in air on a Pd/alumina catalyst at 150°C., and has proposed a "spill-over" mechanism to explain the results. Our results are consistent with our technical catalyst operating by this type of mechanism at room temperature. A possible spill-over mechanism is shown in figure 12. In the first step, a CO molecule from the gas phase arrives at a precious metal site, becomes activated (eg. vibrationally) then spills over onto the tin oxide surface. The CO molecule abstracts an oxygen atom and forms a CO_2 molecule which desorbs back into the gas phase. An oxygen vacancy is left in the surface. Reoxidation of the surface occurs by a similar process in step 2. Oxygen may spill over either as atoms or molecules (eg. dissociative redox or Mars-van Krevelen models); the important step is the refilling of the vacancy. Inhibition occurs when adsorbed CO blocks the resupply of the oxygen. This would indicate that the catalyst can be improved if the CO bond to the surface could be weakened (choice of precious metal, additives, and pretreatment).

CONCLUSIONS

This paper indicates how a catalytic device is developed. There are considerations to be made regarding the means of supporting the catalyst, the method of preparation, both chemical and physical, and an understanding of the way in which the final device will work. None of these can be treated truly in isolation as their interaction is surprisingly complex.

Reference

1. Bond G.C., Fuller M.J., Molloy L.R., Proc. 6th Int. Congr. Cat. 1, 356 (1977).

Acknowledgment

The United Kingdom Atomic Energy Authority would like to thank the D.C.V.D. Ministry of Defense for their cooperation throughout this period of development.

TABLE 1

SPECIFICATION

		AIR PURIFICATION	LASER
Gas composition:	CO -	few %	$< 1\%$
	O_2 -	20%	$< 1\%$
	CO_2 -	few %	20-40%
Temperature :		ambient	ambient
Other requirements:		low $\Delta\rho$	low $\Delta\rho$
		low dust	low dust
Reactor configuration:		single pass	recycle

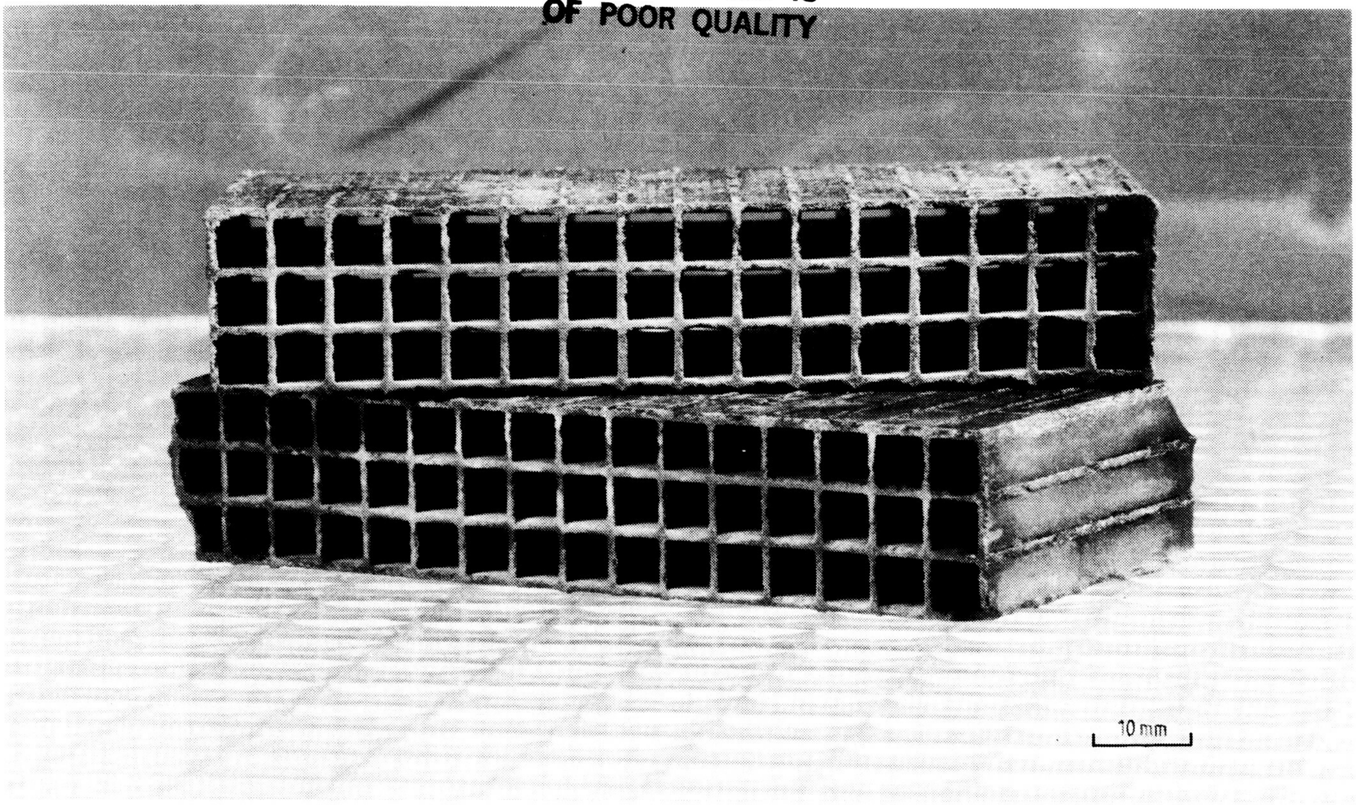

Figure 1. Ceramic monolith coated catalyst.

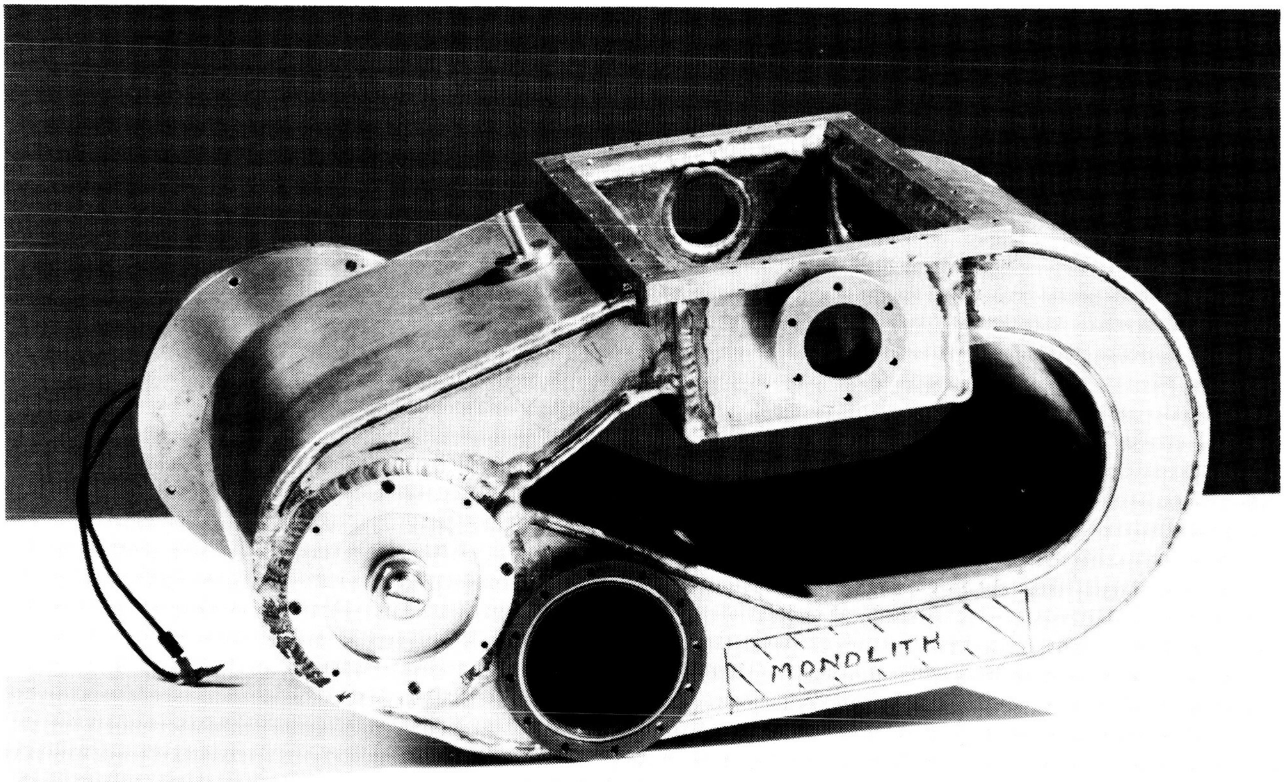

Figure 2. Laser test apparatus.

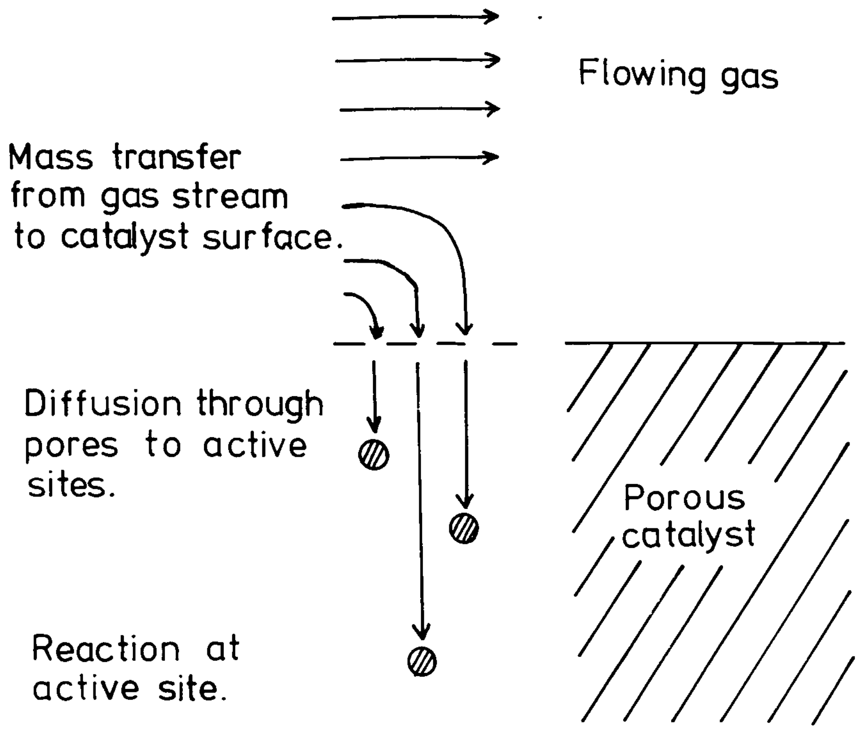

Figure 3. Physical processes in catalysis.

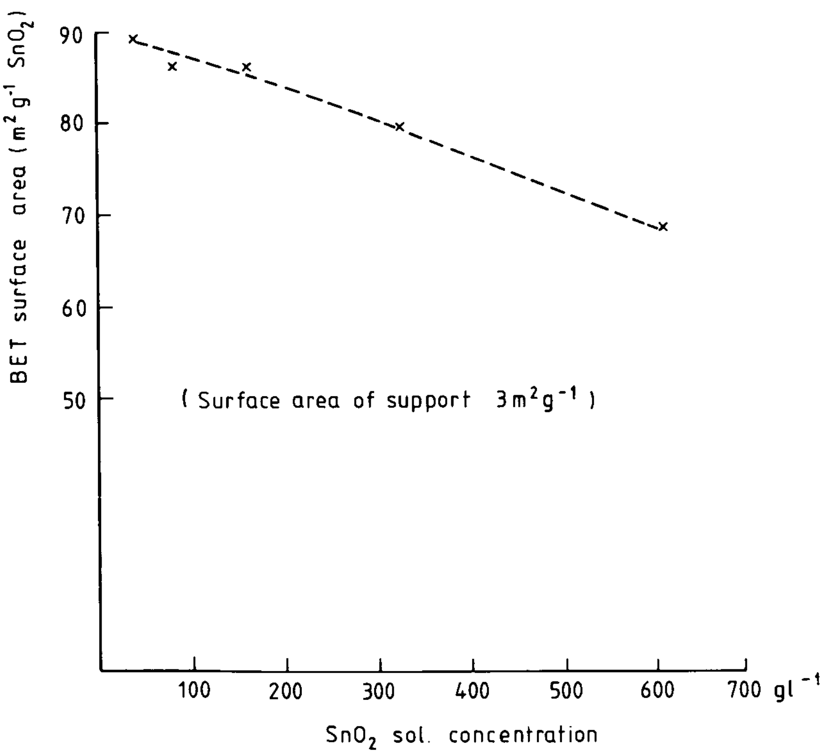

Figure 4. Surface area of SnO_2 calcined on monolith versus SOL concentration used for coating.

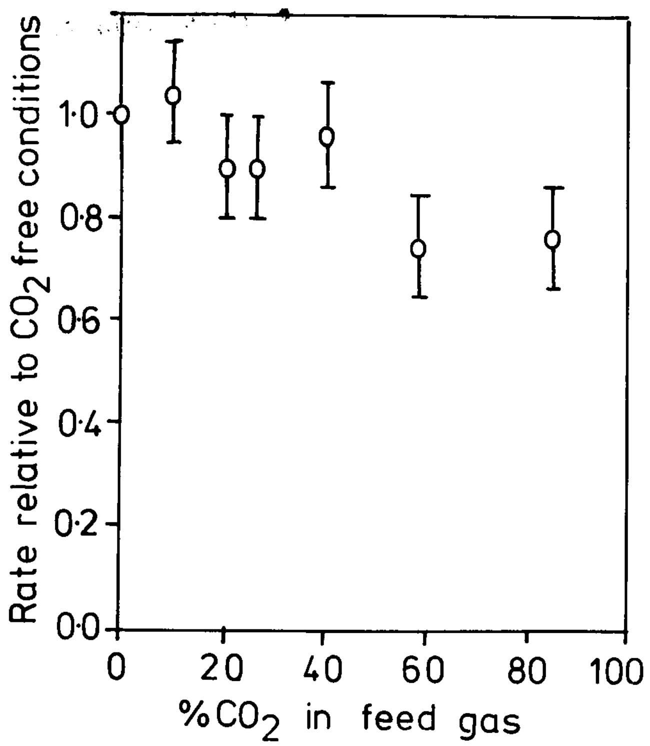

Figure 5. Effect of added CO_2 on the rate of $CO-O_2$ recombination.

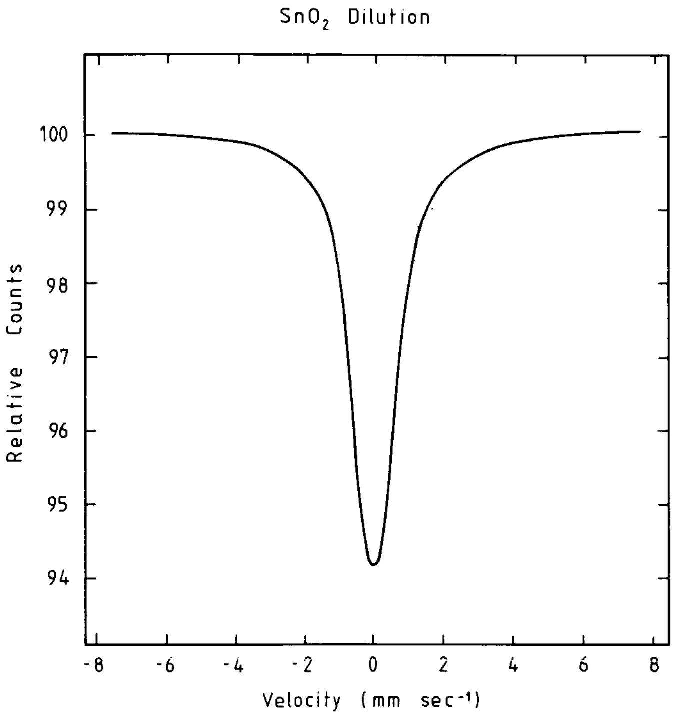

Figure 6. Mössbauer peak position of Sn^{4+}.

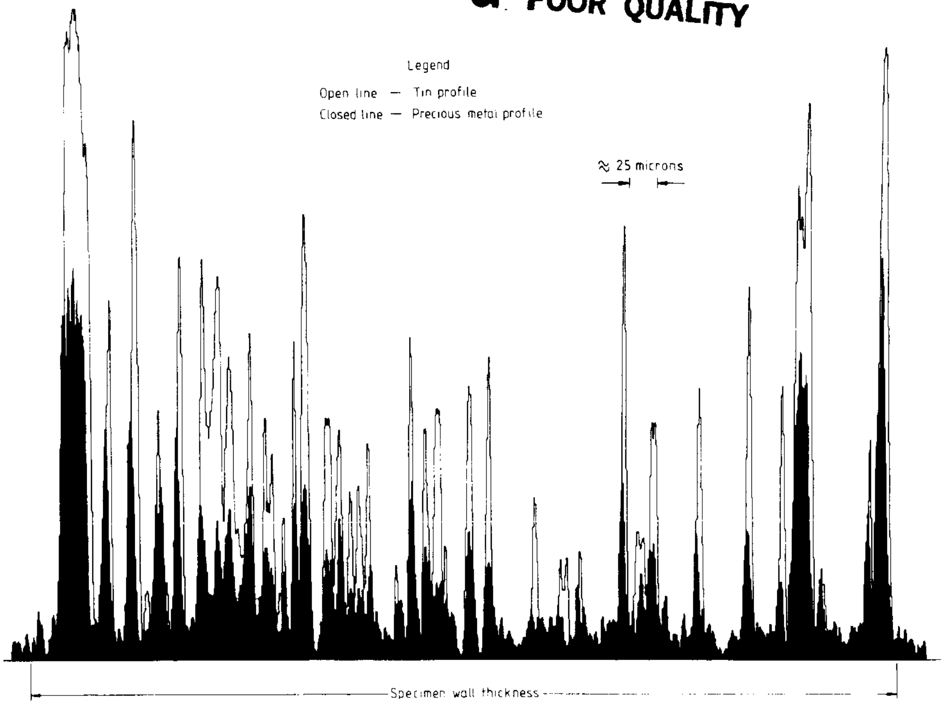

Figure 7. Electron microprobe trace across wall thickness of monolith.

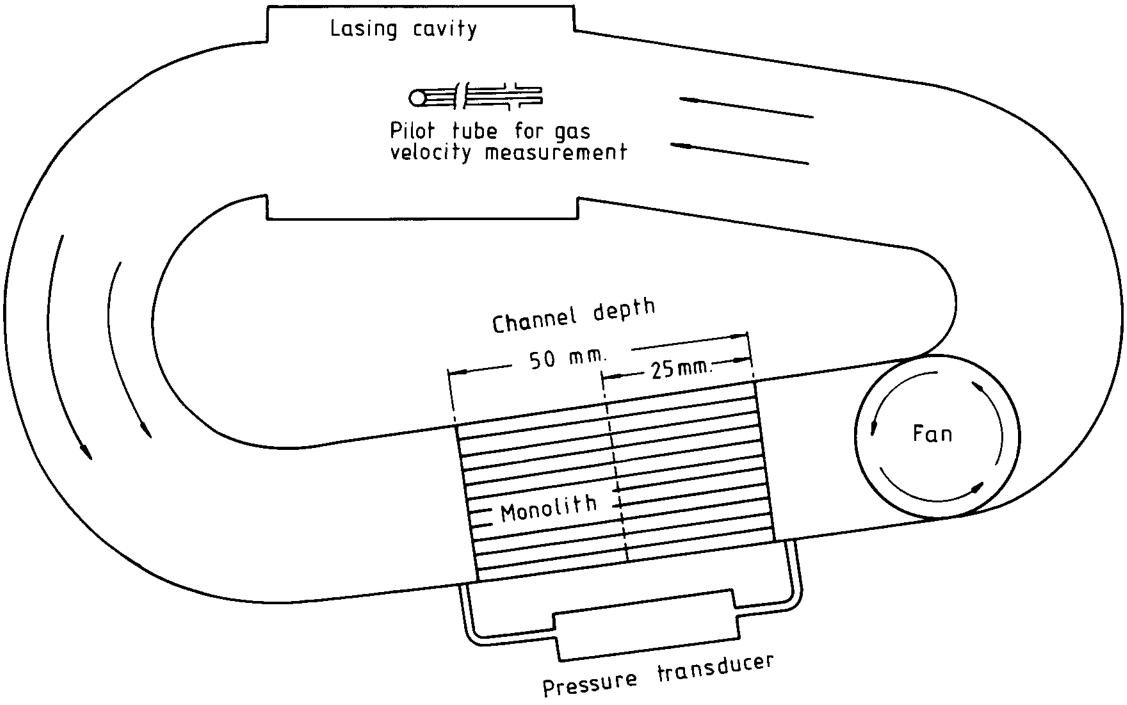

Figure 8. Diagram of pressure drop measurement system.

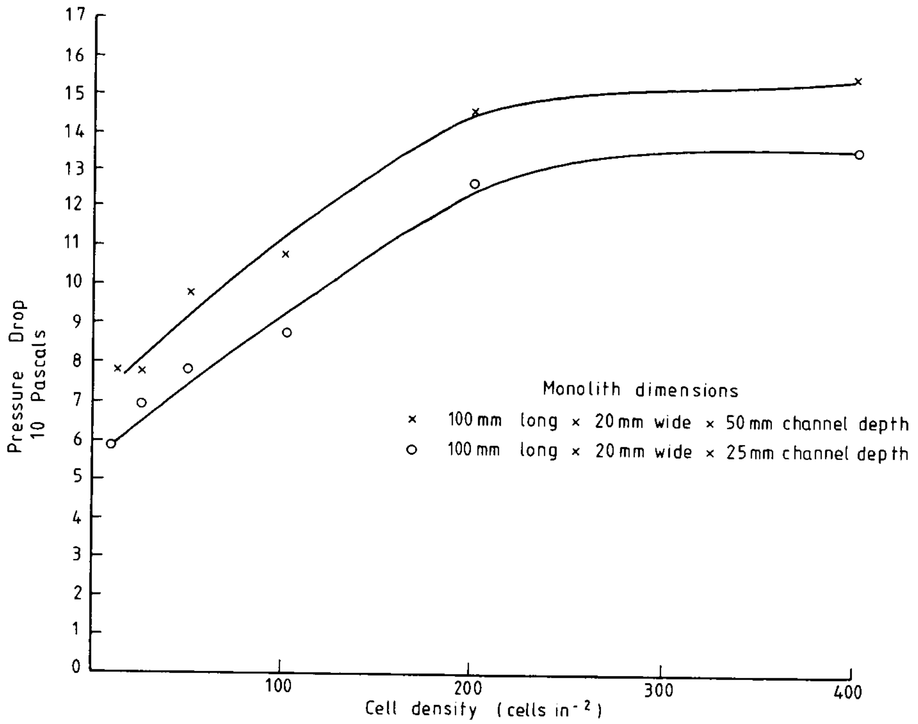

Figure 9. Pressure drop across monolith versus cell density at constant gas velocity (7 mm sec^{-1}).

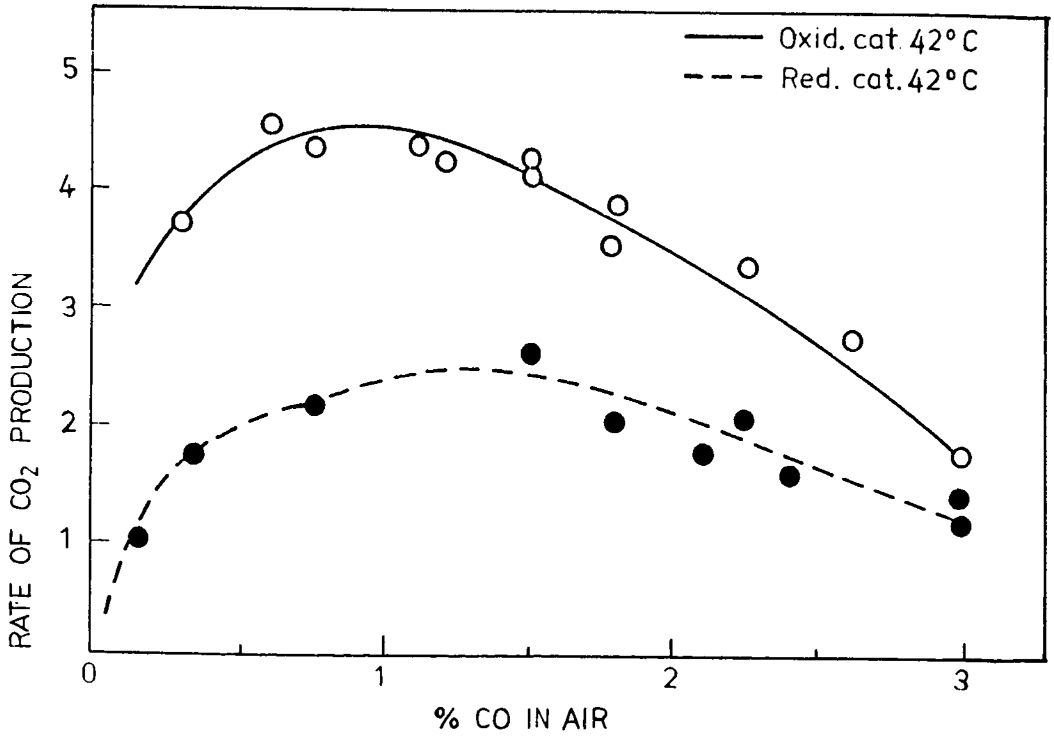

Figure 10. Rate of CO_2 production versus CO in air.

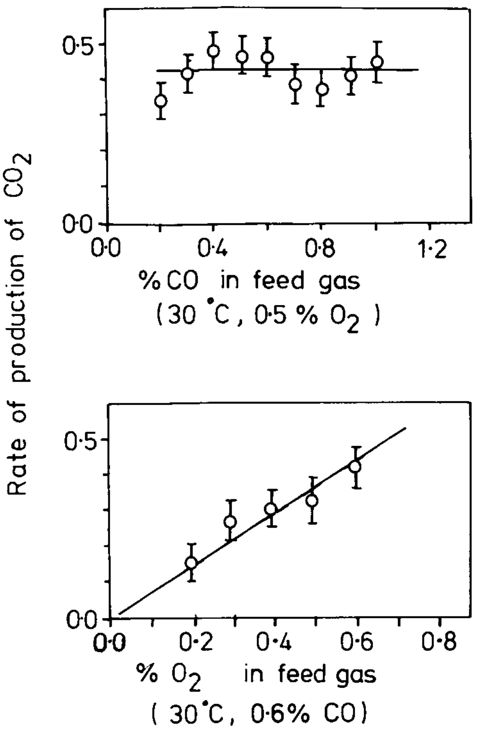

Figure 11. Effect of CO and O_2 partial pressure on the rate of recombination.

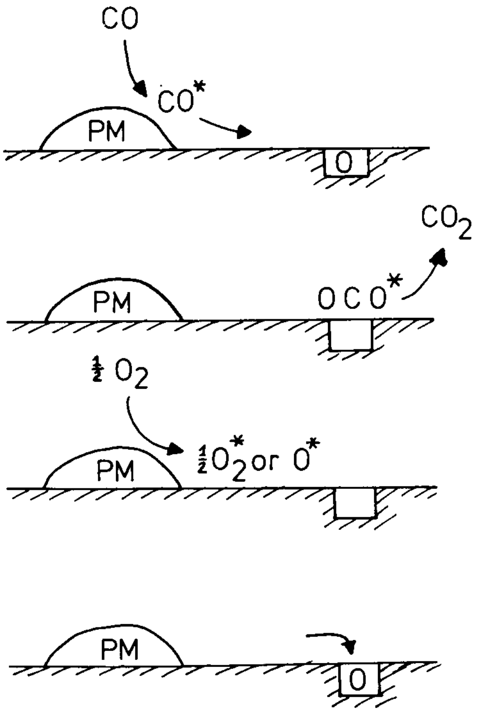

Figure 12. Spillover model (Bond et al.).