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Metal microfibers entrapped catalysts as effective ambient temperature CO oxidation catalysts

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ABSTRACT

CO oxidation reaction on a highly active Pt–CeO_2/SiO_2 catalyst was found to be diffusion controlled at ambient conditions ($T < 50\,^\circ C$; 50–90% RH); therefore, the use of smaller catalyst particles was imperative for optimum Pt utilization. Packed beds (PBs) of smaller particles (dia. < 500 μm) cause problems such as flow maldistribution and channeled flow due to cluster formation. Also these PBs are susceptible to changes in orientations and vibrations resulting in catalyst bypass and reduced activity. Nickel metal microfibrous entrapped Pt–CeO_2/SiO_2 catalysts (MFECs) were developed to circumvent these problems with the PBs. These MFECs outperformed the conventional catalyst PB with equivalent catalyst loading over a wide range of CO concentrations (100–10,000 ppm) and exhibited greater stability. The entrapment of catalyst particles has a significant impact on the heat and mass transport properties of the reactor. Therefore, the effects of transport properties on activity were investigated experimentally using diluted PBs and by reactor simulation using a transient, non-isothermal model to understand the activity improvement by MFECs. Experimental and simulation results showed that while the thermal properties significantly affect the activity, the axial mass dispersion had negligible impact on the activity. MFECs have greater thermal conductivity due to the presence of Ni fibers and the inert thermal mass of the Ni fibers was minimal (33% of the catalyst PB). MFECs have a uniform and more open (void: 0.5–0.8) structure and the entrapment of particles minimizes cluster formation. Due to these better heat and mass transport properties, MFECs outperformed PBs. Also, these MFECs are flexible and pleatable which makes them a potential candidate for CO removal applications.

1. Introduction

Since CO even in trace amounts is harmful to humans as well as the environment [1], low temperature CO removal from air finds applications in many areas ranging from emission control to breathing air purification [2]. Catalytic CO oxidation to CO_2 is the most viable option for CO removal at ambient conditions. At ambient temperature ($T < 50\,^\circ C$) catalytic CO oxidation is difficult to sustain due to the competing nonlinear influences of strong adsorption and self-poisoning (which preferentially accumulates CO on the surface) versus surface oxidation kinetics which removes CO from the surface. Further, water vapor may act as an activity suppressant by either competing with CO for active sites or by blocking the active sites for CO oxidation, for example, in the case of Au/TiO_2 catalysts [3]. After a systematic screening of numerous catalyst formulations (commercial, conventional as well as novel), the authors found that a novel 4%Pt–16%CeO_2/SiO_2 catalyst was highly active (CO conv. > 98%; CO: 100–10,000 ppm; SV: 72,000 h^{-1}) for CO oxidation at ambient conditions ($T \geq 25\,^\circ C$ and 50–90% RH) [4].

The CO oxidation reaction on the Pt–CeO_2/SiO_2 catalyst was found to be diffusion controlled at ambient conditions [4]. Therefore, use of small catalyst particles (<500 μm) was imperative to maximize Pt utilization, reduce cost and minimize the volume of the system. A conventional packed bed (PB) of smaller catalyst particles (dia. < 500 μm) has significant pressure drop and the PB is prone to cluster formation. The particle clustering in the PB could result in channeled flow, flow maldistribution and local bypass of the catalyst [5,6]. Also in the case of PBs, molecular and eddy diffusion (at particle Re > 4) [7] causes appreciable mixing resulting in mass dispersion [8]. Mass dispersion reduces the conversion per pass, as the concentration seen by the catalyst is lower than predicted [9]. Further, these PBs of small particles could get unsettled due to changes in orientation or exposure to vibrations resulting in catalyst bypass and lower activity. To circumvent these problems with the PBs of smaller particles, a catalyst carrier for small particles was needed for this application.

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Nomenclature

C	CO concentration (mol/m^3)
C_S	surface CO concentration (mol/m^3)
C_{IN}	inlet concentration (mol/m^3)
C_P	heat capacity (J/kg K)
Dax	axial dispersion coefficient (m^2/s)
E_a	activation energy (kJ/mol)
k	thermal conductivity (W/m K)
k_r	reaction rate constant (m^3/kg s)
K_A	equilibrium constant
k_0	pre-exponential factor (m^3/kg s)
k_m	mass transfer coefficient (1/s)
L	length of reactor (m)
R	universal gas constant
R_C	rate of reaction (mol/kg s)
R_{CS}	rate of surface reaction (mol/kg s)
T	temperature (K)
T_R	room temperature (K)
t	time (s)
u	superficial velocity (m/s)
z	axial dimension (m)
Greek letters	
ε	bed voidage
λ	thermal diffusivity (m^2/s) = $k/\rho C_P$
ΔH	heat of reaction (kJ/mol)
ρ	density (kg/m^3)
β	surface poisoning dependent activation energy (kJ/mol)
$\beta = 0$	(<750 ppm); $\beta = 1$ (1000 ppm); $\beta = 2$ (1500 ppm); $\beta = 3$ (2000 ppm); $\beta = 4$ (2500 ppm)
θ	surface poisoning = CS/C_{IN}

Catalyst carriers such as a monolith support or a foam support can be coated with smaller catalyst particles to form a uniform wash-coat thickness as small as 50 μm. These catalyst carriers have an open and void structure which minimizes the mass dispersion and offers lower pressure drop. The use of smaller particles minimizes the internal diffusional resistances. Monolith supports have been increasingly used in applications that require greater gas–solid contacting efficiency, for example, environmental applications involving gas phase catalytic reactions use monoliths [10,11]. Also, packed beds are inherently poor conductors of heat due to point particle contacts in the PBs; therefore, a catalyst carrier with greater thermal conductivity could significantly improve the heat transport properties of the system. For example, Visconti et al. have shown that use of metallic monolith improved activity and yield in the case of highly exothermic Fischer–Tropsch synthesis [12]. Also, metallic foams have been pursued in applications demanding higher thermal conductivities [13,14]. Thus, the catalyst carriers significantly affect the heat and mass transport properties of the reactor.

Although monolithic and foam supports offer greater gas–solid contacting efficiency, they suffer from many disadvantages such as lower volumetric catalyst loading (maximum catalyst loading: 10–15%, v/v) and excess inert thermal mass [15]. The CO oxidation reaction is highly exothermic ($-\Delta H_R = 284$ kJ/mol) which can cause appreciable temperature rise in the reactor ($\Delta T \approx 25^\circ$ for 100% conversion of 2500 ppm CO). Under ambient conditions, the temperature rise in the reactor can reduce CO self poisoning and improve reaction kinetics resulting in improved catalytic activity. However, the presence of inert thermal mass would result in lower temperature rise in the reactor during transient state which may cause delayed CO light-off and reduced overall activity. Monolithic and foam supports have significant amount of inert thermal mass (approx. 7–10 times catalyst thermal mass); therefore, they were considered inappropriate for this application.

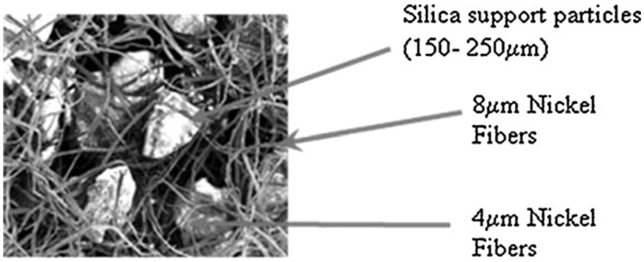

Fig. 1. SEM micrograph of microfibrous entrapped catalysts (MFEC).

Microfibrous entrapped catalysts (MFECs) that offer greater contacting efficiency while maintaining greater catalyst loading (10–50%, v/v) have been developed [16,17]. MFECs have lower inert thermal mass (approx. 1/3rd of the catalyst thermal mass) due to the presence of fibers. These MFECs typically entrap 50–300 μm particles in a 3-dimensional network of 2–20 μm fibers (polymer, ceramic or metal fibers), so the internal diffusional resistances could be minimized. A typical micrograph of MFEC is shown in Fig. 1. The entrapment of particles in a microfibrous mesh minimizes cluster formation and reduces flow maldistribution. MFECs due to their open and uniform structure reduce peaking flow in the reactor and offer lower pressure drop [6]. Axial mass dispersion can be minimized by catalyst dilution with inert [18] and these MFECs could be tailored to minimize dispersion by increasing the voidage of the MFEC (voidage: $\varepsilon = 0.5$–0.9). Also these MFECs can be made out of metallic fibers thereby increasing the thermal conductivity of the reactor [19]. These MFECs are also flexible and pleatable, as shown in Fig. 2, so the packaging issues with small particles could be eliminated. Use of these MFECs has shown significant performance improvements in a number of applications that required greater contacting efficiency and higher catalyst loading [20,21].

During this study, the use of Ni microfibrous entrapped Pt–CeO_2/SiO_2 catalyst for CO oxidation was investigated in detail. The catalyst dilution can minimize axial mass dispersion [18] and addition of an inert material to the PB changes the thermal properties of the system. Therefore, the impact of axial mass dispersion and thermal diffusivity on the reactor performance was studied experimentally using diluted catalyst PBs. The catalyst bed was diluted with inert materials differing in heat capacity and thermal conductivity, namely: silica, nickel or copper powders. Further, the relative impacts of mass dispersion, thermal diffusivity and heat capacity on the reactor performance were analyzed using a 1-D, transient, non-isothermal reactor model.

Fig. 2. Image of rolled MFEC.