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Published on: 01 Sep 2014 - Canadian Journal of Chemical Engineering (Wiley-Liss Inc.)

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Blades, L., Douglas, R., McCullough, G., & Woods, A. (2014). Correlation of Static Ageing Effects on Automotive Catalysts. *Canadian Journal of Chemical Engineering*, *92*(9), 1526-1530. https://doi.org/10.1002/cjce.22012

Published in: Canadian Journal of Chemical Engineering

Document Version: Peer reviewed version

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Correlation of Static Ageing Effects on Automotive Catalysts

L. Blades^{*1)}, R. Douglas, G. McCullough, A. Woods

Abstract

This study identifies and analyses the effect that ageing time and temperature have on the CO lightoff activity of three-way catalyst samples, aged in a static air (oxidising) atmosphere. The bench ageing time (BAT) equation proposed by the Environmental Protection Agency (EPA), which describes ageing as dependent upon time at temperature, was used to calculate a range of oven ageing times and temperatures based on a RAT-A engine bench ageing cycle.

CO light-off tests carried out on cores aged between 800 °C and 900 °C have shown that it is the ageing temperature that has the greatest effect on catalyst deterioration for static ageing testing, with ageing time having little effect. These results were in contradiction to the BAT equation, an industry norm for the ageing of catalysts. This demonstrates that static ageing, whilst showing how temperature affects ageing, gives little or no time effects. The results have shown that static ageing is not representative of actual ageing on a vehicle.

Progressive ageing conducted at a temperature of 1000 °C was shown to cause a decrease in catalyst activity as the ageing time increased. However, even in these extreme conditions, static ageing gave a slower rate of ageing with time when compared to engine ageing as defined by the BAT equation. Overall, static ageing in air has been shown to produce increased ageing due to temperature than predicted by the BAT equation, but less ageing due to ageing time.

Keywords - catalyst ageing, static ageing, catalyst light-off, catalyst performance, correlation

Introduction

Regulations for automotive exhaust emissions are becoming more stringent, requiring the development of more effective catalytic control systems. The three-way catalytic converter is the most common method of reducing these emissions and uses precious metals such as Pt, Pd or Rh, as the catalytic material. Exothermic reactions can cause temperatures within the catalyst reaching higher than 1000 °C, causing thermal deactivation such as sintering of the precious metal particles and the washcoat.^[1-14] At high temperatures the precious metal particles agglomerate, decreasing

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the surface area of catalyst and reducing the catalyst activity. Sintering of the washcoat can also occur, with a decrease in surface area and a loss of internal pore structure. The washcoat undergoes irreversible phase changes, with the alumina transforming from the gamma phase, γ -Al₂O₃, through delta, δ -Al₂O₃ and theta, θ -Al₂O₃, to the stable alpha alumina, α -Al₂O₃, with loss of surface area and hence loss of catalyst activity. Catalyst deactivation can also be caused by catalyst poisoning, by masking or by fouling, resulting in a reduced number of active sites and therefore a reduced catalyst activity.

Due to the increasing complexity of modern automotive aftertreatment systems, and the slow and expensive nature of testing and ageing catalyst samples on-road or on an engine test bench, much more rapid laboratory testing and ageing methods, as well as computer simulation models are now becoming a critical part of the automotive catalyst design phase. A study carried out by Blades et al.^[15] showed how the QUB global catalyst simulation model, which was first developed by McCullough^[16] and later enhanced by Stewart,^[17] could accurately simulate the light-off behaviour of catalyst samples for tests conducted on two different laboratory catalyst test rigs. The model was also able to show that good correlation existed between both methods.

Many laboratory catalyst ageing and testing methods have been conducted as an alternative to the on-road or engine test bench methods. Kallinen et al.^[5] compared engine ageing to thermal ageing in a laboratory, which was performed by static ageing in an oven and dynamic ageing in an infrared furnace. It was shown that static oven ageing, in an oxidising atmosphere, caused the greatest catalyst deterioration of the two laboratory methods, but the infrared furnace ageing correlated better to engine ageing. Hietikko et al.^[6] performed thermal ageing in a tubular furnace for a static oxidising atmosphere, and dynamic inert and reducing atmospheres. This study also showed that the greatest catalyst deterioration occurred for the catalyst sample aged in the static oxidising atmosphere. BET testing was used to show that the thermal deterioration became critical between temperatures of 850 °C and 900 °C. Lassi^[7] also showed that thermal degradation of automotive catalysts begins between temperatures of 800 °C and 900 °C. Fernandes et al.^[8] carried out thermal ageing on catalyst samples in a static air oxidising atmosphere and a dynamic stoichiometric atmosphere. It was shown using CO light-off tests that the oxidising atmosphere caused the greatest deterioration. Moulijn et al.^[9] and Bartolomew^[10] also showed that sintering is more severe in oxidising atmospheres than reducing, and Perrichon et al.^[11] and Gonzalez-Velasco et al.^[12] observed that in oxidising atmospheres sintering of the catalyst support material was most extensive.

The effect that ageing time has on the deactivation of automotive catalyst samples has been analysed in a number of studies. Kallinen et al.^[5] state that catalyst ageing is strongly dependent on

the ageing time. Hietikko et al.^[6] observed that ageing time was a critical variable in the oxidising atmosphere, although secondary to ageing temperature and atmosphere, and had most influence at ageing temperatures below 950 °C. Light-off tests conducted by Fernandes et al.^[8] showed shifts in light-off to higher temperatures as the ageing time was increased at ageing temperatures of 900 °C and 1200 °C. Yang^[13] showed the effect that ageing time had for a dynamically aged catalyst. An increase in ageing time caused a decrease in the noble metal particle dispersion, an increase in sintering and therefore a rise in the noble metal particle average diameter, and also a decrease in CO light-off activity. Research conducted at the Toyota Motor Company by Baba et al.^[18] found that the rate of precious metal sintering is directly proportional to the oxygen concentration of the ageing atmosphere, and therefore increased ageing occurs in oxidising atmospheres.

This study aims to identify and discuss how catalyst ageing in a static environment relates to ageing time and temperature, using laboratory testing methods that are used in industry. The BAT equation is used to determine the ageing times at each ageing temperature for the static ageing procedure.

BAT Equation

Before an automobile manufacturer can introduce a new motor vehicle into commerce, the manufacturer must obtain an Environmental Protection Agency (EPA) and/or CARB certificate of conformity indicating compliance with all applicable emissions standards over the vehicle's useful life period.^[19] Instead of running the vehicle on a road cycle for the full useful life mileage, the EPA proposed that manufacturers can perform accelerated ageing on an engine test bench. The ageing is performed by repeating runs of a bench cycle for a period of time calculated using the standard bench ageing time (BAT) equation.

The BAT equation is used to calculate the appropriate length of time to age a catalyst system on an ageing bench to yield equivalent emission deterioration as running a vehicle on an approved road cycle. The BAT equation is based on an Arrhenius equation which relates chemical reaction rates with temperature. The EPA states the BAT equation as;^[19]

$$t_e = t_h e^{\left(\left(\frac{E_a}{R_0 T_r}\right) - \left(\frac{E_a}{R_0 T_v}\right)\right)}_{(1)}$$

Where:

 $E_a/R_0 = R = Catalyst thermal reactivity coefficient.$

 t_h = The time measured within the prescribed temperature bin of the vehicle's catalyst temperature histogram, adjusted to a full useful life basis.

 t_e = The equivalent time to age the catalyst at the temperature of T_r on the catalyst ageing bench.

 T_r = The effective reference temperature is the constant temperature that would result in the same amount of ageing as the various temperatures experienced during the bench ageing cycle.

 T_v = The mid-point temperature of the temperature bin of the vehicle on-road catalyst temperature histogram.

This equation is important for this research as it allows the time to be calculated for ageing on an accelerated bench cycle, which will produce ageing equivalent to that of a road cycle. In this work the BAT equation has been applied to static ageing in a furnace oven, for times at temperatures equivalent to a RAT-A bench ageing cycle.

Experimental

One standard commercial three-way catalyst, with a volume of 1 litre, a 100 g, 95 % palladium, 5 % rhodium loading, and a channel density of 900 channels per square inch, was used in this study. The catalyst had a cylindrical ceramic cordierite honeycomb structure, onto which an alumina-ceria washcoat was bonded. From this full size catalyst brick four cylindrical cores were extracted using a coring tool, all the way through from the front face to the rear. These cores are referred to as A, B, C and D throughout this study. Each of these cores were then divided into three smaller cored samples, each with a 30 mm diameter and 25 mm length, and labelled 1, 2 and 3. For example, the three cored samples taken from core A were labelled A1, A2 and A3. Figure 1 shows the full size catalyst brick and the one of the 30 x 25 mm cored catalyst samples.

Figure 1 – Cored sample and catalyst brick

Each of the cored samples were de-greened in a furnace oven, in air, at 750 °C for a period of 8 hours in order to achieve reaction stability and to bring all samples to a similar level of activity. This procedure is described by McAtee et al.^[20] Baseline CO light-off tests were conducted for all cored samples in order to show this. These activity tests were performed using the Horiba SIGU 2000. Catalyst light-off is used to indicate the efficiency of an automotive exhaust catalyst and is defined as the temperature of 50 % conversion. The procedure for the CO light-off tests conducted using the SIGU is described by Blades et al.^[15] The gas concentrations used were, 10 % CO₂, 1 % O₂, 0.5 % CO, 5 % H₂O and balance N₂. The space velocity used was 60000 hr⁻¹, giving a flow rate of 17.674 L/min.

The Horiba SIGU 2000 Series Gas Generator and Catalyst Test System generates a simulated exhaust gas, and temperature profile, to allow testing and evaluation of catalyst samples. It is used to test cored samples taken from full size bricks as it is not capable of testing commercial full size catalyst bricks. The SIGU is widely used in the catalyst industry. Figure 2 shows a schematic of the SIGU system.

Figure 2 – Schematic of Horiba SIGU 2000 System

From a series of gas bottles a gas mixture is blended to the required concentration, as inputted by the user. This gas blend then passes through a humidifier section, at which point water vapour is added to the flow if specified. The mixture then enters the reaction furnace where it is heated and passed through the catalyst sample. The gas is vented to exhaust and an analyser can sample both upstream and downstream of the catalyst. Both the Horiba MEXA 7000 and the Horiba MEXA 6000FT gas analysers were used in this study to measure and analyse the exhaust gas concentrations throughout the test. Temperature measurements were taken at the inlet and outlet of the sample for the entire duration of the tests.

After the baseline light-off tests had been carried out on all of the de-greened cored samples, static ageing was conducted in a furnace oven, in air, for ageing temperatures and times calculated using the BAT equation. Samples were aged for ageing times equivalent to 50, 100 and 200 hours of a RAT-A ageing cycle, at 800, 850 and 900 °C. According to the BAT equation, all samples aged for the same equivalent ageing time, no matter what the ageing temperature, should be equivalently aged. Core A1 (aged for 82.85 hours at 800 °C), core C1 (aged at 850 °C for 39.2 hours) and core B1 (aged for 19.75 hours at 900 °C) are all aged to the equivalent of 50 hours on a RAT-A cycle. The EPA recommends an R factor for the standard bench cycle of between 17500 and 18500, depending on the vehicle type, however if a different ageing cycle is used the R value is expected to be different. For this study ageing times were calculated using an R value of 18000. Table 1 shows the ageing procedure carried out on each cored sample.

Table 1 – Ageing times and temperatures for cored samples

Catalyst core D1 was aged at 1000 °C at time intervals of 10 and 20 equivalent ageing hours, progressively up to a total equivalent ageing time of 200 hours for the RAT-A cycle. Table 2 shows the progressive ageing procedure carried out on the cored sample D1.

Table 2 – Ageing times and temperatures for progressive ageing

After each sample had been statically aged it was tested again for CO light-off activity. This was done in order to determine the level of thermal deactivation.

Results

Table 3 shows the results of the baseline CO light-off tests conducted on all of the cored samples after de-greening. It can be seen that all samples show a very similar level of activity, with the light-off temperatures varying by only 8.5 °C.

Table 3 – Baseline CO light-off results

The CO light-off test results for the cored samples after the static ageing procedure, as described in Table 1, are presented in Table 4. The samples taken from core A, which were aged at 800 °C, each show activity very similar to the baseline results, for all ageing times, with a maximum difference of 3.5 °C existing between the baseline and aged light-off temperatures. This would indicate that static ageing, in an oxidising atmosphere at 800 °C has no effect on the CO light-off temperature of these particular formulations of three-way catalytic converters.

Samples C1, C2 and C3, which were aged for the equivalent of 50, 100 and 200 hours respectively at 850 °C, each show an increase in light-off temperature after ageing, but all to a similar level. This indicates that each of the three samples have experienced the same level of thermal deterioration. The difference between the baseline and aged light-off temperature for sample C1 was 8.5 °C, 11.5 °C for sample C2, and 9 °C for sample C3.

The same effect occurs for samples B1, B2 and B3, which were aged for the equivalent of 50, 100 and 200 hours respectively at 900 °C. All of the samples showed an increase in light-off temperature to the same deteriorated level. B1 showed an increase of 29.5 °C from the baseline to the aged level, B2 showed an increase of 33.5 °C, and C3 showed an increase of 35 °C.

Table 4 – CO light-off test results for statically aged samples

Figure 3 – Static ageing results based on equivalent ageing times for a RAT-A cycle

Figure 3 shows the light-off temperature plotted against ageing time for each ageing temperature. It can clearly be seen from the graph that as the ageing temperature increases, so too does the light-off temperature, showing greater thermal degradation of the catalyst. Ageing temperature therefore plays a very important role, as would be expected, for thermal deterioration to occur. It is also clear that, at each temperature, all samples have reached a similar level of degradation and that ageing time has no effect above the initial 50 hours equivalent ageing. The samples aged for 50

hours gives the same level of thermal deactivation as ageing a sample for 200 hours for all of the ageing temperatures tested. It is predicted that the light-off variation between samples is due to a variation in precious metal particles from one core to the next, which is also indicated by the initial baseline light-off test results.

According to the BAT equation each of the samples aged at 50 hours (A1, B1 and C1) should be aged to similar levels, as should the samples aged for 100 hours and those for 200 hours. However, as the ageing time has not had any effect on the light-off temperatures this has not been the case. As the samples are not aged to equivalent levels this suggests that more ageing is occurring than expected. This may be due to the high oxygen concentration of the ageing atmosphere, causing increased catalyst deactivation. From the BAT equation it would be expected that as the ageing time increases the catalyst activity decreases, with a corresponding increase in light-off temperature. This change in light-off temperature is expected to follow a logarithmic trend, with a more rapid increase occurring initially before levelling off. Results have shown that this is not the case for ageing temperatures between 800 °C and 900 °C. Therefore, it can be seen that the BAT equation does not accurately illustrate the catalyst ageing that occurs on a vehicle, for ageing temperatures between 800 °C.

Table 5 shows the results of the CO light-off tests conducted on core D1 after each ageing step of progressive ageing, at an ageing temperature of 1000 °C. The light-off shift is shown in Figure 4. For ageing at this temperature it can be seen that, in most cases, a shift to higher light-off temperatures does occur as the ageing time increases, indicating that ageing time does play a role in catalyst degradation. An initial ageing of 1.18 hours in the oven causes a light-off shift of 45.5 °C from the baseline light-off temperature. After 23.6 hours of ageing the light-off temperature shifted 17 °C further. This is in contrast to ageing at temperatures between 800 °C and 900 °C were ageing time caused no shift in the light-off temperature.

After the initial 1.18 hours of ageing, it can be seen that most ageing occurs in the first 11.8 hours (100 hours equivalent on a RAT-A cycle), with a light-off shift of 11 °C being observed. In the final 11.8 hours of ageing the light-off shift is only a further 6 °C. This indicates that ageing proceeds at a more rapid rate at the lower ageing times. At higher ageing times the change in light-off temperature between each ageing step decreases, showing that most of the catalyst ageing has already occurred. Further ageing of this sample would be required to prove this trend.

From the baseline light-off activity, of sample D1, to the activity after 23.6 hours (200 hours equivalent on a RAT-A cycle) of ageing, the performance has reduced by 40%. However, by using the BAT equation, with the activation energy for CO oxidation of approximately 100 kJ/mol,^[17] it is estimated that the performance after 23.6 hours should only be 5% of the initial performance. Therefore, even though static ageing at 1000 °C has shown a decrease in catalytic activity with respect to ageing time, it is occurring at a much slower rate than when compared to engine ageing as defined by the BAT equation. This suggests that the BAT equation does not relate to static ageing in air, and that static ageing does not accurately represent engine ageing of an automotive catalyst.

Table 5 – CO Light-off test results for progressive ageing at 1000 °C Figure 4 – Light-off temperatures for progressive ageing of sample D1

Conclusion

CO light-off test results conducted on cored catalyst samples, at ageing temperatures between 800 and 900 °C, have shown that under static ageing conditions in air, ageing time has no effect on thermal ageing. Ageing temperature does however play an important role. These results were in contradiction to the BAT equation, which predicts ageing due to time at ageing temperature. Static ageing carried out at an ageing temperature of 1000 °C for a range of ageing times up to the equivalent of 200 hours on a RAT-A cycle, has shown that an increase in ageing time results in decreased activity. However, even in the extreme conditions of 1000 °C, which is close to the sintering temperature of the washcoat, and an oxidising atmosphere, static ageing does not give accurate ageing characteristics with time when compared to engine ageing as defined by the BAT equation. For static ageing, it can be seen that the decrease in catalyst performance is occurring at a much slower rate.

It has been shown that the BAT equation does not apply to static ageing. Static ageing is an ageing method which is widely used in industry, however this research suggests that it is not representative of the dynamic ageing that occurs ageing that occurs on-road, where ageing time has been shown to have an effect. In this study ageing time was only shown to have an effect for an ageing temperature of at least 1000 °C. Static ageing in air has been shown to cause increased ageing due to temperature than predicted by the BAT equation, but less due to time. These effects may be due to the high oxygen concentration of the ageing atmosphere.

Further work on dynamic ageing must be conducted in order to see if any correlation exists between static ageing and dynamic ageing under laboratory conditions. Ageing in various ageing

atmospheres is also required in order to analyse the effects of oxygen concentration in ageing environment.

Nomenclature

BAT	Bench ageing time
BET	Brunauer-Emmett-Teller
CARB	California Air Resources Board
со	Carbon mioxide
CO ₂	Carbon dioxide
Ea	Activation energy (kJ/mol)
EPA	Environmental Protection Agency
H ₂	Hydrogen
H₂O	Water
N ₂	Nitrogen
NO	Nitric oxide
O ₂	Oxygen
Pd	Palladium
Pt	Platinum
QUB	Queen's University Belfast
R	Thermal reactivity coefficient
Ro	Universal gas constant (J/molK)
RAT-A	Rapid ageing test
Rh	Rhodium
te	Equivalent ageing time (h)
t _h	Time within the prescribed temperature bin of catalyst temperature histogram (h)
тнс	Total hydrocarbons

- T_r Reference temperature (K)
- T_v Mid-point temperature of temperature bin on catalyst temperature histogram (K)

Greek Letters

α-Al ₂ O ₃	Alpha alumina
u A1203	

- γ -Al₂O₃ Gamma alumina
- δ -Al₂O₃ Delta alumina
- θ -Al₂O₃ Theta alumina

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