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Review:

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. CO oxidation, hydrocarbon oxidation, hydrodechlorination, and 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 characterization 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
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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,

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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 review 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, USA, 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, 1977, 1983). 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 catalyze different reactions (e.g. one metal catalyzes a hydrogenation-dehydrogenation reaction and the other metal catalyzes 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 emphasizing 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) (Paalanen et al., 2013). The first structural feature (metal particle size) has been widely studied for monometallic 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, Qiao et al. (2011) and Yang et al. (2013) 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. Lucci et al. (2015) and Liu et al. (2016) reported bimetallic single atom alloy catalysts for selective oxidation and formic acid decomposition reactions. The second structural feature, metallic composition, is unique to bimetallic catalysts. A limited 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. (2008) four types of nanostructures are possible for bimetallic catalysts (Fig. 1): (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 considered 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) transfer between two metals 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 prefers 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 research of Ferrando et al. (2008).

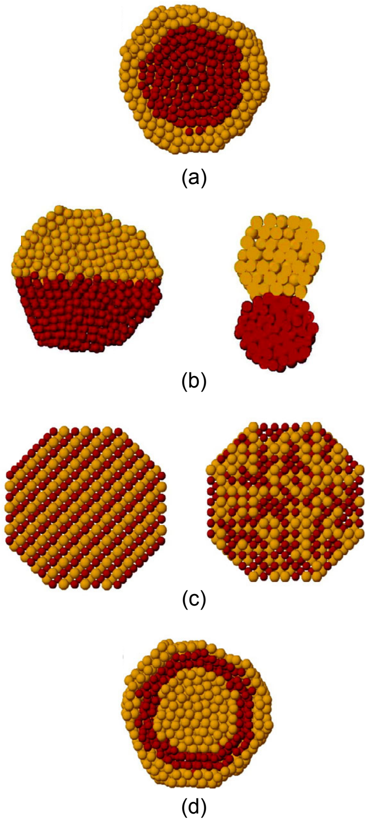

Fig. 1 Schematic representation of different morphologies in bimetallic systems: (a) core-shell morphology; (b) sub-cluster segregated morphology; (c) ordered and random homogeneous alloys morphology; (d) multi-shell morphology. Reprinted from (Ferrando et al., 2008), Copyright 2008, with permission from American Chemical Society

Having discussed the structural features in detail, the next objective is to discuss the synthesis strategies available to tune these structural features.

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 actively materials, a wet-impregnation method is widely used. For simplicity, here we will focus on three strategies to synthesize 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/hydrogenolysis, biomass conversion, reforming, and vinyl acetate synthesis reactions (Edwards et al., 2007; Villa et al., 2007; Hutchings, 2008a, 2008b, 2008c; 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 and 2.5%Au-2.5%Pd/TiO_2 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 do not play any catalytic role and thus should be eliminated. Detailed characterization 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: Some researchers 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, 2015; Prati and Villa, 2014). Supported AuPd nanoparticles prepared by the sol immobilisation method have been found to have excellent particle size control (all bimetallic particles are between 2 nm and 10 nm). In the context of composition, sol immobilisation catalysts displayed a size-dependent compositional 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 2 mol/L HCl solution display excellent particle size control (all bimetallic catalysts are between 2 nm and 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 2 mol/L 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. (2016) further exploited this idea of adding excess chloride ions for Pd-Re bimetallic systems for the hydrogenolysis of glycerol to propanediols. 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 (VOCs), (c) hydrodechlorination, and (d) NO_x decomposition reactions.

4.1 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 involving 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).

$$\mathrm{CO+1/2O_2 \rightarrow CO_2}. \tag{1}$$

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

$$\mathrm{CO+H_2O \leftrightarrow CO_2+H_2}. \tag{2}$$

Due to the reversible nature of this reaction, it is carried out at temperatures substantially higher than CO oxidation using O_2. 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 Pd^0 is reported to be a Langmuir-Hinshelwood model. In addition, there are reports describing PdO as capable of reducing Pd^0 in the presence of CO (Maillet et al., 1997). Bimetallic alloyed nanoparticles alter the activity of their monometallic 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 tuning the Pd-Pd bonds leading to a geometric effect and Pd gaining valence ‘d’ electron 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 O_2 more easily than Au. Au has a high O_2 dissociation barrier (2.23 eV) and higher adsorption energy (−0.17 eV) than Pd-Au alloys, which have a range of −0.71–1.52 eV 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" four-Pd atom cluster, reported to be active for O_2 dissociation, which leads to a decrease in CO oxidation activity. Pd-Au nanoparticles supported on inert supports like SiO_2 or Al_2O_3 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 two 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. (2016) investigated introduction of Pd into a highly active $Au/CeZrO_4$ catalyst and tested the catalyst activity for CO oxidation, WGS reaction, and formic acid decomposition (FAD) (Fig. 2). They observed the 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.

Qian et al. (2017) reported similar observations. They reported 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. 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. (2012) attempted to rationalize Pd-Au interactions with CO and O_2 on Pd-Au (111) surfaces. It was found that "partially-poisoned" Pd ensembles would facilitate the activation of O_2 and subsequent reaction with CO, making Pd-Au alloys potentially highly active for CO oxidation.

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).

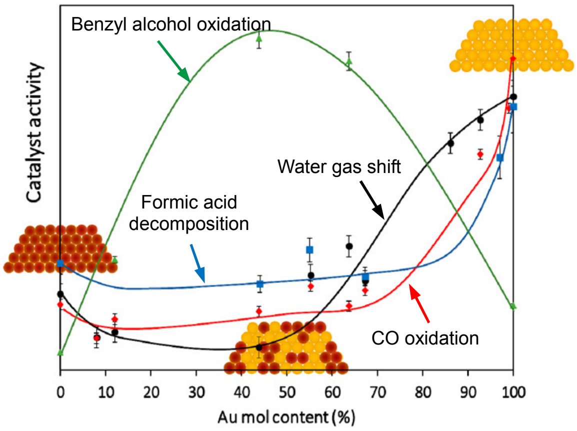

Fig. 2 Catalytic activity of various $Au_xPd_y/CeZrO_4$ catalysts for water gas shift, CO oxidation, formic acid decomposition, and benzyl alcohol oxidation. Reprinted from (Carter et al., 2016), Copyright 2016, with permission from American Chemical Society

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 coordinated than Pt and would segregate to the surface of bimetallic clusters (Harada et al., 1992). The majority of supported Pd-Pt bimetallics have been synthesized by wet impregnation methods. Yashima et al. (2003)

prepared Pt and Pd particles by reaction in microemulsion. Further, the particles were deposited on Al_2O_3 and calcined at 600 °C forming alloyed particles. They reported that a 20:80 Pt-Pd molar ratio gave the most active catalyst. This was contrasted with their wet-impregnated catalyst, which exhibited the highest activity at a 50:50 ratio. Veisz et al. (2005) prepared Pd-Pt powder catalysts using a colloid synthesis. 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 Uner (2008) investigated sequentially impregnated Pd-Pt/Al_2O_3 catalysts. They discovered that sequential impregnation did not result in the formation of alloyed particles. 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. (2009) 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. Bimetallic Pd-Pt nanoparticles supported on CeO_2 were reported in the preferential oxidation of CO in the presence of H_2 (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 synergetic effects are not unprecedented.

4.2 Total oxidation of volatile organic compounds (VOCs)

VOCs are defined as substances of high volatility. Here we will discuss the total oxidation of VOCs that are detrimental to the environment. Therefore, the focus is on the total oxidation of short chain alkanes (methane, ethane, and 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, coating, and many more. Among different catalysts studied for the total oxidation of benzene, Pd and Pt nanoparticles supported on Al_2O_3 were found to be the most promising (Papaefthimiou et al., 1997). It has been reported that Pd^0/Pd^{2+} is involved in this oxidation reaction (Papaefthimiou et al., 1998). Vassileva et al. (1989) reported the effect of metal loading on the catalytic properties of Pd nanoparticles supported on Al_2O_3 and V_2O_5 for the total oxidation of benzene. Ferreira et al. (2004) attributed the higher activity of Pd supported on V_2O_5 to the high amount of V^{4+} species in Pd/V_2O_5-Al_2O_3 catalyst. 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. (2010) 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 temperature to reach the 90% benzene conversion from 292 °C (Pd/MCM-48) to 204 °C (Pd/ZM-40). Tang et al. (2017) applied highly dispersed bimetallic Pd-Ni nanoparticles, supported on SBA-15 for the total oxidation of gaseous benzene. 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., 1999a, 1999b). Some reported catalysts include monometallic Pt and Pd nanoparticles supported on γ-Al_2O_3 and operate in the temperature range of 288–395 °C achieving 50% naphthalene conversion. Similar work was reported by Zhang et al. (2003) who studied a wider range of monometallic catalysts including 1% Pt, 1% Pd, 1% Ru, 5% Co, 5% Mo, and 5% W on γ-Al_2O_3. Brunauer-Emmett-Teller (BET) studies indicated that the metal impregnation resulted in the reduction in surface area compared to the bare Al_2O_3 support. This was proposed to be due to large metal particles filling the pores of the support. Garcia et al. (2006) compared the activity of Pd-V/TiO_2 to Pd/TiO_2 and V/TiO_2 in the total oxidation of naphthalene. It was found that a catalyst with the loading of 0.5% Pd/TiO_2 was more active than bimetallic $Pd\text{-}V/TiO_2$.

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. (2005) investigated Pd-Pt bimetallics for methane combustion. They discovered that small Pt particles in Pd catalysts enhanced resistance to catalyst sintering. The same bimetallic composition was studied by Gremminger et al. (2015). However, the reason for the positive effect of small amounts of Pt is still strongly debated. Maione et al. (2007a, 2007b) proposed a different approach to prepare bimetallic $Pd\text{-}Pt/Al_2O_3$ and $Pd\text{-}Rh/Al_2O_3$ materials 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. Wilburn and Epling (2017) investigated the behaviour of $Pt\text{-}Pd/Al_2O_3$ catalyst for the total oxidation of methane in the presence of sulfur and concluded that the presence of sulfur was less detrimental to CH_4 oxidation activity than the sintering effects associated with reaction temperature changes.

Propane: The total oxidation of propane using Pd-supported nanoparticles has been widely studied and reported. One of the earliest studies of propane combustion was published by Yazawa et al. (1998). They used $Pd/SiO_2\text{-}Al_2O_3$ 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 changed, while the dispersion of Pd was not influenced by the changes in gas feed stream. Garcia et al. (2011) reported the use of vanadium-modified Pd/TiO_2 catalysts for propane total oxidation. It was reported that the co-impregnation of V and Pd enhanced the catalytic activities, with 0.5% Pd/1.5% V/TiO_2 reported to be the most active catalyst. It was found that Pd dispersion and surface site concentration decreased upon the addition of V. The effect of Nb modifiers in Pd/TiO_2 catalysts was studied by Taylor et al. (2008). 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. Hazlett et al. (2017) reported on the $Pd\text{-}Pt/Al_2O_3$ catalyst, known for the total oxidation of CH_4, for CO and C_3H_6 oxidation (Fig. 3). In terms of CO and C_3H_6 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 ratios, catalytic activity is tuned due to the diversity of particles in size and composition.

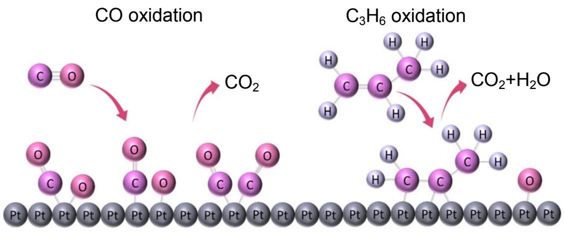

Fig. 3 Schematic representation of the mechanism of bimetallic Pd-Pt nanoparticles-catalyzed oxidation of CO and C_3H_6. Reprinted from (Hazlett et al., 2017), Copyright 2017, with permission from Elsevier

Other hydrocarbons: Haneda et al. (2014) studied the effect of Pd addition on the catalytic performance of Pt/Al_2O_3 for the total oxidation of a mixture of *n*-decane and 1-methylnaphthalene. 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 size Pt was also present at the surface. Moreover, 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).

4.3 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 the 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/Al_2O_3 (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 by Baeza et al. (2015). They 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 larger bimetallic nanoparticles (>4 nm) were related to higher Pd/Rh ratios. Coq and Figueras (2001) in their review focused on the dehydrochlorination of chlorofluorinated compounds using Pd nanoparticles. Bimetallic Pd-In/Al_2O_3 catalysts with different Pd:In molar ratios were applied in the degradation of 4-CP. 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. (2016) reported the use of the Pd-Pt bimetallic nanoparticles 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 allowed for the modulation of the M^0/M^{n+} ratio. When the temperature of the reduction increased, the proportion between metallic Pt and Pt^{n+} also increased (Fig. 4). They attributed high turnover frequency (TOF) to be the result of such combination, which in turn favours the adsorption of reactants onto the catalyst.

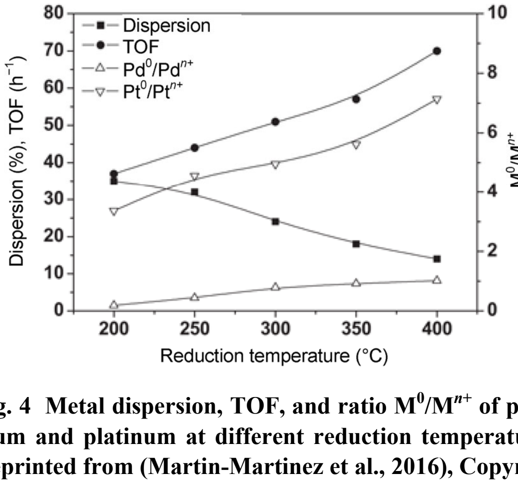

Fig. 4 Metal dispersion, TOF, and ratio M^0/M^{n+} of palladium and platinum at different reduction temperatures. Reprinted from (Martin-Martinez et al., 2016), Copyright 2016, with permission from Springer

Many studies have been performed on Pd-based HDC catalysts, among which Pd-Fe_2O_3 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 Fe_2O_3 and Pd on the activated carbon, which earlier was reported as the best support candidate. Zhang et al. (2017) prepared the catalyst by sequentially depositing Fe_2O_3 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 Fe_2O_3 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. (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. (2011) 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. In the work reported by Nutt et al. (2006) 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. Zhou et al. (2016) investigated Au-decorated Pd supported on carbon nanotubes (CNTs) for the liquid phase hydrodechlorination of 2,4-dichlorophenol (Fig. 5). A range of catalysts with different Au:Pd ratios were 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.

Velazquez et al. (2016) investigated Au-Pd bimetallic supported on Al_2O_3 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. It was shown that the bimetallic catalyst outperformed the monometallic Pd catalyst. Further, high activity of this material was reported in hydrodechlorination of trichloroethylene and perchloroethylene over Pd-Au catalysts to a single-carbon organohalide (Nutt et al., 2006; Heck et al., 2008).

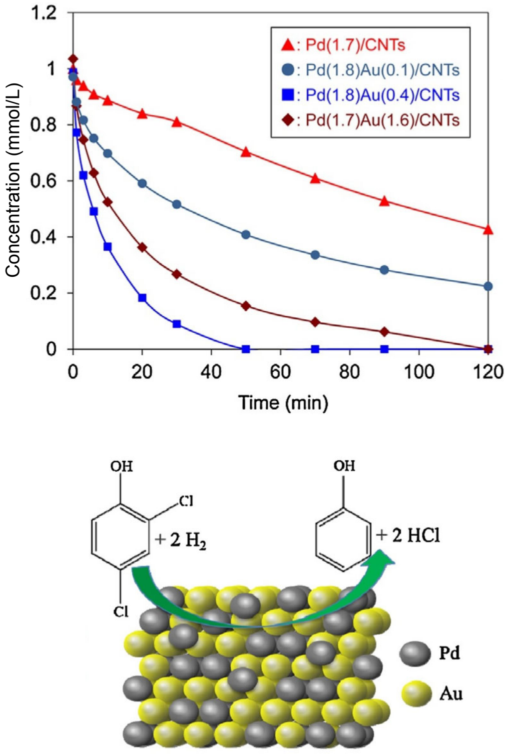

Fig. 5 Schematic representation of 2,4-dichlorophenol converted to phenol via the catalytic HDC method over Pd-Au/CNTs. Reprinted from (Zhou et al., 2016), Copyright 2016, with permission from Elsevier

4.4 NO_x decomposition

Another class of reactions studied using monometallic and bimetallic Pd nanoparticles is that of the NO_x decomposition reactions. Nitrous oxide (N_2O) 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, and Ru catalysts for this reaction. Only a few reports were found dealing with Pd-based bimetallic materials. Wei et al. (2012) applied Pd-Au nanoparticles supported on mesoporous SBA-15 for the decomposition of N_2O (Fig. 6). 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 about 2 nm. High activity of the catalyst was attributed to Pd atoms being isolated into single Pd atoms by Au atoms.

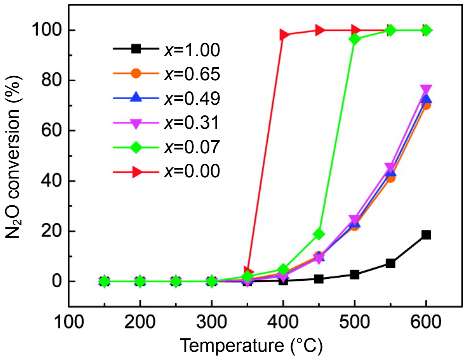

Fig. 6 N_2O conversions vs. reaction temperature over Au_xPd_{1-x}/SBA-15 catalysts. Reprinted from (Wei et al., 2012), Copyright 2012, with permission from American Chemical Society

Similar catalysts were studied by Tzitzios and Georgakilas (2005). In their work Pd (loading 0 to 3% in weight) was combined with 5% 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. They stated that the two components have not formed any alloy, as was indicated by the related X-ray diffraction (XRD) patterns. Unfortunately, no information about the particle size or morphology was reported. In a similar reaction, Masuda et al. (1998) studied the Pd-Ag bimetallic catalyst for the removal of NO_x from diesel exhaust gas. 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. Consul et al. (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. 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.

5 Conclusions

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 modeling 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 characterization 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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中文概要

题　目： **负载型 Pd 基双金属催化剂的设计及其在环境领域的应用**

概　要： 负载型双金属催化剂在很多催化反应中都有着十分重要的意义，包括选择性氧化、加氢/氢解、重整、生物质转化等反应。这一类催化剂的活性、选择性和稳定性取决于颗粒尺寸、组成和形貌等结构特性。针对 Pd 基负载型双金属催化剂体系，本文讨论了其结构特性，并探讨了不同合成方法对结构性质的调控机制。同时，本文阐述了 Pd 基催化剂在环境催化反应中的应用，包括 CO 氧化、烃类氧化、加氢脱氯和 NO_x 分解等反应。尽管在这些领域的研究取得了一定的进展，然而还需要更先进的催化技术来应对一些重大的挑战，如环境修复等。最近，在材料、光谱、显微、催化化学以及工程领域的研究人员的共同努力下，通过先进表征方法、机理研究手段的采用以及构效关系的研究，针对双金属催化剂设计的研究取得了一些新的进展。本篇综述旨在激励相关领域科学家设计合理的新型催化剂体系，以用于未来的绿色及可持续发展。

关键词： 钯；钯合金；双金属催化剂；环境领域的应用