Cohesive strength measurement of catalyst layer: Uniform drying and on-line monitoring

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ABSTRACT

Catalysed chemical reactions usually only occur on the surface of the catalyst, therefore the rate of reaction is dependent on the amount of surface area available. In order to achieve this, the active phase is distributed over a high surface area support material.

In catalytic converters, automotive catalysts are deposited on the interior walls of a ceramic or metallic monolith in the form of a coating. The open structure of the monoliths allows the gases to pass through the catalyst without causing too much pressure drop. The strength of the coated layer is important for the life (and activity) of a catalytic converter. The coated catalyst layer can fail in both cohesive and adhesive manner, and the lack of methods to separately quantify the individual strength has become an issue. For this reason, the current paper proposes an improved method to measure the cohesive strength of a catalytic layer by implementing a uniform drying system for the preliminary method developed in a previous publication (Yang et al., 2016).

The cohesive strength obtained was found to vary with particle size, pH of catalyst suspension, and drying rate of the suspension. In short, a suspension with d_{90} approximately of $9\,\mu m$, pH = 4 and dried under a low drying rate led to a layer with high cohesive strength. Variation in the cohesive strength is explained based on particle mobility and packing behaviour obtained from on-line monitoring of the drying process of a washcoat layer. In addition the cohesive strength is also in close agreement with the DLVO theory except at very low and high pHs where dissolution of the particles may have an influence. A combination of low resistance for particle movement and longer exposure to a drying environment was found to improve the cohesive strength. Particle mobility and packing behaviour which was retrieved on a micrometre length scale from on-line monitoring is one step further to understand the origin of cohesive strength of a coated layer beyond the widely investigated macroscopic preparation conditions such as viscosity and drying rate.

1. Introduction

Catalytic converters are widely employed in petrol and diesel powered vehicles to reduce harmful emissions. In order to achieve this, automotive catalysts are distributed over a high surface area support material in a coated layer which is deposited in the interior walls of a metallic or ceramic monolith. The open structure of the monoliths allows the gases to pass through the catalyst without causing too much pressure drop.

Given the role of the catalyst layer in catalytic converters, it is clear that the mechanical strength of this layer is crucial. The catalytic activ-

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Table 1 – Strength measurement of washcoat layer.		
Method	Principle of measurement	Publication
Ultrasound vibration bath	A coated layer sample is placed in an ultrasound bath and the mass loss of the sample is logged with time.	Giani et al. (2006), Jia et al. (2007), Valentini et al. (2001), Zhao et al. (2003), Jiang et al. (2005), Sun et al. (2007) and Yang et al. (2003)
Thermal shock test	A coated layer sample is subjected to fast moving compressed hot air and the mass loss of the sample is recorded with time.	Zhao et al. (2003), Jiang et al. (2005), Sun et al. (2007) and Yang et al. (2003)
Drop test	A coated layer sample is released from a certain height with the mass loss of the sample after impact registered as strength.	Germani et al. (2007)
Abrasive test	A coated layer sample is rotated against a sand paper of a certain grade. The mass loss of the sample is recorded with the number of rotations of the sample	Ruhi et al. (2006)
Pull off method	The surface of a coated layer sample is covered by an adhesive which is further attached with a punch. The work done required to pull off the punch against the sample is noted down as the strength of the coated layer.	Zhao et al. (2003)
Scratch test	A stylus with a known dimension is employed to scratch a coated layer. The amount of force applied, the displacement travelled by the stylus and the failure pattern resulted can be used to calculate the strength of the layer.	Roth et al. (1987)

ity of catalytic converters depends solely on the availability of catalyst particles dispersed in the coated layer. The mechanical strength of a coated layer can be divided into two types: cohesive strength and adhesive strength. The cohesive strength refers to the strength within the coated layer itself while the adhesive strength is concerned with the bonding strength between a coated layer and the substrate. It should be noticed here in actual service, the coated layer is found to fail in both modes (Yang et al., 2016); therefore both the cohesive and adhesive strength are of equal importance.

Having recognised the utmost importance of the mechanical strength of a coated layer, a number of publications have attempted to measure this property in different ways as seen in Table 1.

Despite the many attempts, all of the testing methods still struggle to differentiate between cohesive and adhesive strength (Yang et al., 2016). For example, the ultrasonic vibration method which is the most commonly used approach may result in the coating sample being partially removed from the substrate and partially detached from the layer itself (the extent of the partial failure depends on a complex combination of the testing environment which includes rate of ultrasound, sample size, relative distance between source of ultrasound and sample, etc.). The same difficulty would be experienced for the other methods published in the open literature (shown in Table 1) because there is no design installed in the testing environment to differentiate between the failure mode of the coated layer.

Given the above gap in strength testing of a coated layer, there is a strong need to devise a new method which is capable of providing separate measurement of the cohesive and adhesive strengths. A new method to separately measure the cohesive strength of washcoat was described in Yang et al. (2016); in this method, a coated layer is prepared in the form of a tablet, the tensile strength of the tablet can then be regarded as the cohesive strength of the coated layer.

However the new method still suffers from one problem that is the tablets made are found to develop splitting into a top fragment and a bottom fragment at some preparation conditions. If this occurs, a cohesive strength value for the whole coated layer becomes difficult to obtain. In respect of this remaining difficulty, the current paper aims to present a method of quantifying the cohesive strength of a coated layer at a comprehensive range of preparation conditions. In addition, the cohesive strength obtained will be reported in Pascal rather than mass loss; Pascal, being the unit of stress, is more scientifically accurate to represent the strength of a material.

A model system for the washcoat drying process employed in this paper was used to study the particle packing process in the washcoat. The drying process was monitored on-line on a micrometre level

Table 2 – Particle size distribution of γ-alumina particles after milling.	
Sample 1	$d_{90} = 9.37\,\mu m$, $d_{50} = 3.76\,\mu m$, $d_{10} = 1.41\,\mu m$
Sample 2	$d90 = 4.11\,\mu m$, $d_{50} = 2.04\,\mu m$, $d_{10} = 0.78\,\mu m$
Sample 3	$d90 = 3.10\,\mu m$, $d_{50} = 1.50\,\mu m$, $d_{10} = 0.57\,\mu m$

to understand how the particles in the washcoat pack under different process parameters to lead to the different cohesive strength obtained.

2. Experimental methods

2.1. Preparation of γ-alumina suspension

The material used to produce the samples reported in this paper was γ-alumina (SCFa140; ex-Sasol) and the suspension prepared by bead milling in the presence of water. A mixture containing 200 g of γ-alumina particles and 300 g of deionised water was milled in an Eiger Mini Mill using yttrium stabilised zirconia beads of 1 mm in diameter at a speed of 3950 rpm. Approximately 70 ml of beads was used in each grinding experiment; this corresponds to 70% of the volume of the grinding chamber in the mill.

Three different particle size distributions in the γ-alumina suspension were obtained from the wet-milling as shown in Table 2. The particle size distribution was measured by laser diffraction using Malvern Mastersizer-3000.

The pH of the γ-alumina suspension was adjusted by HCl (37 wt%) and NH_3 (96 wt%) to decrease and increase the pH, respectively. Only a minimal amount of HCl and NH_3 was required to vary the pH to the desired range, therefore avoiding unnecessary dilution. The pH range tested was from pH = 2 to pH = 10.

2.2. Preparation and experimentation of catalyst tablets

The experimental setup shown in Fig. 1 was employed to produce catalyst tablets from the γ-alumina suspension. 0.6 g of the suspension was added into a tablet die made of fil-