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# Chemical Engineering Design of CO Oxidation Catalysts

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## INTRODUCTION

The purpose of this paper is to present the way that a chemical reaction engineer would approach the challenge of designing a CO oxidation catalyst for pulsed $CO_2$ lasers. CO oxidation catalysts have a long history of application, of course, so it is instructive to first consider the special requirements of the laser application and then to compare them to the characteristics of existing processes that utilize CO oxidation catalysts.

All $CO_2$ laser applications require a CO oxidation catalyst with the following characteristics: (a) active at stoichiometric ratios of $O_2$ and CO, (b) no inhibition by $CO_2$ or other components of the laser environment, (c) releases no particulates during vibration or thermal cycling, (d) long lifetime with a stable activity. In all applications, low consumption of power is desirable, a characteristic that is especially critical in aerospace applications and, thus, catalyst activity at low temperatures is highly desirable. High power lasers with high pulse repetition rates inherently require circulation of the gas mixture and this forced circulation is available for moving gas past the catalyst. Low repetition rate lasers, however, do not inherently require gas circulation, so a catalyst that did not require such circulation would be favorable from the standpoint of minimum power consumption. Lasers designed for atmospheric penetration of their infrared radiation utilize $CO_2$ formed from rare isotopes of oxygen and this application has the additional constraint that normal abundance oxygen isotopes in the catalyst must not exchange with rare isotopes in the gas mixture.

These are the target characteristics. To judge the possibility of using existing CO oxidation catalysts for this application, it is instructive to compare the $CO_2$ laser application to current applications of CO oxidation catalysts.

One of the major applications of CO oxidation catalysts is removing CO from the exhaust of combustion systems. In this emission control application, the thermal energy needed to raise the catalyst to operating temperatures is naturally present and excess oxygen, which tends to accelerate CO oxidation, is either already present or can easily be added by injecting air. Both of these characteristics are not present in the laser application.

Another major use of CO oxidation catalysts is removing low levels of CO that contaminate breathing air. The CO would be present primarily as the partial oxidation product of a combustion process. Situations where contamination of breathing air may occur are in underground mines, inside burning buildings, and aboard submarines. This application differs from the laser application in that it has the advantage that there is always a great excess of oxygen available. However, it also has a disadvantage in common with the laser application in that CO oxidation has to occur at relatively low temperatures (with the exception of the submarine application where power is available for heating).

Thus, the primary challenges of the application of CO oxidation catalysts in $CO_2$ lasers are the need to maximize catalyst activity (a) at low temperatures, (b) in the presence of low relative oxygen concentrations (at or near stoichiometric ratios), and (c) with minimal need for forced convection of gas past the catalyst, in some applications.

On the other hand, there are some nice things about the laser application in comparison with the other applications of CO oxidation catalysts: CO concentrations are initially very low in the laser, sintering and loss of active surface area during operation at high temperatures will not occur, and the gas atmosphere is very clean - for example, in comparison to automotive exhaust gas.

The outline of the next sections of this paper will follow the order that is typically used in the design of any catalytic reactor. First, the mechanism and kinetics of the CO oxidation reaction will be discussed, with indentification of the directions that catalyst development should pursue and recommendations for characterization of catalyst activity. Next, the method of design of a catalytic reactor will be outlined using two different examples relevant to $CO_2$ lasers but using very simple kinetics for illustration.

## MECHANISM OF CO OXIDATION

CO oxidation - or CO-$O_2$ recombination - can occur solely in the gas phase through homogeneous mechanisms, or the reaction can occur on the surface of a solid catalyst through a heterogeneous mechanism. Solid catalysts that catalyze reactions of fluids are called heterogeneous catalysts. Although a heterogeneous catalyst will be required for the laser application, it is instructive to first consider homogeneous mechanisms of CO oxidation.

In almost all systems where the homogeneous reaction of CO with $O_2$ occurs, hydrogen is also present as $H_2$ and/or $H_2O$. This presence of hydrogen has a dramatic effect on the mechanism of CO oxidation in the gas phase. The major steps in this chain reaction mechanism are shown below (ref. 1):

"Wet" Homogeneous Mechanism

| | | | |
|---|---|---|---|
| Initiation | | $\rightarrow$ | OH, H |
| Branching | $H + O_2$ | $\rightarrow$ | OH + O |
| | $O + H_2$ | $\rightarrow$ | OH + H |
| Propagation | OH + CO | $\rightarrow$ | $CO_2 + H$ |

The most difficult step that occurs in any type of CO-$O_2$ reaction is the dissociation of $O_2$. In the presence of hydrogen, this dissociation in the gas phase occurs by the reaction of $O_2$ with H atoms. Also, $CO_2$ is formed not through the reaction of CO with $O_2$ or O atoms but through the reaction of CO with OH radicals. Homogeneous recombination of CO and $O_2$ was accelerated by addition of $H_2$ in the first sealed $CO_2$ TEA laser (ref. 2).

As one would expect, the mechanism is dramatically different in the absence of hydrogen and is much slower:

"Dry" Homogeneous Mechanism

| | | | |
|---|---|---|---|
| Initiation | $CO + O_2$ | $\rightarrow$ | $CO_2 + O$ |
| Branching | $CO_2^* + O_2$ | $\rightarrow$ | $CO_2 + 2O$ |
| Propagation | O + CO | $\rightarrow$ | $CO_2^*$ |

where $CO_2^*$ represents an excited $CO_2$ molecule and the branching step is subject to uncertainty. In fact, some researchers maintain that trace quantities of hydrogen may have been present in most or all published kinetic studies of the "dry" reaction and, thus, that the "dry" reaction may have not been accurately studied to date (ref. 1).

In the reaction of CO and $O_2$ over the surface of a heterogeneous catalyst, the interaction of $O_2$ with the catalyst surface serves to provide the critical step of $O_2$ dissociation. The mechanism can occur easily in the absence of hydrogen on a catalyst surface. There are two major classes of heterogeneous CO oxidation catalysts: (a) "noble metal" or "precious metal" catalysts, and (b) base metal oxide catalysts, or simply "base metal" or "oxide" catalysts. Here, the mechanism for the reaction over a precious metal catalyst such as platinum is shown (ref. 3):

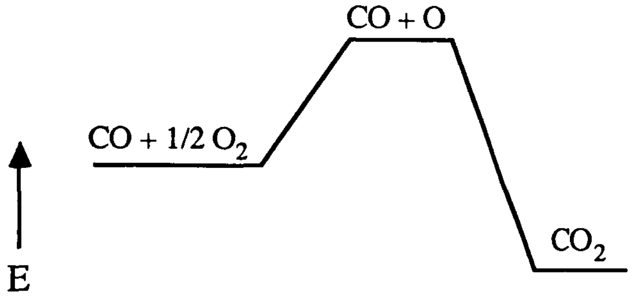
Heterogeneous Mechanism over Precious Metal

$$\begin{aligned} O_2 + 2S &\rightarrow 2O\text{-}S \\ CO + S &\leftrightarrow CO\text{-}S \\ CO\text{-}S + O\text{-}S &\rightarrow CO_2 + 2S \end{aligned}$$

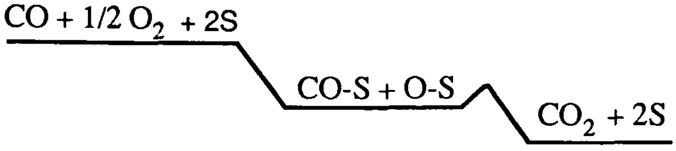
where "S" is a "site" or area on the metal surface that can adsorb one CO molecule or one O atom. The adsorption of oxygen is essentially irreversible at temperatures below 500 °C and the formation and desorption of $CO_2$ is essentially irreversible at all conditions of interest. The fact that CO adsorption requires a smaller area on the metal surface (one S) than does $O_2$ adsorption (2S) is responsible for the strong inhibition of CO oxidation by CO at high CO concentrations or low temperatures. The readily reversible nature of CO adsorption is responsible for the changes in reaction kinetics that occur with changes in temperature, as discussed below.

The contrast between the homogeneous and heterogeneous mechanisms is further emphasized by the following qualitative comparison of the energetics of the two reactions:

Homogeneous Mechanism



Heterogeneous Mechanism over Precious Metal



As shown above, the mechanism over a precious metal catalyst occurs with $O_2$ chemisorbing dissociatively as O atoms bonded on top of the metal atoms that form the surface of the metal. CO molecules adsorb over the same metal surface atoms. Thus, CO and $O_2$ compete for the same surface atoms when they adsorb. This competitive adsorption is responsible for producing the characteristic kinetics (variation in rate with changes in temperature and gas composition) of CO oxidation over precious metals.

The enthalpy or "strength" of adsorption of oxygen atoms is somewhat greater than the strength of adsorption of CO molecules. An $O_2$ molecule, however, requires a large open area on the metal surface in order for it to be able to adsorb than does a CO molecule. As a result of this difference in adsorption area requirements, CO can be said to adsorb "more readily" than $O_2$. This characteristic of CO and $O_2$ adsorption on precious metals means that at ambient temperatures in a stoichiometric mixture of CO and $O_2$, the surface of the metal catalyst will be almost completely covered by adsorbed CO molecules. The rate of reaction will be negligible at this condition of relatively low temperature because $O_2$ molecules can not adsorb on the CO-covered surface and, thus, cannot react. The large CO concentration on the surface is in equilibrium with the CO in the gas. As the temperature of the catalyst is raised, the coverage of the surface by CO will start to decrease since CO adsorption is exothermic. This decrease in surface coverage by CO opens up space on the metal for $O_2$ to dissociatively adsorb. The rate of reaction between adsorbed CO molecules and oxygen atoms is relatively fast, even at ambient temperature, so that once the CO coverage drops such that $O_2$ can adsorb, the rate of reaction will become significant. At a constant and relatively low temperature, the rate of reaction decreases with increasing CO concentration and increases with increasing $O_2$ concentration. The reaction is said to be strongly inhibited by CO at relatively low temperatures. At higher relative temperatures, the surface is primarily covered by adsorbed O atoms and the reaction rate increases with an increase in CO concentration and becomes independent of $O_2$ concentration (refs. 4,5).

The mechanism of CO oxidation over base metal oxide catalysts is qualitatively different from that over precious metals. The mechanism is complex over oxide catalysts, so only general features will be discussed here. Over metal oxides, the reaction proceeds (at least at higher temperatures) through a "redox" mechanism. CO adsorbs on the surface and reacts with oxygen atoms bound in the surface layer of the metal oxide, locally reducing the metal oxide. $O_2$ in the gas phase reacts with and re-oxidizes the metal oxide (ref. 6):

Heterogeneous Mechanism over Base Metal Oxide

$$O_2 + 2\square \rightarrow 2\boxed{O}$$

$$CO + * \rightarrow CO\text{-}*$$

$$CO\text{-}* + \boxed{O} \rightarrow CO_2 + \square + *$$

where * is an adsorption site for CO and $\square$ is an oxygen vacancy in the oxide surface.

The "slow" step in the reaction is the reduction of the oxide by CO. At constant temperatures, the rate of reaction increases with increasing CO concentration and does not change with $O_2$ concentration. These kinetics are dramatically different than those which apply to precious metal catalysts.

The dominant factor in CO oxidation over precious metals is the kinetic competition between CO and $O_2$ for adsorption sites on the metal surface. CO and $O_2$ interact with different locations or sites on oxide catalysts with no competition. The dominant factor in oxide catalysts is the relatively strong bonding that holds oxygen atoms in the oxide and that limits the rate of CO oxidation.

One can say that, in order for reaction to occur at low temperatures, oxygen doesn't adsorb readily enough over precious metal catalysts and adsorbs readily but too strongly over oxide catalysts.

There are two major functions that must be performed by any CO oxidation catalyst:

- adsorb $O_2$ dissociatively,
- adsorb CO next to reactive oxygen atoms.

These critical functions of a CO oxidation catalyst can be used as a framework for catalyst analysis and design of improved catalysts. An optimal catalyst will perform both of these two functions to the correct extent. That is, it will chemisorb $O_2$ readily but not hold the oxygen atoms too strongly, and it will adsorb CO in a manner that CO doesn't compete directly with $O_2$ adsorption.

This framework leads to several ideas for design of an improved catalyst. Starting with a precious metal catalyst, one might try to lower the strength of CO adsorption. While not eliminating the competition between CO and $O_2$, this approach would decrease the extent to which CO inhibits the reaction at a given temperature. Pt and Pd are the precious metals most frequently used in CO oxidation catalysts. They are used because of their resistance to sintering at high temperatures and because of their relative abundance relative to other precious metal catalysts. The relatively low temperature, low volume laser application allows consideration of other metal elements which might have more favorable CO adsorption characteristics. Several additives to metal surfaces have been shown to lower the desorption temperature of CO (ref. 7). CO adsorption over Rh and Pt has been shown to be suppressed when the metal is supported over $TiO_2$ and the support and metal subjected to a high temperature reduction treatment in $H_2$ (ref. 8). Recent research has shown that partial oxides of Ti, or $TiO_2$, migrate from the support to the surface of the metal particles and suppress the adsorption of CO (refs. 9,10). Another possible metal-support interaction that might affect CO adsorption is charge transfer between the support and the metal (refs.11-13).

Starting with a metal oxide, one would like to lower the strength of the bonds that hold oxygen atoms in the surface of the oxide. One possibility is that there are metal oxides that are suitable for the laser application that are not used for other CO oxidation applications because of the different operating conditions. Another possibility is that additives might be found that lower the metal-oxygen bond strength in metal oxides.

So far we have considered modifications to pure precious metal or metal oxide catalysts. The fact that there are two distinct functions that a CO oxidation catalyst must perform suggests that a "compound" catalyst should give improved performance. That is, improved performance should be obtained by an intimate mixture, at the atomic level, of two different materials with optimal properties for the two different catalytic functions required.

Oh and Carpenter (ref. 14) have found that Pt/Rh alloy particles supported on alumina catalyze the CO oxidation reaction at lower temperatures than either of the separate metals. Rh interacts with $O_2$ more strongly than Pt does (refs.15,16). Thus, it is likely, as suggested by Oh and Carpenter, that the mixed-metal catalyst separates the two functions to some extent, with CO adsorbing primarily on Pt atoms and $O_2$ adsorbing primarily on Rh atoms, thus, reducing the inhibition of $O_2$ adsorption by CO.

Currently, the most promising catalyst for the $CO_2$ laser application is a precious metal supported on $SnO_2$ (ref. 17). It is likely that this catalyst is an example of the type of "complex" catalyst that we seek. The primary function of the precious metal may be to adsorb CO. The primary function of the $SnO_2$ may be to adsorb $O_2$. Alternatively or in addition, $SnO_2$ may reduce the strength of CO adsorption over the precious metal, and the metal may reduce the strength of $O_2$ interaction with the oxide. Research needs to be performed to identify the actions of the two components of metal/$SnO_2$ catalysts. Research is also needed to determine the types of contact between the metal and the oxide, e.g., whether oxide species are present on the surfaces of the metal particles, as seems to be the case for the Pt/$TiO_2$ system.

## KINETIC MEASUREMENTS

Once a specific catalyst has been selected for used in a $CO_2$ laser, the next step is to determine the kinetics of the reaction over the catalyst. By this we mean that experimental measurements are performed over the relevant ranges of gas composition and temperature in order to develop a "rate expression." A rate expression (or "equation" or "law") is a mathematical expression that gives the rate of reaction as a function of gas composition and temperature. When performing kinetic studies with heterogeneous catalysts, one must be aware of the fact that heat and mass transfer effects are often present and can interfere with kinetic measurements. Ideally, one would like to determine the reaction rate under conditions where the temperature and composition of the bulk gas is the same as the temperature and composition of the gas immediately near the external surface of the catalyst and within the internal pores of porous catalysts. In some cases, internal transport effects are effectively impossible to eliminate and only "apparent" or "global" kinetics can be measured. However, in that case, it is critical that one is aware of the presence of the heat and mass transport limitations. Kinetic measurements on heterogeneous catalysts are discussed in standard texts (refs. 18,19).

One temptation that understandably occurs during the development of many processes is to make measurements only on working prototypes of the actual system. In this case, measurements would be made only on catalysts installed in working lasers or the bodies of lasers in which synthetic mixtures are injected. The trouble with this approach is that such measurements do not allow for prediction of the magnitude of improvements required or design of other sizes or configurations of the system. We feel that it is imperative that careful kinetic studies be performed in reactors designed for kinetic studies in addition to tests of prototypes.

There are several types of reactors that are used for kinetic studies of heterogeneous catalysts:

- batch reactors
- plug flow reactors
- recycle reactors operating at high recycle ratios.

Each of these types is described in standard texts (refs. 18,19). We suggest that a recycle reactor be considered for kinetic studies of CO oxidation catalysts for $CO_2$ lasers. External temperature and concentration gradients are most easily minimized in recycle reactors and the reaction rate under given conditions of steady-state operation is determined simply by an algebraic equation.

When the performance of different formulations of catalyst is to be compared, it is critical to consider the basis of comparison. For example, for supported precious metal catalysts, the reaction rate per exposed metal atom is the proper measure of performance under given conditions. Different batches of the same composition of catalyst may give different conversions of CO because the metal in each batch is dispersed over the support to a different extent. Alternatively, the metal dispersion may be the same and a chemical difference may account for the difference in conversion. In this case, one must make measurements of the metal particle size and/or metal chemisorption capacity in addition to performing reaction rate measurements.

## DESIGN OF THE LASER/CATALYTIC REACTOR

Once the kinetics of a catalyst have been determined, design of the laser in its function as a catalytic reactor can proceed. Here we illustrate reactor design for two simple cases. First, consider the design of a reactor in which the gas is circulated by a blower past the laser electrodes and past the catalyst in a closed loop. We assume the following:

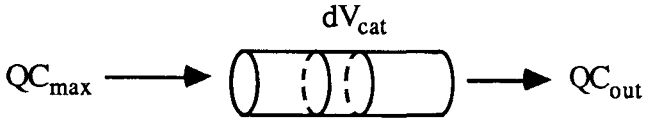
- isothermal conditions,
- a flat gas velocity profile through the catalyst,
- the rate of CO oxidation is proportional to the weight of catalyst (i.e., no diffusional limitations) and the CO concentration but is independent of the $O_2$ concentration.

All of these assumptions most probably will not hold in a real laser. For example, the gas may be in laminar flow past heated catalyst surfaces on which the reaction kinetics are more complicated than the first-order kinetics assumed.

Our objective in this example will be to obtain an expression for the volume of catalyst, $V_{cat}$, required as a function of:

- the gas flow rate, Q ($cm^3/s$),
- the rate of production of CO in the electrode discharge region, $r_{prod}$ (mol/s),
- the rate constant for the CO oxidation reaction over the catalyst, k (1/s), and
- the maximum allowable concentration of CO leaving the discharge zone and entering the catalyst, $C_{max}$ ($mol/cm^3$).

The first step in reactor design is to write molar conservation equations (mole balances) for each key species and to write an energy balance. Since isothermal conditions have been assumed, an energy balance is not required. Mole balances are performed around volumes with uniform conditions, in this case, a differential volume element of the catalyst bed, which may consist of catalyst pellets, for example:



$$\text{accumulation} = \text{in} - \text{out} - \text{reaction}$$

$$0 = QC - Q(C+dC) - kC\, dV_{cat}$$

where C is the concentration of CO at any point. Of course, the concentration of $O_2$ at any point can be determined from the concentration of CO since they will always be in a stoichiometric ratio. More complex rate equations **can** be substituted in for the rate of reaction without increasing the difficulty of the problem. Separating variables and integrating:

$$\int_0^{V_{cat}} dV_{cat} = -\frac{Q}{k}\int_{C_{max}}^{C_{out}} \frac{dC}{C}$$

$$V_{cat} = -\frac{Q}{k}\ln\left(C_{out}/C_{max}\right)$$

$C_{max}$ is specified and $C_{out}$ is determined from the rate of production in the discharge:

$$r_{prod} = Q(C_{max} - C_{out})$$

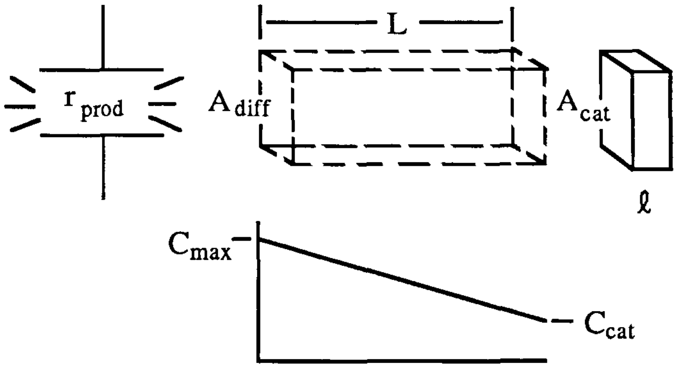
$$V_{cat} = -\frac{Q}{k} \ln(1 - r_{prod} / Q C_{max})$$

And the desired result is obtained. The volume of catalyst required decreases as:

- the activity of the catalyst per unit volume is increased (i.e., k increases),
- the rate of dissociation of $CO_2$ in the discharge decreases,
- the maximum allowable concentration of CO, $C_{max}$, (and, thus, concentration of $O_2$ ) increases

Rearranging the equation, one can see that, for a fixed volume of catalyst, the steady-state concentrations of CO and $O_2$ will increase if the repetition rate of the laser discharge is increased. The utility of such a design equation can readily be seen for evaluating the effects of changes in laser design or operation.

Next we consider a case where there is no forced convection of the laser gas and transport of CO and $O_2$ must occur by diffusion only. This configuration might be feasible in a low repetition rate laser that is constrained to having a small volume and power consumption. In this case, we continue to assume isothermal conditions and a reaction that is first-order in CO and zero-order in $O_2$. However, here we allow for the possibility that the rate of diffusion of CO and $O_2$ in the porous catalyst may be slow with respect to the rate of reaction. The configuration of this laser is shown below in schematic form:



where $C_{cat}$ is the concentration of CO at the external surface of the porous catalyst that has external area $A_{cat}$ (cm$^2$), thickness ℓ (cm) and volume $V_{cat} = A_{cat} \times ℓ$. Diffusion of CO, $O_2$, and $CO_2$ occur between the discharge and the catalyst over a one dimensional diffusion path with length L (cm) and cross sectional area $A_{diff} = A_{cat}$.

At steady-state conditions, the rate of production of CO has to equal the rate of consumption of CO at the catalyst:

$$r_{prod} = r_{rxn} = k\, C_{cat}\, V_{cat}\, \eta$$

For brevity we do not show the derivation that describes the diffusion and reaction of CO within the porous catalyst. This derivation is contained in standard texts (refs.18,19). As a result of diffusional limitations, the concentration of CO and $O_2$ may be lower inside the porous catalyst than at the external surface. The "effectiveness factor " $\eta$ corrects for the lower concentrations of reactants inside the porous catalyst and its value ranges between 0 and 1. For a first-order reaction in a one-dimensional catalyst layer:

$$\eta = \frac{\tanh \phi}{\phi} \quad \text{where} \quad \phi = \ell \sqrt{k/D_{eff}}$$

and where $\phi$ is the "Thiele modulus," which gives a measure of the relative rates of reaction and diffusion, and $D_{eff}$ is the "effective diffusivity" of reactants within the catalyst. The volume of catalyst required is:

$$V_{cat} = \frac{r_{prod}}{k\, C_{cat} \eta}$$

From the steady-state molar conservation equation for CO in the bulk gas:

$$r_{prod} = r_{diff} = D\, A_{diff}\, (C_{max} - C_{cat})/L$$

$$C_{cat} = C_{max} - r_{prod}/(DA\,/\,L)$$

where D is the diffusivity in the bulk gas. And, thus:

$$V_{cat} = \frac{r_{prod}}{k\, \eta\, (C_{max} - r_{prod}/(DA\,/\,L))}$$

Again, the complexity of the problem is not increased by using more complex rate expressions than the first-order equation shown here. The required catalyst volume is now a function of the parameters describing diffusion of CO in the stagnant bulk gas and within the porous catalyst.

There are two limits to effects of diffusion within the porous catalyst. First consider the case where diffusion of reactants is fast relative to the rate of reaction. For this case $\phi << 1$ and $\eta \rightarrow 1$:

$$V_{cat} = \frac{r_{prod}}{k\, (C_{max} - r_{prod}/(DA\,/\,L))}$$

The other limit is the case where the rate of reaction is fast relative to the diffusion of reactants within the catalyst. For this case $\phi >> 1$ and $\eta \rightarrow 1/\phi$:

$$V_{cat} = \frac{r_{prod}}{(\,k^{0.5}\, D_{eff}^{0.5}\,/\,\ell\,)(C_{max} - r_{prod}/(DA\,/\,L))}$$

In this case, quadrupling the activity (i.e., the rate constant, e.g., by adding more precious metal) within a porous catalyst layer of constant thickness $\ell$ only halves the amount of catalyst required. For constant activity, increasing the thickness of the catalyst layer increases the volume of catalyst required. This design equation also serves to illustrate the care that must be taken when trying to measure kinetics over porous catalysts where the effects of diffusion may be important. As another example, note that the rate constant occurs to the 0.5 power. Measurement of overall rates at different temperatures in order to determine an activation energy for the reaction will give a result that is approximately equal to one-half of the real activation energy ($D_{eff}$ is relatively weakly temperature dependent).

## SUMMARY

This brief introduction to catalytic reactor design has emphasized the following points:

- The optimal low temperature catalyst will be a "complex" formulation in which the critical catalytic steps of dissociative $O_2$ adsorption and CO adsorption are performed on separate but intimately mixed catalytic sites.
- It is important to determine rate expressions for catalysts in the absence of heat and mass transport limitations whenever possible.
- Reactors designed specifically for kinetic studies of heterogeneous catalysts should be used, whenever possible, rather than prototype lasers. Once a rate expression is determined for a given catalyst formulation, mathematical models can be developed to explore the use of that catalyst in a variety of different lasers, rather than having the measurements only apply to the specific prototype measurements were made in.
- The performance of different catalyst formulations should be compared on the correct chemical basis - such as comparing rate per exposed metal atom or per unit surface area of metal oxide - rather than on an arbitrary basis such as rate per weight of metal.
- Accurate kinetic measurements allow the development of reactor models that allow exploration of a range of design alternatives.

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