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Designing Pd-based Supported Bimetallic Catalysts for Environmental Applications

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Abstract: Supported bimetallic nanoparticulate catalysts are an important class of heterogeneous catalysts for many reactions including selective oxidation, hydrogenation/hydrogenolysis, reforming, biomass conversion reactions and many more. The activity, selectivity and stability of these catalysts depend on their structural features including particle size, composition and morphology. In this review, we present important structural features relevant to supported bimetallic catalysts focusing on Pd-based bimetallic systems and recently reported strategies to control them through different synthesis methodologies. Further, we focus on a few reactions that are relevant to environmental catalysis *i.e.* (a) CO oxidation, (b) hydrocarbon oxidation, (c) hydrodechlorination and (d) NO_x decomposition where Pd-based catalysts are often used successfully. In spite of much progress in these areas, still there is a need for more advanced catalytic technologies to address the grand challenges like environmental remediation. Some of the recent advances in the design of bimetallic catalysts were made because of the combined efforts of material scientists, spectroscopists, microscopists, catalysis chemists and engineers through *state-of-the-art* characterisation methodologies, mechanistic investigations and structure-activity correlations. This review is aimed at inspiring scientists to rationally design catalysts for a green and sustainable future.

Key words: Palladium, Palladium Alloys, Bimetallic Catalysts, Environmental Applications.

1 Introduction

Sustainably producing energy, chemicals and food without affecting the environment is a grand challenge for our society. There is a rapid growth in the production of chemicals and fuels to meet increasing demand due to population growth and fast economic progress in large developing countries. As a consequence, there has been an increased emission of pollutants having huge environmental impact resulting in climate change and health issues. Hence, there is a pressing need to develop alternative technologies to produce commodity chemicals and fuels from sustainable feedstocks without creating any waste. One of the strategies to achieve this is to design a circular economy where the waste generated in one process is used as a feedstock for another process. Such an approach is very different from our current

“linear” processes where the feedstock is taken from the ground, used for the production of chemicals/fuels and the generated waste is left aside (not recycled). (Moreno et al., 2016; Geissdoerfer et al., 2017) Catalysis will play a crucial role in realising our dream of a green and sustainable circular economy. (Clark et al., 2016) Until now, an enormous amount of effort has been put on developing highly active, selective and stable catalysts that suits the current petroleum feedstock that is composed of mostly non-polar hydrocarbons. In the proposed circular economy, the chemical nature of future feedstocks will be substantially different, and thus there is a need to rationally design new catalysts to suit them. However, the knowledge and science generated through decades of research and development can be used to accelerate our endeavor to develop new catalysts. In an effort to that, here we report a mini re-

view on bimetallic catalysts for environmental applications. In this review we focus on recent developments in designing palladium based bimetallic catalysts for (a) CO oxidation, (b) hydrocarbon oxidation, (c) hydrodechlorination and (d) NO_x decomposition reactions. Supported palladium nanoparticles are extensively examined as catalysts because of their high activity at relatively low temperatures and high tolerance to moisture. (Garcia et al., 2006; He et al., 2010) Palladium has a relatively low activation barrier between the oxidation states of 0 and +2 corresponding to stable d10 and d8 configurations respectively. The ease of shuttling between these two oxidation states is crucial for the oxidative insertion and reductive elimination steps involved in the above-mentioned reactions.

Supported metal catalysts are an important class of heterogeneous catalysts that are widely used in the production of bulk, fine chemicals and fuels. (Anderson and Garcia, 2012) Typically, these catalysts are used for selective oxidation, selective hydrogenation/hydrogenolysis, hydrotreatment and other related reactions. Sinfelt, from Exxon laboratories, developed a new class of supported metal catalysts, called bimetallic catalysts, in the 1970s for reforming reactions and they are currently widely used in the petroleum industries. (Sinfelt, 1983a; Sinfelt, 1983b) Often supported bimetallic catalysts display substantially different catalytic properties from their monometallic analogues. (Ellert et al., 2014) This difference in properties has been attributed to (Ponec, 2001; Alonso et al., 2012):

(a) Geometric effect or ensemble effect: The second metal alters the geometry or dilutes the active metallic site (ensemble) and this effect is also called the “dilution effect”

(b) Ligand effect or electronic effect: The second metal alters the electronic configuration of the active metallic site through electron transfer.

(c) Stabilisation effect: The second metal stabilizes the small metallic active sites by preventing them from sintering and/or preventing coke formation, thereby increasing the stability of the catalyst.

(d) Synergistic effect: Both metals actively participate in the catalytic process by stabilizing the

intermediate or transition state through chemical bonding.

(e) Bi-functional effect: Both metals catalyse different reactions (e.g. one metal catalyses a hydrogenation-dehydrogenation reaction and the other metal catalyses the hydrogenolysis reaction).

From the above arguments it is clear that the catalytic properties of bimetallic catalysts are highly dependent on their structural properties. This trend is similar to supported monometallic catalysts with, however, added complexities because of the presence of the second metal. It is worth emphasising that often the stability of monometallic catalysts is improved by the addition of a second metal. The addition of the second metal prevents metal nanoparticles from sintering during the catalytic reaction. In this review, we will discuss the structural properties of supported bimetallic catalysts followed by a review of recent developments in the strategies to tune these structural properties through appropriate modification of synthesis methods.

2 Structural Features of Bimetallic Catalysts

For supported bimetallic catalysts, the three crucial structural features affecting catalytic properties are: (a) metal particle size, (b) bimetallic composition and (c) morphology (nanostructure). (Sankar et al., 2013) The first structural feature (metal particle size) has been widely studied for mono- as well as for bimetallic catalysts. A number of articles and reviews have been published on the relationship between metal particle size and catalytic properties. (Bell, 2003; Zhong et al., 2003; An and Somorjai, 2012) In many cases, the catalytic activity and particle size have an inverse relationship; however, a number of exceptions have also been reported where an “optimum” particle size is shown to be important. Recently, Zhang et al. have extended the use of the relationship between metal particle size and activity to develop single atom catalysts for selective hydrogenation, oxidation and other reactions. (Qiao et al., 2011; Yang et al., 2013) Flytzani-Stephanopoulos et al. recently reported bimetallic single atom alloy catalysts for selective oxidation and formic acid decomposition reactions. (Lucci et al., 2015; Liu et al., 2016) The second structural feature, metallic composition, is unique to bimetallic catalysts. A limited

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number of studies have been dedicated to the relationship between bimetallic composition and catalytic properties in practical catalysts, because of the complexities involved in controlling this feature. The third structural feature is the nature of arrangement of the two metals in a bimetallic nanoparticle (morphology or nanostructure). According to Ferrando et al. four types of nanostructures are possible for bimetallic catalysts (Fig. 1) (Ferrando et al., 2008): (a) core-shell structure, (b) sub-cluster segregated alloys, (c) random and homogeneous alloys and (d) multi-shell alloys. For the core-shell morphology, a shell of metal atoms surrounds a core of different metal atoms (Fig. 1A). Supported bimetallic catalysts having core-shell morphology have been widely studied for their catalytic properties. The second type of nanostructure, Sub-cluster segregated morphology, is when two metal components have a distinct interface between them (Fig. 1B). Bimetallic systems having this morphology have rarely been reported. Homogeneously or randomly mixed alloy morphology is reported when the two metals are intimately mixed in either an atomically ordered or a statistically random manner (termed “ordered alloys” and “random alloys” respectively) (Fig. 1C). In practical catalysts, the random alloy morphology is more commonly reported than the ordered. In multi-shell morphology there is more than one concentric shell (same metal or different metals) covering the core metal, to form an “onion-like” structure (Fig. 1D). Several factors affect the formation of these morphologies:

(a) Relative strength of the intermetallic bonds compared to the pure monometallic bonds. Intimate mixing of two metals is favoured (ordered or random alloy morphologies) when intermetallic bonds are stronger than the pure monometallic bonds.

(b) Surface energy difference between the two metals. In a core-shell morphology, metal with the lower surface energy will move to the shell and the metal with higher surface energy takes the core,

(c) Atomic sizes – in a core-shell morphology, smaller atoms occupy the core.

(d) Electron transfer – higher electron (charge) between two metals transfer favours intimate mixing resulting in ordered or random alloy morphologies.

(e) Stabilizer ligand – in the presence of a stabilizer ligand, to control the metal particle size, the

metal that has more affinity to the stabilizer ligand preferring the shell position compared in a core-shell morphology.

(f) Electronic/magnetic effects can stabilize specific morphology. For a more in-depth discussion on this topic, readers are referred to the article by Ferrando et al. Having discussed the structural features in detail, the next objective is to discuss the synthesis strategies available to tune these structural features.

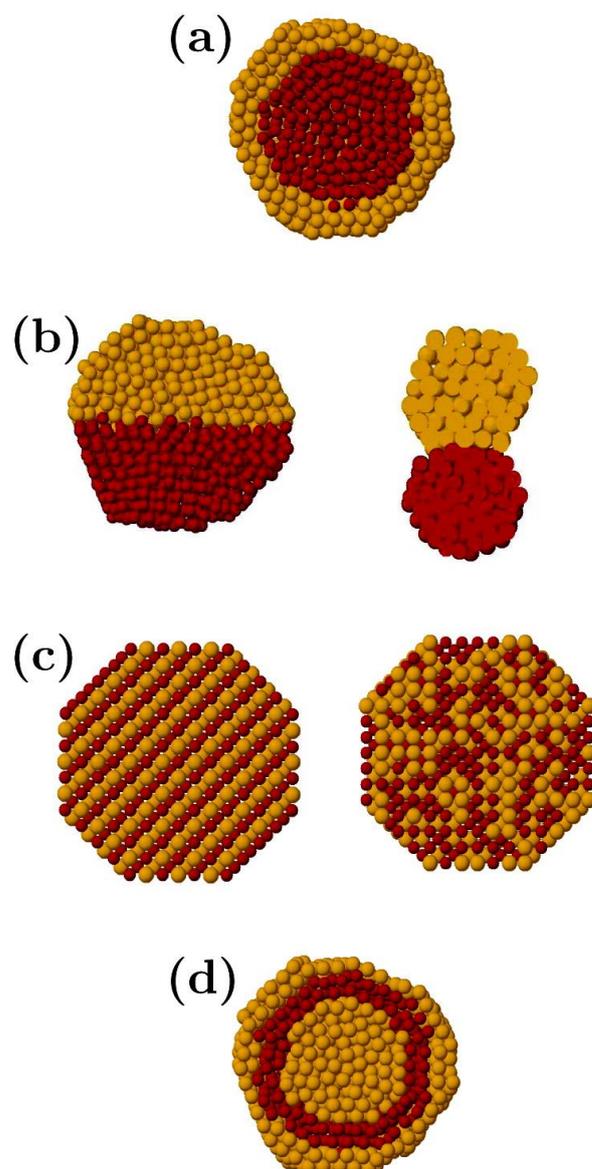


Fig. 1. Schematic representation of different morphologies in bimetallic systems: (a) core-shell morphology, (b) sub-cluster segregated morphology, (c) ordered and random homogeneous alloys morphology, and (d) multi-shell

morphology. Reproduced with permission from ref (Fernando, et al., 2008).

3 Synthesis of Bimetallic Catalysts:

Similar to the synthesis of supported monometallic catalysts, many strategies have been reported for the synthesis of supported bimetallic catalysts including chemical reduction, template assisted synthesis, noble metal induced reduction method, thermal decomposition of metal complex precursors, radiolysis and sonochemical synthesis. (Sankar et al., 2012a) All these methods have certain advantages and disadvantages. However, many of these methodologies are not applicable for preparing catalytically active materials because of non-availability of the metal surface for catalysis and/or lack of stability under reaction or process conditions. For the preparation of catalytically active materials, a wet-impregnation method is widely used. For simplicity, here we will focus on three strategies to synthesise supported AuPd nanoparticles, as representative for Pd based bimetallic catalysts, and how the structural features are tuned by changing the synthesis methodology. Supported AuPd catalysts have been widely reported for many reactions including selective oxidation, selective hydrogenation/hydrogenation, biomass conversion, reforming and vinyl acetate synthesis reactions. (Edwards et al., 2007; Villa et al., 2007; Hutchings, 2008b; 2008c; 2008a; Wang et al., 2008; Dimitratos et al., 2009)

Conventional wet-impregnation: This is the most widely used method for preparation of supported metal catalysts, including bimetallic catalysts. However, catalysts prepared by this method often have a wide particle size distribution. For example, 2.5% Au-2.5% Pd/C & 2.5% Au-2.5% Pd/TiO₂ prepared by the conventional wet impregnation method have bimodal distribution of bimetallic particles i.e. small particles (2-10 nm) and large particles (> 20 nm). In these catalysts, the large particles are catalytically inactive; hence the large particles don't play any catalytic role and thus should be eliminated. Detailed characterisation of them revealed that supported AuPd particles, prepared by conventional impregnation method, display a size-dependent compositional variation. (Hutchings and Kiely, 2013) It is reported that small bimetallic particles (<10 nm) are

palladium rich, medium size bimetallic particles (10-50 nm) are a mixture of palladium and gold and large bimetallic particles (>50 nm) are gold rich. These catalysts displayed a gold core - palladium shell morphology. We have reported supported AuPd nanoparticles synthesized by conventional wet-impregnation as effective catalysts for the solvent free, selective, aerobic oxidation of primary and secondary alcohols to carbonyl compounds and for the direct synthesis of hydrogen peroxide from dilute hydrogen and oxygen. They have been found to be stable for reuse without any deactivation. (Paalanen et al., 2013)

Sol immobilisation: Prati and Rossi et al. developed a sol immobilisation technique to control the particle size distribution using stabilizer ligands like polyvinyl alcohol (PVA) and polyvinyl pyridine (PVP). (Prati and Martra, 1999; Biella et al., 2002; Biella et al., 2003; Villa et al., 2009; Prati and Villa, 2014; Villa et al., 2015) Supported AuPd nanoparticles prepared by the sol immobilisation method have been found to have excellent particle size control (all bimetallic particles are between 2-10 nm). In the context of composition, sol-immobilisation catalysts displayed a size-dependent composition variation. However, the small bimetallic particles (<10 nm) are gold rich, medium size bimetallic particles (10-50 nm) are a mixture of palladium and gold and large bimetallic particles (>50 nm) are palladium rich. (Pritchard et al., 2010) This is the reverse of conventional impregnation catalysts. Sol immobilisation catalysts mostly displayed homogeneous random alloy morphology. Supported AuPd catalysts prepared by the sol immobilisation method have been found to be more active, not stable however, in selective oxidation reactions and direct synthesis of hydrogen peroxide.

Modified impregnation: We recently modified the conventional wet-impregnation method by adding excess chloride ions during the wet-impregnation stage. The addition of chloride ions controls the particle size and composition effectively. Supported AuPd catalysts prepared in a 2M HCl solution display excellent particle size control (all bimetallic catalysts are between 2-8 nm). (Sankar et al., 2012b) The composition of Au in small bimetallic particles (2-8 nm) increases, at the expense of large gold-rich

particles (>20 nm), with the increase in chloride ion concentration during wet-impregnation. Supported AuPd catalysts prepared in a 2M HCl solution do not display any size-dependent compositional variation. All bimetallic particles have similar AuPd composition that matches the initial precursor concentration. All these catalysts have been found to have homogeneous random alloy morphology. These catalysts have been reported to have excellent activity and selectivity for selective oxidation of alcohols and the direct synthesis of hydrogen peroxide. During the course of this investigation, we found that high temperature calcination led to palladium-shell and gold-core morphology and high temperature gas-phase reduction led to homogeneous random alloy structure. (Paalanen, et al., 2013) Li et al. further exploited this idea of adding excess chloride ions for Pd-Re bimetallic systems for the hydrogenolysis of glycerol to propanediols. (Li et al., 2016) This indicates that adding excess chloride ions may be necessary for all palladium-based bimetallic systems to control their structural features. After discussing the structural features and strategies to tune them in bimetallic catalysts, we will now discuss some examples where Pd-based bimetallic catalysts have been tested for reactions relevant to environmental applications.

4 Catalytic Applications of Bimetallic Catalysts

In this section, we will discuss the application of Pd-based bimetallic catalysts for (a) CO oxidation, (b) total oxidation of volatile organic compounds (VOC), (c) hydrodechlorination and (d) NO_x decomposition reactions.

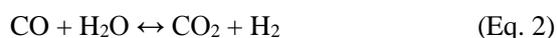
CO oxidation

Carbon monoxide oxidation has been widely studied in academic as well as industrial research, because of its importance in practical applications. Since CO is highly toxic most of the research is focused on environmental protection, in the automotive industry for exhaust gas control and air clean-up. CO can be oxidized to carbon dioxide in the presence of oxygen. Hopcalite is one of the most common catalytic materials used in the industrial processes in-

volving direct oxidation (Eq.1.) (Pitzer and Frazer, 1941) For this industrial catalyst, CO conversion ranges from 60-80% at room temperature depending on a range of factors including catalyst ageing and catalyst calcination temperature. (Hutchings et al., 1996; 1998; Jones et al., 2009)



The second reaction is the water gas shift (WGS) reaction (Eq. 2.), which uses water as oxidant:



Due to the reversible nature this reaction, it is carried out at temperatures substantially higher than CO oxidation using O₂. Commercially WGS reactions are carried out either at 250 °C using platinum catalysts or at 350 °C using iron-based catalysts. (Newsome, 1980; Smith et al., 2010) Often supported precious metal catalysts are used for CO oxidation. Copper, platinum, palladium, silver and gold are the most commonly used metals. These are typically in the form of nanoparticles distributed on oxide or carbon supports, or porous, high surface area sponges. In this review, we will focus on Pd-based bimetallic (Pd-M) catalysts for CO oxidation.

Supported metallic palladium and its oxide (PdO) have been reported to be active for CO oxidation. However, metallic palladium is reported to display better activity. (Cordi and Falconer, 1996) The mechanism of CO oxidation over Pd⁰ is reported to be a Langmuir-Hinshelwood model. In addition, there are reports describing PdO as capable of reducing Pd⁰ in the presence of CO. (Maillet et al., 1997) Bimetallic alloyed nanoparticles alter the activity of their mono-metallic counterparts by changing the geometric structure of the nanoparticle, because of the formation of defect sites, kink steps and edges, and the addition of the new metal leads to a change of electronic structure due to a change in the density of states in the nanoparticle, as described earlier. There have been many studies on the effect of the addition of a second metal to the Pd catalyst and its influence on CO oxidation. One of the most studied examples is the Pd-Au nanoalloys. In this catalyst, it is believed that the synergistic effect comes from Au atoms tun-

ing the Pd-Pd bonds leading to a geometric effect and Pd gaining valence 'd' density from Au via redistribution of electrons. (Suo et al., 2008; Xu et al., 2010) Pd is more active for CO oxidation because of its ability to dissociate O₂ more easily than Au. Au has a high O₂ dissociation barrier (2.23eV) and higher adsorption energy (-0.17eV) than Pd-Au alloys, which have a range of -0.71 -1.52eV for the oxygen adsorption energy. (Chen et al., 2012) The activity of bimetallic Au-Pd catalysts has been a subject of studies for many years and contradictory data have been reported. Several reports attribute a higher activity of the bimetallic catalyst to the synergy between the metals, (Qian and Huang, 2011; Kim and Henkelman, 2013) while others report no particular synergy between Au and Pd. (Venezia et al., 2003; Beck et al., 2007) However, this can be explained by the application of diverse reaction conditions, different supports and catalyst synthesis procedures. It is also reported that, under certain conditions, Pd segregates from Au, leading to a decrease in CO oxidation activity. The migration of Pd breaks the "magic" 4 Pd atom cluster, reported to be active for O₂ dissociation, which leads to a decrease in CO oxidation activity. Pd-Au nanoparticles supported on inert supports like SiO₂ or Al₂O₃ have to be calcined to allow the transfer of electrons from the support to Au and in turn from Au to Pd and this leads to an increased interaction between the 2 metals. (Suo, et al., 2008) In many cases calcination of the material leads to formation of core shell morphology (Au_{core} - Pd_{shell}) which increases the initial rate of CO oxidation. (Beck, et al., 2007) Carter et al. investigated introduction of Pd into a highly active Au/CeZrO₄ catalyst and tested catalyst activity for CO oxidation, water-gas shift reaction (WGS) and formic acid decomposition (FAD) (Fig. 2). (Carter et al., 2016) The authors observed so called anti-synergy for all reactions, as the monometallic catalyst was more active than the bimetallic one. They ascribed the anti-synergy to be related to the particle size. It was concluded that the electronic interaction between Pd and Au, used to explain the synergy observed for selective oxidation reactions, does not have a significant role in WGS, FAD, and CO oxidation under low-temperature gas-phase conditions. Instead, the metal species at the periphery of the supported nanoparticles are implicated in these reactions.

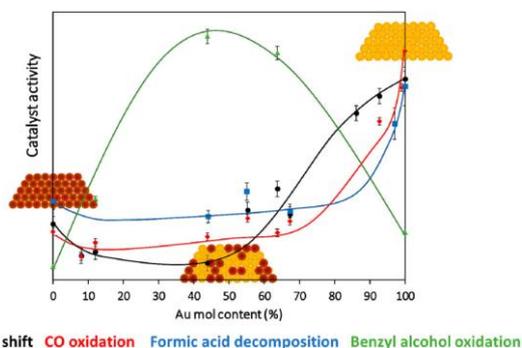


Fig. 2: Catalytic activity of various Au_xPd_y/CeZrO₄ catalysts for water-gas shift, CO oxidation, formic acid decomposition and benzyl alcohol oxidation. Reproduced with permission from reference (Carter, et al., 2016).

Qian et al reported similar observations. They report that alloying Au with Pd reduces the intrinsic catalytic activity for CO oxidation, and continuous Pd atoms on the Au-Pd alloy particles are capable of catalyzing CO oxidation whilst isolated Pd atoms are not. (Qian et al., 2017) In addition to these studies, a few theoretical and experimental studies using model catalysts have predicted that Pd-Au alloy catalysts should be active for CO oxidation. Ham et al. attempted to rationalize Pd-Au interactions with CO and O₂ on Pd-Au (111) surfaces. It was found that "partially-poisoned" Pd ensembles would facilitate the activation of O₂ and subsequent reaction with CO, making Pd-Au alloys potentially highly active for CO oxidation. (Ham et al., 2012)

Another class of bimetallic nanoparticles studied for CO oxidation is Pd and Cu. Monometallic Cu catalysts are reported to be active for CO oxidation reactions. However, they deactivate very fast because of particle sintering, oxidation of Cu metal nanoparticles and formation of OH groups from water. (Kugai et al., 2011b) However, addition of Pd increases Cu stability through electronic modification, making bimetallic Pd-Cu more stable and attractive because of the abundant nature of Cu. (Hungria et al., 2002; Kugai et al., 2011a)

The third group of bimetallic catalysts studied for CO oxidation is Pd-Pt nanoparticles. Pd displays a lower melting temperature and heat of vaporization

than Pt. As a result, it is expected to be lower co-ordinated than Pt and would segregate to the surface of bimetallic clusters. (Harada et al., 1992) The majority of supported Pd-Pt bimetallics have been synthesised by wet impregnation methods. Yashima et al. prepared Pt and Pd particles by reaction in microemulsion. Further, the particles were deposited on Al₂O₃ and calcined at 600 °C forming alloyed particles. The authors reported that a 20:80 Pt-Pd molar ratio gave the most active catalyst. (Yashima et al., 2003) This was contrasted with their wet-impregnated catalyst, which exhibited highest activity at a 50:50 ratio. Viesz et al. prepared Pd-Pt powder catalysts using a colloid synthesis. (Veisz et al., 2005) They reported preferential Pt surface segregation and also reported Pd-Pt alloying. Moreover, the surface segregation has been attributed to the inhibition of Pd oxidation to PdO by Pt. Kaya and Üner investigating sequentially impregnated Pd-Pt/Al₂O₃ catalysts. They discovered that sequential impregnation did not result in the formation of alloyed particles. (Kaya and Uner, 2008) Interestingly, in this system, monometallic Pt and Pd displayed higher activity than the bimetallic catalysts. Pd displayed a higher tolerance to CO self-poisoning than Pt and was attributed to subsurface PdO layers. In a later study, Kaya et al. reported that Pd segregated to the surface of Pd-Pt clusters using Monte Carlo simulations. At a low temperature the bimetallic particles behaved identically to monometallic Pd. (Kaya et al., 2009) Bimetallic Pd-Pt nanoparticles supported on CeO₂ were reported in the preferential oxidation of CO in the presence of H₂. (Parinyaswan et al., 2006) The most active catalyst used for the reaction was prepared using a 1:7 Pt : Pd ratio. In spite of high catalytic activity, deactivation was reported due to poisoning effects of CO. To conclude, there is much evidence of Pt:Pd interaction in bimetallic catalysts. Alloying is possible, and synergistic effects are not unprecedented.

Total oxidation of volatile organic compounds (VOC)

VOCs are defined as substances of low volatility. Here we will discuss the total oxidation of volatile organic compounds (VOC) that are detrimental to the environment. Therefore, the focus is on the total ox-

idation of short chain alkanes (methane, ethane, propane), benzene and polynuclear aromatic hydrocarbons (naphthalene).

Benzene: Benzene, one of the most hazardous aromatic compounds, is emitted by a variety of industries including petrochemical, chemical, steel and coating and many more. Among different catalysts studied for the total oxidation of benzene, Pd and Pt nanoparticles supported on Al₂O₃ was found to be the most promising. (Papaefthimiou et al., 1997) It has been reported that Pd⁰/Pd²⁺ is involved in this oxidation reaction. (Papaefthimiou et al., 1998) Vassileva et al. reported the effect of metal loading on the catalytic properties of Pd nanoparticles supported on Al₂O₃ and V₂O₅ for the total oxidation of benzene. (Vassileva et al., 1989) Ferreira et al. attributed the higher activity of Pd supported on V₂O₅ to the high amount of V⁴⁺ species in Pd/V₂O₅-Al₂O₃ catalyst. (Ferreira et al., 2004) Another strategy reported to increase the catalytic activity of supported Pd catalysts is to increase the metal dispersion by using high surface area supports. He et al. supported Pd nanoparticles on high surface area ZSM-5, MCM-48 as well as on the combined composites of them and tested these catalysts for the total combustion of benzene. All the composite catalysts demonstrated improved catalytic activity reducing the 90% benzene conversion temperature from 292 °C (Pd/MCM-48) to 204 °C (Pd/ZM-40). (He, et al., 2010) Tang et al. applied highly dispersed bimetallic Pd-Ni nanoparticles, supported on SBA-15 for the total oxidation of gaseous benzene. (Tang et al., 2017) Addition of Ni significantly improved the catalytic activity of the Pd catalyst, as full conversion was achieved at 350 °C, compared to 400 °C for the monometallic Pd catalyst. Not many bimetallic catalysts have been reported for the total oxidation of benzene. Hence, there is further scope for developing better bimetallic catalysts for this reaction.

Naphthalene: Supported Pd nanoparticles have been widely used as catalysts in the total oxidation of naphthalene since the 1990s. (Ferrandon et al., 1999b; 1999a) Some reported catalysts include monometallic Pt and Pd nanoparticles supported on γ -Al₂O₃ and operate in the temperature range 288 – 395 °C achieving 50% naphthalene conversion. Similar work

was reported by Zhang *et al.* who studied a wider range of monometallic catalysts including 1% Pt, 1% Pd, 1% Ru, 5% Co, 5% Mo and 5% W on γ -Al₂O₃. (Zhang *et al.*, 2003) BET studies indicated that the metal impregnation resulted in the reduction in surface area compared to the bare Al₂O₃ support. This was proposed to be due to large metal particles filling the pores of the support. Garcia *et al.* compared activity of Pd-V/TiO₂ to Pd/TiO₂ and V/TiO₂ in the total oxidation of naphthalene. It was found that a catalyst with the loading of 0.5% Pd/TiO₂ was more active than bimetallic Pd-V/TiO₂. (Garcia, *et al.*, 2006)

Methane: Pd catalysts are reported to be the most active for the total oxidation of methane under lean conditions. Reduction of Pd to metallic Pd at high temperature was found to lead to lower activity, which confirms that PdO is the active phase for the complete oxidation of methane. Different synthesis strategies, using different supports, have been tried to improve the activity of monometallic Pd catalyst. (Lapisardi *et al.*, 2006) Interestingly, the addition of small amounts of Pt was reported to increase the low temperature activity, especially under wet feed conditions, and also to improve the thermal durability. (Ersson *et al.*, 2003) Strobel *et al.* investigated Pd-Pt bimetallics for methane combustion. He discovered that small Pt particles in Pd catalysts enhanced resistance to catalyst sintering. (Strobel *et al.*, 2005) The same bimetallic composition was studied by Gremminger *et al.* (Gremminger *et al.*, 2015) However, the reason for the positive effect of small amounts of Pt is still strongly debated. Maione *et al.* proposed a different approach to prepare bimetallic Pd-Pt/Al₂O₃ and Pd-Rh/Al₂O₃ material and deposit it by dip coating on FeCr Alloy-type fibers. It was found that bimetallic Pd-Pt catalyst has a better catalytic behaviour than a Pd-based one, which undergoes sintering evidenced by the formation of larger particles agglomerates. (Maione *et al.*, 2007b; 2007a) Wilburn and Epling investigated the behaviour of Pt-Pd/Al₂O₃ catalyst for total oxidation of methane in the presence of sulfur and concluded that the presence of sulfur was less detrimental to CH₄ oxidation activity than the sintering effects associated with reaction temperature changes. (Wilburn and Epling, 2017)

Propane: The total oxidation of propane using Pd-supported nanoparticles has been widely studied and reported. One of the earliest published studies of propane combustion was published by Yazawa and co-workers. (Yazawa *et al.*, 1998) They used Pd/SiO₂-Al₂O₃ and studied the role of the palladium oxidation state and its influence on catalytic activity. It was found that in varying propane to oxygen stoichiometric ratios, the oxidation states of the Pd change, while the dispersion of Pd was not influenced by the changes in gas feed stream. Garcia *et al.* reported the use of vanadium-modified Pd/TiO₂ catalysts for propane total oxidation. It was reported that the co-impregnation of the V and Pd enhanced catalytic activities, with 0.5% Pd/1.5% V/TiO₂ reported to be the most active catalyst. (Garcia *et al.*, 2011) It was found that Pd dispersion and surface site concentration decreased upon the addition of V. The effect of Nb modifiers in Pd/TiO₂ catalysts was studied by Taylor *et al.* It was reported that the inclusion of niobium provided an increase in catalytic activity. This was found to be due to an increase in oxygen mobility after Nb addition. The nature of the Pd was also altered and oxidised Pd was observed. The activity of this catalyst was found to increase with increasing Nb and Pd loading. (Taylor *et al.*, 2008) Hazlett *et al.* reported on the Pd-Pt/Al₂O₃ catalyst, known for total oxidation of CH₄, for CO and C₃H₆ oxidation (Fig. 3). In terms of CO and C₃H₆ oxidation the light-off temperatures for the bimetallic catalysts were generally lower than those for the monometallic catalysts. It was found that by preparing catalysts with different Pd : Pt ratio, catalytic activity is tuned due to the diversity of particles in size and composition. (Hazlett *et al.*, 2017)

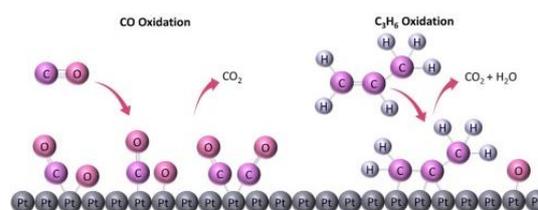


Fig. 3: Schematic representation of the mechanism of bimetallic Pd-Pt nanoparticles catalysed oxidation of CO and C₃H₆. Reproduced with permission from reference (Hazlett, et al., 2017).

Other hydrocarbons: Haneda *et al.* studied the effect of Pd addition on the catalytic performance of Pt/Al₂O₃ for the total oxidation of a mixture of n-decane and 1-methylnaphthalene. (Haneda *et al.*, 2014) Bimetallic Pd-Pt diesel oxidation catalyst showed higher catalytic activity for the total oxidation of hydrocarbons, even after high temperature ageing, than monometallic Pt and Pd catalysts. The optimum Pt/Pd weight ratio was found to be 3: 1. High hydrocarbon oxidation activity was attributed to the enrichment of Pt on the surface of alloyed Pd-Pt particles. In general, Pd-Pt bimetallic catalysts are the most studied system for the oxidation of methane, propane and CO. An effort has been made to understand the Pd-Pt nanoparticles' structure. By using many different characterization techniques, it was finally concluded that Pd segregates to the particle surfaces, leading to a Pt core surrounded by metallic Pd, or small Pd particles dispersed on the Pt core. It has also been shown that Pd surface segregation increased with particle size, and with small particle sizes Pt was also present at the surface. Also, under high temperature oxidizing conditions, some metallic Pd in these bimetallic particles was oxidized into PdO clusters. (Rousset *et al.*, 1998; Van Den Oetelaar *et al.*, 1998)

Hydrodechlorination (HDC)

Chlorinated organic compounds are widely used in agriculture and industry. However, they are highly toxic with carcinogenic, teratogenic and mutagenic properties. Unfortunately, they also possess good thermal and chemical stability, which makes them difficult to decompose. They are mostly present in water, so catalytic decomposition in the liquid phase is required. Among many materials Pd-based catalysts are reported to be the most promising metal for HDC. Since palladium performed well in HDC reactions, it is understandable to add a second component to increase catalytic activity. Catalysts prepared by the addition of Re and Ag to Pd were studied for the HDC of dichloromethane and dichloroethane respectively. Observed increase in activity and selectivity was attributed to the changes in nanoparticle geometry, i.e. the dilution of the Pd surface into smaller

ensembles. (Heinrichs *et al.*, 1997; Bonarowska *et al.*, 1999) Similarly, electronic effects were the main reason for changes in selectivity and activity in the gas phase HDC of chlorobenzene over Pd-Rh/Al₂O₃. (Bodnariuk *et al.*, 1989) Further, bimetallic Pd-Rh nanoparticles, prepared using colloidal methods, with controlled size and structure were tested for the HDC of 4-chlorophenol (4-CP) in the aqueous phase. (Baeza *et al.*, 2015) Authors concluded that redox interactions between both metals are significant for catalytic activity, and this is in agreement with other reports on bimetallic systems. (Harada *et al.*, 1993) The largest bimetallic nanoparticles (>4 nm) were related to higher Pd/Rh ratios. Coq and Figueras in their review focused on the dehydrochlorination of chlorofluorinated compounds using Pd nanoparticles. (Coq and Figueras, 2001) Bimetallic Pd-In/Al₂O₃ catalysts with different Pd : In molar ratios were applied in the degradation of 4-chlorophenol. The research showed that addition of In to the Pd catalyst improved the dispersion of Pd particles and increased the HDC catalytic activity when the In : Pd molar ratio was less than 1/1. (Baeza, *et al.*, 2015) Among the metals used as active phase, Pd and Pt have demonstrated high activity and selectivity to non-chlorinated products. These metals have been used to prepare bimetallic catalysts for the HDC of different chlorinated compounds, including dichloromethane (DCM), where they have shown some advantages compared to the monometallic homologues in terms of activity and/or stability. (Cardenas-Lizana *et al.*, 2013; Gregori *et al.*, 2014) Martin Martinez *et al.* reported the use of the Pd-Pt bimetallic nanoparticle supported on activated carbon for the dechlorination of DCM. They investigated the influence of reduction temperature on the catalyst activity. It was found that the reduction temperature used for the catalyst activation allow for the modulation of the M⁰/Mn⁺ ratio. When the temperature of the reduction increased, the proportion between metallic Pt and Ptⁿ⁺ proportion also increased (Fig. 4). The authors attributed high TOF to be the result of such combination, which in turn favours the adsorption of reactants onto the catalyst. (Martin-Martinez *et al.*, 2016)

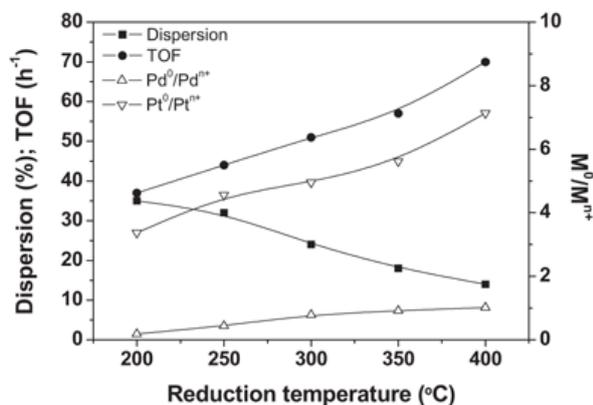


Fig. 4: Metal dispersion, TOF and ratio M^0/M^{n+} of palladium and platinum at different reduction temperatures. Reproduced with permission from reference (Martin-Martinez, et al., 2016).

Many studies have been performed on Pd-based HDC catalysts, among which Pd-Fe₂O₃ has been reported to be particularly effective. (Zhang *et al.*, 2017) However, the ideal support for HDC reactions is a high surface area support. Thus, further improvement of the material resulted from impregnating Fe₂O₃ and Pd on the activated carbon, which earlier was reported as the best support candidate. The authors prepared the catalyst by sequentially depositing Fe₂O₃ and Pd onto an activated carbon support using atomic layer deposition (ALD). Activity and selectivity of the material was higher than that of monometallic Pd/AC (ALD) catalyst which confirms the positive effect of Fe₂O₃ on promoting HDC activity. In another method of preparation of Pd-Fe bimetallic materials, a small amount of Pd was deposited onto zero-valent Fe particles through a facile aqueous replacement reaction. Such an approach was reported by Han *et al.* (Han *et al.*, 2016) It is believed that Pd serves as an indirect catalyst by facilitating the accumulation of active hydrogen species on the Fe surface.

Pd-Au catalysts are often used in the dechlorination reaction in the liquid phase reaction because of their high activity, which is ascribed to geometric and electronic effects. Fang *et al.* investigated the bimetallic Pd-decorated Au nanoparticle catalysts and concluded that Au nanoparticles could stabilize surface Pd atoms in metallic form to increase the active sites and improve the catalytic HDC activity under

ambient-temperature reaction conditions. (Fang *et al.*, 2011) In the work reported by Nutt *et al.* Pd metal was modified with Au in intimate contact such that the interface between Pd and Au atoms provided additional active sites for the HDC of trichloroethene. (Nutt *et al.*, 2006) Zhou *et al.* investigated Au-decorated Pd supported on carbon nanotubes for the liquid phase hydrodechlorination of 2,4-dichlorophenol (Fig. 5). A range of catalysts with different Au:Pd ratio was prepared using the complexing-reduction method. Materials prepared in this way exhibited nanoparticles of Pd and Au mainly in alloy-like structure. The bimetallic catalysts had smaller metal particles and larger numbers of exposed active sites than those of monometallic catalysts. (Zhou *et al.*, 2016)

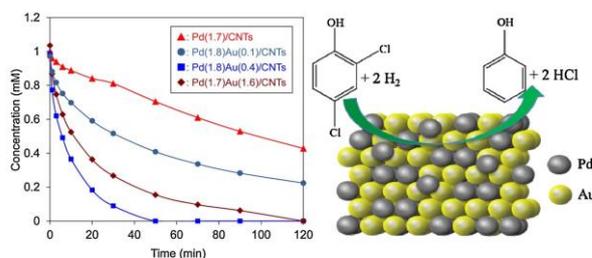


Fig. 5: 2,4-Dichlorophenol can be converted to phenol via the catalytic HDC method over Pd-Au/CNTs and the catalytic activity first increased and then decreased with Au content. Reproduced with permission from reference (Zhou, et al., 2016)

Velazquez *et al.* investigated Au-Pd bimetallic supported on Al₂O₃ for degradation of chloroform, a common groundwater contaminant. Reported data show activity of the catalyst under more realistic conditions: under continuous flow and using actual groundwater. (Velazquez *et al.*, 2016) It was shown that the bimetallic catalyst outperformed the monometallic Pd catalyst. The same authors reported activity of this material in hydrodechlorination of trichloroethylene and perchloroethylene over PdAu catalysts to a single-carbon organohalide. (Nutt, *et al.*, 2006; Heck *et al.*, 2008)

NO_x decomposition

Another class of reactions studied using monometallic and bimetallic Pd nanoparticles is that of the NO_x decomposition reactions. Nitrous oxide (N₂O) is

a toxic and highly devastating greenhouse gas, 300 times more dangerous to the ozone layer than carbon dioxide. Decomposition of N_2O takes place through the dissociation route and most of the current work focuses on the use of monometallic Pd, Rh, Ru catalyst for this reaction. Only a few reports were found dealing with Pd-based bimetallic materials. Wei *et al.* applied Pd-Au nanoparticles supported on mesoporous SBA-15 for the decomposition of N_2O (Fig. 6). (Wei *et al.*, 2012) For the synthesis on nanoparticles they used an adsorption–reduction method. By applying such a preparation method, they achieved highly dispersed and homogeneous Pd-Au alloy nanoparticles with an average metal particle size of ~ 2 nm. High activity of the catalyst was attributed to Pd atoms being isolated into single Pd atoms by Au atoms.

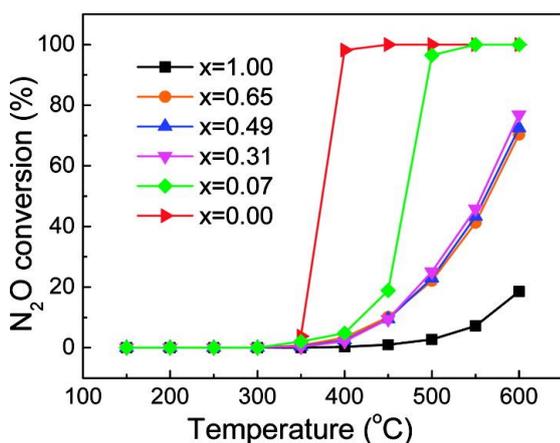


Fig. 6. N_2O conversions vs reaction temperature over $Au_xPd_{1-x}/SBA-15$ catalysts. Reproduced with permission from reference (Wei, et al., 2012)

Similar catalysts were studied by Tzitzios and Georgakilas. (Tzitzios and Georgakilas, 2005) In their work Pd (loading 0 to 3wt%) was combined with 5wt% Ag supported on Al_2O_3 . From the results on N_2O decomposition it was clear that the bimetallic catalyst was significantly more active than the monometallic catalysts. This result was ascribed to a synergistic effect between Ag and Pd. The authors stated that the two components have not formed any alloy, as was indicated by the related XRD patterns. Unfortunately, no information about the particle size or morphology was reported. In a similar reaction,

Masuda *et al.* studied the Pd-Ag bimetallic catalyst for the removal of NO_x from diesel exhaust gas. (Masuda *et al.*, 1998) It was reported that a small amount of Pd improved significantly the catalytic activity in practical conditions. Nitric oxide (NO) is another toxic gas emitted as a pollutant from combustion engines and industrial ovens. Diaz Consul *et al.* in their work published in 2008 dealt with the direct decomposition of NO using a Pd-Mo catalyst supported on Al_2O_3 -thin-layer-modified SiO_2 and Si-MCM-41. (Consul *et al.*, 2008) The catalysts Pd-Mo (Mo was deposited initially) were the most selective, signifying that there was a lower degree of N_2O formation compared with catalysts where Pd was deposited initially (Pd-Mo). It was concluded that these bimetallic catalysts exhibited high activity, due to the stability of nanoparticles caused by the interaction of the Pd and Mo atoms.

Concluding Remarks and Future Perspectives

From the above selected examples, it is clear that bimetallic catalysts have huge potential as catalysts for environmental remediation. However, from the CO oxidation example it is clear that not all bimetallic catalysts are better than their monometallic counterparts. It is crucial to rationally design the synthesis strategy to precisely control the size, composition and morphology of supported bimetallic catalysts. For example, the modified impregnation method, using an excess of chloride ions, can be applied for preparing other Pd-based bimetallic catalysts for the reactions discussed in this review to enhance their catalytic properties. Still this area of controlling particle size, composition and nanostructure of bimetallic catalysts is an emerging field of research. One of the challenges in this area is to understand the relationship between synthesis parameters and resultant nanoparticle structure.

Another important challenge in these bimetallic catalysts is that the real reason for the enhanced catalytic properties is still not known. Most of the reported explanations are speculative. Hence there is a need for an atomic level understanding of bimetallic nanoparticles. Computational modelling should be coupled with experimental methods to understand the

interaction of the two metals in bimetallic nanoparticles and their combined effect on the catalytic properties. Recent results show that metals that do not form alloys in bulk can form intimate random alloy structures at nanoscale. This opens up many more possibilities for bimetallic nanoparticles-based catalysts. Most recent reports on bimetallic catalysts are based on noble metals. By introducing a transition metal in a bimetallic nanoparticle, ideally, we can reduce the use of noble metals by 50% and still enhance the catalytic properties.

Hence, future research should be with close collaboration between material scientists, spectroscopists, microscopists, catalysis chemists and engineers. In situ characterisation of catalysts, under operating conditions, will help to identify the active site for these bimetallic catalysts, which will further help to rationally design catalysts. Although this review focuses on Pd-based bimetallic catalysts, the bigger scientific message can be translated to other bimetallic catalysts.

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