

Study of Carbon Monoxide Oxidation in a Monolithic Converter

S. Chauhan, T. P. K. Grewal, S. K. Agrawal, V. K. Srivastava

Abstract—Combustion of fuels in industrial and transport sector has lead to an alarming release of polluting gases to the atmosphere. Carbon monoxide is one such pollutant, which is formed as a result of incomplete oxidation of the fuel. In order to analyze the effect of catalyst on the reduction of CO emissions to the atmosphere, two catalysts Mn_2O_3 and Hopcalite are considered. A model was formed based on mass and energy balance equations. Results show that Hopcalite catalyst as compared to Mn_2O_3 catalyst helped in faster conversion of the polluting gas as the operating temperature of the hopcalite catalyst is much lower as compared to the operating temperature of Mn_2O_3 catalyst.

Keywords—Carbon monoxide, modeling, hopcalite, manganese oxide.

I. INTRODUCTION

THE main change in the atmospheric air composition is primarily due to the combustion of fossil fuels. An air pollutant when present in excess may cause or contribute to an increase in mortality or serious illness or may pose a potential hazard to human health [1].

The most common sources for CO include car exhaust fumes, smoke from fires, furnaces, gas-powered engines, wood stoves, paint removers containing methylene chloride, tobacco smoke etc [2]. CO from motor-vehicle exhaust is the single most common cause of CO poisoning deaths in the US. Of the 11,547 unintentional CO deaths during 1979–1988, 57% were caused by motor vehicle exhaust; of these, 83% were associated with stationary vehicles. Introduction of CNG has led to 56% less CO emissions as compared to an ordinary diesel bus [3].

The most common cause of release of CO is incomplete combustion of fuel in the internal combustion engines, is likely to occur due to low air-to-fuel ratios in the engine. Human toxicity is often overlooked because CO is tasteless and odorless and its clinical symptoms and signs are non specific. After CO exposure, angina attacks, arrhythmias, and increased level of cardiac enzymes frequently occur [4]. The

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brain and the heart may be severely affected after CO exposure with carboxyhemoglobin (COHb) levels exceeding 20%. Damage occurs because the affinity of hemoglobin for CO is 210 times higher than for O_2 [4].

For decrease in the release of CO from automobiles, monolithic catalytic converters are commonly used. They consist of a honeycomb structure on which a layer of a 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.) is impregnated. Monolith's lighter weight allows more rapid warm up of the catalyst thereby exhibiting higher conversion of pollutants in a shorter period of time [5].

Design and optimization of a catalytic converter is challenging due to the complex interaction between chemical reactions and mass and heat transfer. Experimental test bench measurements are very expensive and time-consuming and, therefore, have to be limited [6]. Furthermore, these experiments are difficult to be interpreted as they concern the details of the different chemical and physical processes taking place inside the honeycomb structure. Hence, reliable numerical simulations can serve as a powerful method to investigate and eventually optimize the performance of catalytic converters [6].

CO released during the warm-up period from the vehicle forms a considerable part of the pollutants released untreated to the atmosphere. Different catalysts have been suggested for its reduction. Modeling for CO reduction using monolith with Mn_2O_3 as the catalyst has been analyzed earlier [7], [8]. However in the study modeling for the reduction of CO using two different catalysts Mn_2O_3 and Hopcalite is carried out. The energy and mass balance equations formed are a set of partial differential equations (PDE) that are solved using Backward Implicit Scheme. Finally a comparison is made between the results derived using the two catalysts Mn_2O_3 and Hopcalite and Hopcalite is found to bring about a faster removal of CO.

II. MATHEMATICAL MODEL

The reaction of CO to form a less harmful gas carbon dioxide is being considered.



A rate expression for the catalytic reaction is given by [9]:

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

where values of k_0 and E are given in Table I for two the catalysts Mn_2O_3 and Hopcalite.

TABLE I

VALUES OF PARAMETERS FOR Mn_2O_3 AND HOPCALITE CATALYSTS		
Quantity	Mn_2O_3 catalyst	Hopcalite catalyst
k_0	1.0669×10^4	4.4150×10^3
	$mol^{0.3} m^{10.7} / m^2 sec$	$mol^{0.3} m^{10.7} / m^2 sec$
E	6.1×10^4 J/gmol	4.6×10^4 J/gmol

A simple one-dimensional model is formed accounting for the mass and heat transfer in the gas and solid phases, the axial heat conduction in the catalyst and the chemical reaction [10].

A. Assumptions

Some major assumptions made during modeling include:

- A channel of the monolith is considered.
- Monolith channel has a circular cross-section and is cylindrical in shape.
- Catalyst concentration is kept constant along the length of the converter.
- Gas phase concentration, temperature and velocity and the solid temperature are uniform across the monolith crosssection.
- Uniform properties are assumed for the flowing gas.
- As the washcoat is assumed to be very thin so diffusion in the washcoat is neglected.
- The physical properties of monolith are constant and independent of monolith temperature.
- Negligible axial diffusion of mass and heat transfer in gas phase.
- Heat transfer by radiation within channels and heat exchange between the substrate and the surroundings at both inlet and outlet faces of the monolith are neglected.
- Heat transfer by radiation is neglected.

B. Modeling Equations

1. Mass Balance for the Gas Phase

The net convective transport of gas in the axial direction (x) and the transfer of reactant mass from gas to solid results in change in concentration with time.

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

where C_g represent concentration of CO in the gas phase (g mole/cm³), C_s represent concentration at the solid surface (g mole/cm³), k_g is mass transfer coefficient (cm/s), S is the geometric surface area per unit reactor volume (cm²/cm³), x is axial length (cm), v is average velocity (cm/s), and t is time (sec).

2. 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, causes a change in gas temperature with respect to time

$$-v \rho_g C p_g \left(\frac{\partial T_g}{\partial x} \right) - h S (T_g - T_s) = \rho_g C p_g \left(\frac{\partial T_g}{\partial t} \right) \quad (4)$$

where ρ_g represents gas density (g/cm³), $C p_g$ is specific heat of gas (J/g K), and h is heat transfer coefficient (J/cm²s K).

3. Mass Balance for Solid Phase

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

$$a(-r)(C_s, T_s) = k_g S (C_g - C_s) \quad (5)$$

where a is catalytic surface area per unit reactor volume (cm²/cm³), and T_s is solid temperature (K).

4. Energy Balance for Solid Phase

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

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

where λ_s is thermal conductivity of wall (J/cm s K), $C p_s$ is specific heat of solid (J/g K), ρ_s is solid density (g/cm³), and ΔH is heat of reaction (J/gmole).

5. 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.

CO concentration at the entrance at all times:

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

Gas temperature at the entrance at all times:

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

Initial solid temperature along the monolith length:

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

The boundary conditions for lagging of solid catalyst entrance and exit:

$$\text{at } x = 0, \quad \frac{\partial T_s}{\partial x} = 0 \quad \text{and at } x = L, \quad \frac{\partial T_s}{\partial x} = 0 \quad (10)$$

$$\text{Also at } x = L, \quad \frac{\partial C_g}{\partial x} = 0 \quad \text{and} \quad \frac{\partial T_g}{\partial x} = 0 \quad (11)$$

Equations (3), (4) and (6) are coupled PDEs. All these equations are made dimensionless [7] and solved using backward implicit scheme [11].

III. RESULTS AND DISCUSSION

At the start of the operation, the converter is at ambient temperature and the entering hot exhaust gas, heats the converter. The catalytic reaction starts once the converter has attained the operating temperature. Due to these reactions a decrease in the concentration of the pollutant CO is observed. The inlet concentration of CO is 1233ppm [12], taken equivalent to a dimensionless value of 1.0000. Figs. 1 and 2 show the variation in the gas conversion with respect to reaction temperature for Hopcalite and Mn_2O_3 catalysts and Fig. 3 shows the exit conversion of the CO gas as it leaves the monolith with respect to time for Mn_2O_3 and hopcalite catalysts.

Fig. 1 shows the conversion of CO with respect to the reaction temperature using Hopcalite catalyst. CO gas at 250°C is introduced in a converter initially at a temperature of 25°C. The hot incoming gas raises the temperature of the converter by transferring heat to it by convection. From these results as shown in Fig. 1, it is observed that at lower temperatures there is hardly any conversion taking place. As reaction temperature reaches 121°C a conversion of about 0.15% is achieved.

As the catalyst gets heated the exothermic catalytic reactions are initiated and the rate of reaction increases due to heat released by these reactions. About 80% conversion is obtained at a reaction temperature of 165°C. For almost complete conversion, a solid temperature of about 180°C is required.

Fig. 2 shows the comparison of the conversion of CO for the two catalysts Mn_2O_3 and hopcalite with respect to the reaction temperature. Initially as seen from the Fig. 2 there is hardly any conversion observed for both the catalysts upto a reaction temperature of about 50°C. About 10% conversion is achieved at a reaction temperature of 110°C using hopcalite catalyst and the same conversion is brought about at 210°C temperature using Mn_2O_3 catalyst. The overall conversion is faster in case of hopcalite catalyst due to the additional presence of copper oxide in the catalyst composition which increases the activity of manganese oxide catalyst [13]. About 50% conversions are obtained at 150°C in case of hopcalite catalyst and at 245°C in case of Mn_2O_3 catalyst. For almost complete conversion, solid catalyst temperature of 180°C is required for hopcalite and 261°C for Mn_2O_3 .

Fig. 3 shows the exit concentration variation with time using both hopcalite [7] and Mn_2O_3 as catalysts. As can be seen, the concentration of gas decreases with time in both cases. Initial dimensionless concentration of CO in the converter is taken as 1.0000 but it decreases as the reaction proceeds due to conversion of CO to carbon dioxide.

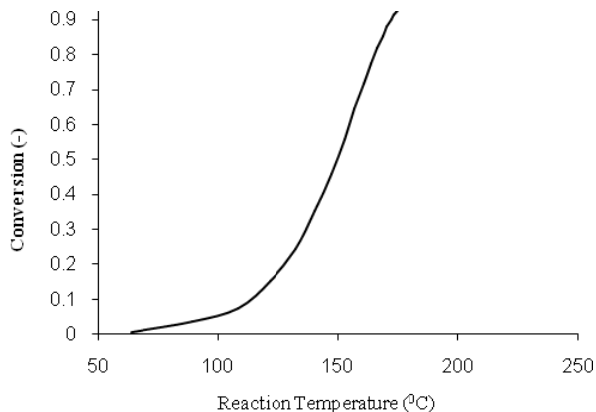


Fig. 1 Conversion of CO with the Reaction Temperature using Hopcalite as a Catalyst

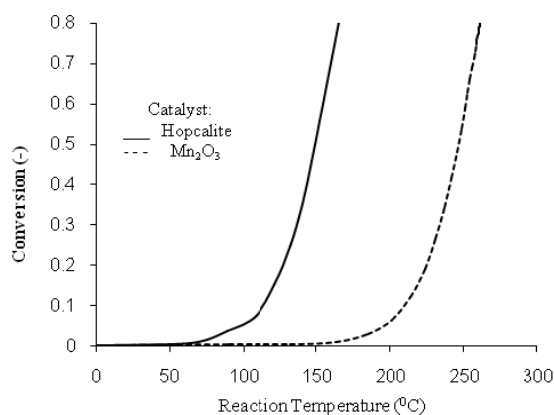


Fig. 2 Conversion of CO with respect to the Reaction Temperature using Hopcalite and Mn_2O_3 as a Catalyst

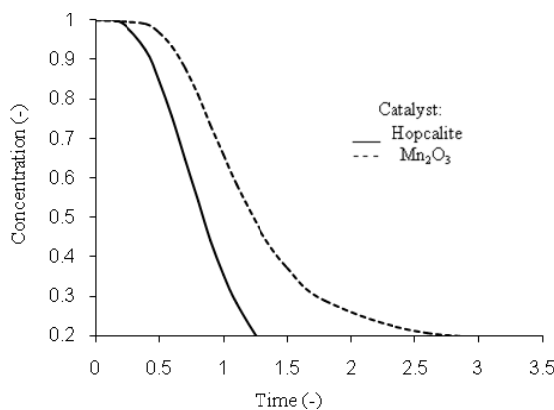


Fig. 3 Exit Concentration variation of CO with respect to dimensionless time for Hopcalite and Mn_2O_3 Catalyst

From the Fig. 3 it is seen that the decrease in concentration is much faster in case of hopcalite as compare to Mn_2O_3 due to the presence of copper oxide in its composition. At dimensionless time 0.80, the dimensionless concentration reduces to 0.5416 for hopcalite and 0.8102 for Mn_2O_3 catalyst.

At dimensionless time 1.50, the concentration is 0.1190 in case of hopcalite and 0.3718 in case of Mn_2O_3 catalyst.

IV. CONCLUSIONS

Development of a model capable of simulating the CO oxidation reaction using one-dimensional model for predicting the CO emissions released to the atmosphere during the warmup period using two different catalysts Mn_2O_3 and hopcalite was carried out. The hopcalite catalyst is a further modification of the Mn_2O_3 catalyst as in the former copper oxide is added which causes an increase in the catalytic activity of the Mn_2O_3 catalyst.

In both cases it was observed that for CO oxidation carried out in the converter channel, initially there is hardly any conversion of the polluting gas till the catalysts reach their 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 CO gas starts only after the incoming gas has heated the solid catalyst to its operating temperature level (i.e. where it achieves the activation energy required to bring about the desired conversion). As the solid temperature increases, the conversion of CO increases. In case of the two catalysts it is seen that hopcalite catalyst due to presence of copper oxide in its composition shows faster initiation of CO oxidation at lower temperatures as compared to the Mn_2O_3 catalyst. At the studied operating conditions, Mn_2O_3 catalyst requires a higher temperature for the conversion of CO gas, therefore hopcalite catalyst is the better option as compared to Mn_2O_3 catalyst for the catalytic oxidation of CO.

REFERENCES

- [1] K. Marilena, E. Castanas, "Human Health Effects of Air Pollution", *Env .Pollution*, vol 151, pp 362-367, 2008.
- [2] J. Varon, P.E. Marik, R.E. Fromm, A. Gueler, "Carbon Monoxide Poisoning: A Review for Clinicians", *J. Emergency Med.*, vol 17, pp 87-93, 1999.
- [3] P.G. Sidhartha, "Present Scenario of Air Quality in Delhi: a Case Study of CNG Implementation," *Atmospheric Environ.*, vol 37, pp 5423-5431, 2003.
- [4] L.D. Procop, R.I. Chichkova, "Carbon Monoxide Intoxication: An updated review," *J. Neur. Sci.*, vol. 262, pp 122-130, 2007.
- [5] R.M. Heck, S. Gulati, R.J. Farrauto, "The Application of Monoliths for Gas Phase Catalytic Reactions", *Chem. Eng. J.*, vol. 82, pp. 149-156, 2001.
- [6] N. Mladenov, J. Koop, S. Tischer, O. Deutshmann, "Modeling of transport and chemistry in channel flows of automotive catalytic converters," *Chem. Eng. Sci.*, vol. 65, pp 812-826, 2010.
- [7] S. Chauhan, T.P.K. Grewal, S. K. Aggarwal, and V. K. Srivastava, "Oxidation of Carbon Monoxide in a Monolithic Reactor", *World Academy of Sci. Eng. and Tech.*, vol 80, pp 1269-1273, 2011.
- [8] S. Chauhan, T.P.K. Grewal, "Carbon Monoxide Combustion", *Proc. of Int. Conf. on Emerging Technol. for Sustainable Environ.* A.M.U. Aligarh, India, pp. 225-228, October, 2010.
- [9] F.C. Buciuman, F. Patcas, T. Hahn, "A spillover approach to oxidation catalysis over copper and manganese mixed oxides," *Chem. Eng. and Proc.*, vol. 38, pp 563-569, 1999.
- [10] S. Chauhan, V.K. Srivastava, "Modeling for Propylene and Propane present in the Exhaust Gases in a Monolithic Catalytic Converter," *Indian Chem. Engr.*, vol.60, pp 301-311, 2008.
- [11] S. Chauhan, V.K. Srivastava, "Modeling Exhaust Gas Pollution Abatement: Part I- Single Hydrocarbon Propylene," *Comput. Math. Appl.*, vol. 55, pp. 319-330, 2008.
- [12] B. Liu, R.E. Hayes, M.D. Checkel, M. Zheng, E. Mirosh, "Reversing flow catalytic converter for a natural gas/diesel dual fuel engine", *Chem. Eng. Sci.*, vol 56, pp 2641-2658, 2001.
- [13] S. Chauhan T.P.K. Grewal, "Development of a Model for Carbon Monoxide Oxidation", *Proc. of the National Conf. on Green Chem.*, Ghaziabad, India, pp. 226-228, Sept 2010.