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Measurement of effective diffusivity in catalyst-coated monoliths

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Abstract

A review is provided about techniques that have been used to evaluate the effective diffusivity of gases in catalyst/washcoat layers, as used in catalytic monoliths.

The importance of making such measurements is described, in order to ensure that the choice of model for effective diffusivity can be verified, and if necessary an appropriate value of tortuosity can be back-calculated. Based on methods described in the literature, it is concluded that, where possible experiments should be performed on actual monolith structures, rather than those that have been reformed. The chromatographic technique is applied to a catalytic monolith and preliminary results of unpublished work are presented. A method of using a cut section from a catalytic monolith in a modified form of 'Wicke–Kallenbach diffusion cell' is also described.

Examples from the patent literature are provided showing, how interest in layered catalyst systems has started to grow, illustrating how diffusion in porous layers can be exploited to develop 'designer catalyst systems'.

Keywords: Reaction engineering; Reactors; Catalytic combustion; Monoliths; Effective diffusivity; Modelling; Kinetics

1. Introduction

The more general use of catalytic monoliths is described in a number of review articles, e.g. [1–12] and in [13–15]. In this paper, the application of such systems to support combustion reactions is considered.

In a catalytic monolith, the walls of the channels may be coated with a high surface area washcoat that contains the dispersed catalyst(s) in a porous structure, or the walls of the monolith structure may contain the catalyst as an integral part. For the reactants to reach an active catalytic site, they need to diffuse into the porous structure. This transport process is known as intra-phase diffusion and is just one of a number of steps in a catalytically supported reaction. Neither experimentalists nor developers of reaction engineering models of catalyst combustion systems, can afford to neglect whether or not diffusion in the catalyst/washcoat layer is or is not a significant factor. In the majority of cases, its catalytic combustion reactions are so fast, that diffusion in the catalyst/washcoat layer soon starts to reduce the overall rate of reaction. Although, this aspect was considered in the 1970s in some early theoretical studies of effectiveness factors for the oxidation of CO over autocatalysts (e.g. [16]), it has taken a considerable amount of time to be more generally accepted. Just by looking at a few review articles on the application of catalytic combustion, it should be clear that this requires serious consideration (e.g. [17,18]).

A general discussion of how kinetic parameters may be falsified by intraparticle transport limitations is provided in [19]. If comparative experiments are being

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performed with catalyst systems that have varying pore structures, or the intention is to determine kinetic rate expressions, then it is essential to check if diffusion in the catalyst system is significant or not, and then to decide on appropriate action. An example of such a consideration is presented in [20], where the use of an annular reactor is described. This has a thin coating of catalyst (10–40 μm) on the outside of the central tube and reactants flow in the annular gap (0.1–0.3 mm) at a linear velocity of 2–10 m/s. Groppi et al. [21], being familiar with both experimental and mathematical modelling techniques used them in a complimentary manner to design an annular reactor that would enable both inter- and intra-phase mass transfer effects to be minimised.

If a catalytic monolith is used as a membrane reactor, then pressure gradients may exist across the porous layers containing the catalyst. Further information on diffusion in membrane structures may be obtained in [22], however, in general in a catalytic monolith there are no pressure gradients across the free space in the channel and the porous layer at the wall. The movement of reactants or products in the porous structure occurs by a process known as diffusion. Three different types of mechanism are possible. These consist of ordinary bulk diffusion, Knudsen diffusion, and surface diffusion. Bulk diffusion occurs when the mean free path of the molecule is much smaller than the pore diameter, so collisions between gas molecules occur more frequently than between the molecules and the pore walls. If the pore diameter were reduced in size, such that collisions between the molecules and the pore walls became more frequent, then Knudsen diffusion would be more dominant. As described in [23, p. 136], “when a molecule strikes the pore wall it does not bounce like a tennis ball. Rather the molecule is instantaneously adsorbed and re-emitted in a random direction. The direction in which the molecule is emitted bears no relation to its original direction before the collision and, it is this randomness which provides the characteristic feature of a diffusive process”.

In [24], a review is provided of three-dimensional random network models of catalyst support structures. To illustrate how a molecule may move from a wide to a narrow pore, a possible path of collision with molecules and the walls is illustrated in Fig. 1.

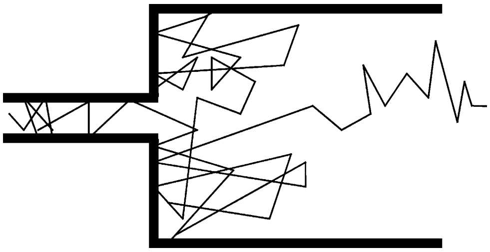

Fig. 1. Trace of a particle in a macropore connected to a micropore structure, adapted from [24].

In a review article by Krishna and Wesselingh [25], further information on intra-phase diffusion and generalisation to multicomponent mixtures may be obtained.

It is well recognised in the literature that both bulk and Knudsen diffusion mechanisms apply in catalytic monoliths. The third possible mechanism is known as surface diffusion. In this case it is possible for adsorbed molecules on the surface of a structure to move along the surface in the direction of a concentration gradient, however, according to Ruthven [23, p. 137], significant physical adsorption is seen as a prerequisite for the contributions from surface diffusion to be noticeable, and this requires temperatures not too far above the boiling point of the species considered. In most catalytic combustion applications, temperatures are elevated, molecules are chemisorbed (thin mono-layer), and therefore surface diffusion is unlikely to be of any significance, however, if diffusion experiments were to be performed at milder conditions (e.g. ambient), with hydrocarbons that could be close to their boiling points (e.g. hexane), then this aspect would need to be considered. Direct measurement of surface diffusion is not easy as this proceeds in parallel with gas phase diffusion in the porous structure. Ruthven [23, p. 138] refers to a method in [26], which involves making measurements over a wide range of temperatures, in order to deduce contributions to flux from surface diffusion.[1]

The combined effects of bulk and Knudsen diffusion processes in a porous structure are represented by a term known as the effective diffusivity. This is based

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[1] The term ‘surface diffusion’, as used in this paper, should not be confused with the migration of species that form part of the support structure in a catalyst, which is also know as ‘surface diffusion’.

on the total cross-sectional area of the porous layer and includes porosity and tortuosity either explicitly or implicitly.

In reviewing the literature, although there are plenty of papers on the subject of diffusion in catalyst pellets, there is relatively little work published on diffusion in catalytic monoliths. Even when looking at the literature on the development of mathematical models of monolith reactors, there is little evidence of the validation of the methods used to model effective diffusivities in the system studied. Siemund et al. [27], after developing a model of a three-way catalytic converter and then comparing it with experimental data, conclude that "theoretical and experimental effort must be put on internal diffusion".

In gathering data from the literature, work on the measurement of effective diffusivities in monolith catalyst supports used for the selective catalytic reduction of NO_x has also been included, as the experimental techniques are considered relevant.

2. Why is it necessary to measure the effective diffusivity in a catalytic washcoat?

Although throughout the literature there are many examples of different types of models that could be used to determine the effective diffusivity in a catalyst pellet, if they are to be applied to a catalytic monolith, then it is necessary to perform measurements on the distribution of pore sizes and respective pore volumes in the structure in order to make use of the models. In addition, in some models it is necessary to know the tortuosity in order to be able to apply a model. Hayes et al. [28], in making a comparison of the random-pore model developed by Wakao and Smith [29], and the parallel pore model by Wheeler [30], showed that for a gamma alumina monolith washcoat, that significant differences can be obtained in the values of effective diffusivity calculated. Values calculated using the random-pore model were three times and seven times larger then measured values for the cordierite and washcoat, respectively. When using the parallel pore model, provided a tortuosity factor of 8.5 and 8.1 was assigned to the support and washcoat, respectively, a match was obtained. This work has led to the development of a simple methodology to the selection of a suitable method of representing the effective diffusivity terms. By performing a measurement of effective diffusivity in a sample of washcoated monolith, then the choice of model can be verified, and if necessary an appropriate value of tortuosity can be back-calculated. These expressions can then be used in the model of the catalytic combuster.

As an aside, a study by Sharma et al. [31], of 13 commercial catalysts and supports, using helium, nitrogen, and *n*-butane as tracers is informative and illustrates with measurement and worked examples the complexity of this topic. The data was analysed using different pore models and the tortuosity factors were back-calculated and compared. Although tortuosity was found to vary with particle porosity, there was considerable spread in the data and a simple relationship could not be assumed. In general, there were similar results obtained for the three tracers studied except for a few instances, e.g. in experiments with butane over some of the materials significant adsorption was suspected. In another material, substantially high values of tortuosity were determined with nitrogen (rather than helium) and this was attributed to severe pore constriction as a result of calcining at high temperatures.

3. Measurement of effective diffusivity

One of the more well known classical methods of determining the effective diffusivity of a catalyst pellet was developed by Wicke and Kallenbach [32], by measuring the steady state counter diffusion through a pellet mounted in a cell. This apparatus is now known as the Wicke–Kallenbach diffusion cell. A cylindrical shaped pellet is mounted in the cell, with the sides sealed and the flat sides of the pellet each face a separate chamber, see Fig. 2. A concentration difference between the chambers provides the driving force to create a flux across the pellet, which is measured and used to calculate the effective diffusivity.

A transient method could also be applied using the same design of diffusion cell. A pulse of tracer could be injected into the stream feeding the upper chamber and the transient response in the output stream in the upper or lower chambers could be measured (e.g. [33,34]). A comprehensive review of such measurements has been provided in Park and Do [35].

In another classical approach, the pellets are contained in a packed bed, and a pulse (or step change)

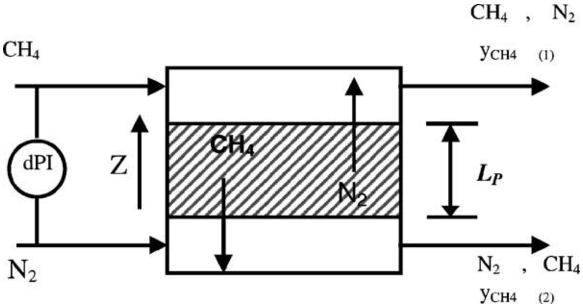

Fig. 2. Diagram of apparatus for steady state diffusion experiments in porous catalysts, adapted from [13, p. 569]).

of non-adsorbing and non-reacting tracer is introduced into the bed. The resulting transient response is measured in the outlet stream and then analysed. The spread of the tracer provides an indication of dispersion and the extent of intra-phase diffusion in the catalyst pellets.

Although the steady-state method is widely used, it suffers from the disadvantage, that because of the way in which the pellet is mounted in the diffusion cell, the method relies on the flow of gas from one side of the pellet to the other, so the dead-end pores and the pores to which access has been restricted because of the method of mounting are excluded from contributing to the flux. For catalyst pellets, comparative studies of steady state and transient methods are numerous in the literature (e.g. [36]).

Some of the techniques that have been developed for pellets, may be adapted to make measurements on a catalyst-coated monolith, however, the thin nature of this layer (10–150 μm), small mass of catalyst/washcoat per unit volume of monolith and the high open free area of the channels (60–90%) presents some interesting challenges.

One approach could involve the preparation of a washcoat slurry and then either:

(a) casting it into the shape of a pellet, or
(b) crushing samples of washcoated material and then pressing the material into the shape of a pellet.

Although these approaches are possible, the morphological form of the pellet may not be representative of the way in which the thin layer is formed in a monolith.

To overcome this problem, the following approaches have been considered.

3.1. *Measurement of flux through the wall of a single monolith channel (6 mm i.d.)*

Beeckman [37], report results from measurements of diffusion through neighbouring channels in a monolith, that had the catalyst material incorporated into the actual porous support structure of the monolith (this did not have a washcoat). In this application the diameter of the monolith channels was about 6 mm. A diffusion cell was constructed, by cutting a single channel from the monolith and this was then mounted in a larger diameter tube. As a result of a concentration gradient on either side of the wall, the flux of NO through the wall of the tube was measured and hence the effective diffusivity was determined. The method and theoretical analysis for co-current and counter-current flow conditions are also described in [13, p. 570].

If a catalyst is incorporated into the monolith structure, then this method may be appropriate, however, any contributions from the dead-end pores are excluded from this assessment.

3.2. *Using a zirconia solid electrolyte element as an oxygen ion pump*

In Mezedur et al. [38], effective mass diffusivities are measured using a zirconia oxygen sensor. Although this is an interesting technique, the support needs to be carefully constructed, and then it has to be coated with a washcoat slurry. In this paper, interesting data is provided on the washcoat in a catalytic converter. It is shown to be a highly porous layer, having different pore-size distributions at different pore length scales.

3.3. *Measurement of flux through a composite structure from the centre channel (about 3 mm i.d.) to its surrounding neighbours*

Hayes et al. [28], adapted the method described in [37] and used it on a catalyst/washcoated monolith structure. The measured values of flux were then obtained for a composite structure consisting of three layers: (a) washcoat, (b) cordierite, and (c) washcoat, see Fig. 3. By performing experiments on an uncoated

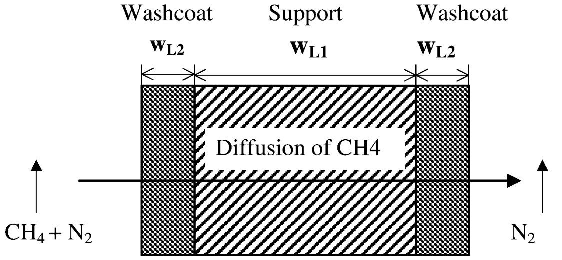

Fig. 3. Cross-section of substrate and washcoat layer showing thickness and diffusion direction, adapted from [28].

monolith and then a coated structure, the effective diffusivity in the individual layers may be calculated by assuming that a resistance in series model may be applied.

In this approach, it is assumed that there is no effect from the interface between the washcoat and the support structure. By performing experiments on samples prepared with differing thickness of washcoat, this assumption can be tested. It is shown that the key to success in predicting the effective diffusivity of the catalyst/washcoat layer lies in the choice of model and value of tortuosity used, which for a γ-alumina catalyst/washcoat layer [28] is about 8.1.

However, this method could not be used on an impervious support structure, e.g. metal monolith.

3.4. Chromatographic method applied to particles in a packed bed

Santos et al. [39], describe the use of a chromatographic method to evaluate the effective diffusivity of a catalyst, used for the selective catalytic reduction of NO_x in emissions from power plants. In the commercial application, monolith structures are used, however, in their experiments they packed a 0.0107 m i.d. column with particles, claiming to have used a catalyst of the same composition and morphology as that of a commercial monolith—unfortunately they did not explain how they achieved this. However, it should be possible to crush a monolith into a powder for such experiments. Although, if the monolith has a washcoat applied to the surface, then it would be difficult to interpret the resulting data as the composition of the particles would vary in the bed. Some could consist of substrate, others the washcoat, and some contain both.

3.5. Chromatographic method applied to a monolith structure in a tube

If applied to a section of monolith, the chromatographic method has the advantage that the contribution of any dead-end pores may be taken into account. The pathway followed by the tracer is similar to that encountered for reactants and products, however, besides the usual problems of tracer injection, entrance effects and measurement of the exit stream, there are a number of new problems to be overcome. For example:

(a) The ratio of the volume of the porous layer (washcoat) per total monolith volume is relatively small. This leads to the problem of having a relatively small volume of porous structure to accommodate the tracer and enable a discernable response to be detected.
(b) The channels could have an open free area (approximately 1 mm in hydraulic diameter) and under experimental conditions at which this type of experiment would be performed, a developing profile in the inlet section, followed by laminar flow conditions, would add considerable dispersion to the tracer, as it flows down the channels of the monolith.
(c) The distribution of washcoat is not uniform around the perimeter of the channel and may also vary in the axial direction. This adds a complication to the way in which the results would need to be interpreted.

This method could be used on a washcoat/catalyst-coated impervious support structure, e.g. metal monolith.

To test the feasibility of this method, code was used to simulate the transient response from a monolith to a pulse input of non-reacting tracer. The conditions simulated are summarised in Table 1. The results of one of the simulations are presented in Fig. 4. For a residence time of 5 s in the system, then a discernable difference in the shape of the measured output should be obtained, provided that on-line measurement is sufficiently fast.

3.6. Using a CSTR applied to a monolith structure

Moller and O’Connor [40], describe the use of a CSTR to measure the effective diffusivity in catalyst

Table 1
Conditions used to simulate the application of the chromatographic method to a monolith (courtesy of R.E. Hayes, University of Alberta, Canada)

Channel shape	Circular
Channel size	1.1 mm internal diameter
Washcoat thickness	50 μm
Substrate thickness	75 μm
Mean pore diameter	12.6 nm
Tortuosity factor	6
Washcoat porosity	0.67
Knudsen and bulk diffusion both considered in the washcoat	
Inlet temperature	550 K
Pressure	101325 Pa
Calculated residence time for plug flow in an uncoated channel	5 s
Model used	One dimensional gas flow and two dimensional washcoat, single channel model with the Taylor Aris dispersion model
A square input pulse of 2 s duration was applied	

pellets. This approach may also be viable for a catalytic monolith. By cutting sections of monolith and mounting them inside a spinning basket (with the axis facing the direction of rotation), or in a chamber through which fluid is internally re-circulated (e.g. with an impeller), then gas film mass transfer may be minimised. The author is not aware of the method being used to determine intra-phase diffusion for a monolith, however, Bennett et al. [41] did use a spinning basket to determine the reaction kinetics for a catalytic coated monolith.[2]

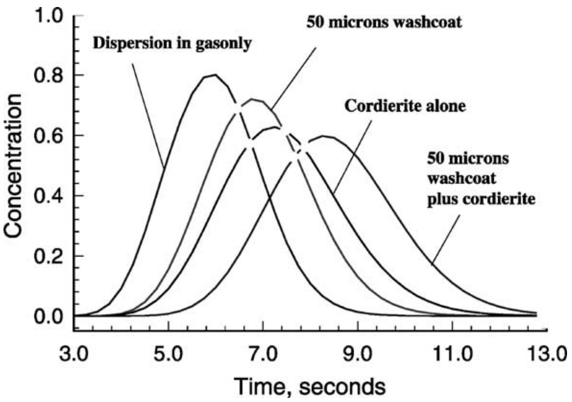

Fig. 4. Simulating a transient response from a monolith to a pulse input in tracer for conditions summarised in Table 1 (courtesy of R.E. Hayes, University of Alberta, Canada).

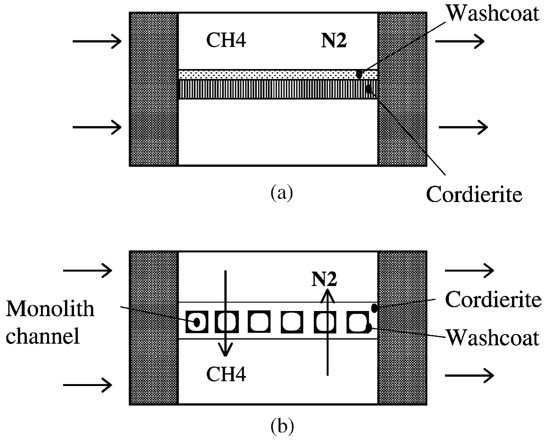

Fig. 5. (a) Using a thin wafer of cordierite that is then coated with catalyst/washcoat and mounted in a diffusion cell; (b) extension of method to a multichannel structure.

3.7. *Using a flat plate of cordierite coated with a washcoat, in a diffusion cell*

In more recent and yet unpublished work at the University of Bath (UK) it has been shown that a flat and thin wafer of cordierite can be cut from a monolith structure. This wafer is then coated with a thin layer of catalyst/washcoat that is then calcined and conditioned at conditions representative of a commercial unit. The coated wafer is then sealed in a modified form of the 'Wicke–Kallenbach diffusion cell' (see Fig. 5(a)) and experiments are performed. The transient method although technically feasible, has been found to be prone to errors associated with the very low value of residence time across the thin wafer, relative to other time delays in the system, however, the steady state method is shown to produce reliable results. The positioning of a thin washcoated plate in this type of diffusion cell, does not suffer from the associated mounting problems of a catalyst pellet in a conventional diffusion cell. Access to the sides is not denied and neither is it significant, however, contribu-

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[2] If referring to this paper the reader is also advised to consult [42], for a correct re-interpretation of some of the mass transfer coefficients.

Table 2
Summary of pore volume and pore-size analysis obtained from mercury porosimetry [28]

Material	Mesopores		Macropores	
	Mean pore diameter (nm)	Porosity	Mean pore diameter (nm)	Porosity
Cordierite	0	0	3500	0.36
Plain washcoat	10	0.58	500	0.10
Washcoat with Pd	10	0.41	400	0.06

tions from dead-end pores are neglected in the analysis. This method has now been extended to cut section from a coated monolith, performing experiments on a composite multi-cell structure, see Fig. 5(b). A special feature of this approach is the development of a technique to test coated monoliths from a production run.

4. Pore size and pore volume in catalytic monoliths

Although the classification of pores according to their size diameter does vary in the literature, the classification adopted by the International Union of Pure and Applied Chemistry (as reported in [43, p. 25] is as follows:

- Micropores: <20 A (2 nm).
- Mesopores: 20–500 A (2–50 nm).
- Macropores: >500 A (50 nm).

An example of such data is shown in Table 2. In [28], it is shown how to perform measurements on samples of (a) cordierite and (b) cordierite with washcoat, and then how to back-calculate the pore size and pore volume data for the washcoat. Experimental measurements, on a sample of cordierite support structure from a monolith, show that it consists mainly of macropores, with a mean pore diameter of 3500 nm and 0.36 porosity. On the other hand, the catalyst/washcoat layer consists mainly of mesopores with a mean pore diameter = 10 nm and porosity = 0.41, the porosity of the macropores is very small (=0.06).

5. The effect of chemical reaction on effective diffusivity

This remains a topic over which there has been a lot of debate in the literature for catalyst pellet systems. It adds another complication and discussions in [44,45] are relevant.

This topic is not covered in any detail in this paper as more of a basic understanding of diffusion in catalytic monoliths needs to be acquired before this more advanced aspect can be considered.

6. Future work

6.1. Fractal pore structures

It is clear that more information needs to be acquired on the topology of the pore network and the morphology of the pores. Coppens and Froment [46], in promoting an approach to understand catalyst pore structures, based on mathematical ‘fractals’, state that “The tortuosity factor lumps too much information to be an adequate catalyst parameter and its use is not to be recommended in future work.” This approach appears somewhat harsh, as many researchers have only in the last decade come to terms with the significance of intra-phase diffusion in catalytic combustion applications and few still remain to be convinced. In [46], they explain that the wide range of values reported for tortuosity has been explained by the influence of the network topology, of pore constrictions and of pore-size distribution effects. They argue that because of fractal pore tortuosity, the average distance covered by a diffusing molecule between two neighbouring sites is larger than the free flight distance between these sites. In simplified terms, fractals (from Latin *fractus*, meaning broken) describe the discontinuity that is encountered in moving from point to point in a porous structure. The path is very irregular and discontinuous, see Fig. 6. It is not smooth and regular as visualised by simplified and smooth cylindrical shaped channels of pore structures. By using scanning electron microscopy (SEM), the structure of the washcoat can be seen, see Plate 1. This provides

Fig. 6. Visualisation of a fractal pore, adapted from [47].

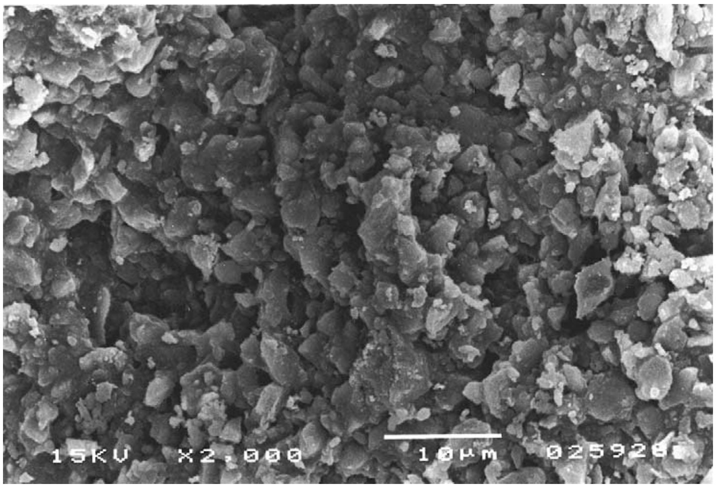

Plate 1. SEM of a section of washcoat in the corner of a cell, showing the size and shape of particles, see [13, p. 568] for further information.

evidence to support this type of thinking. It is clear that the structure is bidisperse and is constructed of microporous aggregates with a network of macropores in between. The size and shape of the aggregates is variable and discontinuous. Further examples of SEMs of γ-alumina washcoats are available in [48–50]. The size and shape of the particles is very much dependent on the method of preparation of the washcoat.

6.2. *Network of cracks in the washcoat*

In addition, cracks may be found in the surface of the washcoat, e.g. see [13, p. 568]. These probably occurred during the drying/calcining process. This network of cracks provides additional access to the washcoat structure, although its significance has not yet to the authors knowledge been quantified.

6.3. *Layered systems for 'designer catalysts'*

In [51], the catalytic combustion of methane is studied and it is illustrated how mathematical modelling techniques can be combined with experimental work to study the effect of additional layers of non-catalytic washcoat, applied as a diffusion barrier. The motivation for this work was to study whether or not these layers may be used to limit the rate of reaction and hence control catalyst temperatures under certain operating conditions. It was shown that even a thin diffusion barrier (e.g. 10 μm) was sufficient to reduce the conversion of methane from 78 to 15%.

Over the last decade, many catalyst manufacturers have taken more of an interest in this topic, as they have recognised its importance and opportunities. For example, manufacturers of catalytic converters have started to make use of these thin layers to engineer a composite catalyst layer (e.g. see SEM in [52]), with different reactions promoted in the different layers. The patent literature, in the field of catalytic converters for the purification of exhaust gases from internal combustion engines, is full of examples of how layered catalyst systems are designed and could work. For example:

(a) In Frestad et al. [53], the 'catalytical coating' consists of at least two washcoat layers. In 'a preferred embodiment one layer contains 75–100% by weight of the total amount of Pt and also contains Rh, while another layer contains the remaining amounts of Rh and Pt, respectively'. Pt and Rh are the catalysts. Many other examples are provided in this patent of preferred embodiments wherein different combinations of components are contained in the two layers. An explanation of advantages is offered: by layering this 'emphasises the unique properties of the different noble metals'. Different reactions can occur in the layers and in the bottom layer reactant composition is affected by reactions that have occurred in the outer layer. Diffusional resistance in these layers clearly plays an important role. The layers can also be designed to contain cerium oxide in one of the layers and hence exhibit an oxygen storage capacity.

(b) In Hayashi et al. [54], another two layer washcoat system is described, but the use of cerium is more of a key feature. The bottom washcoat layer includes at least cerium, zirconium, and palladium, and the top washcoat layer includes at least platinum, rhodium, barium, and cerium. The content of cerium in the top layer is set smaller than that in the bottom layer. It is claimed that "this causes the hydrocarbon conversion performance of rhodium and the nitrogen conversion performance of platinum in the top washcoat layer to be balanced properly, while maintaining the hydrocarbon conversion of palladium in the bottom washcoat layer, thereby providing an improved exhaust gas purification performance as a whole". It is also claimed that, by keeping the platinum and palladium in separate layers, the formation of the platinum–palladium alloy under high temperature conditions can be suppressed. In this example, diffusion and reaction steps are carefully balanced in the top washcoat. The layers are designed to promote different reactions in the two layers and also to physically separate the platinum and palladium.

(c) In Ishij and Nishizawa [55], the main feature of this invention, is to adsorb hydrocarbons on one of the layers, when the exhaust gas temperature from the engine is low. This occurs in the bottom layer on a material such as a zeolite. This is coated with a top layer consisting of materials such as palladium and rhodium, as precious metal catalysts, which support the three-way catalytic reactions to control emission, however, the bottom layer only extends along part of the length of the monolith, and a section before the outlet only consists of the top layer. In some cases, the layer may comprise a higher concentration of the three-way catalysts. In this design, it is claimed that, performance of the catalytic converter under cold start conditions, is improved.

(d) In Kachi and Nishizawa [56], there are now three layers in the scheme. The bottom layer acts as a hydrocarbon trap and contains zeolites. The middle and outer layer both contain noble metals as catalysts, however, the concentration of catalyst in the outer layer, is claimed to be higher than in the middle layer.

In a second embodiment of the invention, a fourth layer is added to the scheme. This now consists of a bottom layer, which 'may include alumina or silica as a main component'. This layer is thickened at the corners of the cell and serves the purpose of reducing the amount of material required in the hydrocarbon trap layer, which is then coated on top. The next two layers consist of the noble metal catalysts.

The modelling of such systems clearly necessitates the inclusion of diffusion in catalytic layers. In addition, the use of additional materials to store oxygen (e.g. cerium oxide, [57]) and to trap hydrocarbons (e.g. zeolites), would necessitate additional special consideration of the composite nature of the washcoat/catalyst structures.

6.4. *Varying the catalyst distribution along the monolith and in the radial direction in the washcoat*

Information on how the catalyst is distributed throughout the washcoat layer, will also become more important as the level of sophistication in the modelling of diffusion increases. From published data in [13, pp. 583–585], it is evident that depending on the method of coating, the distribution of catalyst can vary significantly throughout the layer. Cominos and Gavriilidis [58], show how by preparing axially non-uniform catalytic monoliths, advantages may be gained in the performance of the system.

7. Concluding remarks

It is clear that both experimentalists and mathematical modellers of catalytic combusters need to consider intra-phase diffusion in the catalytic structure.

When choosing a method to use for the measurement of effective diffusivity, it is important to consider how representative is the material on which measurements are made. If possible, measurements on actual monolith structures should be performed.

Looking at the progress made in the use of layered systems for catalytic converters, it is clear that there are opportunities to exploit diffusion characteristics and to develop 'designer catalyst systems'.

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