Chemical Engineering Journal 271 (2015) 188–194

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Direct measurements of gas diffusivity in a washcoat layer under steady state and heated conditions

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HIGHLIGHTS

- Gas diffusivity in simulated washcoat layer at heated condition was measured.
- W–K type diffusion cell was developed to measure gas diffusivity at heated condition.
- Temperature dependence of gas diffusivity was discussed.
- Mean Transport Pore Model was used.

ARTICLE INFO

Article history:
Received 1 December 2014
Received in revised form 4 February 2015
Accepted 6 February 2015
Available online 14 February 2015

Keywords:
Catalyst
Diffusion
Porous material
Pore size distribution
Washcoat layer

ABSTRACT

A Wicke–Kallenbach-type counter-current diffusion cell was developed to measure gas diffusivity in a ZrO_2 based simulated washcoat layer under heated conditions, by using components with high thermal resistance and designing a sample holder. Gas diffusivity was measured between room temperature and 673 K. Two pairs of gases, N_2/Ar and C_3H_6/Ar, were used in the measurements. The temperature dependence of gas diffusivity was consistent with theory of gas diffusion. This verified validity of measurements under the heated conditions. The result of the measurement was successfully analyzed by Mean Transport Pore Model. The transport parameters from the Mean Transport Pore Model were evaluated as the geometric factor ψ of 0.19 and the mean diffuse pore radius r of 272 nm. With these parameters, the difference between actual operating conditions of monolithic catalysts and experimental conditions in this research can be bridged.

1. Introduction

Recent papers have demonstrated that typical catalytic reactors may be operated in the region of significant diffusion limitation [1–10]. Monolithic catalysts coated in a catalyst layer on a honeycomb-type substrate may be relatively unaffected by the diffusion limitation. This is because the catalyst layer, which is known as a washcoat layer, is thin. However, many papers have reported that the diffusion limitation can affect the performance of monolithic catalysts [11–20]. Recently, simulation studies that take the diffusion limitation into account were reported by Kota [19] and Shakya [20]. Kota et al. studied the micro-kinetics of NO_x storage and reduction on $Pt/BaO/Al_2O_3$ monolith catalyst [19]. They discussed the impact of washcoat layer diffusion and its effect on kinetic parameters, and developed a micro-kinetics model for NO_x reduction with H_2, CO, and C_3H_6 [19]. Shakya et al. ran simulations on of dual-layer and dual-brick Cu–Fe/SCR catalysts and revealed that the influence of gas diffusion was more significant in dual-layer than in dual-brick catalyst [20].

In order to design a washcoat layer to avoid the diffusion limitation, either an evaluation of diffusion limitation or an understanding of diffusion phenomena is required. Kolaczkowski et al. researched heat and mass transfer in methane combustion with monolithic catalysts [21]. They estimated the temperature dependence of the activation energy and reported that the reaction was limited by transport processes over temperatures of 770 K. Many methods to examine gas diffusivity in the washcoat layer have been reported [22–25]. Beckman [22] and Hayes [23] reported that the method for cutting a flow cell out of monolithic catalysts was suitable for monolithic catalysts of larger diameter of cells (above 2 mm). However, for smaller cells on the order of 1 mm, which are often used for three-way catalysts of automobiles, this flow cell method is not practical. For smaller cells, methods reported by Stary [24] and Zhang [25] were more suitable. Stary et al. measured the diffusivity of He and Ar through a washcoat layer using gas

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http://dx.doi.org/10.1016/j.cej.2015.02.033
1385-8947/

Nomenclature

C_i	molar concentration of component i (mol/m^3)
$D_{eff,i}$	effective diffusion coefficient of component i (m^2/s)
$D^k_{eff,i}$	effective Knudsen diffusion coefficients of component i (m/s)
$D^b_{eff,ij}$	effective binary bulk diffusion coefficient of the pair $i-j$ (m^2/s)
D^b_{ij}	binary bulk diffusion coefficient of the pair $i-j$ (m^2/s)
K_i	Knudsen diffusion constant of component i (m/s)
M	molecular weight
N_i	molar diffusion flux of component i (mol/m^{2}s)
R	gas content
r	mean transport pore radius (m)
r_e	capillary radius
y_i	molar fraction of component i
α_i	$\alpha_i = 1-(M_i/M_j)^{1/2}$
ψ	ratio of transport pore porosity and tortuosity
z	length in the diffusion direction (m)
σ_{AB}	collision integral
Ω_{AB}	Lennard–Jones potential parameter

chromatography [24]. Zhang et al. measured the diffusivity of CO through a washcoat layer with a modified Wicke–Kallenbach-type diffusion cell [25]. In these studies, direct measurement of gas diffusivity was not possible, because the washcoat layer could not be separated from the substrate. Hence, the gas diffusivity through the washcoat layer must be obtained by deducting the gas diffusivity of the substrate. This is problematic in the evaluation of transient diffusion phenomena, which is important in real catalysis such as automobile exhaust catalysis.

In our previous paper, we reported a direct measurement of gas diffusivity [26]. A sample was prepared by coating a slurry on a metal mesh and a subsequent drying-calcination process. This sample simulated the pore structure of an actual washcoat layer, which had been determined in the drying process of a coated slurry. Since the metal mesh had no diffusion resistance, gas diffusion in the simulated washcoat layer could be measured directly. An actual washcoat layer consists not only of ZrO_2 but also CeO_2, Al_2O_3, and many types of mixed metal oxides. When the direct measuring method is used in the actual R&D process, the material contained in the slurry should be selected on the basis of the components in the actual washcoat layer.

These conventional studies, including ours, had one common problem in that the gas diffusivity was measured at room temperature, whereas monolithic catalysts are employed over a wide temperature range. For example, VOC combustion catalysts operate in the range of 373–673 K [27], while for catalytic gas turbine combustors used in power generation, a monolithic catalyst is employed at 1073 K [28]. When an automotive catalytic converter is employed in the FTP cycle, the catalyst temperature is in the range of 300–1073 K [29]. There have been no studies of gas diffusivity through the washcoat layer at temperatures greater than room temperature. This may be due to the difficulty of using diffusion cells under heated conditions, e.g., because epoxy resin or rubber O-rings, which prevent gas from leaking from the diffusion cell, cannot be used under these conditions.

In this research, we have focused on directly measuring gas diffusivity in a simulated washcoat layer under heated conditions. We developed a Wicke–Kallenbach-type diffusion cell with heat-resistant properties, and the validity of measurements under these conditions was verified by two methods: measurement of the temperature dependence of gas diffusivity and analysis based on the Mean Transport Pore Model (MTPM) [30].

2. Experimental

2.1. Development of Wicke–Kallenbach-type diffusion cell for use under heated conditions

Fig. 1(a) shows a cross-sectional view of the cell developed in this research. A photograph of the cell is shown in Fig. 1(b). As shown in Fig. 1(a), a simulated washcoat layer separates the upper and lower compartments. In our previous paper [26], the cell was made with Pyrex glass@ and a rubber O-ring was used to prevent gas from leaking from the diffusion cell. In the current study, the cell was made from SUS304, with a metal O-ring, enabling measurements under heated conditions. Gas diffusivity was measured at temperatures below 673 K to avoid a chemical reaction between the evaluating gas and SUS304. The volume reducer shown in Fig. 1(a) was employed to control the linear rate in the diffusion cell. The gas for evaluation, N_2 or C_3H_6, was fed into the lower compartment. N_2 was selected as an example of a main component of the gas phase in a monolithic reactor. C_3H_6 was selected as an example of a reactant gas in catalysis. The paired gas that was used along with the gas to be evaluated was Ar since it is suitable for use with a thermal conductivity detector (TCD). Although Ar may not be present when a monolithic reactor is employed, the main purpose of this research was to investigate the gas diffusion phenomena. By using MTPM [30], the effective diffusion coefficient measured in this research may be converted to an effective diffusion coefficient under a N_2 atmosphere.

2.2. Sample

In our previous study [26], the simulated washcoat layer was applied to a metal mesh by dip coating using a slurry containing ZrO_2 powder and zirconium nitrate. After dip coating, the sample

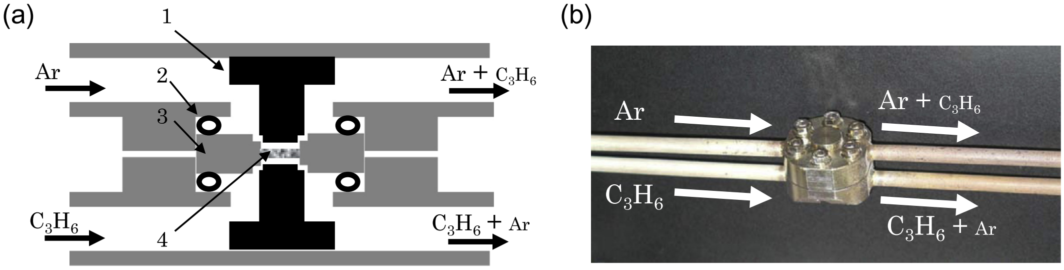

Fig. 1. (a) The Wicke–Kallenbach-type counter-current diffusion cell: (1) gas current control section, (2) metal O-ring, (3) SUS section to fix to metal mesh, and (4) simulated washcoat layer. (b) Photograph of the diffusion cell.