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A Review of Measurement Techniques of Mechanical Properties of the Catalyst Layer in Catalytic Converters

Existing methods and two new methods to measure the cohesive and adhesive strength of a catalyst layer are reviewed

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A catalyst support is often used to disperse a catalyst material to enhance the contact area for reaction. In catalytic converters, a coating called the catalyst layer contains both the catalyst support and catalytically active material. Given the role of the catalyst layer in catalytic converters, its mechanical strength is of great importance as it determines the service life of catalytic converters. This review paper therefore summarises a number of methods which are currently used in the literature to measure the strength of a catalyst layer. It was identified that the methods applied at present could be divided into two groups. All methods regardless of the group have been successfully used to investigate the effect of a range of formulation and process parameters on the strength of a catalyst layer. In terms of measurement principles, Group 1 methods measure the strength based on mass loss after the layer sample is subjected to a destructive environment of choice. Group 2 methods tend to give more direct measurements on the strength of bonding between particles in a catalyst layer. Therefore, strength data generated by Group 2 methods are more reproducible between different researchers as the results are less dependent on the testing environment. However, methods in both groups still suffer from the fact that they are not designed to separately measure the cohesive and the adhesive strength of a catalyst layer. Two new methods have been recently proposed to solve this problem; with these methods, the cohesive and adhesive strength of a catalyst layer can be measured separately.

1. Introduction

Fossil fuels have been widely used as a source of power, improving human lives but creating environmental problems at the same time. Emissions from using fossil fuels are found in a number of sectors such as production processes, domestic and commercial activities. But the most significant source of emissions is from transportation. For this reason, conventional vehicles are widely required by state law to be fitted with a catalytic converter to comply with air quality standards. Harmful emissions (nitrogen oxides (NOx), carbon monoxide (CO) and unburnt hydrocarbons (HC)) are converted to environmentally friendly species in the catalytic converter to increasingly low levels.

The conversion reactions are catalysed by certain catalytically active materials which are palladium, platinum and rhodium. As shown by Equations (i)–(iii), Pd and Pt are used for oxidation reactions to neutralise CO and HC while Rh is used for reduction reactions to remove NOx (1).

$$\text{Hydrocarbon} + O_2 \xrightarrow{Pt/Pd} CO_2 + H_2O \quad \text{(i)}$$

$$CO + O_2 \xrightarrow{Pt/Pd} CO_2 \quad \text{(ii)}$$

$$NOx + CO \xrightarrow{Rh} N_2 + CO_2 \quad \text{(iii)}$$

The catalytically active materials cannot provide satisfactory conversions on their own; they are often dispersed over a catalyst layer in order to enhance the contact area to promote reaction rates (2). The catalyst layer itself is then coated on the surface of channels of a monolith (also termed as the substrate) which has a honeycomb structure to avoid excessive pressure drop as the exhaust gas passes. The concept can be seen in **Figure 1**.

It could be seen that the catalyst layer plays an important role in the design of the catalytic converter, regarding dispersing the catalytically active material. In particular, the mechanical strength of a catalyst layer determines the service life of a catalytic converter (3–5) because loss of the catalyst layer directly corresponds with loss of catalytically active material, causing a reduced conversion potential for the catalytic converter. This review paper will therefore present and discuss a range of methods which are reported in the literature to measure the mechanical strength of the catalyst layer in catalytic converters.

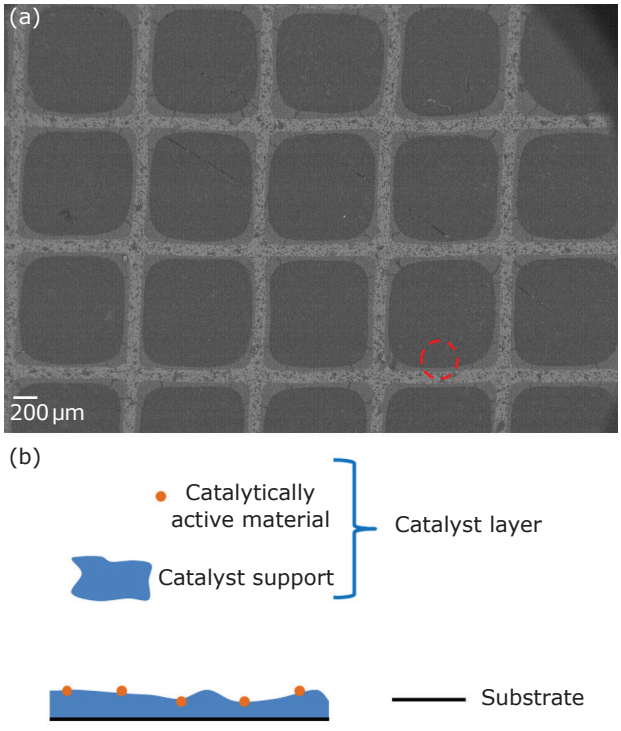

Fig. 1. (a) Details of the coating on the surface of channels in a monolith; (b) an expansion of the circled area

2. Manufacturing Procedure of Catalyst Layer

In this review, the various strength measurement techniques that are used to quantify the strength of a catalyst layer are discussed. This often requires an understanding of the formulation and process parameters to prepare the layer sample. Therefore, a brief introduction to the manufacturing procedure of a catalyst layer is given here.

The catalyst support in the catalyst layer can be made from a variety of materials. Aluminium oxide (Al_2O_3, also called alumina), titanium dioxide (TiO_2, also called titania), silicon dioxide (SiO_2, also called silica) or a mixture of silica and alumina can all be used. The reasons that these materials are a good choice is related to their satisfactory refractory properties and high surface area to volume ratios (6–8).

A catalyst layer carrying the catalytically active material is conventionally manufactured in one of two ways. The first method which is called the precipitation pathway is shown in **Figure 2** (9). The meaning of precipitation refers to a deposition process of catalytically active material in the form of a catalyst layer. A diagram showing the second method, an impregnation pathway, is shown in **Figure 3** (9). The main difference between the two routes is that in the precipitation method, the catalyst support and the catalytically active material are deposited together in one process; while in the impregnation pathway, the catalyst support of the catalyst layer is deposited first followed by a separate introduction of the catalytically active material (10).

In both methods, a suspension is obtained after the first processing step, which is wet milling. Study has shown that milling performed in the presence of water leads to a stronger catalyst layer compared with dry milling in the case of alumina (11). The possible explanation behind the observation is that wet-milled alumina particles are more positively charged and therefore become more mobile in the suspension; during the later drying process, wet-milled particles are able to travel to more favourable packing sites under drag force from the drying water to generate a higher strength for the catalyst layer (12). The solid content of the suspension is important in terms of obtaining a catalyst layer of required thickness and good uniformity. A very low solid content would

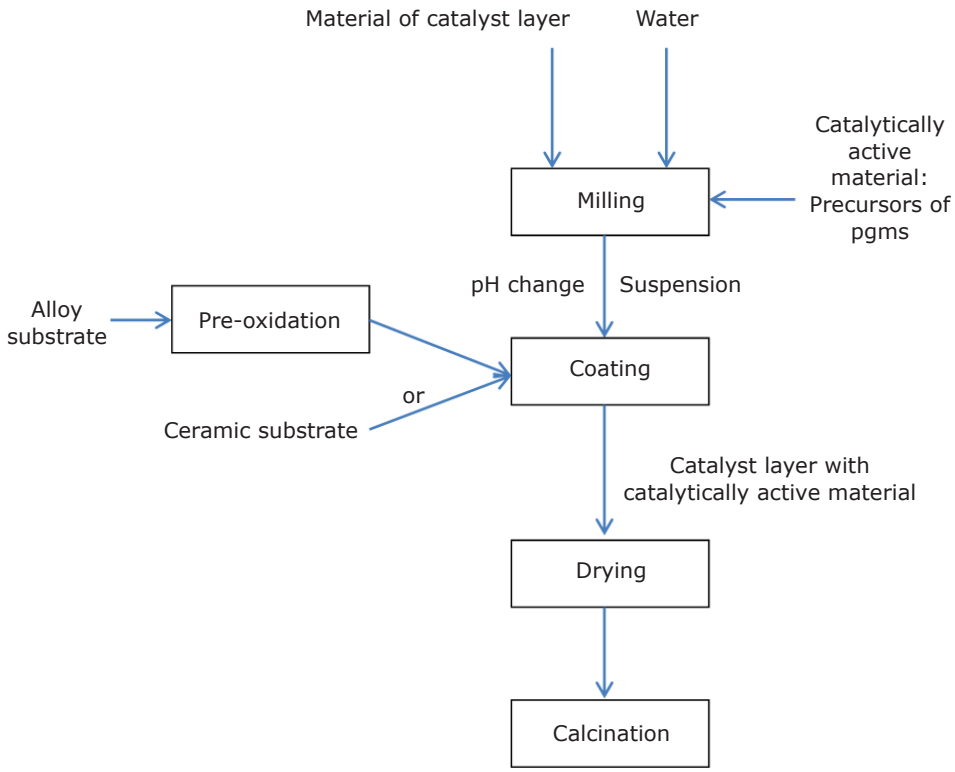

Fig. 2. The manufacturing process of a catalyst layer by precipitation (9)

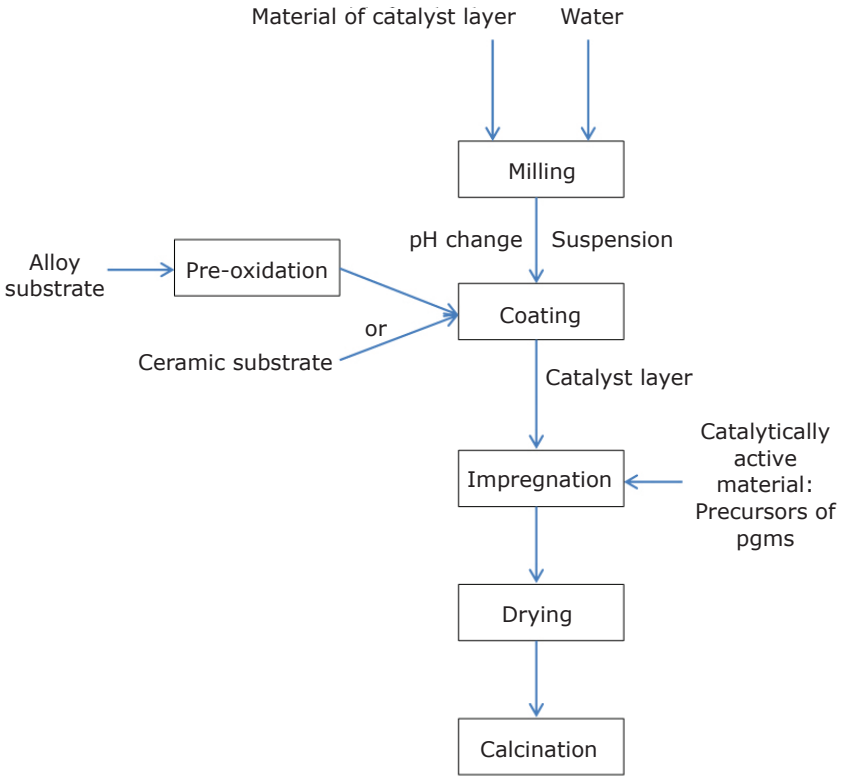

Fig. 3. The impregnation pathway to prepare a catalyst layer (9)

need a number of coating steps in order to achieve a desired loading of the catalyst layer while a very high solid content, which significantly increases the viscosity of the suspension, would lead to uneven coating. Therefore an optimum solid content exists at around 40 wt% (13).

The suspension is then subjected to pH adjustment. The suspension would contain particles only for the catalyst support of the catalyst layer in the impregnation route and particles for both the catalyst support and the catalytically active material in the precipitation route. Both particle size and the level of particle dispersion in the suspension are highly significant to the strength of a catalyst layer. Researchers have shown that smaller particles would produce a stronger catalyst layer irrespective of the material choice of the catalyst support (6, 14) because of a greater contact area being available with particles of smaller size. However, a mixture of different sized particles is needed to achieve a crack-free catalyst layer as small particles often function as the binding bridge between large particles to form a structurally continuous body (15). A high level of dispersion between particles is recommended to produce a strong catalyst layer; as particles become flocculated, the strength of the catalyst layer produced tends to drop (3–5). The definition of dispersion or flocculation is related to the isoelectric point of the particles in the suspension. If the pH of the suspension is on the acidic side of the isoelectric point, the particles are regarded to be dispersed while if the pH of the suspension is above the isoelectric point, the particles are in a flocculated state. Particles in the dispersed state are more easily rearranged under drying force to form more favourable packing; however, particles in the flocculated state are more stagnant and therefore pack less efficiently during drying to form the catalyst layer.

The coating of the suspension onto the monolith can be done in two ways. The first way, which is called dip-coating, requires the substrate to be manufactured into a monolith first, followed by pouring the suspension through the monolith or sucking the suspension into the monolith. The second way has the order reversed, but is only applicable for FeCrAlloy® substrates. The suspension is first of all coated onto the substrate which is then coiled to form a monolith (16). The coated substrate is then dried and calcined at a much higher temperature than the drying temperature. The drying process has been studied and it was shown that a slow and uniform drying process tends to result in an increase in the strength of the catalyst layer (3, 4). The calcination process is known to improve the strength of the catalyst layer after drying due to sintering (17).

The substrate can be built from an alloy material called FeCrAlloy® which consists of mainly iron with a moderate amount of chromium (20–30%) and a minor amount of aluminium (4–7.5%) or a ceramic material called cordierite which has a chemical formula of $2MgO•2Al_2O_3•5SiO_2$. In terms of building the monolith structure, FeCrAlloy® sheets are first corrugated and then folded to create a monolith. If using cordierite, monoliths are made from a paste containing precursors which is extruded and the cordierite is formed during the firing process.

3. Overview of Methods to Quantify the Strength of Catalyst Layer

A number of methods have been applied in the current literature to quantify the strength of the catalyst layer and these methods can be mainly classified into two groups as can be seen in **Table I**. Group 1 methods have a common characteristic in that they measure the strength of a catalyst layer based on mass loss of the sample which has been exposed to certain testing environments. In contrast, Group 2 methods report the strength of the catalyst layer based on units of stress or work done which give a more direct measure of the bonding strength between particles in a catalyst layer.

3.1 Group 1 Methods

3.1.1 Ultrasonic Vibration Test

As can be seen in **Table I**, the ultrasonic vibration bath is one of the most common methods currently used to evaluate the strength of a catalyst layer in literature. This strength test is conducted by exposing a sample of the catalyst layer to ultrasound of known magnitude in an ultrasonic bath for a set duration; the mass loss from the sample is then measured and used as an indication for the strength of the catalyst layer. The ultrasound is transferred by a liquid and acts to weaken the bonding between particles of the catalyst layer (18). A schematic diagram showing the experimental setup for the ultrasonic vibration test is shown in **Figure 4**.

Samples of the catalyst layer with their substrate were subjected to an ultrasonic vibration test in which they were immersed in petroleum ether

Table I Summary of Existing Techniques for Measuring the Strength of a Catalyst Layer

	Group 1 method					Group 2 method	
Reference	**Ultrasonic vibration test**	**Simulated environment**	**Thermal shock**	**Drop test**	**Abrasive test**	**Pull-off method**	**Scratch test**
(19)	✓	–	✓	–	–	✓	–
(22)	✓	–	–	✓	–	–	–
(26)	–	–	–	–	✓	–	–
(27)	–	–	–	–	✓	–	✓
(27)	–	–	–	–	✓	–	–
(8)	✓	–	–	–	–	–	–
(23)	✓	–	–	–	–	–	–
(20)	✓	–	–	–	–	–	–
(21)	✓	–	✓	–	–	–	–
(24)	✓	–	✓	–	–	–	–
(6)	–	✓	–	–	–	–	–
(14)	–	✓	–	–	–	–	–
(15)	✓	–	–	–	–	✓	–
(25)	–	✓	–	–	–	–	–

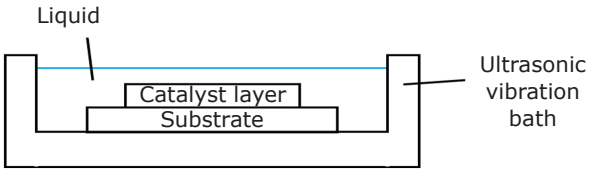

Fig. 4. Schematic diagram for the experimental setup of an ultrasonic vibration test

and treated for 0.5 min to 30 min and the weight loss after exposure was reported as a function of a time (19). Nine different samples were prepared and the weight loss results reported together with another two strength tests used in the study. Optimum conditions for preparing the sample resulted in a weight loss of 2.79% from the ultrasonic test, which was in agreement with the other two strength tests. This meant that the strongest catalyst layer could be achieved by: (a) pre-oxidising FeCrAlloy® at 950°C for 10 h; (b) coating the substrate with a primer sol and calcining at 800°C for 3 h; (c) coating with a γ-alumina suspension and calcining at 900°C for 2 h. However, the ultrasound conditions in terms of frequency and power were not given.

The effect of concentration of nitric acid (HNO_3) on the weight loss of the catalyst layer suggested that a HNO_3:Al_2O_3 ratio <2.9 mmol g^{-1} led to minimum weight loss (20). The researchers also investigated the drying and calcination temperatures. It was found that drying temperatures >100°C had no influence on the strength of the catalyst layer; in terms of calcination temperature, the lowest weight loss was at 900°C for 10 h on a FeCrAlloy® substrate. However, the actual weight loss number was not given.

The coating method was changed to electrophoretic deposition in another study (21). The calcination temperature was investigated, indicating that a higher calcination temperature led to a stronger catalyst layer. The addition of aluminium powder during the process of electrophoretic deposition was found to improve the strength of the catalyst layer. It was also shown that the use of lanthanum nitrate ($La(NO_3)_3$) solution in the deposition process increased the strength of the catalyst layer. Overall, a strong catalyst layer was associated with a weight loss of around 44%.

Petroleum ether was employed as the medium to transmit ultrasound with an ultrasonic frequency of 42 kHz, a power of 130 W and a duration of 30 min (22). In this work, it was determined that the size of particles in the suspension and the use of a binder in the suspension would play an important role in the strength of the catalyst layer. A smaller particle size would increase the strength; when the particle size was increased above 28 μm, the use of binder would dominate the strength. The strength data from the ultrasonic test were also checked

using the drop test and both results agreed with each other.

In another study, samples were immersed in an ultrasonic bath for 30 min, however no other conditions were mentioned (8). Catalyst layers were successfully prepared by depositing pseudoboehmite as a precursor of γ-alumina by a sol-gel method to fill the porous structure of FeCrAlloy® foam; the sol-gel dispersions consisted of 20% pseudoboehmite in 0.9% (w/w) HNO_3 and were aged for 72 h to reach an appropriate viscosity to produce a uniform and reproducible layer. Strong layers were quoted with a weight loss of about 4% for single layer coating and 6% for double layer coating in this work.

A low intensity ultrasonic vibration environment was claimed not to cause any noticeable breakage (23); therefore the test was performed with a power of 1000 W and a frequency of 25 kHz for 20 min, 40 min, 60 min and 80 min. The optimum conditions for preparing a strong catalyst layer were found to be: (a) 900°C for FeCrAlloy® pre-oxidisation; (b) 70°C for sol drying and 120°C for suspension drying; (c) 900°C for calcination. Strong catalyst layers had a weight loss of 8.4% to 18.3% during the ultrasonic test.

An ultrasonic vibration was carried out at a power of 220 W and a frequency of 40 kHz for 20 min (24). This research investigated the effect of apparent viscosity of the suspension and determined that a lower viscosity was beneficial for creating a strong catalyst layer whose weight loss was around 2%.

The effects of a range of formulation and process parameters have also been examined on the strength of catalyst layer using the ultrasonic bath test (15). The conditions for the test were 300 W and 60 Hz for 0.5 h in the presence of petroleum ether. From all of the parameters investigated, a strong catalyst layer was found to have a weight loss as low as 4.5%.

From the above review, it can be seen that a range of weight loss values has been observed for what is regarded as a strong catalyst layer, ranging from as low as 2–3% to as high as 40–45%. This suggests that strength data obtained from the ultrasonic vibration test is highly sensitive to the testing environment which consists of different vibration power, frequency, time and geometry of the vibration bath.

3.1.2 Simulated Environment Test

The second method in Group 1 is termed the simulated environment test. It has also gained some popularity in the current literature as a way to test the strength of a catalyst layer. The principle of this method is that a high velocity flow of hot air is passed in parallel directions over a catalyst layer sample (as can be seen in **Figure 5**) with the mass loss of the sample after the test being recorded as an indication for the strength of the catalyst layer. The high velocity of the hot air flow acts to detach particles from the catalyst layer.

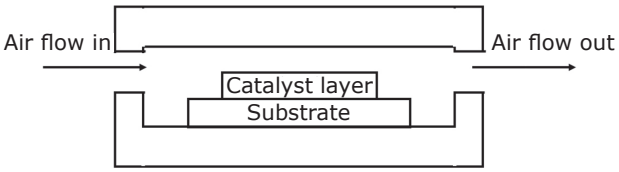

Fig. 5. Schematic diagram for the experimental setup of a simulated environment test

The strength of a catalyst layer produced from suspensions of γ-alumina powders prepared from different routes was tested using a high velocity air flow parallel to the surface of the sample. The strength of the catalyst layer was reported based on mass loss of the monolith as a function of time (6). The temperature of the air was set to 800°C and the free volume velocity was set to 100,000 h^{-1}. This set of conditions was chosen to replicate the exhaust system of car engines. The results suggested that a smaller particle size would help to increase the strength of the catalyst layer. A strong catalyst layer was associated with a 5% weight loss after the treatment. The same testing method in a similar study suggested that a strong catalyst layer would correspond to roughly 4% weight loss (25).

The testing method applied to γ-alumina (6) was also used for zirconia and titania (14) to measure the strength of the catalyst layer. The dependence of the strength of the catalyst layer (prepared from zirconia powder) on particle size was studied and it was found that a smaller particle size led to an increase in strength. It was also determined that titania powder demonstrated better strength for a catalyst layer than the other powders. Strong catalyst layers of both zirconia and titania were measured to have a 0.5% weight loss.

3.1.3 Thermal Shock Test

In a thermal shock test, catalyst layer samples are subjected to rapid temperature changes and the thermal stress developed in the process could

cause the catalyst layer sample to fail. The strength of a catalyst layer is then measured based on the mass loss of the sample after such exposure. The conditions employed in a thermal shock test were heating a catalyst layer sample to 950°C for 20 min and subsequently quenching it in water at 25°C (19); the same procedure was repeated ten times before the weight loss was measured. The best preparation conditions for the catalyst layer resulted in a 0.02% weight loss, which was in agreement with the other two strength tests (ultrasonic vibration and pull-off) performed in the same study.

Another thermal shock test (21) involved heating catalyst layer samples to 400°C and cooling quickly to room temperature. Both a higher calcination temperature and the addition of alumina powder during the deposition process improved the strength of the catalyst layer, which was in agreement with the other strength test method (ultrasonic vibration) used in the study. A strong catalyst layer was found to have a weight loss of 4%.

A thermal shock test was carried out in a muffle at 500°C for 1 h and 750°C for 5 h and cooled down immediately to room temperature afterwards (24). The research investigated the effect of apparent viscosity of the suspension and determined that a lower viscosity was beneficial for creating a strong catalyst layer whose weight loss was around 21%.

3.1.4 Drop Test

A drop test was conducted by dropping a catalyst layer sample in a monolith from a certain height (50 cm) on a hard surface with the channel of the monolith facing down; the weight loss arising from the drop was recorded to indicate the strength (22). The test can be said to work using the kinetic energy developed in the fall to break the bonding between particles. A range of weight loss (from 1% to 60%) was obtained from catalyst layers prepared by adding different binders into the suspension.

3.1.5 Abrasive Test

An abrasive test utilised a NUS-1 (Suga, Japan) abrasion tester (26). In the tester, the sample was designed to constantly move against an abrasive material which consisted of particles of 12 μm. The abrasive material was also rigidly fixed and set to apply a normal load of 3 N on the sample. The abrasive action was then repeated for 400 cycles at fixed velocity of 0.04 m s^{-1}, equalling a total distance of 25 m. Equation (iv) was then used to calculate a wear rate which served as an indicative parameter for the strength of the catalyst layer. The method was applied to study the strength of a catalyst layer coated on two different substrates (bare mild steel and phosphated mild steel achieved by chemical pretreatment). The results suggested the wear rate of a catalyst layer coated on bare mild steel had a rapid increase from the start of wearing until a sliding distance of about 18 m while the layer coated on phosphated mild steel only started to show such increase from a sliding distance of 12 m, suggesting phosphated mild steel provided better adhesion. The uncoated mild steel curve on both graphs served as a reference, indicating the service life of the different catalyst layers; the end of the service life of a catalyst layer was reached when the measured wear rate became the same as that of the uncoated mild steel.

$$\dot{W} = \frac{\Delta m}{\rho l} \quad \text{(iv)}$$

Another study which employed the abrasive test slid a catalyst layer prepared on a plate of grey cast iron against a cylinder (27). A contact pressure of 100 MPa and a sliding velocity of 0.04 m s^{-1} were used. It was found that the uncoated surface presented a straight-line relationship while the catalyst layer delayed the wear by about 50 min. This corresponded to a sliding distance of 120 m. A similar setup was used in another study where a catalyst layer coated on grey cast iron was rubbed against a cast iron disc at a pressure of 200 MPa and a 20 h running time was determined before the wear started to appear (26).

3.2 Group 2 Methods

3.2.1 Pull-Off Test

The pull-off test, as seen in **Figure 6**, measures the force that is required to pull off a catalyst layer from a substrate (19). In this research, the interface shear strength was then calculated using Equation (v). The punch was travelling at a constant speed of 10 mm min^{-1} during the test. The strongest catalyst layer gave an interface shear strength of 20 MPa, which was in agreement with the other two strength tests (ultrasonic vibration bath and thermal shock) performed in the study.

$$\tau_{interfacial} = \frac{F}{S} \quad \text{(v)}$$

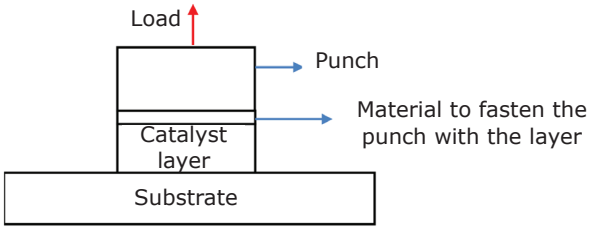

Fig. 6. Schematic diagram showing the experimental setup of the pull-off method

Another version of the pull-off test was designed to measure the work required to pull off a catalyst layer from a substrate (15). The work done was calculated by finding the area under a force over displacement curve when the force reached the point that the catalyst layer failed. It needs to be noted that this version of the pull-off test began with a compression by the punch on the sample of the catalyst layer, followed by decompression and finally pull-off. Therefore, a negative stress was present initially due to decompression before the positive stress from the pull-off action was applied.

An annular support which had an inner diameter of 2.1 cm and an outer diameter of 4.4 cm was used to firmly place a catalyst layer sample underneath. A carbon tape which had a diameter of 2.5 cm was cut to the size of the circular end of the probe (diameter = 1 cm) to connect the probe and the sample to facilitate the test. The probe withdrawal speed was set to be 10 mm min^{-1}. The investigation suggested that smaller particles led to an increase in all of the three measurement quantities concerned.

3.2.2 Scratch Test

The experimental setup of the scratch test (27) can be seen in **Figure 7**. A sample of catalyst layer was scratched with an increasing load by a stylus with a diamond tip with a defined curvature. The critical load at which the catalyst layer began to detach from the substrate was recorded and used to indicate the strength of the catalyst layer. The critical point was determined by acoustic emission and confirmed by inspection in a microscope. The critical load was found to be in an inversely proportional relationship with the length of spalling and there was a critical layer thickness above which the critical load for fracture stopped increasing.

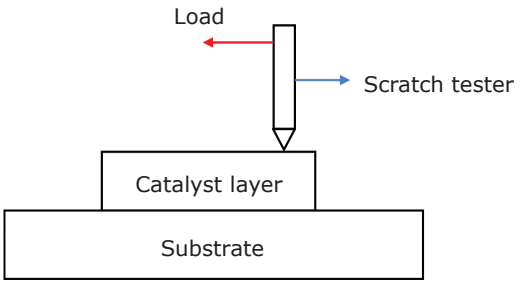

Fig. 7. Schematic diagram showing the experimental setup of the scratch test

4. Evaluation of Measurement Methods

4.1 Group 1 Methods Evaluation

Four methods are classified in Group 1. All of the methods in this group use mass loss of the sample as a way to represent the strength of the catalyst layer. The mass loss is triggered by an external effect applied to the sample, for instance an ultrasonic vibration in the ultrasonic vibration bath or kinetic energy in the drop test. Two problems are associated with the measurement techniques in Group 1.

The first problem is that the strength results obtained cannot be compared between different authors, although many authors have normalised their mass loss results and therefore report the strength results using percentage of mass loss (Equation (vi)).

$$\%m = \frac{\Delta m}{m_o} \qquad \text{(vi)}$$

This problem is represented in **Figure 8** where a wide range of weight loss values reported for a strong catalyst layer in different publications can be seen. The strongest catalyst layer in one work (24) is said to have a weight loss of only 2 wt% however work elsewhere (21) quotes the strongest layer having a weight loss of 45 wt%. The varying maximum sliding distance of the catalyst layer shown in **Table II** also indicates the same problem. The maximum sliding distance refers to the sliding distance in the abrasive test before the wear rate starts to rise. According to **Table II**, the strongest catalyst layer can have a maximum sliding distance of either 120 m or 12 m, which are widely different from each other.

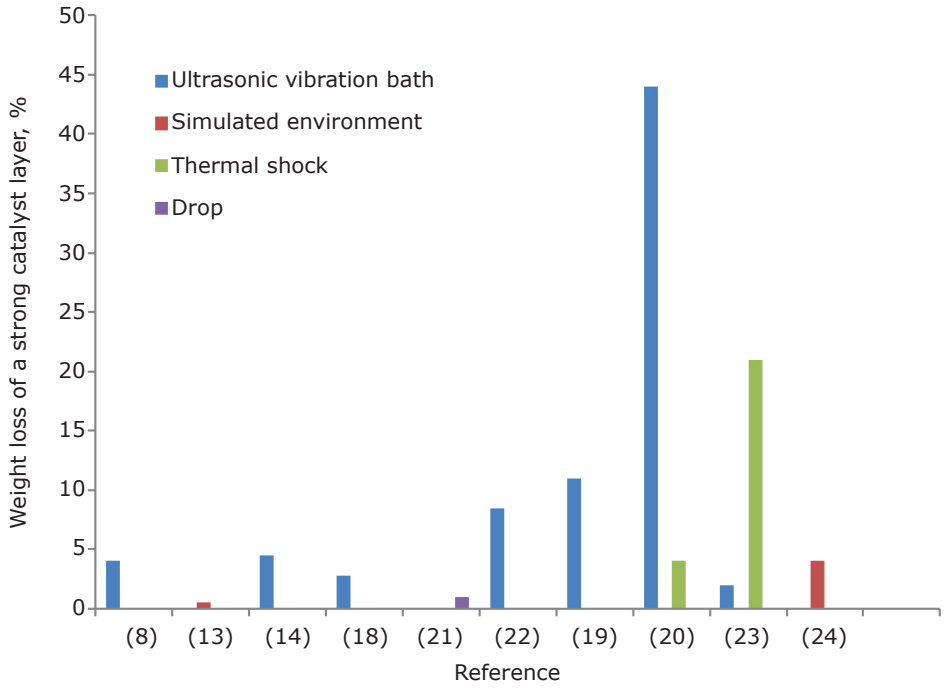

Fig. 8. Range of weight loss for a strong catalyst layer mentioned in different publications

Table II Maximum Sliding Distance of a Strong Catalyst Layer in Different Publications

	Normal compression	Abrasive size, μm	Sliding velocity, m s^{-1}	Reference	Maximum sliding distance, m
Abrasive test	3 N	12	0.04	(26)	12
	100 MPa	–	0.04	(27)	120

The first problem is due to the fact that these results are not independent of the testing environment. For example, in the case of using an ultrasonic vibration bath test to quantify the strength of the catalyst layer, if the experimental conditions (power, frequency, medium, duration) of the ultrasonic bath used are different, one can hardly make a reliable comparison in the layer strength obtained by different studies. As can be seen in **Table III**, the experimental conditions from research that applied the ultrasonic vibration test are different in most of the key testing parameters and in certain cases (8, 19, 20, 21) some of these parameters are not even given. One could also notice that a much higher frequency of ultrasound in Jiang *et al*. (40 kHz) (24) compared with Adegbite *et al*. (0.06 kHz) (15) did not result in a higher weight loss; this could be because of a lower power and shorter exposure time in Adegbite *et al*. (15). However it is unknown at the moment how much decrease in the frequency would correlate to the lower power and exposure duration employed in the study by Jiang *et al*. (24). Without the same testing environment, it would be hard to compare the strength of a catalyst layer across different studies and therefore conclude on the standards of a strong catalyst layer.

As can be seen in **Table II**, **Table IV** and **Table V**, similar problems as in the case of the ultrasonic vibration test exist in the thermal shock test, the simulated environment test and the abrasive test; the experimental conditions are different in most key testing conditions such as the hot and cold temperatures in the thermal shock test and the normal compression in the abrasive test. The difference in experimental conditions makes it difficult for different researchers to compare their results and agree on what is regarded as a strong catalyst layer.

In the case of simulated environment, it could be seen that the three publications (6, 14, 25) which applied this testing method employed the same

Table III Summary of Experimental Conditions and Results of the Ultrasonic Vibration Bath Method

Reference	Power, W	Frequency, kHz	Exposure time, min	Medium	Weight loss, %
(19)	–	–	30	Petroleum ether	2.79
(20)	–	–	30	Petroleum ether	11
(21)	–	–	30	Petroleum ether	44
(2)	130	42	30	Petroleum ether	–
(8)	–	–	30	–	4
(23)	1000	25	80	Water	8.4
(24)	220	40	20	Water	2
(15)	300	0.06	30	Petroleum ether	4.5

Table IV Summary of Experimental Conditions and Results of the Simulated Environment Method

Reference	Free volume velocity, h^{-1}	Temperature, °C	Weight loss, %
(6)	100,000	800	5
(25)	100,000	800	4
(14)	100,000	800	0.5

Table V Summary of Experimental Conditions and Results of the Thermal Shock Method

Reference	High temperature, °C	Duration, h	Low temperature, °C	Repetition	Weight loss, %
(19)	650	0.33	25	10	0.02
(21)	400	–	25	1	4
(24)	500	1	25	1	21
	750	5			

testing environment. However, from the arguments that are presented for the other testing methods in Group 1, it could be expected that further publications employing a simulated environment would suffer from the difficulty of comparison between different authors if they do not apply the exact same testing conditions. As for the drop test, given the fact that there is currently only one publication which applied this test, it would be difficult to make further comments on the results of this test.

Due to the fact that the origin of the strength of the catalyst layer is bonding between particles in the catalyst layer (cohesive) and bonding between these particles and substrate (adhesive), any indirect measurement of these bonding strengths can be affected by external factors as seen above.

A second problem for Group 1 methods is that the design of the method does not contain a way to control the failure pattern of a catalyst layer. The meaning of this statement is that a catalyst layer sample under test could fail either by the cohesive or the adhesive mode (as seen in **Figure 9**), depending on the weakest point of bonding.

From the operation principle of the ultrasonic test as described in **Figure 4**, it could be expected that the catalyst layer could fail both in the cohesive and the adhesive mode. The solution medium that is used in the ultrasonic vibration test could either remove an upper portion of the catalyst layer or penetrate to the interface between the catalyst layer and the sample and detach the catalyst layer at this interface. Similar arguments could be applied for the rest of the methods in Group 1. As can be seen in the operation principles of these methods shown earlier, there is not a mechanism designed in the method to control the failure pattern. The external force aimed to test the strength of the

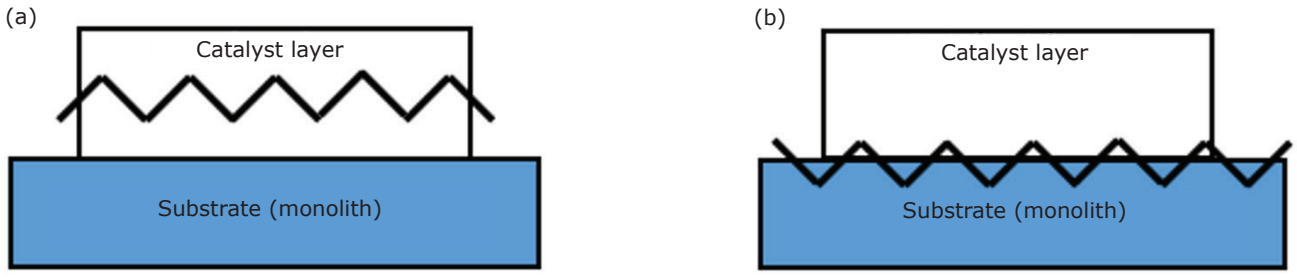

Fig. 9. Two failure modes of a catalyst layer: (a) cohesive mode; (b) adhesive mode

catalyst layer could destruct the catalyst layer in any direction, therefore a mixed result between the cohesive strength and the adhesive strength may be obtained.

However, as seen in the introduction, a catalyst layer in operation could fail in both the cohesive and the adhesive mode, suggesting that both the cohesive and the adhesive strength are important for the durability of a catalyst layer; it is essential not to mix the cohesive and the adhesive strength in any strength measurement of a catalyst layer.

4.2 Group 2 Methods Evaluation

According to the operation principles for Group 2 methods as described in **Figure 6** and **Figure 7**, it could be seen that Group 2 methods are designed to provide more direct measurement of the bonding strength between particles in order to tackle the first problem mentioned above. The explanation is given as below.

The pull-off method measures the stress required to cause the catalyst layer to fail. The stress is determined by the force at the breakage divided by the area over which this force is applied. In comparison with the great dependence of strength results from weight-loss based methods as seen before, the stress results obtained here would be less dependent on the experimental conditions of the test, for example the size of the sample can be accounted for and the testing speed of the pull-off punch (due to the brittle nature of the catalyst layer). Therefore, the stress obtained is a direct measurement of the bonding strength between particles of the catalyst layer at the failure locations and may be better reproduced by different researchers. In the end, a criterion for a strong catalyst layer in terms of stress can be set. Similar arguments can be made for the scratch method which is designed to generate a critical force value above which the catalyst layer under testing starts to crack.

Although Group 2 methods have made improvements on the reproducibility of strength results, it could be seen that they are still unable to differentiate between the cohesive and the adhesive failure as explained below; therefore the second problem still remains. In the case of the pull-off test, it can be understood that the pulling load in this method would simply cause the weakest point across both the cohesive and the adhesive strength to fail, therefore there is no mechanism involved to control the failure pattern in order to differentiate between the two modes of failure. In the scratch test, while the scratch tester is moving across a catalyst layer, the force it applies could not only cause the catalyst layer to fail from the layer itself but may also lead the catalyst layer to detach from the interface between the layer and the substrate; therefore, the cohesive and the adhesive strength results are again mixed. For the last Group 2 method, density measurement could give an overall determination of the strength of the catalyst layer while there can be a distribution of density across the thickness of the catalyst layer. This would suggest that the cohesive and adhesive strength of the catalyst layer can be considerably different.

5. New Developments in Measurement

From the discussion in the previous section, it can be seen that there is a need for a robust method in the study of strength of a catalyst layer, which could produce a more direct and distinct measurement of the strength of bonding between particles within a catalyst layer and between these particles and the substrate, based on scientific fundamental quantities for mechanics such as stress (16).

Given this understanding, new improvements have started to be made recently as an attempt to solve the remaining limitations (3, 4).

In this research, a catalyst layer has been made in the shape of a tablet under controlled conditions and the tensile strength of the tablet (as calculated by Equation (vii)) was determined as the cohesive strength of the layer.

$$\sigma = \frac{2F}{\pi Dt} \quad \text{(vii)}$$

The experimental setup involved using a cylindrical die made of filter paper; suspension with known particle size distribution and pH was then added to the die, followed by drying in controlled temperature and relative humidity conditions. Once the suspension was dried, tablets were removed from the dies and subject to calcination. The use of filter (4) was found to generate a uniform drying environment to avoid segregation of particles during drying, which was initially experienced in previous experiments (3). The outcome of this research was that the cohesive strength of a catalyst layer could be separately measured based on the unit of stress. The effects of various preparatory parameters including particle size, pH, relative humidity during drying and calcination temperature were successfully investigated.

Another technique has been described to separately measure the adhesive strength of a catalyst layer based on the unit of stress (5). The technique is based on a scraper which is designed to fail a catalyst layer sample at the interface between the sample and the substrate. Equation (viii) was then used to determine the adhesive strength. As the scraper is initially moving at the interface, a friction force is encountered. This friction force is treated as a background when computing for the effective breakage force (ΔF). The displacement travelled by the scraper from the point that the scraper first touches the catalyst layer to the point that the first breakage of the sample is noticed is regarded as the effective displacement (Δl). The technique has been successfully applied to quantify the adhesive strength of a catalyst layer prepared under different conditions such as pH of suspension and surface roughness and porosity of substrate.

$$\tau_{adh} = \frac{\Delta F}{W\Delta l} \quad \text{(viii)}$$

The new methods presented in this section have been successfully used to test the strength of a catalyst layer under different preparation conditions such as particle size, pH of suspension, drying condition and substrate characteristics. However, at the moment, these new methods have only been tested on γ-alumina; a wider range of powder materials to make a catalyst layer would need to be tried before these new methods gain more popularity in the literature.

6. Conclusions

Given the increasingly stringent emission standards, many vehicles are required by law to be fitted with a catalytic converter to combat harmful emissions. In a catalytic converter, the catalyst layer plays an important role to disperse catalytically active material to accelerate the conversion reactions; therefore the mechanical strength of a catalyst layer is of extreme importance. A lot of researchers have investigated the effect of different formulation and process parameters on the strength of the catalyst layer. This review has therefore summarised a range of strength measurement techniques to quantify the strength of the catalyst layer. There are seven main methods which are widely used in the current literature for this topic. These methods can be divided into two groups according to their measuring principles. Group 1 methods contain five methods which are designed to measure the strength of a catalyst layer based on mass loss of the layer after certain treatments. The treatment often features an external destructive environment such as ultrasonic vibration, a high-pressure gas flow or a temperature cycle. There are two drawbacks associated with Group 1 methods. The first problem is that a weight-loss based strength measurement cannot be reproduced between different researchers as the results are dependent on the testing environment and the second problem is the inability to differentiate between the cohesive and the adhesive strength of the catalyst layer. Group 2 methods tend to give results which are independent of the testing environment, eliminating the first problem; however, the second problem still remains as the measuring principle of Group 2 methods did not contain a mechanism to control the failure pattern of a catalyst layer. Certain new methods to solve both problems have been recently developed in the literature, a wider use of these methods on

different powder materials to make a catalyst layer would be needed.

Nomenclature

D	tablet diameter
F	breakage force
ΔF	effective breakage force
l	sliding distance
Δl	effective displacement
m_o	original mass
$\%m$	percentage of mass loss
Δm	weight loss
s	overlapping area
t	tablet thickness
W	width of scraper
$\dot{W}$	wear rate
σ	tensile strength
τ_{adh}	adhesive strength
$\tau_{interfacial}$	interfacial shear strength
ρ	density

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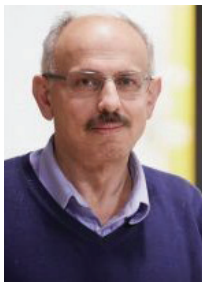

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