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Criterion for extinction of CO oxidation in a catalytic monolith

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The extinction of CO oxidation occurring on the Pt catalyst in a monolithic reactor depends on the interplay of the reaction kinetics and mass and heat transfer. In particular, it may be related to a first-order kinetic phase transition from the high-reactive regime to the low-reactive regime. For this scenario, we obtain the criterion for extinction.

KEY WORDS: extinction; ignition; kinetic phase transitions; mass-transport limitations; monolithic catalytic reactor; CO oxidation; Pt.

1. Introduction

Catalytic monoliths are widely used for emission control in vehicles [1] (for some other applications, see Ref.[2]). The early monoliths were ceramic. At present, the metallic monolith structures are provided as well in certain niche markets. Schematically, the monolith can be viewed as a solid with a series of parallel channels with a diameter of about 1 mm, so that each channel represents a tube reactor. The walls of channels are coated by a high-surface-area washcoat (e.g., by metal oxide such as γ-Al_2O_3) with thickness of about 30 μm, providing the support for the dispersed active phase (e.g., noble metals such as Pt or Rh).

As usual in catalysis, the performance of monolithic reactors depends on the interplay between reaction kinetics and mass and heat transfer. During the past two decades, various aspects of this interplay have been analyzed in numerous publications (see [3–6] and references therein). Special attention was paid to *ignition* (or *light-off*) occurring with increasing inlet temperature. Physically, the ignition is related to instability and self-acceleration of exothermic reactions due to the heat release. Before ignition, the system is in a low-reactive state and the mass-transfer limitations are typically negligible. After ignition, the system is in a high-reactive state and the reaction rate is usually controlled by mass transport.

With decreasing inlet temperature, one can observe reaction *extinction*, i.e., the transition from a high-reactive state to a low-reactive state. Recent experimental studies of oxidation of CO [7,8] and propane and propene [8] in a monolithic reactor with the Pt/γ-Al_2O_3 catalyst indicate that in the case of propane the ignition and extinction kinetics are nearly identical. For CO and propene, in contrast, the extinction temperature is appreciably lower than the ignition temperature.

Theoretically, to our knowledge, the conditions for extinction in a monolithic reactor in general and for CO oxidation in particular have not been analyzed in detail. As one of the first steps in this field, we discuss in this Letter the likely scenario of extinction of CO oxidation.

At fixed temperature, the kinetics of CO oxidation on Pt or Rh are known [9] to often exhibit bistability as schematically shown in figure 1. During the low-reactive regime observed at relatively high CO pressure, the surface is primarily covered by CO and the reaction rate is controlled by O_2 dissociation. During the high-reactive regime at relatively low CO pressure, in contrast, the surface is mainly covered by oxygen and the reaction rate is proportional to CO pressure. The stepwise changes in the reaction rate, observed with increasing or decreasing reactant pressure, represent first-order kinetic phase transitions.

The ignition in CO oxidation typically occurs before the corresponding kinetic phase transition. For this reason, the analysis of ignition can be performed even if one ignores kinetic phase transitions. In contrast, the extinction in CO oxidation may be related to the kinetic phase transition from the high-reactive regime to the low-reactive regime. Below, we show how it may occurs. Specifically, we discuss extinction in a uniform washcoat layer (Section 2) and also in a single spherical pellet (Section 3). The former part (Section 2) of our work contains our main results. The latter part (Section 3) is complementary (it may be of interest for the interpretation of the reaction kinetics in the case when the distribution of the active phase in the washcoat is non-uniform [7,8]).

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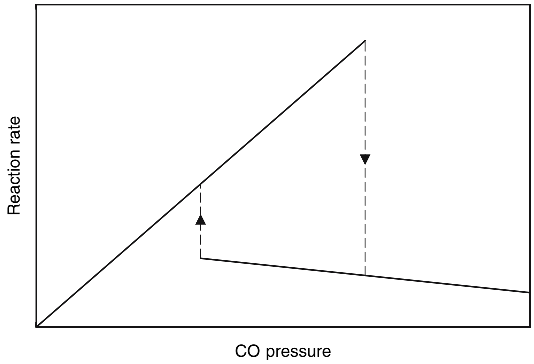

Figure 1. Schematic dependence of the rate of CO oxidation on Pt on CO pressure. The dashed lines indicate kinetic phase transitions.

2. Extinction in a washcoat layer

Let us consider CO oxidation in a uniform washcoat layer at given temperature and CO and O_2 concentrations in the channel. If temperature is appreciably above the extinction temperature, $T > T_{ex}$, the high-reactive regime can be maintained in the whole washcoat layer, i.e., at $0 \le z \le L$, where z is the transverse coordinate, and L is the washcoat-layer thickness ($z = L$ corresponds the boundary between the wascoat and gas phase). With decreasing temperature, the critical CO concentration, u_{cr}, will decrease and eventually it will be lower than the CO concentration in the channel, $u_{cr} < u_{ch}$. Thus, the high-reactive regime will be impossible at $z \simeq L$. Inside the layer, this regime may however still be stable and accordingly the reaction will not be extinguished. With further decrease of temperature, the conditions for realization of the high-reactive regime will not hold in the whole layer (at $0 \le z \le L$) and the reaction will be extinguished.

To obtain the criterion for extinction, we should scrutinize the situation when the high-reactive regime occurs in the depth of the washcoat layer, i.e. at $0 \le z \le l < L$, and to analyse the conditions of its existence. In our treatment, we assume that oxygen is in excess and that during the high-reactive regime the reaction is first order in CO. In this case, the conventional reaction-diffusion equation for CO concentration at $0 \le z \le l$ is

$$D\frac{d^2u}{dz^2} - ku = 0, \quad (1)$$

where k is the reaction rate constant, and D is the CO diffusion coefficient in the washcoat. At $z = l$, we have

$$u(l) = u_{cr}. \quad (2)$$

At $z = 0$, the no-flux boundary condition is expressed as

$$\left.\frac{du}{dz}\right|_{z=0} = 0. \quad (3)$$

The text-book solution of equation (1) with these boundary conditions is

$$u(z) = u_{cr}\cosh(\kappa z)/\cosh(\kappa l), \quad (4)$$

where $\kappa = (r/D)^{1/2}$ is the inverse diffusion length. The CO diffusion flux at $z = l$ is given by

$$J = D\kappa u_{cr}\tanh(\kappa l). \quad (5)$$

At $l < z \le L$, the system is in the low-reactive state. Neglecting the reaction rate in this case, i.e., using equation (1) with $k = 0$, we have

$$u(z) = u_{ch} - (u_{ch} - u_{cr})(L - z)/(L - l). \quad (6)$$

The corresponding diffusion flux at $z = l$ is expressed as

$$J = D(u_{ch} - u_{cr})/(L - l). \quad (7)$$

The diffusion fluxes given by equations (5) and (6) should be equal, i.e., we should have

$$\kappa u_{cr}\tanh(\kappa l) = (u_{ch} - u_{cr})/(L - l). \quad (8)$$

This condition can be rewritten as

$$\kappa(L - l)\tanh(\kappa l) = (u_{ch} - u_{cr})/u_{cr}. \quad (9)$$

The right-hand part of equation (9) is independent of l. The left-hand part equals zero at $l = 0$ and $l = L$ and reaches maximum between these values of l as shown in figure 2. If $(u_{ch} - u_{cr})/u_{cr}$ is lower than this maximum, equation (9) has two solutions. An elementary analysis indicates that the solution with the higher/lower value of l is stable/unstable, respectively. If $(u_{ch}-u_{cr})/u_{cr}$ is higher than the maximum of the left-hand part of equation (9), equation (9) has no solutions, and accordingly the high-reactive regime does not occur. Thus, equation (9) defines the extinction criterion. Specifically, the extinction takes place when $(u_{ch} - u_{cr})/u_{cr}$ is equal to the maximum of the left-hand part of equation (9).

The criterion formulated above is local. In general, it should be complemented by calculation of temperature along the channels. The latter is beyond our present goals (it can be done e.g. in analogy with Ref. [6]). Physically, it is clear that the criterion formulated will first be fulfilled near the inlet of the reactor and then the extinction front will rapidly propagate downstream.

3. Extinction in a spherical pellet

Let us now consider CO oxidation in an active spherical pellet surrounded by inactive washcoat. This case is similar to that treated above. In particular, the high-reactive regime can be maintained at $T > T_{ex}$ in the whole pellet, i.e., at $0 \le r \le R$, where r is the radial coordinate, and R is the pellet radius. With decreasing temperature, the critical CO concentration, u_{cr}, will decreases and eventually it will be lower than the external CO concentration, i.e., the concentration near

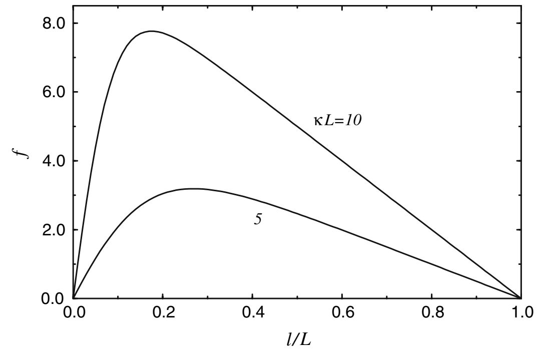

Figure 2. Left-hand part of equation (9), f, as a function of l/R for $\kappa L = 5$ and 10.

the pellet, $u_{\rm cr} < u_{\rm ex}$. Thus, the high-reactive regime will be impossible at $r \simeq R$. Inside the layer at $0 \le r \le l < R$, this regime may however still be stable and accordingly the reaction will not be extinguished. With further decrease of temperature, the conditions for realization of the high-reactive regime will not hold in the whole pellet (at $0 \le z \le R$) and the reaction will be extinguished.

At $0 \le r \le l < R$, the high-reactive regime is described as

$$D\frac{1}{r^2}\frac{d}{dr}r^2\frac{du}{dr} - ku = 0. \tag{10}$$

At $r = l$ and $r = 0$, we should have

$$u(l) = u_{\rm cr} \text{ and } \left.\frac{du}{dr}\right|_{r=0} = 0. \tag{11}$$

The corresponding solution of equation (10) is

$$u(r) = \frac{u_{\rm cr} l}{r}\frac{\sinh(\kappa r)}{\sinh(\kappa l)}. \tag{12}$$

At $l < r \le R$, the system is in the low-reactive state. Neglecting the reaction rate in this case, we have

$$u(r) = u_{\rm ex} - (u_{\rm ex} - u_{\rm cr})\left(\frac{1}{r} - \frac{1}{R}\right)\bigg/\left(\frac{1}{l} - \frac{1}{R}\right). \tag{13}$$

At $r = l$, the diffusion fluxes determined by equations (12) and (13) should be equal. Using this condition, one can easily get

$$u_{\rm cr}\kappa l\frac{\cosh(\kappa l)}{\sinh(\kappa l)} = \frac{u_{\rm ex}R - u_{\rm cr}l}{R - l}. \tag{14}$$

This equation implicitly defines the extinction criterion. Specifically, the extinction occurs when the equation has no solution. Compared to equation (9), equation (14) is more cumbersome. Often, it can however be simplified. If for example $u_{\rm cr}$ is appreciably lower than $u_{\rm ex}$, one can drop $u_{\rm cr}l$ in the left-hand part of equation (14) and obtain

$$\kappa l\frac{\cosh(\kappa l)}{\sinh(\kappa l)} = \frac{u_{\rm ex}R}{u_{\rm cr}(R - l)}. \tag{15}$$

In general, the concentration $u_{\rm ex}$ should be obtained self-consistently by solving the reaction-diffusion equation for the whole washcoat layer. If during extinction l is appreciably lower than R, one can neglect the concentration gradients near the pellet and identify $u_{\rm ex}$ with average local concentration in the washcoat outside the active pellets. Taking into account that the extinction is expected to start near the channel and then to rapidly propagate into the washcoat layer, one can replace $u_{\rm ex}$ by the concentration near the cannel, i.e., by $u_{\rm ch}$.

4. Conclusion

We have derived the criteria for extinction of CO oxidation in a uniform washcoat layer and also in an active spherical pellet. At present, the application of these criteria is far from straightforward, because our knowledge of the CO-oxidation kinetics on Pt (or Rh) is still limited. The low- and high-reactive regimes of CO oxidation can accurately be described at UHV conditions [9] (under these conditions, Pt is in the metallic state in both cases). To interpret the ignition and extinction kinetics observed in monolithic reactors (e.g. in Refs. [7, 8]), we need however the accurate kinetic data at atmospheric pressure. Under the latter conditions, the low-reactive regime is basically the same as at UHV, and accordingly the ignition kinetics can accurately be described. In contrast, the high-reactive regime is expected to be complicated by surface-oxide formation as it was directly observed by STM [10] (see also related discussion of oscillatory kinetics of CO oxidation [11] and Monte Carlo simulations [12]). The corresponding mechanistic details are far from complete. In addition, due to complications related to inevitable diffusion limitations, the accurate kinetic parameters for the reaction kinetics during the high-reactive regime are still lacking. For these reasons, one can hardly accurately calculate k,κ and $u_{\rm cr}$.

Finally, we may also notice that without surface-oxide formation the rate of CO oxidation on Pt during the high-reactive regime might be comparable with the impingement rate and accordingly might be influenced by diffusion in a single pore [13]. Due to surface-oxide formation, the rate is however much lower (see the discussion in Ref. [11]), the diffusion limitations in a single pore are negligible, and one can use equations (1) and (10) in order to describe diffusion.

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