Bimetallic Catalysts for Volatile Organic Compound Oxidation

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Abstract: In recent years, the impending necessity to improve the quality of outdoor and indoor air has produced a constant increase of investigations in the methodologies to remove and/or to decrease the emission of volatile organic compounds (VOCs). Among the various strategies for VOC elimination, catalytic oxidation and recently photocatalytic oxidation are regarded as some of the most promising technologies for VOC total oxidation from urban and industrial waste streams. This work is focused on bimetallic supported catalysts, investigating systematically the progress and developments in the design of these materials. In particular, we highlight their advantages compared to those of their monometallic counterparts in terms of catalytic performance and physicochemical properties (catalytic stability and reusability). The formation of a synergistic effect between the two metals is the key feature of these particular catalysts. This review examines the state-of-the-art of a peculiar sector (the bimetallic systems) belonging to a wide area (i.e., the several catalysts used for VOC removal) with the aim to contribute to further increase the knowledge of the catalytic materials for VOC removal, stressing the promising potential applications of the bimetallic catalysts in the air purification.

Keywords: VOCs; bimetallic catalysts; air purification

1. Introduction

Volatile organic compounds (VOCs) are a wide group of organic compounds characterized to boiling points less than 250 °C at room temperature and at atmospheric pressure [1]. Due to their carcinogenic and toxic nature, most VOCs are considered major causes of air pollution. Indeed, their emission in the environment leads to the formation of secondary dangerous compounds, due to the occurrence of chemical reactions with other airborne pollutants such as NOx and SOx, which results in the formation of tropospheric ozone and photochemical smog [2,3]. Long exposure to these pollutants leads to serious problems for human health [4,5]. Global economic and industrial development over the years has caused an exponential increase of anthropogenic VOC emission [6]. VOC discharges include outdoor sources, such as transport, industrial and petrochemical processes, etc., and indoor sources, such as household products, solvents, office materials, cleaning products, domestic cooking, etc. [7]. The emitted VOCs encompass alkanes, paraffins, olefins, aromatics, alcohols, ketones, aldehydes, esters, sulfur/nitrogen-containing VOCs, and halogenated VOCs. Among them, the most common and toxic are benzene, phenol, toluene, styrene, formaldehyde, propylene, and acetone [8], whereas Cl-VOCs and in general halogenated VOCs, due to their inherent stability and toxicity, are also very dangerous [9].

Different technologies have been developed for VOC treatment, and they can be divided into nondestructive and destructive VOC removal. The former include adsorption, membrane separation, and condensation [10–12]. Among these, the adsorption process is considered one of the most efficient treatments, owing to a low energy consumption, relatively low operation cost, and simple operations for the adsorption/regeneration of the adsorbent [12,13]. With adsorption, it is possible to
remove, without the generation of dangerous byproducts, a low/medium concentration of VOCs (<1000 mg/m³) [1]. Regarding destructive (i.e., oxidative) processes, the most commonly used ones are thermal (not-catalytic) combustion and catalytic oxidation, both of which can be applied to treat a medium/high concentration (>5000 mg/m³) of VOCs [14,15]. In particular, catalytic conversion has some advantages compared to thermal incineration; indeed, this process has become more popular than noncatalytic treatments. Catalytic oxidation allows converting VOCs into less toxic substances, such as carbon dioxide and water, in a temperature range much lower than thermo-oxidation [16,17]. Specifically, with catalytic conversion, the operating temperature range is 200–500 °C or even lower, whereas in thermal incineration, temperatures are higher (800–1200 °C). Lower temperatures permit reducing the production of dioxins and NOx. Furthermore, catalytic oxidation is more versatile and cheaper, especially when it comes to processing low concentrations of organic compounds [18]. In recent years, new technologies have been applied for the elimination of VOCs at low concentrations, namely, the advanced oxidation process (AOP), e.g., photocatalytic degradation, ozone treatment, Fenton oxidation methods [19,20], biodegradation [21], and phytoremediation [22].

Due to the economic and technological advantages of catalytic oxidation, widespread efforts have been committed to the selection of high-performing catalysts for this process. However, considering the large number of organic molecules and the problematic nature of VOCs mixtures, the design and optimization of catalytic materials are challenging tasks. Both noble and transition metals have been widely used as catalysts for either nonhalogenated or halogenated VOCs [23–25]. Notwithstanding their high costs, the supported noble-metal catalysts are widely applied due to their intrinsic features, such as resistance to deactivation, ease of regeneration, and highly catalytic performance [26–28]. These features strictly depend on the synthetic procedure adopted for the preparation of the supported metal catalyst, as well as the type of metal salt precursor, the metal loading, the kind of support, and the particle size [29–31]. Furthermore, VOCs and air/oxygen content, total gas stream rate, and employed reactor (membrane reactor, fixed-bed reactor, etc.) are key parameters that can affect overall catalytic activity [32–34].

In the literature, there are many studies that deeply analyze single or various parameters that influence the final results of catalytic oxidation applied to VOC treatment, including the catalysts used [16,35,36], the nature of VOCs [2,9,37], the combination of different technologies [1,38], the type of reactor [39], or the performances in practical applications [40].

One of the less explored strategies to enhance the catalytic activity of supported noble/transition metal catalysts is the addition of a second metal (noble and/or transition) to the first one. This work analyzes a little aspect of the VOC catalytic treatment topic: the advantages of using supported bimetallic catalysts with respect to monometallic counterparts, focusing on the morphological, chemophysical, and textural properties of these peculiar materials, and how these features can influence the catalytic activity.

This review aims to enlarge the scientific panorama about VOC removal through catalytic oxidation, focusing on the bimetallic catalysts, an aspect not yet systematically examined in the literature.

2. Bimetallic Catalysts for VOC Oxidation

Bimetallic nanoparticles (NPs) are a kind of materials formed by two different metals and characterized with peculiar features [41,42]. Specifically, they can show new properties resulting from the combination of features arising from the monometallic counterparts. Usually, the obtained physicochemical properties of bimetallic systems give a holistic result, i.e., the final properties are not the simple additive features of the monometallic analogs, but in many cases, it is possible to exploit a great improvement with new properties due to the presence of synergistic effects [43,44]. Since their application in the field of petrochemistry [45], bimetallic systems are being widely applied in heterogeneous catalysis in various reactions, such as hydrogenation [46,47], reforming [48,49], H2 production and purification [50–53], and oxidation [54–56]. Recently, they have also been applied in the biomedical field [57].
On the basis of the morphology of the bimetallic system, it is possible to classify the main arrangements into three typologies: core–shell or multishell structures, heterostructures, and random or homogeneous alloys (Figure 1) [43,44,58].

![Possible morphologies of bimetallic nanoparticles](image)

**Figure 1.** Possible morphologies of bimetallic nanoparticles (one metal in red, the other in dark yellow): (a), (b) core–shell system; (c) multishell system; (d) subcluster segregated systems; and ordered (e) and random (f) homogeneous alloys. Reprinted (adapted) from [58], Copyright 2008, American Chemical Society.

Various factors influence the final morphology of bimetallic systems: (1) the intrinsic strength of the bonds between the two metals in comparisons to the strength of the bonds between the two monometallic constituents (in particular, if the resulting alloy bond strength is greater, reciprocal mixing is preferred, and, in the opposite case, the segregation of the two metals is favored); (2) the balance in the surface energy of the metals, where the monometallic element that owns the lower surface energy will move to the surface, establishing a shell structure, while the metal with the smaller atomic sizes will collocate to the core; (3) the mixing is favored when an electron/charge transfer between the metallic counterparts is verified; and (4) magnetic effects can influence the final structure between the two metals [44,58,59].

The morphologies are also strictly affected by the preparation method adopted. In general, the synthesis of the bimetallic systems can be carried out with the solid-state or with the solution methods [60–62]. The latter are preferred because solid-state techniques require high temperatures and long times for annealing procedures, thus decreasing the surface area of the bimetallic catalyst and affecting catalytic performance in a crucial way. By contrast, with solution methods, it is possible to control the nucleation and growth processes by modifying the reaction parameters.

In the main catalytic reactions, the bimetallic system is supported on a specific support [63]. The commonly used techniques for the preparation of supported bimetallic catalysts are: impregnation [64,65], co-precipitation [66,67], deposition–precipitation [50,68], thermal decomposition [69], and chemical reduction [70]. The choice of a proper support is another key feature that strongly influences the catalytic activity of the bimetallic system. In particular, for VOC oxidation, and for oxidation reactions in general, the utilization of an active support (i.e., having redox properties and lattice oxygen mobility), for example, CeO$_2$ or Fe$_2$O$_3$, can contribute to the formation of a synergistic effect involving both the metals and the same support [68,71], whereas other supports, with high surface areas, such as zeolites, silica, alumina, etc., favor the high dispersion of the metal species and, therefore, the interaction between the metals and the same support [16,72].

Since the first works of Haruta and co-workers [73], gold-based catalysts have generated many investigations focused on the catalytic properties of this peculiar metal. With respect to the platinum-
group catalysts, gold’s properties are in some cases superior; consequently, the supported gold-based materials have found many applications in catalytic reactions dealing with environmental protection and energy production [50,72]. In the specific field of VOC catalytic oxidation, gold-based catalysts play a key role. For these reasons, bimetallic alloys with gold are firstly examined.

2.1. Gold-Based Bimetallic Catalysts

The important role of gold-based catalysts in heterogeneous catalysis was disclosed through the high activity of this metal in CO oxidation and selective oxidations [74,75]. After these studies, many works dealing with this catalyst have emerged, widely expanding the use of gold catalysts [72,76]. With respect to the other commonly used noble metals, namely, Pt and Pd, gold catalysts show peculiar features such as resistance to O₂ poisoning and high selectivity. Another key parameter that strictly affects the catalytic activity of Au catalysts is size-dependence: To be active, gold particles must be, in general, smaller than 5 nm, which balances the proportion of the low coordination surface active sites (edges and corners) [77].

For other applications, as well as for VOC oxidation, the catalytic activity of gold-supported samples is affected by many factors: (a) gold–support interaction; (b) gold loading; (c) the valence state of gold; (d) the adopted synthesis and pre-treatment conditions utilized; and (e) the concentration and nature of the chosen VOC target [78,79]. Among the monometallic gold catalysts employed for VOC oxidation, the Au/CeO₂ sample showed a great performance in the oxidation of oxygenated molecules, i.e., aldehydes, ketones, esters, and alcohols [72]. It was reported that the high activity was related to the enhancement in the surface oxygen reducibility/mobility of the CeO₂ support. The oxidation mechanism followed a Mars–Van Krevelen (MvK) mechanism, where the ceria lattice oxygens were actively involved in the oxidation pathway [68,80] (Figure 2).

![Figure 2. Lattice ceria oxygens of Au/CeO₂ catalyst involved in catalytic oxidation of formaldehyde. Reprinted (adapted) from [80], Copyright 2014, American Chemical Society.](image)

Nevertheless, the application of gold catalysts to industrial level is limited due to certain drawbacks, such as the decrease of activity in the presence of high concentration of moisture and the aggregation of gold nanoparticles at high temperatures [81,82].

Gold-based bimetallic systems are considered a useful solution to overcome the cited limitations, due to the combination of properties from the gold and the second metal. Among the various metals employed to be joined with gold, it has been found that Pd, Ag, and Cu show a high miscibility, and these systems can be prepared with a wide range of methodologies [83,84], whereas Pt, Ru, Co, Fe, and Ni are only partially or not at all miscible with gold [84]. Consequently, Au-Pd followed by Au-Ag and Au-Cu are the most utilized gold-based bimetallic catalysts for VOC oxidations.
2.1.1. Au-Pd Catalysts

Gold is miscible with palladium in all compositions; consequently, while the formation of gold–palladium alloys is favored, the segregation of single metals was, in fact, avoided [76,83]. In Table 1 are reported some of the experimental results of the application of the Au-Pd systems in catalytic oxidation of various VOCs (T90 = temperature at which the 90% of conversion was achieved).

In particular, Hosseini et al. [85] synthesized Au-Pd catalysts supported on mesoporous TiO2 for the removal of toluene, propene, and a gaseous mixture of both. Interestingly, they found that catalytic activity is influenced by the morphology of the core–shell structure with the best performance shown with the Au-core/Pd-shell. By contrast, with the reverse morphology (Au-shell/Pd-core) the catalytic activity was lower, due to the lower affinity of gold for oxygen adsorption (in this case, the rate determining step of the reaction that followed a Langmuir–Hinshelwood mechanism) caused by the poor ability of gold to polarize oxygen molecules. In the same context, Barakat et al. [86] investigated the catalytic stability of bimetallic Au-Pd/doped TiO2 samples under severe testing conditions (exposing the catalyst to 110 h of a gaseous toluene/air stream). The bimetallic catalyst maintained a good activity even after a long time. The interaction between the Nb-doped TiO2 support and the Au-Pd system allowed obtaining a cycle-like activity of the catalyst. This oscillatory behavior was related to the existence of carbonaceous compounds adsorbed on the surface of the spent catalyst that, together with the formed OH radicals, favored the reduction of palladium. The redox process of palladium was linked to the cyclic-like activity of the bimetallic sample (Figure 3).

Figure 3. Catalytic oxidation of toluene under ageing condition over Au-Pd/Nb-TiO2 catalyst. Figure from [86].
Table 1. Comparison between different supported Au-Pd bimetallic catalysts in catalytic oxidation of various volatile organic compounds (VOCs).

| Catalyst  | Preparation Method | Support    | VOC         | To (°C) | Ref. |
|-----------|--------------------|------------|-------------|---------|------|
| 1% Au-0.5% Pd  | core–shell         | TiO₂       | toluene     | ≈200 °C  | [85] |
| 1% Au-1% Pd    | chemical reduction | MnO₂       | toluene     | ≈180 °C  | [87] |
| 1% Au-1% Pd    | chemical reduction | Co₃O₄      | toluene     | ≈160 °C  | [88] |
| 1% Au-0.5% Pd  | core–shell         | TiO₂       | propene     | ≈190 °C  | [85] |
| 3% Au-1% Pd    | deposition–precipitation | CeO₂-5%Fe₂O₃ | benzene | ≈95 °C    | [89] |
| 1% Au-1% Pd    | deposition–precipitation | CeO₂   | benzyl alcohol | ≈120 °C | [90] |
| 2% Au-2% Pd-0.2% Fe | chemical reduction | MnO₃      | α-xylene    | ≈210 °C  | [91] |

1 Nominal concentration, weight percentage (wt%).

Regarding toluene degradation, Xie et al. [88] studied the catalytic performance of the bimetallic gold–palladium system supported on three-dimensionally ordered macroporous (3DOM) Co₃O₄. The bimetallic sample showed a much higher activity compared to its nonmetallic counterparts, with a To of about 100 and 30 °C lower compared to monometallic gold and palladium, respectively. The peculiar features of the 3DOM supports (such as higher porosity and ordered pore channels) were also exploited by the same authors [91], who utilized an Au-Pd bimetallic sample prepared via chemical reduction, but employing the Mn₂O₃ as support. The bimetallic catalysts confirmed the higher activity compared to monometallic gold and palladium in the oxidation of different VOCs, such as methane and α-xylene. To further boost catalytic activity, doping with Fe of the Au-Pd/3DOM-MnO₂ catalyst allowed modifying the structural properties of the alloy NPs. With this modification, oxygen activation and the methane adsorption ability were increased, enhancing, as final result, the overall catalytic activity.

Catalytic performance in various mixtures of VOCs (toluene/m-xylene, ethyl acetate/m-xylene, acetone/m-xylene, and acetone/ethyl acetate) was examined by Xia et al. [87] on Au-Pd prepared via chemical-reduction-supported αMnO₂ nanotubes. In this case, the authors focused on an MvK-like mechanism with the mutual interaction of the Au-Pd nanoparticles with the α-MnO₂ that improved the mobility/reactivity of the surface lattice oxygen of the support. In catalytic oxidation of VOC mixture, the rate-determining step is the competitive adsorption between the various VOCs on the surface of the catalyst. With the bimetallic catalyst, the authors measured the total oxidation of a single component and of the VOC mixture at T < 300 °C. The same bimetallic sample also showed a high catalytic stability in the long time (50 h) on stream experiments.

Tabakova et al. [89] focused their work on the removal of benzene utilizing an Au-Pd bimetallic system synthetized by deposition–precipitation and supported on Fe-doped CeO₂. The superior performance of the bimetallic catalyst with respect to the monometallic ones was highlighted through comparison of the To, which was ≈95 °C for the bimetallic sample, ≈180 °C for the Pd/Fe-CeO₂, and ≈190 °C for the Au/Fe-CeO₂. In addition, in this case, the synergistic interaction between the alloy nanoparticles and the support enhanced the mobility of the ceria surface lattice oxygen, further boosted by doping with iron. Moreover, this strong interaction facilitated the nucleation of the noble metal particles on the surface of cerium oxide.

Benzyl alcohol oxidation on Au-Pd bimetallic catalysts was extensively studied by the research group of Prati et al., and an exhaustive comparison of the performance, in this reaction, of the bimetallic Au-Pd systems present in the literature, together with a deep analysis of the various adopted preparation methods are reported in [83]. The same research group [76,83] studied the catalytic behavior of different bimetallic systems composed of Au and various other metals supported on activated carbon prepared using the sol immobilization methodology. Interestingly, they found a structural correlation depending on the second metal utilized. Specifically, an alloy structure was obtained using Pd and Pt, whereas a core–shell morphology was attained with Ru, while with Cu, a phase segregation of this metal, instead of gold, was favored. In the benzyl alcohol tests, the bimetallic synergistic effect was exploited only with copper and palladium.

The strong interaction between gold and palladium, beneficial for catalytic oxidation of benzyl alcohol, was also examined by Li et al. [90] using CeO₂ with different morphology as support. The
different morphology of cerium oxide (rod, cube, and polyhedrons), where gold/palladium nanoparticles were deposited–precipitated (Figure 4), affected the catalytic performance. Specifically, the Au-Pd supported on ceria rod showed a higher benzyl alcohol conversion with respect to the samples supported on CeO$_2$ cubes and CeO$_2$ polyhedrons and was thus related to the smaller particle size of ceria rod compared to the other CeO$_2$ supports; moreover, this particular morphology also favored a higher concentration of ceria oxygen defects, enhancing the mobility/reducibility of the ceria surface oxygens. By contrast, the sample supported on the CeO$_2$ cube exhibited the highest selectivity in benzaldehyde.

Kucherov et al. [92] investigated the performance of mono- and bimetallic gold-based catalysts for the removal of dimethyldisulfide (DMDS), an S-VOC. They corroborate the performance of Au-Pd catalysts also for this type of VOC. The bimetallic sample supported on TiO$_2$ demonstrated a stable performance and assisted with the removal of DMDS at T < 155 °C with the formation of SO$_2$ and elemental S.

**Figure 4.** TEM (Transmission electron microscope) and HRTEM (High-resolution transmission electron microscope), images of: Au-Pd/CeO$_2$-rod (a, b); Au-Pd/CeO$_2$-polyhedron (c, d); and Au-Pd/CeO$_2$-cube (e, f) catalysts. Figure from Ref. [90], Copyright 2020, Elsevier.
2.1.2. Au-Ag and Au-Cu Catalysts

The establishment of a strong interaction between gold and silver with the formation of an alloy or of bimetallic clusters was investigated by our research group both in VOC oxidation and in \( \text{H}_2 \) purification towards the preferential oxidation of CO (PROX reaction) [50,53,68]. In particular, we evaluated the catalytic activity of Au-Ag and Au-Cu bimetallic samples supported on \( \text{CeO}_2 \) toward the degradation of 2-propanol and ethanol. A higher activity was found of the gold–silver sample with respect to Au-Cu and the monometallic counterparts. The higher activity of the gold–silver system was correlated to a higher mobility/reactivity of ceria surface oxygens, due to a strong synergistic interaction between the gold–silver nanoparticles and the cerium oxide. A linear correlation was stated considering the \( T_{50} \) of alcohol oxidation and the TPR (temperature-programmed reduction) initial temperature, i.e., the temperature at which the reduction of ceria surface oxygens started considering the analyzed samples (Figure 5). The Au-Ag/CeO\(_2\) catalyst displayed the lowest reduction temperature and \( T_{50} \).

![Figure 5](image)

**Figure 5.** Temperature at which the 50% of conversion of ethanol and 2-propanol was achieved (\( T_{50} \)) versus TPR (temperature-programmed reduction) initial temperature: (filled diamond) Au-Ag/CeO\(_2\); (filled circle) Au-Cu/CeO\(_2\); (filled square) Au/CeO\(_2\); (filled triangle) Ag/CeO\(_2\); (times) Cu/CeO\(_2\). Figure from [68], Copyright 2015, Springer Nature.

Nagy et al. [93] studied the performance of Au-Ag nanoparticles supported on SiO\(_2\) synthetized from the adsorption of bimetallic colloids in the oxidation of benzyl alcohol. The authors focused their research on the crucial importance of the molar ratio between the two metals. In particular, a synergistic effect was verified that reflects a higher activity at a low Ag/Au molar ratio (best result Ag/Au = 23/77). For the authors, the synergy is activated by the optimal concentration of the two metals, which increased the activation of both oxygens from gas-phase and from the support. In the same context, a correlation between catalytic activity and the concentration of gold and silver was measured by our research group in the PROX reaction [50] with a higher concentration of gold or silver with respect to the second metal that was detrimental for the overall catalytic performance, whereas the best results were obtained with an approximately equal concentration of gold and silver (1% wt-1% wt).

The crucial importance of the molar ratio between gold and the other metal was also stated in the review of Bracey et al. [94], focused on the Au-Cu system. Specifically, in one of the analyzed works, the following order of reaction in catalytic oxidation of propene is reported: AuCu (1:3 molar ratio)/TiO\(_2\) > AuCu (1:1 molar ratio)/TiO\(_2\) > AuCu/TiO\(_2\) (3:1 molar ratio) > Au/TiO\(_2\). The content of copper, in fact, strongly influenced the dispersion of the metal nanoparticles, with a high amount of copper in the alloy that caused a decrease in the size of the metal particles, thus contributing to enhancing the activity and selectivity into propene oxide [95]. In the same review, it was illustrated that, when investigating another reaction, such as selective oxidation of benzyl alcohol to benzaldehyde, the more active bimetallic catalyst was the sample with the higher concentration of gold (the catalyst AuCu/SiO\(_2\) with a molar ratio of 4:1). Similarly to the previous examples, the
bimetallic catalyst was prepared by impregnation, but in this case, a higher concentration of gold is fundamental to achieve a high selectivity (98%) to benzaldehyde.

The above-discussed literature data on AuCu bimetallic catalysts were mainly focused on the selective oxidation of VOCs, whereas the work of Nevanperä et al. [96] dealt with catalytic oxidation of DMDS with bimetallic gold-based catalysts (Au-Cu and Au-Pt) supported on γ-Al₂O₃, CeO₂, and CeO₂-Al₂O₃ prepared by surface redox reduction. Among the examined supports, the alumina gave the best results, whereas the addition of gold enhanced the catalytic activity of both monometallic copper and platinum samples, Au-Cu catalysts being the most active system. Interestingly, the authors noted that the same Au-Cu catalyst led to the formation of dangerous byproducts, such as carbon monoxide and formaldehyde. This was attributed to the high concentration of reactive surface oxygens favored by the presence of copper oxide and to the dissociation of the oxygen that started at a lower temperature with respect to the monometallic samples, with the consequent modification of the surface acid and basic sites of the bimetallic catalyst. By contrast, selectivity towards CO₂ and H₂O was higher in the Au-Pt sample.

2.1.3. Other Au-Based Bimetallic Catalysts

As discussed in the last examined work, among the other Au-based bimetallic catalysts, the Au-Pt system exhibited promising performance in VOC oxidation [96–98].

Kim et al. [97] investigated catalytic oxidation of toluene employing the Au-Pt/ZnO-Al₂O₃ catalyst prepared by impregnation in air or H₂. They found that the bimetallic sample prepared in air led to an increase of the gold particle size and a decrease of the Pt with respect to the same particles synthetized in H₂ stream, where an inverse correlation was verified (the gold size decreased, and the platinum size increased). Due to the crucial importance of the gold nanoparticles that facilitated the total oxidation of toluene and that increased the reduction of the surface oxygen of the mixed oxide support, the catalytic performance was higher with the bimetallic sample synthetized in H₂ stream and calcined at 400 °C (Pt and Au mean size of about 5 nm). In another study [98], the same authors correlated the catalytic activity of the same bimetallic samples, even in the total oxidation of toluene, to the molar ratio of gold and platinum, finding the following order of activity: Pt₇₅Au₂₅ > Pt₆₇Au₃₃ > Pt₁₀₀Au₀ > Pt₅₀Au₅₀ > Pt₃₃Au₆₇ > Pt₂₅Au₇₅ > Pt₀Au₁₀₀. The small amount of gold promotes the total oxidation of toluene due to the formation of a strong metal–metal interaction.

The good affinity of gold with noble metals was also confirmed via the catalytic performance in VOC removal of the Au-Ru system [99,100]. Sreethawong et al. [99] investigated catalytic oxidation of methanol over gold–ruthenium samples prepared through impregnation and supported on SiO₂. The characterization measurements (TPR, SEM, and XRD) suggested the occurrence of an interaction between the two metals exploited with a particular composition (3.32 wt%Ru–0.61 wt% Au), which led to obtaining a good catalytic activity, notwithstanding the fact that the two metals were not miscible in their bulk phase. Interestingly, if alumina was used as support, the formation of byproducts (methyl formate, formic acid, dimethyl ether, and formaldehyde) other to CO₂ was detected, with an increase of methanol conversion. Catalytic oxidation of methanol was also analyzed by Calzada et al. [100] with Au-Ru/TiO₂ catalysts prepared by deposition–precipitation with urea. The authors highlighted that the synergistic effect between the two metals was activated at a low conversion temperature (from room temperature to T = 50 °C), with a dependence on the bimetallic atomic ratio (the best-performing one was Ru: Au 0.75:1). Interestingly, the DRIFT (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) CO spectra (Figure 6) illustrated as the interaction between the two metals decreased CO adsorption in the Ru surface sites in the Ru-Au 0.75:1 sample, an indication of the modification of the surface gold sites.
The modifications of the bimetallic surface sites due to interaction between the two metals strongly occurring with the Ru:Au 0.75:1 ratio were the reason behind the higher catalytic activity of this bimetallic sample compared to those of the monometallic catalysts and the Ru:Au 1:1 sample. In addition, in this case, the formation of formates as intermediates of the oxidation reaction was verified.

Catalytic activity in the total oxidation of toluene of the Au-Ir bimetallic catalyst supported on TiO2 was studied by Torrente-Murciano et al. [101]. Similarly to the previous case, the synergistic interaction between the two metals allowed them to sensibly decrease the T90 that was ≈230 °C for the bimetallic sample, ≈250 °C for the monometallic gold, and ≈270 °C for Ir/TiO2. The key factors that deeply influenced catalytic activity were the strong metals–support interaction exploited with the bimetallic system, which also permitted diminishing the loss of activity due to the metals sintering at high temperatures. Furthermore, the intimate contact between iridium and gold modified the bimetallic surface-active sites enhancing oxygen activation.

In the work cited in Section 2.2, Kucherov et al. [92] demonstrated a good activity of Au-Rh supported on HZSM-5 zeolite into the oxidation of the DMDS in SO2 at 290 °C. In this case, the zeolite support, owing to a high surface area, favored a high dispersion of the metals, a feature that is beneficial for catalytic activity.

Regarding gold–copper bimetallic systems, there are certain studies with other transition metals, utilized together with gold for VOC oxidation. Au-Co and Au-Fe interaction were principally investigated. In the examined works, the gold atoms interacted with the second metal present as a doping agent of the support [102–104].

Solsona et al. [102] synthetized gold nanoparticles anchored on cobalt containing mesoporous silica (UVM-7). The interaction between gold and cobalt permitted increasing catalytic activity in the oxidation of toluene and propane with respect to Au/UVM-7 and Co/UVM-7 catalysts. The presence of gold enhanced the reducibility of cobalt, present as CoOx at the Au-Co interface, thus facilitating the redox cycle of cobalt, with an MvK-like mechanism, which boosted catalytic oxidation of VOCs. In the same context, Albonetti et al. [103,104] deeply investigated the catalytic behavior of gold catalysts supported on mesoporous silica (SBA-15) via an iron oxide layer obtaining the Au/FeOx/SBA-15 composite. The good dispersion of nanosized gold favored the incidence of a strong synergism between gold and iron that led to an optimal activity in the combustion of methanol (T90 ≈ 140 °C).

As a conclusion of this generic overview of gold-based bimetallic catalysts applied at VOC oxidation, it is possible to recognize some fundamental features of these peculiar catalysts: (a) the essential action of the nanosized gold that is able to establish a metal–metal surface interaction with...
a wide range of both noble and transition metals; (b) the occurrence of a synergism between the two metals that allows sensibly decreasing the light-off temperatures of VOC oxidation; (c) the synergistic effect, which is not simply the addition of the single characteristics of the corresponding monometallic samples but leads to exploring new physicochemical properties; (d) the mutual interaction between the two metals which also strongly influences metals–support interaction (in particular, if the support is a reducible oxide (CeO2, MnOx, CoOx, etc.), the gold-based bimetallic cluster increases the mobility of the surface oxygen of the support, enhancing, in this way, catalytic oxidation towards an MvK mechanism). If the support is a nonreducible or hardly reducible oxide (TiO2, SiO2, and zeolites), the high dispersion of the bimetallic alloy and the modifications of the metals surface active sites allow enhancing oxygen adsorption, improving, as a final result, the overall catalytic performance. The most employed preparation methods of the supported gold-based bimetallic catalysts are impregnation (wet or wetness), deposition–precipitation, and chemical reduction.

2.2. Other Bimetallic Catalysts

Among the other noble metals, the most employed catalysts for catalytic oxidation of VOCs are platinum-based materials [16], and similarly to gold, platinum has shown a good affinity with palladium [105–108]. In general, as can be seen from Table 2, the use of noble-metals-based bimetallic catalysts has allowed obtaining a good performance in the removal of VOCs, whereas the utilization of transition-metals-based materials has led to shift at high temperatures in the total conversion of VOCs. However, especially in recent years, the necessity to reduce the amount of expensive noble metals has led to exploring a new synergism between noble and transition metals.

Fu et al. [105] prepared, for the hydrothermal method, a Pt-Pd bimetallic sample supported on mesoporous silica. Comparably to the catalytic behavior of gold-based samples, the synergism between the two metals allowed obtaining a superior performance in the removal of toluene with respect to the monometallic samples, with an improvement in the reducibility of palladium, involved in the redox cycle PdO→Pd(0), and in oxygen adsorption capability.

Table 2. Comparison between different supported bimetallic catalysts in catalytic oxidation of various VOCs.

| Catalyst | Preparation Method | Support | VOC | T90 (°C) | Ref. |
|----------|--------------------|---------|-----|----------|------|
| 0.2%Pt-0.1%Pd | hydrothermal | Silica MCM-41 | toluene | ≈170 °C | [105] |
| 0.3%Pt-2%Pd | impregnation | γ-Al2O3 | benzene | ≈225 °C | [106] |
| 2%Ru-5%Co | impregnation | TiO2 | benzene | ≈200 °C | [109] |
| 1%Ru-5%Ce | impregnation | TiO2 | chlorobenzene | ≈275 °C | [110] |
| 18%Mn-0.1%Pd | impregnation | γ-Al2O3 | formaldehyde/methanol | ≈80 °C | [111] |
| 15%Mn-5%Cu | impregnation | γ-Al2O3 | toluene | ≈380 °C | [112] |
| 1.3%Fe-1.75%Ag | ionic exchange | ZMS-5 | ethyl acetate | ≈250 °C | [113] |

1 Nominal concentration, weight percentage (wt%).

The good catalytic activity of the Pt-Pd system was also confirmed by Kim et al. [106] in the degradation of benzene. Catalysts were synthetized via wetness impregnation on γ-Al2O3. Metal–metal interaction was favored by the formation of small and uniform particles and, as stated in the previous paragraphs, a specific amount ratio between the two metals (the optimum in the cited work is 0.3 wt% Pt–2% wt Pd). A higher concentration of platinum led to a remarkable decrease in activity due to the blockage of the active sites. The same authors in another paper [107] confirmed with a deep XPS (X-ray photoelectron spectroscopy) analysis the crucial role of the ratio between the metals to avoid the obstruction of the catalyst surface sites. The removal of methanol, acetone, and methylene chloride was instead studied by Sharma et al. [108], utilizing ceramic Raschig rings coated with Pt and Pd on fluorinated carbon. The authors measured a higher activity of the bimetallic catalyst with respect to monometallic ones. Furthermore, the hydrophobic nature of this particular bimetallic catalyst allowed obtaining a 90% of degradation of methanol and acetone at about 150 and 300 °C respectively, whereas 60% of degradation was achieved at 400 °C for the methylene chloride. In this case, a good correlation was established with a semi-empirical Langmuir–Hinshelwood...
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model, which is able to predict the oxidation rate of each VOC in a gas mixture (methanol, acetone, and methylene chloride).

Ethanol adsorption and oxidation were investigated by the research group of Wittayakun et al. [114] with a Pt-M (M = Co, Cu, Mn) sample supported on silica MCM-41. Among the transition metals, cobalt gave the best results, and in particular, the bimetallic 0.5 wt% Pt–15 wt% Co exhibited the best ethanol adsorption and CO₂ desorption. Interestingly, the authors identified two different reaction mechanisms considering the platinum monometallic sample and the bimetallic platinum–cobalt one (Figure 7).

![Figure 7. (a) Ethanol oxidation mechanism on 0.5 wt% Pt/MCM-41; and (b) ethanol oxidation mechanism on 0.5 wt% Pt–15 wt% Co/MCM-41. Figure modified from [114]. Copyright 2012, Elsevier.](image)

Specifically, in the monometallic sample after the adsorption of ethanol, a formation was verified of a parallel adsorbed acetaldehyde, further converted into monodentate acetate and at end, dissociated and desorbed as carbon dioxide, methane, and water (Figure 7a). In the bimetallic catalyst, by contrast, the ethoxy species reacted with the adsorbed oxygen to give a bidentate acetate species that was transformed into carbon dioxide (Figure 7b). The modification of the ethanol adsorption led to a higher ethanol conversion with the monometallic platinum sample in comparison with the bimetallic Pt-Co sample that, conversely, showed a higher catalytic stability. Even with the bimetallic platinum-based catalysts, Chantaravitoon et al. [115] examined the performance of a Pt-Sn/γ-Al₂O₃ catalyst prepared with impregnation, for the oxidation of methanol. The authors noted from the temperature-programmed desorption (TPD) measurements of methanol oxidation that on the bimetallic catalyst, methanol decomposed as H₂ and CO and the desorption peaks shifted at higher temperatures, increasing the amount of Sn. In addition, in this case, the monometallic Pt catalyst exhibited a better performance compared to the bimetallic one; however, the addition of a small amount of Sn (<5 wt%) reduced the deactivation of the catalyst in the long-time tests.

In addition, Ru-based bimetallic compounds were discreetly studied for VOC oxidation [109,110,116]. Liu et al. [109] prepared Ru-M (M = Co, Mn, Ce, Fe, Cu) samples supported on TiO₂, evaluating catalytic performance in the degradation of benzene. Among the various metals, 1% wt Ru-5% wt Co showed the best activity; the presence of ruthenium, in fact, increased the reducibility...
of $\text{Co}_3\text{O}_4$. The authors stated also that the presence of water vapor inhibited benzene oxidation at $T = 210 \, ^\circ\text{C}$.

The total oxidation of propene was examined on Ru-Re/$\gamma$-Al$_2$O$_3$ by Baranowska et al. [116]. As discussed before, this nonconventional combination between these two metals also allowed increasing catalytic stability in the consecutive tests instead of the overall catalytic activity, which remained superior with the monometallic Ru sample. The addition of Re (the best composition being 5% wt Ru–3% wt Re) hampered the formation of RuO$_2$ agglomerates. In this way, the dispersion of ruthenium is favored, allowing a higher stability compared to monometallic ruthenium catalysts. Ye et al. [110] performed a catalytic test regarding chlorobenzene removal with Ru-Ce/TiO$_2$ samples prepared via impregnation. Interestingly, on the basis of the crystalline phase of titanium dioxide, the catalytic activity changed. At 280 $^\circ\text{C}$, the bimetallic sample showed a conversion of 91% and 86% if supported on TiO$_2$:rutile and TiO$_2$:P25 (80% anatase, 20% rutile), respectively. The mixed crystalline phase of P25 was the best support for the monometallic ruthenium catalyst. By contrast, with respect to the work of Baranowska et al. [116] for this reaction and with the titanium dioxide support, dispersion was not the major parameter that affected catalytic activity; indeed, on 1%wt Ru–5% wt Ce/TiO$_2$ (rutile), the abundant RuO$_2$ clusters favored both catalytic activity and stability.

Interaction with Ce/CeO$_2$ was also investigated by Yue et al. [117] but utilizing palladium. The performance of the bimetallic catalyst Pd-Ce/ZMS-5 synthetized through impregnation was evaluated on the degradation of methyl ethyl ketone (MEK). The presence of cerium oxide considerably increased the acid sites of palladium, enhancing at the same time the re-oxidation of Pd and boosting, in the end, the overall MEK degradation rate through an MvK mechanism.

Another bimetallic catalyst with palladium was prepared by Arias et al. [111]. In this work, the synergistic effect between palladium and manganese was explored utilizing alumina as support. The authors followed the oxidation of a VOC mixture (formaldehyde/methanol), concluding also in this case that an MvK-like mechanism was the reaction pathway, with the interaction between palladium and manganese favoring the oxidation of VOCs due to the activation of the reactive lattice oxygen of PdO and MnO$_2$.

Various bimetallic samples were tested for catalytic oxidation of VOCs, studying both the physicochemical properties and the catalytic activity of silver-containing samples [113,118–120]. In particular, Jodaei et al. [113,118] tested different Ag-M bimetallic samples supported on ZMS-5 zeolite obtained via ionic exchange. The authors investigated the catalytic combustion of ethyl acetate, finding this order of activity and stability: Fe-Ag/ZSM-5 > Co-Ag/ZSM-5 > Mn-Ag/ZSM-5 > Ag/ZSM-5. The high dispersion of silver was favored by an optimal amount of iron (1.3 wt% Fe–1.75 wt% Ag), thus activating a synergistic effect between the two metals. In the same context, Izadkhah et al. [119] made a theoretical model for the removal of ethyl acetate. In particular, considering the preparation condition, the formulation, and loading of the promoter of silver, with their algorithm, it was possible to identify the optimal catalyst for this reaction. Among the first transition metal series, the bimetallic catalyst that exhibited superior performance compared to the monometallic silver was Fe-Ag/ZSM-5, thus confirming the experimental results of Jodaei et al. [113,118], Ni-Ag/ZSM-5 and V-Ag/ZSM-5.

Complete oxidation of formaldehyde at $T < 90 \, ^\circ\text{C}$ was obtained by Qu et al. [120] with Ag-Co/MCM-41 silica. The key feature able to sensibly increase catalytic performance with respect to the monometallic silver was electron transfer between silver and cobalt that enhanced the reducibility of cobalt oxide, increasing, at the same time, the activation of surface oxygen on the bimetallic catalyst. Furthermore, the high metal–metal support interaction (SMMI) at the optimal Ag/Co mass ratio (3:1) favored a faster adsorption–dissociation of formaldehyde on the Ag species with respect to the Co$^{3+}$ sites (Figure 8), thus decreasing the light-off temperature of VOC oxidation.
On the same support (MCM-41 silica), Pârvulescu et al. [121] synthesized with the hydrothermal method various Co-based bimetallic mesostructures (Co-V, Co-La, Co-Nb) characterized by a high surface area and narrow pore size distribution. The oxidation of styrene and benzene was deeply influenced by the addition of a second metal component. Indeed, although the addition of La did not result in any synergistic effect, the addition of vanadium favored the oxidation of benzene, whereas the addition of niobium facilitated the removal of styrene, demonstrating that the presence of the second metal changed the surface-active sites of cobalt.

Similarly to cobalt, copper-based bimetallic catalysts also showed a good activity in the removal of VOCs [112,122,123]. Kim et al. [112] found an optimal interaction between Mn and Cu for the total oxidation of toluene. The order of activity considering other transition metals as a second component was: 5% wt Cu-15% wt Mn/γ-Al2O3 > 5% wt Co-15% wt Mn/γ-Al2O3 > 5% wt Ni-15% wt Mn/γ-Al2O3 > 15% wt Mn/γ-Al2O3 > 5% wt Fe-15% wt Mn/γ-Al2O3. The interaction between Mn and Cu favored a high dispersion of manganese, increasing, at the same time, the mobility/reducibility of manganese oxide. The oxidation of toluene was studied recently by Djinović et al. [122], who had examined the performance of monometallic CuO and bimetallic Cu-FeOx composites supported on KIL-2 silica. The utilization of two reducible oxides allowed increasing the amount and reactivity of oxygen species, which included adsorbed (O− and O2−) and lattice (O2−) oxygens at the Cu-FeOx interface, providing a substantial decrease of T90 that was ≈350 °C for the bimetallic cluster instead of ≈450 °C of monometallic copper oxide, whereas the FeOx/KIL-2 silica reached only 30% of toluene conversion at 450 °C.

Abdullah et al. [123] investigated the oxidation of a Cl-VOC mixture (dichloromethane (DCM), trichloroethylene (TCE) and trichloromethane (TCM)) with Cu-Cr/ZMS-5. Interestingly, in this case, the presence of water vapor in the gas feed enhanced the total oxidation to CO2. The presence of water vapor favored the formation of reactive carbocations. Furthermore, H2O was beneficial in blocking chlorine-transfer reactions. Indeed, an important deactivation effect was found with the bimetallic catalyst at a higher Cl/H gas feed ratio, and chlorination led to a decrease in metals’ reducibility that resulted in a low degradation efficiency. The reaction was driven by an MvK mechanism.

At this point, it is possible to highlight some differences through comparison of the catalytic performance of gold-based bimetallic samples with the others reported above. For the nongold-containing samples category, supports with a high surface area or with a tunable pore size distribution (silica, zeolite, alumina, etc.) were preferred to favor the dispersion of the active metals. Platinum-based samples gave the best results, with a second metal that in many cases enhances catalytic stability rather than overall VOC conversion. Although noble-metals–bimetallic catalysts showed the best performance, in recent years, in order to reduce the high cost of these catalysts, the addition or replacement of at least one of the noble metals with a cheaper transition metal is an interesting approach to reduce the total material cost while maintaining an acceptable catalytic activity.
### 3. Bimetallic Catalysts for the Photocatalytic Oxidation of VOCs

The urgent request for a “greener” and sustainable industrial chemistry has driven a huge field of research towards alternative ways to treat VOCs instead of catalytic combustion. Among the various AOPs (see the Introduction section), photocatalytic oxidation is the most applied process. With respect to catalytic thermal oxidation, this technique allows working at room temperature, exploiting the chemophysical processes activated by an appropriate light radiation interacting with the surface of a semiconductor photocatalyst [40,124–126]. Specifically, dangerous organic compounds are oxidized by hydroxyl, and super oxide radicals are generated by the interaction between the photoelectrons and photoholes of the photocatalyst with water and oxygen. These photoelectrons and photoholes are formed when an adequate wavelength ($\lambda \leq \lambda_g$, of the semiconductor) irradiates the photocatalyst [127,128]. The most used photocatalysts are metal oxides or sulfides such as TiO$_2$, ZnO, WO$_3$, ZrO$_2$, CeO$_2$, Fe$_2$O$_3$, ZnS, and CdS, and among them, TiO$_2$ and ZnO are the most used [129,130]. Due to its properties, such as its nontoxicity, relatively low cost, and high activity, especially under UV irradiation, titanium dioxide was deeply investigated both in academic and industrial research [124,126]. With a band gap varying from 3.0 to 3.2 eV depending on the crystalline form, TiO$_2$ is able to exploit only 5% of solar radiation, thus limiting its practical applications. Photothermocatalytic oxidation is a multicatalytic approach that accepts the contemporaneous utilization of a light source to activate the photocatalyst, and thermal heat to boost the conversion of organic molecules and to increase the yield to CO$_2$. A proper structural and/or chemical modification of titanium dioxide together with this multicatalytic approach can be considered a suitable solution to decrease the total energy consumption, maintaining the high conversion values typical of thermocatalytic oxidation of VOCs [131–133]. Another connected strategy to increase the photocatalytic performance of titanium dioxide under solar/visible light irradiation is doping with metal or nonmetal elements [134–136], and a not yet largely explored strategy is the combination of a bimetallic alloy with TiO$_2$ [137,138]. The same metals typically employed for catalytic oxidation of VOCs, such as Au, Ag, Pt, Pd, and Cu in the nanoparticle size, if irradiated with (usually) a visible light irradiation, allow exploiting the localized surface plasmon resonance (LSPR) through collective oscillations of the electrons in the surface of the metal nanoparticles. This effect, combined with the photocatalytic properties of TiO$_2$, is a performance solution to obtain a visible-light-driven photocatalyst [124,139,140]. In addition, for this particular application, bimetallic compounds can help to overcome some of the drawbacks of single metals. For example, the LSPR of some noble metals such as Pd, Pt, and Rh is not efficiently activated by solar irradiation, and a possible combination with the most effective plasmonic metals, such as Au, Ag or Cu, leads to taking advantages of both the LSPR effect and of the reactive catalytic behavior of the other noble metals [137].

For the above considerations, in VOC photo-oxidation, the most investigated system was the Au-Pd bimetallic compound joined with a semiconductor photocatalyst [141–145]. In these materials, the good affinity of gold and palladium, already discussed in terms of thermocatalytic performance (Section 2.1.1.), is in this case utilized to increase the photocatalytic performances of titanium dioxide or of another semiconductor oxide.

Colmenares et al. [141] synthetized an Au-Pd/TiO$_2$ photocatalyst with the original technique of sonophotodeposition (Figure 9). The bimetallic sample exhibited high activity (83%) and good selectivity (70%) in the partial oxidation of methanol to methyl formate after 120 min of UV irradiation (125 W mercury lamp $\lambda_{max} = 365$ nm). Although the bimetallic catalyst showed a low selectivity to CO$_2$ ($<30$%), demonstrating that this approach is better suitable for selective oxidation than the total oxidation of VOCs, the reported material synthesis and adopted reaction conditions are a fascinating way to obtain results with an energy-efficient procedure and a selective photocatalyst in a short time and under mild conditions.
Figure 9. Sonophotodeposition setup before (a) and during the deposition procedure (b): (1) batch photoreactor; (2) argon line; (3) switched off 6 W UV lamp; (4) ultrasonic bath; (5) switched on 6W UV lamp; (6) reflux condenser; and (7) lamp cooling system (20 °C). Figure from [141], Copyright 2015, John Wiley and Sons

In a further study, the same research group [142] developed a density functional methodology to analyze the reaction mechanism of the selective photo-oxidation of methanol on the bimetallic Au-Pd/TiO₂ sample. The theoretical investigation showed, as with the formation of a synergistic interaction between gold and palladium, a superior photoelectron–hole separation, was verified in comparison with the monometallic samples. Furthermore, it was shown that to favor total photo-oxidation to CO₂, the dissociation of molecular oxygen should be driven preferentially on Pd to favor the formation of PdO sites, where complete oxidation (no methyl formate formation) to carbon dioxide occurred.

Cybula et al. [143] investigated the performance of an Au-Pd bimetallic sample supported on rutile TiO₂ synthetized with a water in oil microemulsion methodology, in the photocatalytic oxidation of toluene and phenol under visible light irradiation (25 LEDs (λₓᵧₓ = 415 nm)). In particular, the authors focused on the effect of calcination temperature on materials’ preparation. The bimetallic sample calcined at 350 °C achieved 65% of toluene degradation and 22% of phenol conversion after 60 min of visible light irradiation. The performances were inferior compared to the photoactivity of monometallic palladium (79% in the toluene degradation and 24% in the phenol removal); however, the synergistic effect combined with a strong metals–support interaction was better exploited in the UV-vis tests, where the intrinsic photoactivity of rutile TiO₂ also made a substantial contribution in removal efficiency. In fact, with the bimetallic sample, 100% of phenol degradation was achieved after 60 min of irradiation instead of the 56% of Pd/TiO₂.

The interaction of the gold–palladium compound with other semiconductors was examined by the research group of Zhang et al. [144,145]. The photocatalytic oxidation of the trichloroethylene was studied on Au-Pd/BiPO₄ nanorods and on Au-Pd/MoO₃ nanowires. Interestingly, with the deposition of the Au-Pd alloy on the surface of the BiPO₄ nanorod, the photocatalytic degradation rate increased quickly, being about 25 times higher compared to that achieved with bare BiPO₄. The authors proposed, on the basis of the characterization measurements, the reaction mechanism illustrated in Figure 10. Under visible light irradiation (solar simulator with a 440 nm cut-off filter), Au-Pd/BiPO₄ were excited due to the LSPR of the Au-Pd alloy. An effective charge carrier separation was achieved due to electron transfer from the conduction band (CB) of BiPO₄ to the Au-Pd surface interface, whereas the photoholes remained confined in the valence band (VB) of BiPO₄. Subsequently, the same photoelectrons present in the surface of the Au-Pd alloy reacted with the oxygens in the gas-phase that were successively reduced into superoxide radicals. These radicals together with the holes in the VB of BiPO₄ oxidize the trichloroethylene in water and carbon dioxide.
The synergistic effect between gold and palladium nanoparticles that permitted increasing charge carrier separation, enhancing in this way photocatalytic activity, was verified, also employing MoO3 nanowires as a semiconductor photocatalyst [145].

The exploration of the synergistic effect with a bimetallic alloy in the photocatalytic oxidation of VOCs has not yet been largely investigated in the literature, and only a few examples are present considering other compounds instead of the Au-Pd system [146–149]. The possibility of favoring a selective oxidation route due to the high selectivity of gold–silver nanoparticles was examined by Han et al. [146] even in partial oxidation of methanol to methyl formate. In this case, the Au-Ag/TiO2 powders prepared via chemical reduction showed good results with a methanol conversion of 90% and a selectivity to methyl formate of about 85% under UV irradiation (500 W high pressure mercury lamp, $\lambda_{\text{max}} = 365$ nm). Similarly to the Au-Pd systems, the bimetallic alloy enhanced the photoelectron–photohole separation with electron transfer from the conduction band of TiO2 (excited by the UV irradiation) to the gold–silver surface interface.

Another alloy with silver, i.e., Ag-Pt, was studied by Zielińska-Jurek et al. [147] in the photo-oxidation of toluene under visible light irradiation (LEDs, $\lambda_{\text{max}} = 415$ nm). The authors found an interesting correlation regarding the order of deposition of the Ag-Pt/TiO2 photocatalysts prepared by sol–gel. In particular, the best sample (best photoactivity) was the material where the silver precursor was added before the platinum one. It was fundamental, in fact, to obtain particles with a definite size and dispersion (Ag-Pt size between 6–12 nm). In this way, it was possible to increase the toluene degradation rate with respect to the monometallic samples. By contrast, the bimetallic sample prepared with a simultaneous addition of metals precursors on TiO2 gave a lower photoactivity and different metal size and distribution. The authors concluded that platinum size had a greater influence than silver in determining overall photocatalytic activity. Recently, the same research group evaluated photocatalytic performance in both toluene and acetaldehyde degradation and of Penicillium chrysogenum, a dangerous fungus present in the indoor environment with Ag-Pt/TiO2 and Cu-Pt/TiO2 samples [148]. Both bimetallic samples showed a higher fungicidal activity under visible light irradiation than bare TiO2, whereas in VOC degradation, the Ag-Pt system was better-performing compared to Cu-Pt. The peculiar activity of both bimetallic samples was ascribed to the interfacial charge transfer process between the two metals and the TiO2 confirmed by the quenching of fluorescence (i.e., intensity diminution of the TiO2 photoluminescence bands) due to the presence of the metal alloy.

Wolski et al. [149] studied the mechanism of methanol photo-oxidation on bimetallic Au-Cu catalyst supported on Nb2O5 with an in operando IR methodology under both UV and visible light irradiation. Interestingly, they found that photocatalytic activity is strictly related to the light sources used and to the number of Brønsted/Lewis acid sites present on the surface of the catalysts. Specifically, under visible light irradiation, the synergism between gold and copper led to an increase in the amount of Bronsted/Lewis acid sites on the niobia, with a consequent higher activity of
bimetallic samples compared to that of monometallic and pure Nb2O5 samples. Furthermore, the total oxidation to CO2 was favored. By contrast, with UV light irradiation, the major activation of niobia (Eg ≈ 3.2 eV) favored selective oxidation into dimethoxymethane, formaldehyde, and methyl formate.

In this short chapter, the state-of-the-art of the application of bimetallic structures as chemical modifiers of conventional and unconventional semiconductor photocatalysts was examined. This approach is relatively new, and the effects of alloy synergism on the photocatalytic process are currently under investigation. The promising results, especially obtained by combining the LSPR effect of both noble and transition metals with semiconductor photoactivity, together with a possible multicatalytic strategy (i.e., a photothermo atalytic approach employing a bimetallic/semiconductor catalyst and a solar/visible light source) could in the future be a fascinating strategy to develop a greener and sustainable technology applied to the removal of volatile organic compounds.

4. Conclusions

In this review, the application of bimetallic catalysts for VOC oxidation was examined in terms of catalytic activity and physicochemical properties. Among the various systems, gold-based bimetallic catalysts exhibited a good performance in the degradation of a wide range of VOCs. The presence of nanosized gold was essential to decreasing the light-off temperature of VOC oxidation, whereas interaction with the second metal allowed increasing the reactivity of the employed support or enhancing oxygen activation. Although platinum-based bimetallic samples usually did not overcome the degradation yields achieved with the monometallic platinum catalysts, they showed a substantial improvement of catalytic stability due to the synergistic effect between platinum and the second noble or transition metal. Finally, the application of the already stated synergisms in catalytic thermo-oxidation, for example, strong Au-Pd interaction, can be successfully transferred to new technologies for VOC abatement, such as photocatalytic oxidation, with the exploitation of new mutual effects such as surface plasmon resonance combined with the high reactivity of noble/transition metals. This can be a promising strategy to achieve significant progress in the technologies applied to the improvement of air quality.

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