

CO OXIDATION IN A CARBERRY REACTOR: MANIFESTATION OF REACTION KINETICS BY CONTROLLED REACTION / TRANSPORT

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Introduction

Thin-walled honeycombed substrates find extensive use as catalyst supports in automobile catalytic exhaust converters. Of special interest is the investigation of CO oxidation kinetics since CO is the main pollutant in automobile exhaust gases.

The oxidation of CO over noble metal catalysts has been studied for many years.

In **Table 1**, the most important kinetic data presented in literature are given.

The available data for external mass transfer in monoliths and the existing correlations for mass transfer coefficients differ up to an order of magnitude with predictions. In an early work, Hawthorn³⁾ presented the correlation for *Sh* number as a function of *Re* and *Sc* numbers. Votruba *et al.*¹³⁾ reported a somewhat different correlation resulting during evaporation from a honeycomb body. Another correlation for the mass transfer coefficient is given by Arashi *et al.*¹⁾, deduced from experiments under reacting conditions. A similar expression to that published by Votruba *et al.*¹³⁾ for mass transfer correlation is reported by Ullah⁹⁾. The plots of the correlations mentioned above are given in **Fig. 1**.

In the present work, an attempt was made to investigate the coupling of kinetics and external mass transfer in experimental data obtained from a specially designed Carberry²⁾ type reactor. The reactor used was a spinning basket catalytic reactor where the catalyst (*Pt*, *Rh* over γ -Al₂O₃, on monolithic ceramic substrate) rotated in the reacting gas stream. This particular configuration enables the experimental measurement of catalytic reaction rate as a function of reacting gas velocity through monolithic cata-

lyst and the estimation of external mass transfer rates in monoliths is thus possible. A proper mathematical model which includes intrinsic kinetics and external mass transfer was used. In this way, intrinsic kinetics of carbon monoxide oxidation have been estimated in order to elucidate the important kinetic parameters and the influence of external mass transfer.

1. Experimental

1.1 Catalyst

The catalyst used in the kinetic experiments consisted of a monolithic cordierite substrate, donated by Corning, with 400 cells-in⁻² (62 cells-cm⁻²), wall thickness of 0.12 mm and porosity of 0.19 ml·g⁻¹ (measured by mercury penetration porosimetry) which was coated with an active layer containing mainly of alumina and the precious metals (platinum and rhodium). This coating was loaded on the monolithic substrate using a wet impregnation procedure. The ceramic substrate was dipped into an aqueous slurry which was the product of a wet milling process (Vlachou *et al.*, 1992). The solids consisted of γ -Al₂O₃: 87.43 %, *Pt*: 1.36 %, *Rh*: 0.14 %, CeO₂: 1.82 % and La₂O₃: 9.25 % on a dry basis. The prepared catalyst was then dried at 110°C for 1 hour, calcined at 600°C for 2 hours and reduced in a hydrogen flow of 200 ml·min⁻¹ at 400°C for 2 hours.

1.2 Experimental setup

A Carberry reactor was used as shown in **Fig. 2**. The monolithic catalyst was attached to a rotating shaft inside the reactor chamber. Each of the two branches of the shaft behaves as a differential reactor which is swept by the surrounding gas environment several thousand times per

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Table 1. Kinetic rate equations for CO oxidation

Voltz ¹²⁾	$R_{CO} = \frac{1.83 \times 10^{12} e^{-\frac{22600}{T}} (CO)(O_2)}{\left[1 + 0.655 e^{\frac{1730}{T}} (CO)\right]^2}$ $\{R_{CO}\}: \text{mol.ft}^{-3} \cdot \text{s}^{-1}$	Pt / Al ₂ O ₃ 6-8 mesh alumina spheres
Hegedus ⁵⁾	$R_{CO} = \frac{10^{12} \cdot T \cdot e^{-\frac{15000}{RT}} \cdot (CO) \cdot (O_2)}{\left[1 + 4.5 \times 10^5 \cdot T \cdot e^{\frac{2000}{RT}} \cdot (CO)\right]^2}$ $\{R_{CO}\}: \text{mol.cm}^{-2} \text{Pt} \cdot \text{s}^{-1}$	Pt / Al ₂ O ₃ pellets
Oh ⁸⁾	$R_{CO} = \frac{6.699 \times 10^9 e^{-\frac{12556}{T}} (CO)(O_2)}{T \left[1 + 65.5 e^{\frac{961}{T}}\right]^2}$ $\{R_{CO}\}: \text{mol.cm}^{-2} \text{Pt} \cdot \text{s}^{-1}$	Pt / Al ₂ O ₃ monolithic type catalyst
Varma ¹⁰⁾	$R_{CO} = \frac{1.21 \times 10^{22} e^{-\frac{26000}{RT}} (CO)(O_2)}{\left[1 + 4.12 \times 10^6 e^{\frac{1900}{RT}} (CO)\right]^2}$ $\{R_{CO}\}: \text{mol.gcat}^{-1} \cdot \text{min}^{-1}$	0.1% (Pt:Rh = 10:1) / Al ₂ O ₃ , 10% CeO ₂ , 2% NiO, monolithic
Harold ³⁾	$R_{CO} = \frac{2.7 \times 10^{16} e^{-\frac{21430}{RT}} (CO)(O_2)}{\left[1 + 360 e^{\frac{3800}{RT}} (CO)\right]^2}$	0.3% Pt/Al ₂ O ₃ spherical pellets, thin exterior spherical shell
Koberstein ⁶⁾	$R_{CO} = \frac{2.7^{13} \cdot e^{-\frac{21800}{RT}} \cdot (CO)(O_2)}{\left[1 + 0.36 e^{\frac{3850}{RT}} \cdot (CO)\right]^2}$ $\{R_{CO}\}: \text{mol.m}^{-3} \cdot \text{s}^{-1}$	(Pt/Rh: 1/5) / Al ₂ O ₃ , monolithic

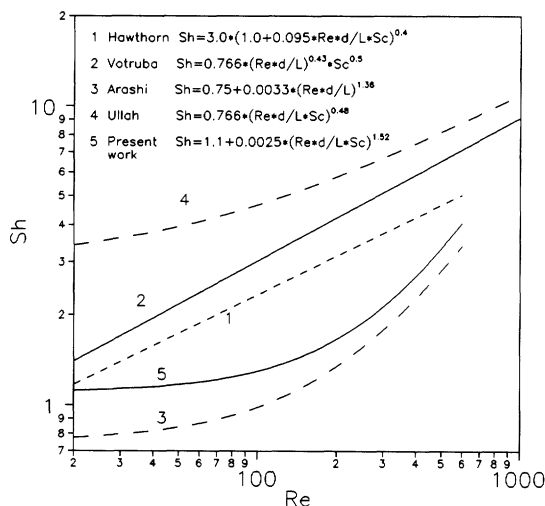
minute. We assumed that rotational velocities used assured perfect mixing. The samples from the reactant and product streams were analyzed using a gas chromatography apparatus (HP-5710B) equipped with two columns, namely a 80-100 mesh silica gel and a 5A 80-100 mesh molecular sieve, connected in series with a thermal conductivity detector.

1.3 Experimental conditions and experimental data

Kinetic data were obtained as outlet concentration of carbon monoxide for a set reactor inlet gas concentrations, reactor gas temperatures and feed flow rates. Reactor temperature was varied over the range of 150-240°C. Reactor pressure was maintained close to atmospheric. Carbon monoxide concentration was varied over the range of 3.0-3.3 % (v/v) and oxygen concentration was varied over the range of 1.6-2.1 % (v/v). Total mass flow rate was varied over the range of 15.9-17.1 mg/s.

2. Results

A series of experiments were carried out and reaction rate data versus reactor gas velocity are plotted in **Fig. 3**. By analyzing the gas mixture at the reactor inlet and outlet the material balance was verified and the rate of carbon monoxide oxidation was calculated. A quite strange behaviour in the reaction rate was observed at temperatures of $T = 423^\circ\text{K}$ and $T = 433^\circ\text{K}$. The reaction rate decreased as gas velocity increased implying that the external mass transfer coefficient, k_c , increases. This k_c increase causes a rise in the catalyst interphase CO concentration.

**Fig. 1** Comparison of literature and present work approximations of external mass transfer

This effect indicates an inverse-law dependence of kinetic rate equation on carbon monoxide concentration which can be attributed to carbon monoxide inhibition. It should be noted here that reaction kinetics with a first order inhibition term lead to a monotonous rate decrease in contrast with that of second order which causes the rate to pass through a maximum. At higher temperatures, where the rate controlling step was the external mass transfer, this behaviour was not observed; however, it can be observed in cases where the external mass transfer rate is too fast compared to CO oxidation rates.

An additional observation is that greater reaction rates for lower temperatures (by 10°C) have been achieved. This phenomenon can also be explained in terms of the interaction between mass transfer and chemical reaction with inhibition term. In cases where mass transfer imposes a lower CO concentration, then an increase in the reaction rate is expected since the inhibition term is reduced. The latter rate increase may exceed the reaction rate observed for a slightly higher temperature and at different (perhaps much higher) CO concentration.

The reactor model combines a heterogeneous catalytic reaction and mass transfer from the bulk fluid to the gas-solid interface. Under steady state conditions, the reaction rate on the catalyst surface equals the rate of external carbon monoxide diffusion from the bulk region to the gas-catalyst interphase:

$$r_{CO} = \frac{k_0 e^{\left[-\frac{E}{R_s T_s}\right]} (CO)^*}{\left[1 + k_1 e^{\left[\frac{\Delta H}{R_s T_s}\right]} (CO)^*\right]^2} = k_c [(CO)_f - (CO)^*] \quad (1)$$

From the equation above the kinetic parameters k_0 , E , k_1 , ΔH along with the external mass transfer coefficient k_c are determined by nonlinear fitting. The initial values for the kinetic parameters and external mass transfer coefficient were adopted from the literature, the algebraic equation is solved via a Newton Method and the rate of reaction is calculated by means of interphase concentrations. The para-

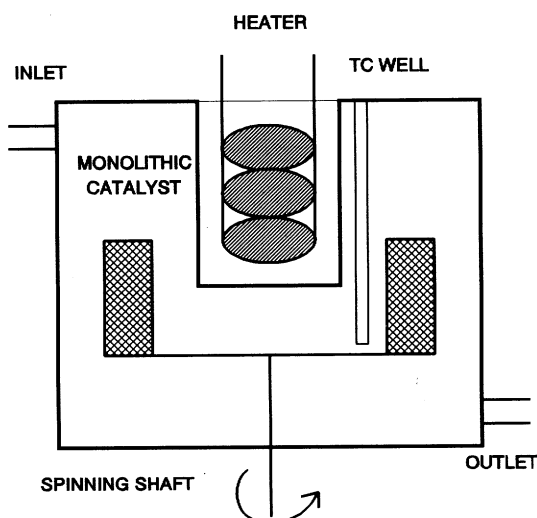


Fig. 2 Spinning basket reactor

meter values were determined so that the discrepancy between the calculated and experimental reaction rates would be minimized. In determining parameter values, we used the Marquardt-Levenberg non-linear optimization method⁷. The parameters were varied until convergence was reached.

The experimental runs were fitted by the model described above and the values of the estimated kinetic parameters are: $k_0 = 2.55 \cdot 10^8 \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{kg}^{-1}$, $k_1 = 1.88 \cdot 10^7 \text{ m}^3 \cdot \text{kmol}^{-1}$, $E = 56.1 \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta H = 7.5 \text{ kJ} \cdot \text{mol}^{-1}$. The external mass transfer coefficient, k_c , is predicted by equation 5 proposed in this work as shown in Fig. 1. The kinetic model predictions agree well with the experimental data on synthetic gas mixtures. The maximum deviation between predicted and experimental reaction rates was 20 %.

Nomenclature

$(\text{CO})_f$	= Carbon monoxide bulk concentration	$[\text{kmol} \cdot \text{m}^{-3}]$
$(\text{CO})^*$	= Carbon monoxide interphase concentration	$[\text{kmol} \cdot \text{m}^{-3}]$
d	= Monolith channel diameter	$[\text{m}]$
$D_{\text{CO}, \text{N}_2}$	= CO-N ₂ diffusion coefficient	$[\text{m}^2 \cdot \text{s}^{-1}]$
E	= Arrhenius activation energy	$[\text{kJ} \cdot \text{mol}^{-1}]$
k_0	= Arrhenius pre-exponential factor	$[\text{m}^3 \cdot \text{s}^{-1} \cdot \text{kg}^{-1}]$
k_1	= Inhibition kinetic constant	$[\text{m}^3 \cdot \text{kmol}^{-1}]$
k_c	= External mass transfer coefficient	$[\text{m} \cdot \text{s}^{-1}]$
L	= Monolithic catalyst length	$[\text{m}]$
r_{CO}	= Carbon monoxide oxidation rate	$[\text{kmol} \cdot \text{sec}^{-1} \cdot \text{kg}^{-1}]$
Re	= Reynolds number, $Re = \rho u d / \mu$	

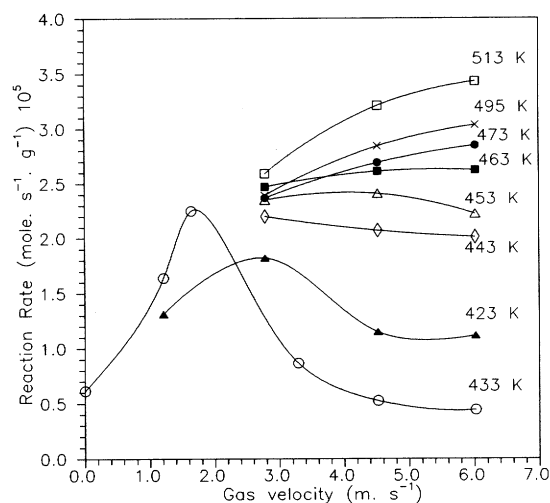


Fig. 3 Experimental data for CO kinetics

Sc	= Schmidt number, $Sc = \nu / D_{\text{CO}, \text{N}_2}$	
Sh	= Sherwood number, $Sh = k_c d / D_{\text{CO}, \text{N}_2}$	
T_w	= catalyst temperature	$[\text{K}]$
u	= Gas phase velocity	$[\text{m} \cdot \text{s}^{-1}]$
ΔH	= Adsorption activation energy	$[\text{kJ} \cdot \text{mol}^{-1}]$
μ	= Gas phase viscosity	$[\text{poise}]$
ν	= Gas phase kinematic viscosity	$[\text{m}^2 \cdot \text{s}^{-1}]$
ρ	= Gas phase density	$[\text{kg} \cdot \text{m}^{-3}]$

Literature Cited

- 1) Arashi, N., Y. Hishinuma, K. Narato, F. Nakajima and H. Kuroda: *Int. Chem. Eng.* **22**, 489-494 (1982)
- 2) Carberry, J.J.: *Ind. Eng. Chem.*, **56**, 39-46 (1964)
- 3) Harold, M.P. and Dan Luss: *Ind. Eng. Chem. Res.*, **26**, 2099-2106 (1987)
- 4) Hawthorn, R.D.: *AIChE Symposium Series*, **137**, 428-435 (1974)
- 5) Hegedus, L., S. Oh and K. Baron: *AIChE J.*, **23**, 632-641 (1977)
- 6) Koberstein, E. and G. Wannemacher: 'Catalysis and Automotive Pollution Control', p. 155-172, Elsevier, Amsterdam (1987)
- 7) Marquardt, D.: *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963)
- 8) Oh, S. and J. Cavendish: *Ind. Chem. Eng. Prod. Res. Dev.*, **21**, 29 (1982)
- 9) Ullah, U. and S. Waldram: *Chem. Eng. Sci.*, **47**, 2413-2418 (1992)
- 10) Varma, A. and B. Subramaniam: *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 512-516 (1985)
- 11) Vlachou, V., D. Goula and C. Philippopoulos: *Ind. Eng. Chem. Res.*, **31**, 364-369 (1992)
- 12) Voltz, S., C. Morgan, D. Liederman and S. Jacob: *Ind. Eng. Chem. Prod. Res. Dev.*, **12**, 294 (1973)
- 13) Votruba, J., O. Mikus, Khue Nguen, V. Hlavacek and J. Skrivacek: *Chem. Eng. Sci.*, **30**, 201 (1975).