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Oxidation of Carbon Monoxide in a Monolithic Reactor

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***Abstract*—**Solution for the complete removal of carbon monoxide from the exhaust gases still poses a challenge to the researchers and this problem is still under development. Modeling for reduction of carbon monoxide is carried out using heterogeneous reaction using low cost non-noble metal based catalysts for the purpose of controlling emissions released to the atmosphere. A simple one-dimensional model was developed for the monolith using hopcalite catalyst. The converter is assumed to be an adiabatic monolith operating under warm-up conditions. The effect of inlet gas temperatures and catalyst loading on carbon monoxide reduction during cold start period in the converter is analysed.

***Keywords*—** carbon monoxide, catalytic, modeling, monolith

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I. Introduction

CONVENTIONAL combustion carried out in power plants, industrial processes and on road vehicles emit many pollutants like carbon monoxide, hydrocarbons, oxides of nitrogen (NOx), sulphur dioxide, Pb, particulates etc. All these processes lead to severe degradation of environment. It has been reported that transportation and fuel combustion are one of the major sources of carbon monoxide release to the atmosphere. During transport the most common cause of release of carbon monoxide is incomplete combustion due to low air-to-fuel ratios in the internal combustion engines.

Carbon monoxide reduces the oxygen taking capacity of haemoglobin and converts it to carboxyhaemoglobin and therefore causes many health problems. Any exposure to ambient air with carbon monoxide levels greater than 100 ppm is dangerous to human health. The amount of carboxy haemoglobin formed depends on the duration of exposure, concentration in air, ventilation and individual susceptibility [1]. So, oxidation of carbon monoxide to carbon dioxide is very important environmentally and industrially. The catalyst enables the reaction to occur at much lower temperatures than required by a conventional thermal oxidation. Due to due to the lower operating temperatures such processes precluding the formation of toxic compounds [2].

A monolithic catalyst is most commonly used for these type of applications. The main advantages of monolith are low-pressure drop, high-geometric surface, robustness, strength and low weight [3]. They are made by applying a layer of catalytically active component or appropriate support (e.g. Al_2O_3, SiO_2, ZrO_2, carbon, zeolites, etc.) containing one or more catalytically active components (Pt, Pd, Rh, zeolites, etc.) impregnated to the walls (or inside the walls) of the basic, most frequently inert monolith structure [4]. Modified alumina-washcoated supports offer high surface area and excellent catalyst adhesion [5]. Due to higher geometric surface areas monoliths exhibit higher conversion of pollutants.

Highly active catalysts are desirable leading to complete oxidation within short residence time [2]. Although noble metal catalysts like Platinum, Palladium are the best available and most active catalysts for carbon monoxide oxidation having low poisoning and more water tolerant but in view of their depleting resources, base metal oxides are showing more promise. The ceramic monoliths are operated essentially adiabatically, because of their low thermal conduction and the lack of radial mixing that yield a poor heat transfer to the walls [6].

Experimental work as compared to modeling proves to be very expensive and time-consuming and, therefore, has to be limited. Hence, reliable numerical simulations can serve as a powerful method to investigate and eventually optimize the performance of catalytic converters, Understanding the temperature and species profiles inside the converter is an important step in the development of highly optimized catalytic systems [7].

In this paper, a one-dimensional model for carbon monoxide catalytic oxidation reaction was considered, taking into account the gas and the solid phase, mass and energy balance equations. The equations formed are partial differential equations. All these equations are coupled and solved using Backward Implicit Scheme. The effect of changes in inlet gas temperature and catalyst loading on conversion of the reactant gas were studied using hopcalite catalyst.

II. Mathematical Model

The oxidation reaction of carbon monoxide is considered.

$$CO + ½\ O_2 \rightarrow CO_2 \quad (1)$$

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The rate expression for the catalytic reaction is given by [8]:

$$(-r)(C_s, T_s) = k_0 \exp^{(-E/RT_s)} C^{0.7} \quad (2)$$

where values of k_o and E are 4.4150×10^3 $mol^{0.3}ml^{0.7}/m^2sec$ and 4.6×10^4 J/gmol.

The model is based on the following assumptions [9] and the governing equations.

A. Assumptions

Some major assumptions made during modeling include:

1) A single circular cross-sectional channel of the monolith is considered.
2) The noble metal concentration is kept constant.
3) Gas phase concentration, temperature and velocity and the solid temperature are uniform across the monolith cross-section.
4) Uniform properties are assumed for the flowing gas.
5) The diffusion in the washcoat is neglected.
6) The physical properties of monolith are constant and independent of monolith temperature.
7) Negligible axial diffusion of mass and heat transfer in gas phase.
8) Heat transfer by radiation within channels is neglected.
9) Heat exchange between the substrate and the surroundings at both inlet and outlet faces of the monolith are neglected.

B. Modeling Equations

Mass balance for gas phase:

The mass balance includes the net convective transport of gas in the axial direction represented by x, the transfer of reactant mass from gas to solid and the accumulation term.

$$v\left(\frac{\partial C_g}{\partial x}\right) + k_g S(C_g - C_s) = \left(\frac{\partial C_g}{\partial t}\right) \quad (3)$$

where C_g and C_s represent the concentration of carbon monoxide in the gas phase and at the solid surface ($gmole/cm^3$), k_g is mass transfer coefficient (cm/s), S is the geometric surface area per unit reactor volume (cm^2/cm^3), v is average velocity (cm/s), x is axial length (cm), and t is time (sec).

Mass balance for solid phase:

The rate of mass transfer of the reactant from gas to solid phase is taken equal to the reaction taking place at the catalyst surface.

$$k_g S(C_g - C_s) = a(-r)(C_s, T_s) \quad (4)$$

where T_s is solid temperature (K), and a is catalytic surface area per unit reactor volume (cm^2/cm^3).

Energy balance for the gas phase:

The net convective transport of gas in the axial direction results in the heat transfer from the gas to the solid wall.

$$-v\rho_g Cp_g\left(\frac{\partial T_g}{\partial x}\right) - hS(T_g - T_s) = \rho_g Cp_g\left(\frac{\partial T_g}{\partial t}\right) \quad (5)$$

where T_g is gas temperature (K), ρ_g represents gas density (g/cm^3), Cp_g is specific heat of gas (J/g K), and h is heat transfer coefficient (J/cm^2s K).

Energy balance for solid phase:

The energy balance takes into account the heat conduction in the solid wall in axial direction, heat transfer between the gas and the solid wall, heat released due to heterogeneous chemical reaction at the wall surface and the net accumulation of heat in the solid wall.

$$\lambda_s\left(\frac{\partial^2 T_s}{\partial x^2}\right) = -hS(T_g - T_s) - a(-\Delta H)(-r)(C_s, T_s) + \rho_s Cp_s\left(\frac{\partial T_s}{\partial t}\right) \quad (6)$$

where λ_s is thermal conductivity of wall (J/cm s K), Cp_s is specific heat of solid (J/g K), ρ_s is solid density (g/cm^3), and ΔH is heat of reaction (J/gmole).

Initial and Boundary Conditions:

At the start of the operation the monolith is present at the ambient temperature and is suddenly exposed to hot exhaust gas from combustion chamber.

Carbon monoxide concentration and temperature at the entrance at all times:

$$C_g(0,t) = C_g^0 \quad (7)$$

$$T_g(0,t) = T_g^0 \quad (8)$$

Initial solid temperature along the monolith length:

$$T_s(x,0) = T_s^0 \quad (9)$$

The boundary conditions for lagging of solid catalyst at:

the monolith entrance $x = 0$, $\frac{\partial T_s}{\partial x} = 0$ (10)

the monolith exit $x = L$, $\frac{\partial T_s}{\partial x} = 0$ (11)

$$x = L, \quad \frac{\partial C_g}{\partial x} = 0 \tag{12}$$

$$x = L, \quad \frac{\partial T_g}{\partial x} = 0 \tag{13}$$

Equations (3), (5), and (6) are partial differential equations. They are solved in dimensionless form using the following expressions:

$$C = \frac{C_g}{C_g^0} \tag{14}$$

$$T_g^{'} = \frac{T_g}{T_g^0} \tag{15}$$

$$T_s^{'} = \frac{T_s}{T_s^0} \tag{16}$$

$$z = \frac{x}{L} \tag{17}$$

$$t^{'} = \frac{t}{t_0} \tag{18}$$

where C, $T_g^{'}$, $T_s^{'}$, z, and t' are all dimensionless. L is converter length (cm) and t_0 is time at start of operation (s).

C. Dimensionless Equations

Combined Mass balance equations:

Combining (3) and (4) and solving them using dimensionless expressions used in (14)-(18) gives:

$$\left(\frac{\partial C}{\partial z}\right) = -\theta_1\left(\frac{\partial C}{\partial t^{'}}\right) - \psi_1 C e^{\left(-E/RT_s\right)} \tag{19}$$

$$\text{where } \psi_1 = \frac{Lak_0}{v} \tag{20}$$

$$\theta_1 = \frac{L}{vt_0} \tag{21}$$

Energy balance equation for gas phase:

Making (5) dimensionless by using (15)-(18) gives:

$$\left(\frac{\partial T_g^{'}}{\partial z}\right) = -\theta_2\left(\frac{\partial T_g^{'}}{\partial t^{'}}\right) + \delta_1\left(T_s^{'} - T_g^{'}\right) \tag{22}$$

$$\text{where } \theta_2 = \frac{L}{vt_0} \tag{23}$$

$$\delta_1 = \frac{SLh}{v\rho_g Cp_g} \tag{24}$$

Energy balance equation for solid phase:

Making (6) dimensionless by using (14)-(18) gives:

$$\left(\frac{\partial T_s^{'2}}{\partial z^2}\right) = -\psi_2 C e^{\left(-E/RT_s\right)} + \alpha_1\left(T_s^{'} - T_g^{'}\right) + \phi_1\left(\frac{\partial T_s^{'}}{\partial t^{'}}\right) \tag{25}$$

$$\text{where } \psi_2 = \left(C_g^0\right)\frac{aL^2\left(-\Delta H\right)k_0}{\lambda_s T_g^0} \tag{26}$$

$$\alpha_1 = \frac{ShL^2}{\lambda_s} \tag{27}$$

$$\phi_1 = \frac{\rho_s Cp_s L^2}{\lambda_s t_0} \tag{28}$$

where ψ_1, ψ_2, θ_1, θ_2, δ_1, ϕ_1, and α_1 are dimensionless quantities.

Initial and boundary conditions in dimensionless form:

$$C\left(0, t^{'}\right) = 1.00 \tag{29}$$

$$T_g^{'}\left(0, t^{'}\right) = \frac{T_g}{T_g^0} \tag{30}$$

$$T_s^{'}\left(z, 0\right) = \frac{T_s}{T_s^0} \tag{31}$$

$$z = 0.0, \quad \frac{\partial T_s^{'}}{\partial z} = 0 \tag{32}$$

$$z = 1.0, \quad \frac{\partial T_s^{'}}{\partial z} = 0 \tag{33}$$

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$$z = 1.0, \quad \frac{\partial C}{\partial z} = 0 \tag{34}$$

$$z = 1.0, \quad \frac{\partial T_g^{'}}{\partial z} = 0 \tag{35}$$

Equations (19), (22), and (25) are partial differential equations and along with initial and boundary conditions given by (29) to (35) represent the model in dimensionless form.

III. Methadology For Solution

As all these above equations are coupled; hence they are solved at the same time. The results for these partial differential equations are arrived at after solving them using the Backward Implicit finite difference numerical scheme [10].

IV. Results And Discussion

The hot exhaust gas enters the cold converter initially at 25^0C and starts heating the converter. The catalytic reaction starts only the converter has achieved its operating temperature. Once the reaction starts a decrease in the concentration of the pollutant carbon monoxide is observed. The inlet concentration of carbon monoxide has a dimensionless value of 1.0000 and the results are obtained and analysed for decrease in the dimensionless concentration upto 0.2000. Fig. 1, 2 and 3 shows the variation in the gas exit concentration with time for different inlet gas temperatures and Fig. 4 shows the decrease in conversion with aging of the catalyst.

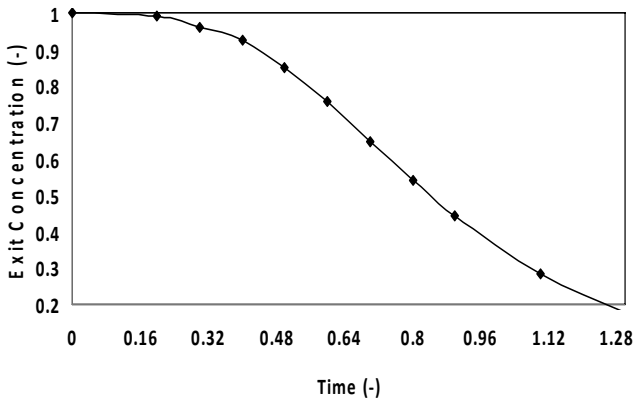


Fig. 1 Exit Concentration variation of Carbon Monoxide with respect to dimensionless time for Hopcalite Catalyst

Fig. 1 represents the exit concentration of gas with respect to time for an inlet gas temperature of 160°C. Initially there is hardly any change in concentration of carbon monoxide as the converter has not attained its operating temperature. At dimensionless time 0.30 the exit dimensionless concentration is 0.9624. However with increase of time as the converter gets heated, the conversion of gas becomes more pronounced. At dimensionless times 0.70 and 0.90 the exit dimensionless concentrations are 0.6479 and 0.4421 respectively.

Fig. 2 represents the exit concentration of gas with respect to time for different inlet temperatures of the gas. Results are analysed for decreasing the inlet gas temperatures to 140°C from 160°C. Initially there is hardly any difference in conversion of carbon monoxide for these different inlet gas temperatures. As can be seen from Fig. 2 at dimensionless time 0.30 the exit dimensionless concentrations are 0.9710 and 0.9624 for inlet gas temperatures of 140°C and 160°C respectively. However with increase of time the effect of increase in gas inlet temperature on the conversion of gas becomes more pronounced. At time 0.90 the exit dimensionless concentrations are 0.6606 and 0.4421for inlet gas temperatures of 140°C and 160°C respectively. It is observed that fast conversion occurs at higher values of inlet temperatures of the gas.

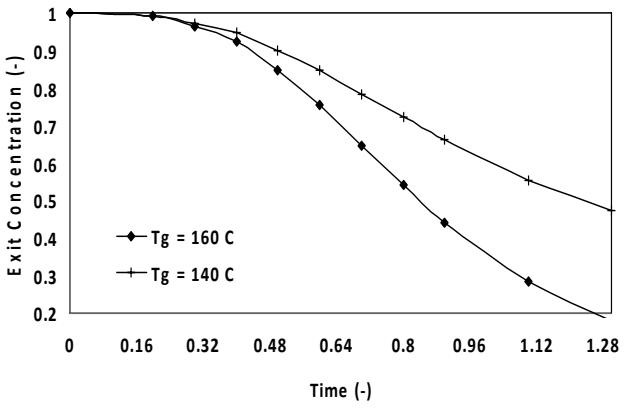


Fig. 2 Exit Concentration variation of Carbon Monoxide with respect to dimensionless time for inlet gas temperatures of 140^0C and 160^0C

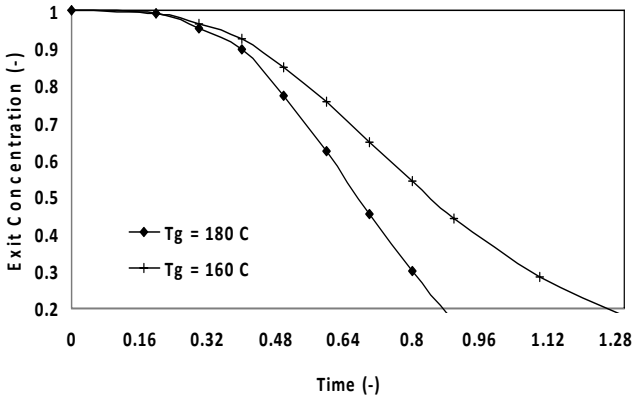


Fig. 3 Exit Concentration variation of Carbon Monoxide with respect to dimensionless time for inlet gas temperatures of 160^0C and 180^0C

Fig. 3 represents the exit concentration of gas with respect to time for inlet gas temperatures of 160°C and an increased inlet gas temperature to 180°C. As observed in Fig. 2 initially there is hardly any conversion of carbon monoxide for these different inlet gas temperatures. At dimensionless time 0.30

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the exit dimensionless concentrations are 0.9624 and 0.9515 for inlet gas temperatures of 160°C and 180°C respectively. As time increases an appreciable change in the exit concentrations of the gas at these temperatures is observed. At dimensionless time 0.80 the exit dimensionless concentrations are 0.5416 and 0.2998 for inlet gas temperatures of 160°C and 180°C respectively. So increased gas conversion is found to occur at higher inlet gas temperatures.

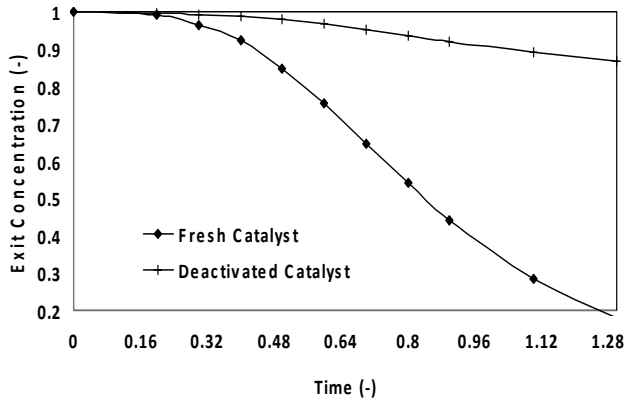


Fig. 4 Exit Concentration variation of Carbon Monoxide with respect to dimensionless time for a fresh and deactivated catalyst

Fig. 4 represents the exit concentration variation with respect to time for different values of catalyst loading for carbon monoxide gas. Data available in literature with regard to loading levels of the catalyst show that for a typical in use catalyst, the standard loading is taken as 268 cm^2/cm^3 (roughly 15% of fresh loading level of 1,700 cm^2/cm^3). At dimensionless time 0.40, the dimensionless exit concentrations are 0.9252 and 0.9885 for fresh catalyst and the deactivated catalyst respectively. At dimensionless time 0.90, the dimensionless exit concentrations are 0.4421 and 0.9194 for fresh catalyst and the deactivated catalyst respectively. It is observed that the faster conversion of carbon monoxide occurs at higher loading of the catalyst.The SI unit for magnetic field strength H is A/m. However, if you wish to use units of T, either refer to magnetic flux density B or magnetic field strength symbolized as $\mu_0 H$. Use the center dot to separate compound units, e.g., "$A \cdot m^2$."

V. Conclusion

A one-dimensional model developed was simulated to analyse the conversion of the gas carbon monoxide for different inlet gas temperatures and catalyst loading. In both cases it was observed that initially there is hardly any conversion of the polluting gas till the catalyst reaches the operating temperatures. This is due to the fact that initially when the converter is started, the solid temperature being very low (ambient temperature), it does not favour the start of catalytic reactions. The conversion of carbon monoxide gas starts only after the incoming gas has heated the solid catalyst to its operating temperature level, when the activation energy required to bring about the desired conversion is achieved.

An increase in carbon monoxide conversion due to increase in inlet gas temperature is observed. At higher gas temperature more heat is supplied to the catalyst, so the catalytic reactions get activated faster bringing about the desired conversion in a short span of time. Also in case of a fresh catalyst, the higher catalyst loading favours faster conversion of the carbon monoxide gas as compared to the deactivated catalyst. This is due to the fact that in the former case more catalyst is available for the reaction, thereby increasing the rate of catalytic reaction. Catalyst loading decreases as the catalyst deactivates (caused by use over a period of time) decreasing the conversion of carbon monoxide.

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