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Review article

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## **Recent Advances in Gasoline Three-Way Catalyst Formulation – A Review**

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## Abstract

Development of three-way catalyst (TWC) technology has been critical in maintaining air quality regulations for gasoline engines via the conversion of pollutants from the internal combustion engine exhaust. The development of improved TWC formulations is an important challenge for automotive industry. Indeed, in order to meet increasingly stringent environmental regulations around the world, the development of more efficient catalysts depends on a complete understanding of the many parameters related to TWC design. In this review paper, some of these parameters are examined in relation to TWC performance, and especially low temperature activation performance, with a focus on more recently published work. In particular, washcoat composition, platinum group metal ratios and loading, and substrate design are considered. The effect of these parameters with regard to the conversion efficiency of carbon monoxide, unburned hydrocarbons, and nitrogen oxides pollutants is summarized.

## Keywords

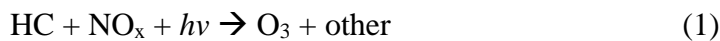
Three-way catalyst, ceria, zirconia, alumina, oxygen storage capacity, platinum group metals, washcoat

## 1. Introduction

Global air pollution caused by human activities and industries has been a major public health concern, particularly in urban areas. The impact to health services and society at large is significant, and the majority of cities worldwide do not meet World Health Organization (WHO) air quality guidelines.<sup>1,2</sup> Recognition of this problem led to the introduction of legislations controlling and imposing limitations on pollutant emissions at the exhaust of vehicles. These legislations led to the development of catalytic converter technology in the 1970s to control and treat these pollutants. While gasoline engine exhaust composition can

vary based on design and driving conditions, typical operating conditions are 0.5 vol. % CO, 3500 ppm HC, 900 ppm NO<sub>x</sub>, 0.17 vol. % H<sub>2</sub>, 10 vol. % H<sub>2</sub>O, 10 vol. % CO<sub>2</sub>, 0.5 vol. % O<sub>2</sub>, and the balance N<sub>2</sub>.<sup>3</sup> Initially, Pt/Pd or Pt/Rh oxidation catalysts were developed to limit hydrocarbon and carbon monoxide emissions, later developing into three-way catalysts (TWCs) which also convert NO<sub>x</sub> emissions.<sup>4</sup>

While carbon monoxide levels are controlled because of its very high toxicity, hydrocarbons and NO<sub>x</sub> are dangerous because they react to form photochemical smog in the presence of sunlight:<sup>4</sup>



Satisfactory emission control is achieved within a three-way catalyst via the simultaneous oxidation of carbon monoxide and hydrocarbons to carbon dioxide and water, and the reduction of nitrogen oxides to nitrogen gas. However, other reactions, such as the water-gas shift reaction or reaction of pollutants with water or hydrogen, can occur as well.<sup>3</sup>



Three-way catalyst design consists of a monolith substrate, high surface area washcoat with oxygen storage promoter materials, the active catalyst (platinum-group metals, or PGMs), and promoter materials.<sup>4</sup> The substrate has a honeycomb structure and is usually made from cordierite, but metallic foil substrates have been developed as well. The washcoat contains a doped alumina-based material (Al<sub>2</sub>O<sub>3</sub>) due to its high surface area and good thermal stability and resistance to sintering. Ceria (CeO<sub>2</sub>) or ceria-based materials are used as a promoter due to ceria's oxygen storage capacity (OSC). Without any OSC function, the ratio of oxygen to

fuel needs to be tightly controlled with a specific stoichiometric ratio to achieve the best conversion rates, typically an air-to-fuel ratio of 14.7:1 (Figure 1).<sup>3,5</sup> This is because while CO and hydrocarbons are converted to CO<sub>2</sub> under oxidizing conditions, the reduction of NO<sub>x</sub> to N<sub>2</sub> only shows good conversion efficiency under reducing conditions. However, cerium ions can easily switch between 3+ and 4+ oxidation states via the creation and regeneration of oxygen vacancies, which allows the ceria-containing catalyst material to store oxygen from the exhaust stream when it is in stoichiometric excess, promoting conversion of NO<sub>x</sub>, as well as release oxygen to the exhaust stream when it is deficient, promoting conversion of CO and hydrocarbons to CO<sub>2</sub>. This expands the air-to-fuel ratio ‘window’ under which acceptable catalyst performance is achieved for all three reactants.<sup>6</sup> Typically, a CeO<sub>2</sub>-ZrO<sub>2</sub> blend is used to improve thermal stability. Pt or Pd are used as the active oxidative catalyst, with Rh included for the reduction of NO<sub>x</sub> to N<sub>2</sub>.<sup>3,5</sup>

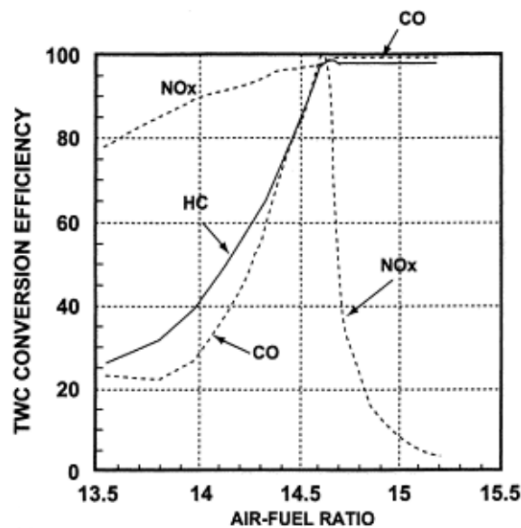


Figure 1. Three-way catalyst performance in terms of CO, HC, and NO<sub>x</sub> performance as a function of air/fuel ratio. Reproduced with permission from Elsevier.<sup>7</sup>

In addition to promoting reducibility, ceria stabilizes the noble metal catalysts in a dispersed state, hindering sintering at high temperatures via the formation of oxidized Pt-O-Ce bonds in

presence of oxygen.<sup>8</sup> Because cerium can easily cycle between oxidation states, it allows the Pt to return to a more catalytically active metallic state during stoichiometric conditions (Figure 2). In contrast, a similar mechanism does not exist for Pt/alumina systems.

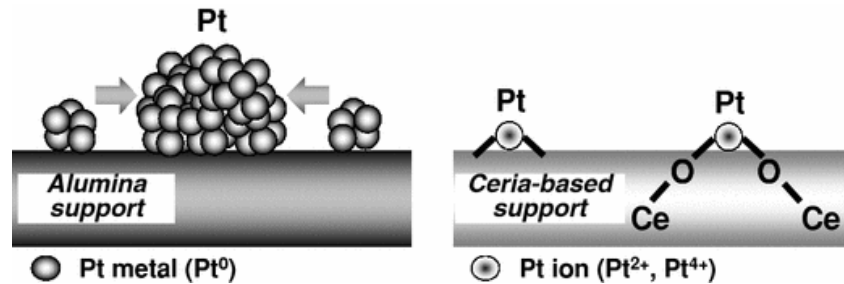


Figure 2. Sintering inhibition on Pt/ceria compared with Pt/alumina support. Reproduced with permission from Springer.<sup>8</sup>

A significant shortcoming in modern TWC design is cold-start performance during the initial minutes of a vehicle journey. TWCs depend on the elevated temperatures provided by the engine exhaust to operate with satisfactory conversion rates. During this start-up period, the low engine exhaust temperature (typically <250 °C) only slowly raises the temperature of the catalyst itself.<sup>9</sup> However, good conversions are typically only achieved at temperatures > 300 °C.<sup>10</sup> Cold-start emissions can account for a high proportion of total trip emissions – sometimes up to 50% in urban areas where shorter trips are the norm.<sup>11,12</sup> Therefore, strategies to either enhance low-temperature catalytic performance or heat the three-way catalyst more quickly will have the largest impact on improving overall TWC performance.

The focus of this review will be on the design of three-way catalysts to enhance light-off temperatures and low-temperature catalytic performance. In particular, the effect of washcoat composition, precious metal catalyst loading (Pt, Pd, and/or Rh), and substrate design will be examined.

## 2. Washcoat Composition

Alumina ( $\text{Al}_2\text{O}_3$ ) is the main material in most TWC washcoat formulations due to its stability at high temperatures.<sup>10</sup> A ceria ( $\text{CeO}_2$ )-based material is typically dispersed over or incorporated into the alumina layer to provide oxygen storage capacity to the TWC, enhancing conversion rates. Generally, a ceria-zirconia ( $\text{CeO}_2$ - $\text{ZrO}_2$ ) solid solution is used instead of pure ceria – the inclusion of zirconium ions into ceria's crystal lattice can enhance the material's oxygen storage capacity and improve thermal stability. This is important because TWCs can be exposed to extremely high temperatures (800-1000 °C) for extended periods of time. Exposure of ceria to these temperatures leads to severe sintering phenomena. This can cause a number of issues that affect TWC performance: loss of surface area, loss of available reactive oxygen within the ceria lattice, further sintering of the active metal catalyst, and reduction in contact area between the ceria and alumina washcoat. However, using ceria-zirconia somewhat mitigates these issues. Additionally, the 'controlled deposition' of ceria-zirconia onto alumina can prevent its transformation from high surface area  $\gamma$ -alumina to its low surface area  $\alpha$  form.<sup>3,5</sup>

Thermal stability of TWC materials can be further improved by the addition of other 'promoter' elements, such as alkaline earth metals or any of the trivalent rare earth metals.<sup>13</sup> While  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  solid solutions with a composition of  $x = 0.4$ - $0.6$  have been shown to have good OSC values compared with other Ce/Zr ratios, these materials also undergo phase separation after long-term (>100 h) aging at 1000 °C. However, the introduction of trivalent rare earth metals (Y, La, Pr, Nd) can stabilize the material – resulting in an improved surface area and higher OSC value after long-term aging. Dopants can also improve ceria's oxygen storage capacity.<sup>14</sup>

The type of oxide support can influence the oxidation state and dispersion of Pt, Pd, or Rh catalysts, and thus affect performance. This can inform which washcoat layer a particular metal catalyst will be deposited onto. For instance, ceria and titania supports improve the reducibility of Pd particles to form metallic Pd, which generally provides better low-temperature performance than Pd/Al<sub>2</sub>O<sub>3</sub>.<sup>15</sup> On the other hand, Rh has the potential to interact too strongly with Ce-rich supports, forming Rh-O-Ce bonds. ZrO<sub>2</sub> has been reported as a more beneficial support for preserving catalytically active metallic Rh after aging in air.<sup>16</sup>

Below, various aspects of washcoat composition are discussed, and results from literature are summarized in Table S1 in Supporting Information. Results are shown in terms of light-off temperature (T<sub>10</sub> and/or T<sub>50</sub>) for conversion of CO, HCs, and NO<sub>x</sub>. T<sub>10</sub> and T<sub>50</sub> are defined as the temperatures at which 10% and 50% conversion are achieved, respectively. Experimental parameters are summarized in Table S2 in Supporting Information, with select values shown in Figure 3.

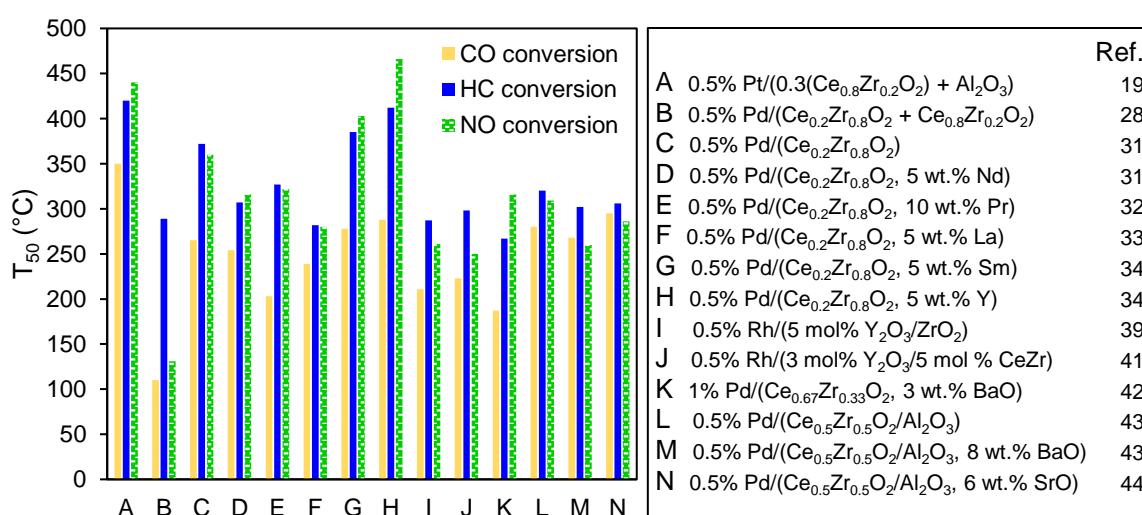


Figure 3. Select T<sub>50</sub> values of CO oxidation, hydrocarbon oxidation, and NO reduction for catalysts with various washcoat compositions.



## 2.1 Addition of ceria-zirconia to washcoat

Compared with pure alumina washcoats, ceria-zirconia shows many improvements for three-way catalysis. Lang *et al* examined the effect of using either  $\text{CeO}_2\text{-ZrO}_2$  or  $\text{Al}_2\text{O}_3$  as a support material for a Pd catalyst, finding that for CO oxidation, the Ce-Zr catalyst showed clear improvements in terms of light-off temperature.<sup>17</sup> For HC oxidation, while light-off performance was similar, the Ce-Zr catalyst was able to achieve full conversion at a lower temperature than the alumina catalyst. Zheng *et al* performed a similar study, using commercial BASF washcoat materials and a Rh-based catalyst.<sup>18</sup> They found that Rh and alumina had strong metal-support interactions, leading to the formation of rhodium aluminate and catalyst deactivation, while Rh-CeZr interactions were weaker and more reversible, allowing the Rh to remain in its catalytically active  $\text{Rh}^0$  state. For both metals, deposition on CeZr was advantageous compared with deposition on  $\text{Al}_2\text{O}_3$  due to ease of oxygen vacancy formation in CeZr (Figure 4). Because CeZr can create oxygen vacancies by releasing oxygen from its lattice structure, it can quickly provide this oxygen to react with CO and hydrocarbons, allowing them to oxidize to  $\text{CO}_2$ . In contrast,  $\text{Al}_2\text{O}_3$  does not have the capability to generate oxygen vacancies, so reactions proceed more slowly by reacting directly with oxygen adsorbed on the surface of Pd.

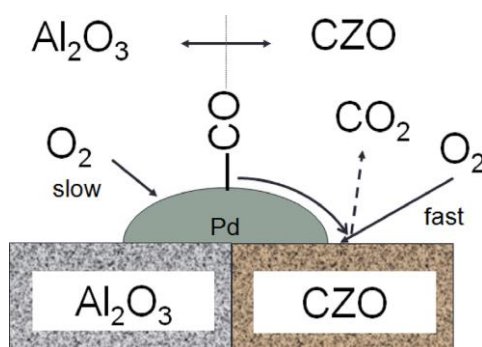


Figure 4. Oxidation of CO on Pd/Al<sub>2</sub>O<sub>3</sub> vs. Pd/CeO<sub>2</sub>-ZrO<sub>2</sub>. Reproduced with permission from Elsevier.<sup>17</sup>

Ozawa *et al* looked into modification of alumina with ceria, producing three catalysts: Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/(CeO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>), and Pt/(Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>).<sup>19</sup> Here, the incorporation of ceria and zirconia into the washcoat material improved light-off performance for HC and NO oxidation. The ceria-zirconia both inhibited sintering of Pt and provided additional OSC. While this study examined the addition of CeZr materials to already-synthesized alumina, Chen and Chang developed a novel Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/ZrO<sub>2</sub> mixed oxide material, in which Ce, Zr, and Al precursor materials were simultaneously coprecipitated into a single material.<sup>20</sup> This was compared as a washcoat material for a Pd-based catalyst with a more traditional CeO<sub>2</sub>/ZrO<sub>2</sub> mixed oxide physically blended with Al<sub>2</sub>O<sub>3</sub>. They found that the Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/ZrO<sub>2</sub> washcoat was more thermally stable – inhibiting sintering of both the Pd particles and the ceria-zirconia component of the washcoat, which improved low-temperature catalytic performance. In a ‘real-world’ test, Chen and Chang attached the catalysts to a 3.5 L GTDI engine on a 2010 model vehicle with low-temperature exhaust. Here, while both materials showed similar performance for NO<sub>x</sub> removal, the Al<sub>2</sub>O<sub>3</sub>/CeO<sub>2</sub>/ZrO<sub>2</sub> was superior in terms of HC conversion.

The choice of where to deposit PGM catalysts on the washcoat can have a significant influence on TWC performance. Yamamoto and Tanaka explored this by designing a TWC containing both Al<sub>2</sub>O<sub>3</sub> and a CeZr component, but only depositing Pd particles on either the alumina or ceria-zirconia, not both.<sup>21</sup> They found that under static operating conditions, the Pd-Al<sub>2</sub>O<sub>3</sub> catalyst performed better due to improved dispersion of Pd particles on the washcoat, but under dynamic conditions (more realistic – with fluctuating concentrations of O<sub>2</sub>, H<sub>2</sub>, and CO), the Pd-CeZr catalyst showed better performance because it had enhanced resistance to sintering.

## 2.2 Ceria-zirconia ratio

Many different ceria-zirconia ratios have been employed in TWC designs.<sup>22,23</sup> In the first generation of CeZr-based washcoat materials developed in the late 1980s, Zr was introduced in quantities up to 20 mol % to provide thermal stability. This limitation was due to the chosen production method – impregnation of already-synthesized ceria powders in an aqueous zirconium nitrate solution. Several years later, second-generation CeZr materials were developed in which any molar ratio of ceria and zirconia could form nearly perfect solid solutions. In 1998, third-generation alumina-ceria-zirconia materials were developed, using  $\text{Al}_2\text{O}_3$  particles interspersed amongst CeZr particles to inhibit sintering (Figure 5). This design uses the more thermally stable  $\text{Al}_2\text{O}_3$  particles as a ‘diffusion barrier’ between CeZr particles, preventing them from sintering and agglomerating into larger particles at high temperatures. This preserves the oxygen storage capacity of the washcoat material, which would otherwise decrease with sintering and loss of surface area upon high temperature exposure.

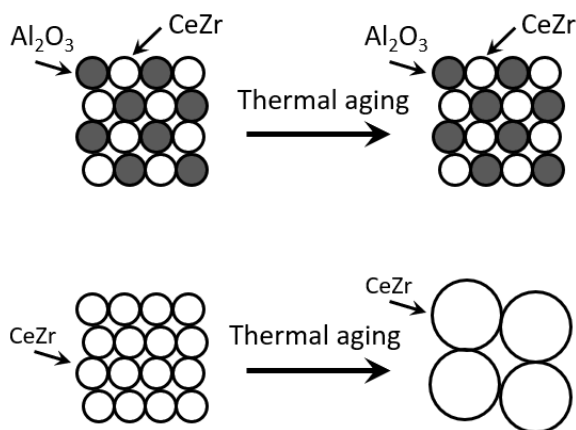


Figure 5. Sintering behaviour of CeZr and CeZr/ $\text{Al}_2\text{O}_3$  particles upon aging.

Typically ceria-zirconia materials with approximately 40-60% ceria content are considered to have the highest OSC, and thus enhanced catalyst performance.<sup>13,24</sup> Priya *et al* find that  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  has the highest OSC, while Madier *et al* report that  $\text{Ce}_{0.63}\text{Zr}_{0.37}\text{O}_2$  has the highest

OSC.<sup>25,26</sup> In a more complex mixed oxide experiment, Priya *et al* also synthesized a series of  $\text{Ce}_{0.6}\text{Zr}_{(0.4-x)}\text{Al}_{1.3x}\text{O}_2$  oxides ( $x = 0, 0.1, 0.2, 0.3, \text{ and } 0.4$ ), finding that  $\text{Ce}_{0.6}\text{Zr}_{0.2}\text{Al}_{0.26}\text{O}_2$  had the highest oxygen storage capacity.<sup>27</sup> However, such materials can undergo phase separation into separate Ce-rich and Zr-rich particles at high temperatures. Lan *et al* examined this phenomenon by synthesizing  $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ ,  $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ ,  $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ , and a physical mixture of  $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2 + \text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ , as a support for a Pd-based TWC.<sup>28</sup> They found that using a physical mixture of Ce-rich and Zr-rich particles from the beginning was advantageous compared with the 50-50 CeZr material (which would separate into Ce-rich and Zr-rich phases anyway). This material contained numerous interfacial boundaries between different crystallites, which both hindered high-temperature sintering and provided more lattice defects, improving OSC.

Other design considerations can inform Ce-Zr ratio choice as well. For instance, while materials with higher Ce levels can store and release the most oxygen, they do so more slowly than Zr-rich materials, which release smaller amounts of oxygen, but more quickly. Aoki *et al* proposed a system in which the front half of a TWC contains a Zr-rich washcoat and the rear half a Ce-rich formulation.<sup>29</sup>

## 2.3 Rare earth and alkaline metal promoters

In addition to Ce, Zr, and Al, rare earth and alkaline earth metals are often used as promoters to further improve OSC and thermal stability. Guo *et al* synthesized a series of  $\text{Ce}_{0.35}\text{Zr}_{(0.65-x)}\text{Nd}_x\text{O}_2$  supports for use with a Pt-Rh catalyst.<sup>30</sup> The inclusion of Nd in the washcoat improved OSC and catalytic activity up to 15 mol % Nd – with higher levels of Nd, performance declined.  $\text{Ce}_{0.35}\text{Zr}_{0.5}\text{Nd}_{0.15}\text{O}_2$  was shown to be the best-performing washcoat material out of those tested.

Wang *et al* examined the addition of Nd, Pr, La, Sm, or Y dopants in a Zr-rich Pd/Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> catalyst (3-10 wt. % dopant levels).<sup>31-34</sup> In agreement with Guo *et al*, Nd improved catalyst performance, although here 5% Nd-Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> was the washcoat material with the best low-temperature performance. The addition of La (5 wt. %) and Pr (8-10 wt. %) also improved catalytic activity, but Sm and Y-doped catalysts performed poorly, resulting in higher light-off temperatures than the undoped Pd/CeZr catalyst. Of the materials examined in these studies, the Pr-doped Pt/CeZr catalyst showed the best performance – with fresh catalyst light-off temperatures (T<sub>50</sub>) of 152, 200, 174, and 157 °C for CO, HC, NO, and NO<sub>2</sub> removal, respectively. After calcination at 1100 °C for 4 h, light-off temperatures were 203, 332, 336, and 203 °C for CO, HC, NO, and NO<sub>2</sub>, respectively.

The same group also examined the same dopants for a Ce-rich Pd/Ce<sub>0.67</sub>Zr<sub>0.33</sub>O<sub>2</sub> catalyst (molar ratio of dopant to Ce – 1:8).<sup>35</sup> All dopants improved catalytic activity compared to the undoped Pd/CeZr, due to improved interactions between PdO and the catalyst support. Out of the five dopants, Pr and Nd showed the best low-temperature activity. This was attributed to a more homogeneous solid solution being formed, compared with the La, Sm, or Y-doped materials. The T<sub>50</sub> of aged catalysts was as low as 267 °C for HC oxidation, 267 °C for NO reduction, and 186 °C for NO<sub>2</sub> reduction (Figure 6).

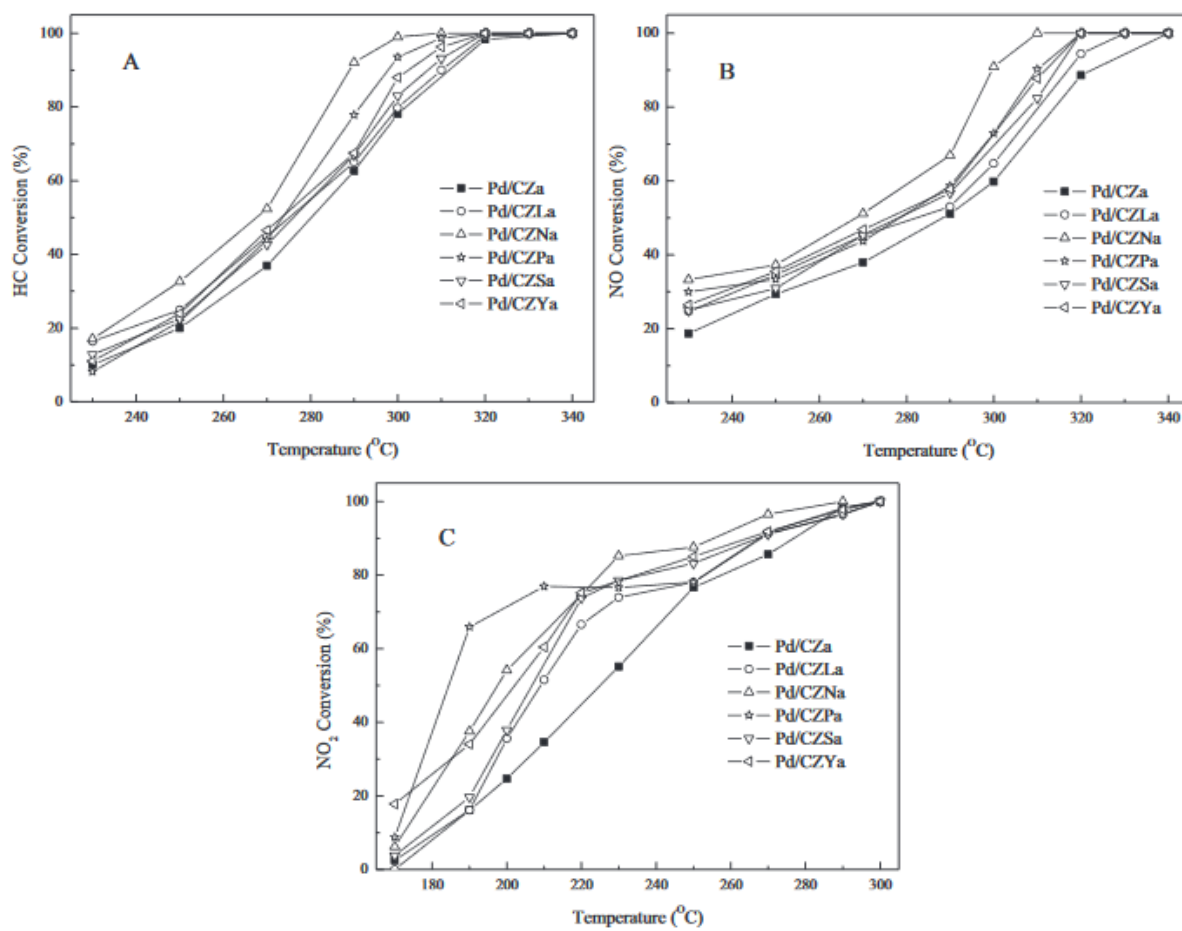


Figure 6. Conversion rates of HC, NO, and NO<sub>2</sub> for aged Pd/CeZrM catalysts (M = Nd, Pr, La, Sm, Y) under stoichiometric conditions. Reproduced with permission from Elsevier.<sup>35</sup>

Zhou *et al* also looked into the effect of Y, Nd, and Pr dopants, synthesizing a series of Pd/(0.4CeO<sub>2</sub>/0.5ZrO<sub>2</sub>/0.05La<sub>2</sub>O<sub>3</sub>/0.05M) catalysts (M = Y<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, or Pr<sub>2</sub>O<sub>3</sub>).<sup>36</sup> Light-off temperatures achieved were slightly higher than those reported for the ceria-rich Nd- or Pr-containing catalysts of Wang *et al*, despite a higher Pd loading (1 wt. % vs. 0.5 wt. %). This is potentially due to higher zirconia content reducing OSC in the washcoat material.

The effect of Y or La dopants on a Pt+Rh/CeO<sub>2</sub>-ZrO<sub>2</sub>-M<sub>x</sub>O<sub>y</sub>/(3 wt. % La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) catalyst was investigated by Jiaxiu *et al*.<sup>37</sup> The catalysts were hydrothermally aged for 5h at 1000 °C. In agreement with Wang *et al*'s study on Ce-rich washcoat materials, both dopants improve metal dispersion and low-temperature catalyst performance, particularly after aging. This

study shows that the beneficial effect of rare earth dopants is maintained even with alumina included in the washcoat composition.

In a similar study, Papavasiliou *et al* compared the performance of a Pt/Al<sub>2</sub>O<sub>3</sub>/Ce<sub>0.4</sub>Zr<sub>0.5</sub>La<sub>0.1</sub>O<sub>1.95</sub> catalyst with a commercial Pt-Rh TWC.<sup>38</sup> The synthesized catalyst had a Pt loading of 0.5 wt. %, while the commercial catalyst's metal loading was 2.25 wt. %. In this study, two versions of synthetic exhaust were used – one without H<sub>2</sub>O and CO<sub>2</sub>, as is often reported in the literature, and one with 10% each H<sub>2</sub>O and CO<sub>2</sub> to simulate a more realistic 'real-world' exhaust. For the experiment including H<sub>2</sub>O and CO<sub>2</sub>, the synthesized Pt/AlCeZrLa catalyst showed better low-temperature performance than the commercial catalyst, despite a much lower metal loading. However, the opposite was true for the experiment without H<sub>2</sub>O and CO<sub>2</sub> in the exhaust stream, underlining the need to make such experiments mirror real-world conditions as closely as possible (Figure 7).

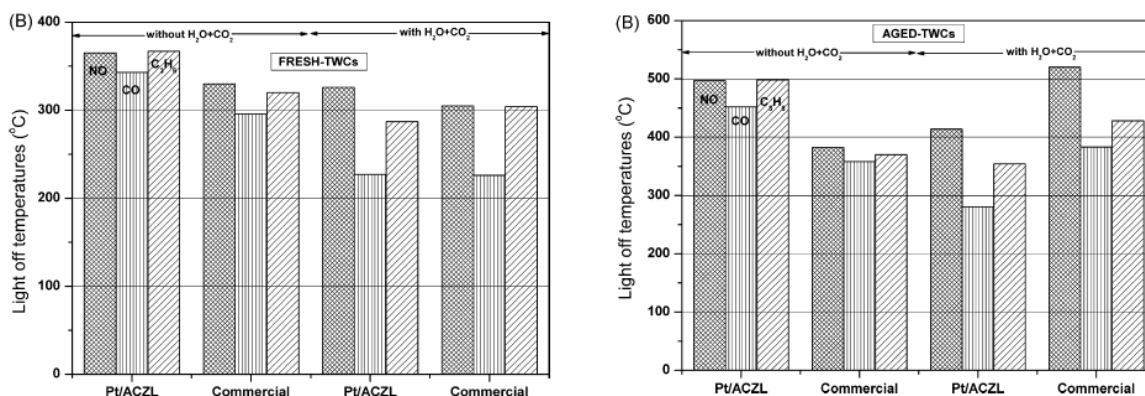


Figure 7. Light-off temperatures ( $T_{50}$ ) of fresh and aged Pt/Al-Ce-Zr-La and commercial catalysts, under simulated exhaust conditions (with or without H<sub>2</sub>O and CO<sub>2</sub>). Reproduced with permission from Elsevier.<sup>38</sup>

Zirconia-based oxides can be used to support Rh particles to avoid unfavorable interactions between Rh and ceria. Haneda *et al* examined the use of 5 mol % doped ZrO<sub>2</sub> as a support for a Rh catalyst.<sup>39,40</sup> La, Pr, Nd, Y, Ce, Sm, Gd, Tb, and Dy were chosen as potential dopants. In

contrast to the ceria-based formulations discussed above, Haneda *et al* report that the inclusion of La, Pr, and Nd reduce catalyst performance for the Rh/ZrO<sub>2</sub> system. However, Y, Ce, Sm, Gd, Tb, and Dy improve catalytic activity. The best-performing catalyst support was Y-doped ZrO<sub>2</sub>. The level of improvement compared with undoped Pd/ZrO<sub>2</sub> was correlated with the level of Rh dispersion. In particular, Rh interactions with Y<sub>2</sub>O<sub>3</sub> helped stabilize the Rh particles in a dispersed state and prevent sintering, thus improving catalytic activity. Haneda *et al* have also reported that adding 5 mol % CeO<sub>2</sub> to the Rh/Y-ZrO<sub>2</sub> catalyst system further improves performance due to enhanced catalyst reducibility.<sup>41</sup> However, higher levels of Ce reduce performance by allowing for excessively strong Rh-ceria interactions which create stable, inactive oxidized Rh particles.

Yang *et al* and Lan *et al* looked into the addition of BaO to Pd/CeO<sub>2</sub>-ZrO<sub>2</sub> and Pd/CeO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, respectively.<sup>42,43</sup> Yang *et al* found that it was possible to synthesize a homogeneous single-phase Ce/Zr/Ba solid solution with enhanced reducibility. For catalysts aged in air for 4h at 1100 °C, the 5 mol % BaO catalyst showed the best performance for HC and NO removal. However, CO oxidation was negatively impacted due to the Ba doping inhibiting Pd-CO interactions, which decreased the number of active sites for CO oxidation on the catalyst surface. Including alumina in the washcoat composition, Lan *et al* found that with lower (4-6 wt. %) BaO levels, the Ba would preferentially combine with Al<sub>2</sub>O<sub>3</sub>, acting as a stabilizer. At 8 wt. % BaO, some of the Ba enters the Ce/Zr phase, forming a solid solution with enhanced oxygen mobility, reducibility, and thermal stability. However, at 10 wt. % and above, segregation of a separate BaO phase occurs, which distorts the catalyst's physical structure and has a negative impact on catalytic activity. 8 wt. % was determined to be the ideal BaO level in the Pd/CeO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system.



Lan *et al* also examined the impact of incorporating SrO into a similar Pd/CeO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> TWC.<sup>44</sup> Similarly to BaO, SrO strongly interacts with the alumina phase to improve thermal stability. A two-phase Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>-SrO/Al<sub>2</sub>O<sub>3</sub> nanostructure is formed, improving reducibility, stability, and Pd dispersion. However, while improvements in catalytic activity were seen compared to a Pd/CeZrAl catalyst, the SrO-doped TWC did not outperform the BaO-doped system in terms of light-off temperature. Yang *et al* also looked into other alkaline metal dopants, synthesizing Mg, Ca, Sr, and Ba-doped Pd/CeO<sub>2</sub>-ZrO<sub>2</sub> TWCs.<sup>45</sup> In agreement with Lan *et al*, they found Ba was the best-performing dopant, while the inclusion of Mg actually reduced thermal stability and catalyst performance.

## 2.4 Alternative washcoat materials – zeolites as a HC and NO<sub>x</sub> trap

Zeolites can be included as a washcoat component as a ‘cold trap’ for reactants – adsorbing them in ambient conditions and releasing them at higher temperatures. Zeolites are a group of microporous, Al and Si-containing materials. Their large network of mesopores and micropores provide them with a good adsorption ability. HC trap designs utilizing zeolite materials have been in use since the 1990s, with various systems demonstrating improved low-temperature performance.<sup>46</sup> Factors that can limit zeolite HC trap effectiveness include thermal stability, desorption below 200 °C (below light-off temperatures), reversibility of adsorption process, and different behavior for different HCs. For instance, while higher molecular weight HCs (such as toluene) are taken up by zeolite materials to a high degree, lighter molecules such as propene are only lightly adsorbed, and can desorb from the trap at temperatures far below light-off.<sup>47</sup>

Kustov *et al* examined the use of Li, Na, and K-modified ZSM-5 zeolite materials for toluene adsorption (Figure 8).<sup>48</sup> They found that Li or Na doping (to 5 wt. % and 2.5 wt. %, respectively) provided the largest advantages for toluene storage, as well as high-temperature

desorption (between 200 and 400 °C). ZSM-5 was chosen for this study due to its higher thermal stability and good pore structure compared with many other common zeolites.

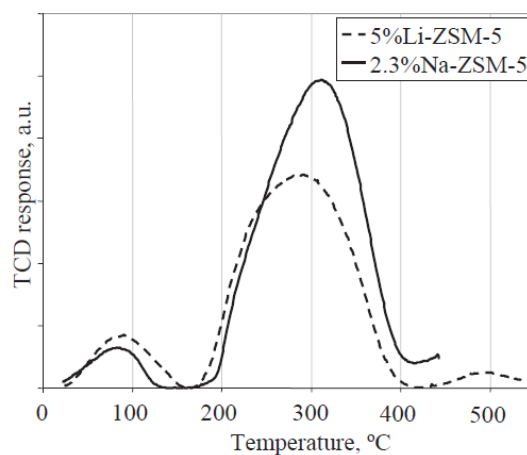


Figure 8. Temperature-programmed desorption of toluene from ZSM-5 zeolites. Reproduced with permission from Elsevier.<sup>48</sup>

Design considerations for HC traps may need to take into account more than just successful HC uptake. Bugosh and Harad investigated the use of a BEA zeolite as a dodecane trap, as well as its performance incorporated into a Pt/Pd/BEA/Al<sub>2</sub>O<sub>3</sub> TWC.<sup>46</sup> They found that while higher levels of BEA improved hydrocarbon adsorption, as expected, the adsorbed dodecane had an inhibitory effect of CO oxidation – higher levels of pre-adsorbed HCs shifted the light-off curve of CO to higher temperatures. Burke *et al* examined the effect of water in the exhaust stream on HC adsorption in Na-BEA and La-BEA zeolites.<sup>49</sup> They found that, compared with a H<sub>2</sub>O-free test run, the presence of water significantly decreased the adsorption of propene and toluene, and adsorption of water was favored. The authors suggest the incorporation of a more hydrophilic zeolite in combination with BEA may be a strategy for dealing with water in vehicle exhaust.

There are a large number of possible zeolite materials, and many have been used as HC trap materials, including Y zeolite, ZSM-5 (MFI), USY, BEA, mordenite, FAU, and FER with

varying SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of 1 to 150.<sup>48</sup> Therefore, a comprehensive examination of zeolite properties, correlated to performance, is desired. Westermann and Azambre looked into the effectiveness of six different zeolites for use in a HC trap: HY-15 and H $\beta$ -12.5 (large pores), HZSM5-5.5 and 5A-2 (medium pores), HFER-10 (small pores with 2D structure), and HMOR-10 (large pores but 1D structure).<sup>50</sup> They used decane, toluene, and propene as representative heavy and light HC molecules. Their findings were that HY-15, 5A-2, and H $\beta$ -12.5 preferentially adsorbed decane over toluene, while HFER-10 was skewed toward propene adsorption. However, HMOR-10 and HZSM5-5.5 showed less preferential ‘single-file’ adsorption behavior and higher desorption temperatures, more favorable for cold-start applications. The behavior of different zeolite materials was attributed to the quantity of acid sites, the Si/Al ratio, the degree of microporosity, and the pore size – the optimum pore size was determined to be 5.5 to 6 Å for toluene and 4 to 5 Å for propene. The relationship between acidity and microporous volume on hydrocarbon adsorption capacity is shown in Figure 9.

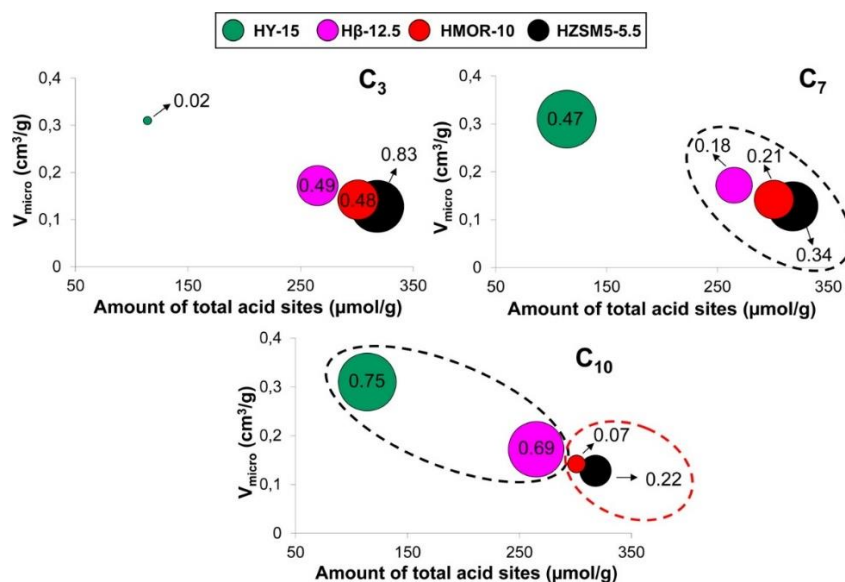


Figure 9. Influence of acidity and microporous volume on the total adsorptive capacity of various zeolite materials for propene ( $\text{C}_3$ ), toluene ( $\text{C}_7$ ), and decane ( $\text{C}_{10}$ ). The adsorptive capacity ( $\text{mmol g}^{-1}$ ) is represented by the size of the circles. Reproduced with permission from the American Chemical Society.<sup>50</sup>

More recent research has also focused on using zeolites as a NO<sub>x</sub> cold-start trap. Murata *et al* report a study looking at 1 wt. % Pd, Pt, or Rh-loaded ZSM-5 zeolite for TWC use.<sup>51</sup> They found that Pd/ZSM-5 adsorbed NO up to 0.4 g<sub>NO</sub> L<sub>cat</sub><sup>-1</sup>, compared with approximately 0.03-0.04 g<sub>NO</sub> L<sub>cat</sub><sup>-1</sup> for Pt/ZSM-5, Rh/ZSM-5, and Pd loaded on other supports (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>). This adsorbed NO could be reduced to N<sub>2</sub> while heated under a slightly reducing atmosphere. In a real-world engine test using a traditional close-coupled Pt/Rh TWC and a Pd/ZSM-5 underfloor catalyst, NO<sub>x</sub> emissions during the initial cold-start period were reduced from 200 to 50 ppm.

### 3. Platinum Group Metal Loading

Platinum, palladium, and rhodium are the common platinum group metals (PGMs) employed as the active component in three-way catalyst designs. Pt and Pd are used for the oxidative component of three-way catalysis, while Rh is necessary to control NO<sub>x</sub> emissions. The choice of using Pt or Pd is mainly economic – in the 1990s, Pd was more common because it was less expensive, but increasing demand for Pd led to a surge in price, and Pt-based formulations were developed instead.<sup>52</sup> It should be noted that Pd and Pt are not interchangeable without other design considerations – Pd is typically less stable than Pt, which must be accounted for.<sup>21</sup> Rh is the most expensive of the three metals, and 80% of global Rh demand is for TWC use. This has driven the development of low-Rh formulations. While rhodium-free Pd-only TWCs have been produced, they typically do not have very good NO<sub>x</sub> removal capabilities.<sup>52,53</sup> Recent results are summarized below and in Table S3 in Supporting Information.

#### 3.1 PGM loading quantities and ratios

From Johnson Matthey, Cooper and Beecham reported a study comparing TWC activity across a range of Pt, Pd, and Rh loadings and relative ratios.<sup>54</sup> (Figure 10) All catalysts tested

were either Pd/Rh or Pt/Rh and were aged at 950 °C for 80 h (correlating to 160000 km of road use). Loadings were chosen to match the ‘lower end’ of PGM loadings in commercial catalysts. Their findings were that increasing Pt or Pd loading only slightly improved the catalyst performance for HC and NO<sub>x</sub> removal and decreasing the amount of Pt or Pd only slightly reduced catalytic activity. In contrast, increasing or decreasing the amount of Rh had a more significant benefit in improved catalytic activity (in terms of light-off temperature). Additionally, Pd slightly outperformed Pt under most testing conditions. The authors note that while low-Rh formulations have become common due to the high cost of rhodium, this may not make sense in terms of performance. Their conclusions are that increasing Rh levels should boost TWC performance, while Pd or Pt loadings can probably be decreased for cost savings, if necessary.

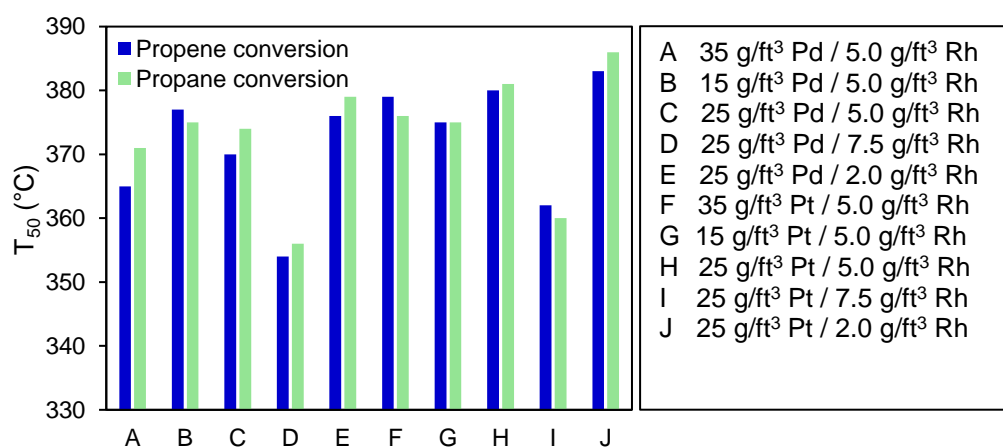


Figure 10. T<sub>50</sub> conversion values of hydrocarbons for a catalyst with different Pt, Pd, or Pd loadings and ratios.<sup>54</sup>

Alikin and Vedyagin examined different Rh loadings (0.01 to 1 wt. %) on a CeO<sub>2</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> washcoat material for three-way catalysis.<sup>55</sup> As expected, they report that higher Rh loadings improve light-off temperatures. They also found that if the Rh loading is too low (0.1 wt. % or below), strong Rh-ceria interactions upon high-temperature aging lead to a loss

of catalytic activity. For Rh levels higher than this, performance improves because most of the Rh remains catalytically active.

Theis *et al* examined varying Pd loadings on Al<sub>2</sub>O<sub>3</sub> catalysts (0 to 4 wt. % Pd).<sup>56</sup> They found that increasing the Pd loading from 0 to 2 wt. % led to an improvement in catalyst performance for CO, HC, and NO removal. However, this improvement was not linear – and the performance of the 4 wt. % sample was very similar to that of the 2 wt. % sample, suggesting that under the experimental conditions used, there are only diminishing or no returns for adding Pd above 2 wt. %.

Kang *et al* also examined Pd loading's impact on TWC performance, looking at commercial catalysts with Pd loadings of 0.10 to 1.24 wt. % (20 to 240 g/ft<sup>3</sup>) Pd.<sup>57</sup> The washcoats were alumina with 3% ceria and 1% each BaO and La<sub>2</sub>O<sub>3</sub>. Similarly to Theis, Kang found that TWC performance increased nonlinearly with increasing Pd content, finding only small differences in catalysts with more than 0.42 wt. % (80 g/ft<sup>3</sup>) Pd.

Jeong and Choi investigated different ratios of Pd, Pt, and Rh in a TWC with a double-layer washcoat consisting of Al<sub>2</sub>O<sub>3</sub> and an undisclosed amount of Ce, Zr, and La.<sup>58</sup> (Figure 11) Unlike many other reports in the literature, real exhaust gas (from a 5 hp gasoline engine) was used in this study. In agreement with Cooper and Beecham, they found that Pd-based catalysts had better light-off temperatures than Pt-based catalysts. The optimum Pd:Rh ratio in this study was 18:1 – this catalyst outperformed others with equivalent levels of Rh, but either higher or lower Pd loadings. However, this result does not necessarily contradict the results of Cooper and Beecham because catalysts with higher Rh loadings with equivalent Pd levels were not tested.

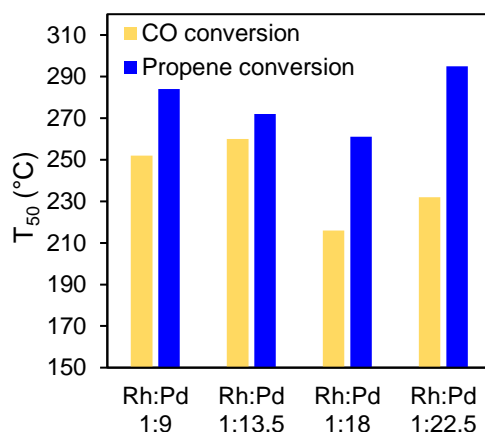


Figure 11.  $T_{50}$  conversion values of hydrocarbons for a catalyst with different Rh:Pd ratios.<sup>58</sup>

In other studies in which only CO oxidation or NO removal with CO were considered, Phan and Kureti report that in a Pd/Al<sub>2</sub>O<sub>3</sub> system for CO oxidation, the light-off temperature improves up to 2 wt. % Pd, with higher Pd levels not providing additional performance.<sup>59</sup> Martínez-Arias *et al* report that, between 0.05, 0.5, and 1.0 wt. % Pd/Al<sub>2</sub>O<sub>3</sub>, increasing Pd provides improved performance for CO and NO removal. However, CO desorption from Pd is a rate-limiting step due to strong CO-Pd interactions.<sup>60</sup> Di Monte *et al* report that for a Pd/Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, 2.8 wt. % Pd provides better light-off performance for CO and NO removal than 0.7 wt. % Pd.<sup>61</sup> Finally, Anderson *et al* report that loading more Pt in a Pt/Rh/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalyst material improves performance for CO oxidation.<sup>62</sup>

### 3.2 Additional considerations for TWC metal loading

Three-way catalysts may be designed with distinct washcoat layers, with separated active metals either to improve activity or prevent sintering. Catalyst deactivation has been partially attributed to the formation of Pd-Rh alloys at high temperatures in catalyst formulations which originally had separate Pd and Rh particles.<sup>63</sup> For example, Rh can be placed in a top layer where it is exposed to the various reductant species in the exhaust gas, before the reactants diffuse to a lower Pt- or Pd-containing layer where oxidation takes place.<sup>52</sup> Jeong

and Choi's TWC study, discussed in the previous section, employed a double-layer washcoat with Pd/Pt and Rh components in different layers.<sup>58</sup> In another experiment, Shinjoh *et al* reported a TWC in which Pt was supported on a ceria-based oxide material and Rh was supported on a zirconia-based oxide to prevent sintering after high-temperature aging. This was achieved through the high level of interaction between metal and support, with Pt-O-Ce and Rh-O-Zr bonds preventing high-temperature particle agglomeration. This design outperformed a conventional catalyst design in terms of light-off temperature.<sup>64</sup> It also avoided excessive Rh-Ce or Rh-Al interactions, which can cause the formation of a highly oxidized inactive form of rhodium.<sup>41,65</sup>

In contrast to designs with separate metal components, other recent research has shown that some bimetallic alloy designs can improve catalytic performance or stability, not just cause deactivation. Vedyagin *et al* developed an alloyed 0.2 wt. % Pd-Rh/Al<sub>2</sub>O<sub>3</sub> catalyst (Pd:Rh ratio 3:2) which was more stable than an identical catalyst with separate Rh and Pd particles.<sup>66</sup> Interactions between Pd and Rh in the alloyed metal particles prevented Rh from diffusing into the washcoat phase, a potential cause of rhodium deactivation. However, despite improved stability, the bimetallic alloy catalyst showed worse light-off performance than a similarly prepared Rh-only catalyst. This was explored further in a following study, looking at different Pd:Rh ratios (3:2, 7:3, and 4:1).<sup>63</sup> The catalyst with the highest level of Rh demonstrated the strongest Pd-Rh interactions, and thus the highest level of stability after aging at 1000 °C. However, it should be noted that in both studies, a similarly prepared Rh-only catalyst had better low-temperature performance than any of the alloyed catalysts – their only advantage is stability.



The reason why such alloy catalysts perform more poorly than pure Rh, despite better stability, is that Pt and Pd strongly interact with CO – adsorbing it to the point of hindering the other TWC reactions by blocking reaction sites. This interferes with Rh’s catalytic activity in Pt-Rh or Pd-Rh alloys. To mitigate this, Haneda *et al* designed an iridium-rhodium catalyst – Ir does not adsorb CO as strongly as Pt or Pd, so should not hinder HC/NO<sub>x</sub>.<sup>53</sup> They found that the inclusion of Ir (unlike the Pd-Rh alloy catalysts above) at a 1:9 Ir:Rh ratio improved activity beyond that of a Rh-only catalyst, as well as enhancing stability (Figure 12). The authors state that the use of Ir could be a strategy to reduce Rh levels in TWC design. This could be useful from an economic point of view – Ir is less expensive than Rh.<sup>67</sup>

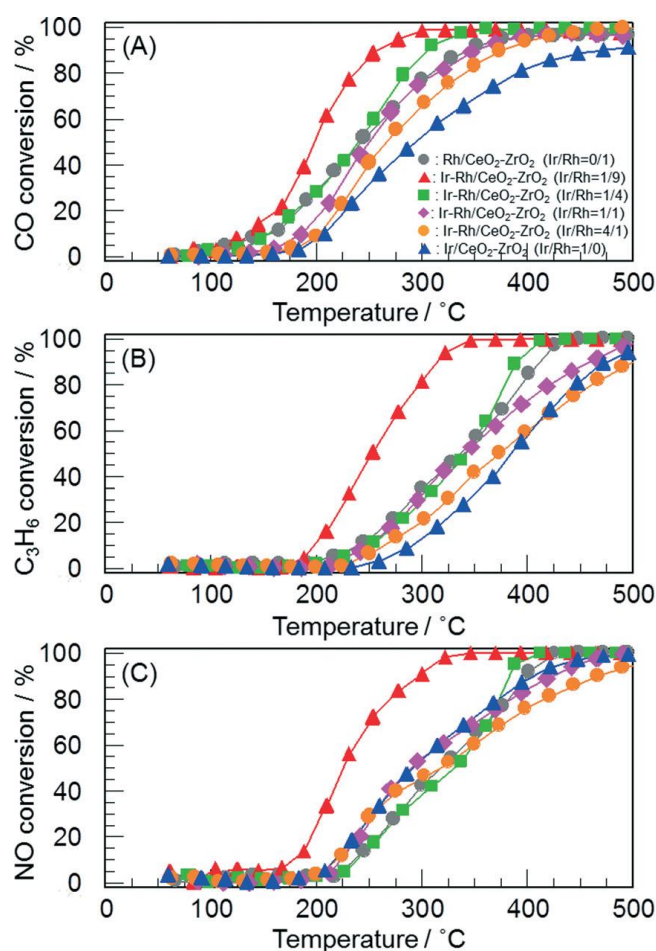


Figure 12. CO, HC, and NO conversion rates for Rh and Ir/Rh-based catalysts. Reproduced with permission from the Royal Society of Chemistry, permission conveyed through Copyright Clearance Center, Inc.<sup>53</sup>

## 4. Monoliths

The two most common monolith designs for TWCs are cordierite ceramic or metallic foil. Extruded cordierite monoliths are the most popular design on the market due to their good thermal shock resistance, chemical resistance and low coefficient of thermal expansion – cordierite’s melting temperature is approximately 1450 °C and it resists oxidation.<sup>68</sup> This makes cordierite a good material to withstand the harsh conditions TWCs are exposed to.

However, there are limits to how thin cordierite monolith walls can be manufactured. In contrast, metallic monoliths can have a frontal open area of about 90%.<sup>68,69</sup> This provides a higher geometric area per volume for catalyst deposition and allows lower flow resistance and back pressure. While cordierite monoliths are more common, metallic monoliths can be found in certain niche applications, such as large trucks or high-performance sports vehicles in which the low pressure drop is more desirable. An additional advantage of metallic monoliths is high thermal conductivity, allowing faster heating of the catalyst. However, their coefficient of thermal expansion is also larger than that of cordierite monoliths, meaning special bonding techniques must be employed to ensure the washcoat material adheres to the monolith.

Santos *et al* find that with identically prepared ceramic and metallic substrates, the ceramic monoliths provide better CO and HC conversions than metallic monoliths at low space velocities ( $< 50000\text{-}70000\text{ h}^{-1}$ ).<sup>68</sup> However, at higher space velocities, metallic substrates provide better conversions due to a larger surface area and improved mass transfer properties. This is because at higher space velocities the TWC reactions are mass-transfer limited, providing an advantage to the metallic substrate.

Reducing the mass of a monolith can improve its performance. Otsuka *et al* developed a ‘super-light’ monolith with a 20% increase in porosity levels.<sup>70</sup> This monolith had the same pressure drop and thermal stability as a conventional monolith, but provided extra surface area for washcoat deposition while maintaining the same wall thickness (2 or 3 mil) and cell size. Overall, emissions were reduced by approximately 10% compared with the conventional monolith. Kikuchi *et al* compared monoliths with 600, 900, and 1200 cells, with wall thicknesses of 4.3, 2.5, and 2.0 mil, respectively.<sup>71</sup> They found that maximizing the number of cells and minimizing wall thickness and overall substrate mass improved TWC performance.

Chang *et al* report a novel substrate made from an extruded zeolite material, instead of cordierite or metal foil.<sup>72</sup> This was done in the investigation of zeolites as a ‘HC trap’ washcoat material, which have been shown to be able to adsorb and store HCs below the light-off temperature and release them at a higher temperature. However, zeolites can only be loaded to approximately 2 g/in<sup>3</sup> on a traditional ceramic monolith because of increasing back pressure and processing constraints if the washcoat layer is too thick. Therefore, Chang *et al* developed an extruded zeolite-based monolith, containing about 4 g/in<sup>3</sup> zeolite material. When combined with a Pd/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-CeO<sub>2</sub> catalyst and washcoat, TWC low-temperature performance was improved compared with a similar catalyst with a ceramic monolith. Additionally, the zeolite monolith catalyst trapped approximately 85% of HC emissions in a 30 second storage test, compared with 64% for a more traditional zeolite-on-cordierite catalyst (Figure 13).

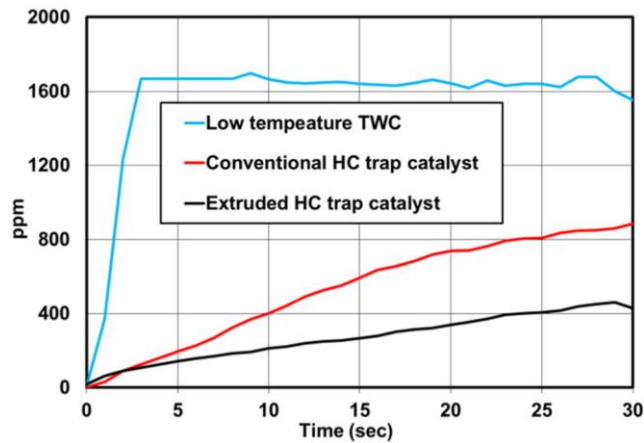


Figure 13. Hydrocarbon storage capacity during a 30 second trap test at 80 °C. Reproduced with permission from SAE International, permission conveyed through Copyright Clearance Center, Inc.<sup>72</sup>

## 5. Conclusions

Three-way catalytic converters are essential for reducing gasoline engine powered vehicle pollutants emissions to regulation levels. This review has shown the recent range of research investigating the numerous factors that impact the three-way catalyst design. One such factor is the design of washcoat formulations. Ceria-zirconia is added to alumina washcoats to improve oxygen storage capacity. While ceria-zirconia materials with 40-60% ceria are typically used due to their high oxygen storage capacity, good results have also been achieved with other formulations, such as a mixture of Ce-rich and Zr-rich particles. An additional consideration is the use of Zr-rich formulations to avoid unfavorable interactions between Rh and ceria. Oxygen storage capacity and thermal stability of the washcoat can be further improved with the addition of low levels of rare earth or alkaline metal promoters, and the inclusion of zeolites to act as a hydrocarbon or NO<sub>x</sub> cold trap should be considered as well.

Another key factor in three-way catalyst design is the loading and ratio of platinum group metals. Pt/Rh or Pd/Rh are the most commonly used metals – Pt or Pd for oxidative reactions,

and Rh for NO<sub>x</sub> reduction. While the use of Pt or Pd has often been based on economic decisions, performance differences mean the two metals are not interchangeable without other design considerations. While low-Rh designs have been introduced due to the higher cost of Rh, this may have a larger negative impact on catalyst performance than decreasing the loading of Pt or Pd. More novel catalyst designs such as the use of bimetallic alloys show potential in reducing Rh loading without sacrificing performance.

Monolith design choices also influence three-way catalyst performance. Metallic monoliths may be chosen instead of the more common cordierite-based monoliths in applications where a lower pressure drop is desirable. Highly porous cordierite monoliths have been shown to improve performance by increasing the surface area available for washcoat deposition, and novel zeolite-based monoliths offer a potential way to increase the total zeolite loading in a catalyst beyond that of what traditional cordierite monolith designs allow.

Overall, a good understanding of how various washcoat compositions, PGM particles, and the monolith interact to form an effective catalyst is necessary for the further development of three-way catalysts with better performance, particularly at low temperatures where current catalyst designs are not very active. While the development of this technology thus far has provided numerous environmental benefits, with increasingly stringent air quality and emissions regulations in the US, Europe, China, and elsewhere, the need for further progress in emissions control technology is clear.

## 6. Funding

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