

# Recent advances in photo-assisted preferential CO oxidation in H<sub>2</sub>-rich stream

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Photocatalysis plays a key role in CO preferential oxidation (CO-PROX) in H<sub>2</sub>-rich streams thanks to the great performance this reaction can achieve when it is light driven, at atmospheric pressure and room temperature, with negligible hydrogen loss. This short review is an attempt to summarize the most recent advances in photo-PROX focused mainly on the most popular strategies to improve TiO<sub>2</sub> photocatalytic activity, as well as on the active phases used, paying special attention to the synthesis and deposition of noble metal nanoparticles because of their outstanding properties. In this work, we critically review these results with the aim of finding general indications about the main characteristics of the catalysts and the optimal operating conditions of photo-assisted CO-PROX reaction.

## Addresses

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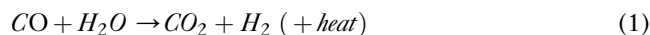
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## Introduction

The depletion of fossil fuels, together with the massive greenhouse gases emissions, has led the scientific community to the quest of clean and environment-friendly energy resources that must meet the efficiency requirement to be feasible on a large scale, reducing the strong reliance of industrialized and emerging countries on nonrenewable energy sources. Hydrogen is considered as a clean energy carrier [1] that can be used as feedstock for low-temperature fuel cells such as polymer electrolyte fuel cells (PEMFCs), which

also have higher electrical efficiencies compared with internal combustion engines. The industrially established process for hydrogen production is by hydrocarbons' catalytic reforming at high temperature. Nevertheless, alternative processes are being developed to promote the decarbonization of the energy sector, including thermochemical, electrolytic or photolytic ones such as alcohols reforming and autothermal reforming [2], biomass gasification [3] and photo-electrochemical water splitting [4].

Although steam reforming is the most economical method, carbon monoxide is produced as by-product, so water gas shift reaction (reaction (1)) must be carried out to reduce the CO content to ca. 1% [1]:



However, further CO purification [5] is required before entering a PEMFC, as the platinum electrode is easily poisoned by CO, thus lessening the cell power generation performance [6]. Different approaches, as selective diffusion, pressure swing adsorption, hydrogen membrane separation, selective CO methanation [7] and preferential oxidation of CO to CO<sub>2</sub> (CO-PROX) have been considered to eliminate the traces of CO in the hydrogen stream with a minimum hydrogen loss, the latter being the most effective technology because of its efficiency and mild operation conditions (P<sub>atm</sub> and T = 30 to 200 °C).

## CO preferential oxidation

CO preferential oxidation (CO-PROX) in hydrogen-rich streams is interesting, given the possibility of coupling this reaction to low-temperature PEMFCs, therefore avoiding the need of hydrogen storage and allowing its use for automotive applications as well as for both stationary and portable power generation [8].

The following reactions (Eq. 2–3) can occur in a CO-PROX system:



Both reactions are irreversible, exothermic and competitive. In the first reaction (Eq. (2)), an excess of oxygen has to be provided ( $\sim 2$ ). In the second step, a substantially higher oxygen excess factor ( $\lambda$ ) of 2–4 is used, which is then processed with the remaining CO to reduce the CO concentration to less than 10 ppm.

Equation (3) is highly undesirable because of the consumption of hydrogen needed to feed a PEMFC; nevertheless, as 100% selectivity is not possible, H<sub>2</sub> oxidation takes place and H<sub>2</sub>O forms, reducing the activity and selectivity of the catalyst.

Several factors affect oxidation rate and selectivity in CO-PROX reaction: supports and promoters' properties as well as chemical status of the metallic phase. Also, surface coverage by CO molecules depends on reaction parameters such as CO partial pressure, reaction temperature and/or H<sub>2</sub>, O<sub>2</sub> and CO gases ratios [9].

#### Noble metal catalysts

Platinum-group metal (Pt, Pd, Rh and Ru) catalysts supported on inert structures, such as alumina or silica, have been traditionally applied in this reaction. Pt-based catalysts have been widely studied, but their use in PEMFCs at room temperature remains a challenge because of their high sensitivity to CO poisoning. To weaken CO adsorption, promoters [10] or reducible oxides, such as CeO<sub>2</sub>, can be used as supports [11], with an enhancement of activity in comparison with nonsupported Pt-based catalysts. Ru and RuO<sub>2</sub> catalysts supported on silica and zeolites have presented a high activity in the range 80–160 °C [9,12,13], hindering methanation and reverse water gas shift reactions and also showing an excellent selectivity towards CO oxidation in the presence of H<sub>2</sub>, as CO would preferentially adsorb in the Ru surface, hampering the interaction between H<sub>2</sub> and Ru active sites [14].

#### Transition metal oxide catalysts

Transition metal oxides, such as Co, Fe, Cu or Zn oxides, have also shown considerable activity in the PROX reaction at low temperatures, especially CuO–CeO<sub>2</sub> system reporting close values to those of noble metals [15,16] but with great selectivity for CO<sub>2</sub> formation, thanks to both the supply of oxygen adsorption sites from the Ce<sup>3+</sup>/Ce<sup>4+</sup> pair which creates surface oxygen vacancies and the improvement of the redox properties. In addition, iron oxide has also shown a significant promotional effect, also because of its role as oxygen reservoir [17].

#### Au-based catalysts

Gold had been regarded as a catalytically inert metal until Haruta et al. [18] demonstrated the supported gold catalysts' outstanding activity in the low-

temperature CO oxidation reaction. It has been reported that the catalytic activity of these Au-based catalysts is closely related to the size of gold particles, nanometric ones being the most active [19]. Moreover, the catalytic activity also relies on the nature of the support material [20]. Reducible oxides as TiO<sub>2</sub> [21], Fe<sub>2</sub>O<sub>3</sub> [22] or CeO<sub>2</sub> [23] supports show great ability to provide reactive oxygen to the active Au sites, which significantly enhances the catalytic activity.

#### Photo-PROX

Despite the good performance of Au/TiO<sub>2</sub>-based catalysts in CO-PROX reaction, their catalytic activity can be further improved when it is light driven because of two main reasons: TiO<sub>2</sub> is an n-type semiconductor showing a striking photoactivity in a wide range of reactions [24–27] and Au nanoparticles (NPs) present a remarkable photoresponse behaviour, thanks to their optical properties due to the local surface plasmon resonance, a collective oscillation of free (weakly bonded) electrons excited by an oscillating electric field, such as that of light [28]. This fact opens up the opportunity to a new research line focused on the study of light-driven CO-PROX. Table 1 shows some examples of photocatalysts used for the so-called photo-PROX, and it is clearly noticeable that Au supported on TiO<sub>2</sub>, despite the very low metal loading, outstands as the benchmark photocatalyst for this reaction.

#### Synthesis strategies of TiO<sub>2</sub>

Titania is regarded as the photocatalyst per excellence; it is a widely spread, nontoxic, low-cost material, thermally and chemically stable and with notable optical properties [6]. Intrinsic properties such as particle size distribution, mean pore size, specific surface area and crystal structure are reported to be determining in its photocatalytic performance [34]. TiO<sub>2</sub> naturally exists in three crystallographic polymorphs [36]: rutile (tetragonal), brookite (orthorhombic) and anatase (tetragonal) phases. Controlling anatase–rutile transition through thermal treatment (calcination) is crucial [37] because the combination of these two polymorphs in variable proportions (usually 10–30 wt%) has shown higher efficiency than pure phases [34].

Besides, modifying titania morphology can also improve its activity, as amorphous titania hardly shows photoactivity even under UV irradiation, demonstrating the relevance of crystallinity and morphology [38]. Thus, the synthesis method rises as a pivotal step to obtain highly active TiO<sub>2</sub>-based catalysts. Apart from calcination temperature as mentioned above, the synthesis pH is also determining to obtain anatase or rutile phases: basic conditions in a hydrothermal synthesis produce anatase, whereas with acidic treatment, rutile polymorph is preferred [32].

**Table 1****Catalysts used in photo-PROX reaction in recent years.**

| Catalyst                            | % wt Au | Type of reactor        | Reaction temperature (°C) | CO conversion (%) | CO <sub>2</sub> selectivity (%) | Ref. |
|-------------------------------------|---------|------------------------|---------------------------|-------------------|---------------------------------|------|
| Au/TiO <sub>2</sub>                 | 1.0     | Fixed-bed flow reactor | 25                        | 25                | 60                              | [29] |
| Au/TiO <sub>2</sub> @CuO            | 1.0     | Fixed-bed flow reactor | 25                        | 70                | 85                              | [29] |
| Mo-MCM-41                           | 1.0     | Closed system          | 20                        | 98                | 98                              | [30] |
| Au/ZnCo <sub>2</sub> O <sub>4</sub> | 0.94    | Fixed-bed flow reactor | 25                        | 61.7              | 64.5                            | [31] |
| Au/TiO <sub>2</sub> nanorods        | 1.0     | Fixed-bed flow reactor | 30                        | 40                | 100                             | [32] |
| Au/TiO <sub>2</sub> -PANI           | 1.0     | Fixed-bed flow reactor | 25                        | 55                | 80                              | [33] |
| Au/Meso-TiO <sub>2</sub>            | 0.47    | Fixed-bed flow reactor | 30                        | 95                | 69                              | [34] |
| AuCu/SBATi                          | 1.5     | Fixed-bed flow reactor | 30                        | 80                | 80                              | [35] |

Another strategy is incorporating titania NPs into mesoporous materials with uniform pore channels and long-range ordering structures, such as MCM-41 or SBA-15 [39,40], which allows the introduction of titanium species both on the external surface and in the pore channels of these ordered materials maintaining their organized mesoporous structure and high surface area.

### TiO<sub>2</sub> limitations

The photocatalytic oxidation of a reactant on TiO<sub>2</sub> can be generally summarized in four sequential stages [41]: (1) generation of charge carriers by UV–visible irradiation; (2) separation and migration of these photo-generated carriers; (3) trapping of photogenerated carriers to produce active species; and (4) reactant oxidation by either active species or photogenerated holes.

The most restrictive limitation in TiO<sub>2</sub>-based applications, other than the rapid recombination rate of the photogenerated electron–hole pairs within its particles, is the need to use ultraviolet irradiation ( $\lambda < 387$  nm) to promote an electron from the valence to the conduction band (band gap: 3.2 eV anatase, 3.0 eV rutile) [42]. UV irradiation promotes O<sub>2</sub> and CO adsorption at TiO<sub>2</sub> surface and inhibits H<sub>2</sub> chemisorption by hindering the process by which hydrogen adatoms react with lattice oxygen [43]. However, only 5% of the incident solar spectrum consists of UV light, the rest being visible (ca. 45%) and infrared light (50%). For this reason, the development of new materials photoactive in the visible light range seems very appealing so that an efficient use of sunlight can be accomplished.

### TiO<sub>2</sub> nonmetal doping

First approaches to narrow titania's band gap consisted of transition metal doping [44,45] and the use of TiO<sub>2</sub> reduced forms, but both techniques resulted in long-term unstable catalysts because doped metals acted as electron–hole recombination sites [46].

Conversely, nonmetal doping with C [47], N [48], S [49] and combination of thereof [50], replacing oxygen in the lattice of TiO<sub>2</sub>, is also of interest, because these

elements can modify titania cell parameters and reduce the pristine band gap and/or the Fermi level, as well as enhance charge carriers separation.

For example, N-doped TiO<sub>2</sub> tested in pollutants photodegradation in aqueous media accomplished 13.6% and 7.8% of improvement under visible and UV light than pure TiO<sub>2</sub>, respectively [51]. The incorporation of F increases the acidity because of the interaction of Ti<sup>4+</sup> and F<sup>-</sup> ions that supplies Ti<sup>3+</sup> cations on the surface, obtaining a band gap narrowing of 0.2–0.6 eV [52]. Also, semimetal doping with B has proved to enhance visible light photoresponse, thanks to the mixed valence band formed between boron and oxygen, as it can be incorporated into the TiO<sub>2</sub> crystal lattice forming a solid solution [53].

### Au NPs supported on TiO<sub>2</sub>

Undoubtedly, the best strategy to accomplish good photocatalytic performance in the visible region is coupling titania with noble metals such as Ag, Pd, Pt and especially Au, thanks to their exceptional optical properties and notable reactivity at low temperatures, especially when using noble metal NPs, as they can act as electron sinks for conduction band electrons in TiO<sub>2</sub> and promote charge carriers separation, improving the quantum yield [28,54,55]. Although oxygen dissociation is the rate-limiting step in CO-PROX reaction over Au-based catalysts because it is inhibited on single gold crystal [56], when supported on TiO<sub>2</sub>, it has shown remarkable photoactivity, suggesting that this reaction takes place at the metal-support interface. Moreover, gold can form alloys with a second, more widespread, economical metal on which oxygen adsorption and activation occur easily [35,57]. Besides displaying outstanding optical properties due to the local surface plasmon resonance phenomenon [28], Au nanoparticles supported on a semiconductor give rise to a Schottky barrier, formed when at the metal–semiconductor interface, there is an energy difference between titania conduction band and gold Fermi level that creates electron states within the band gap. This potential barrier reduces the recombination rate between electrons and holes, as titania electrons are trapped in the

metal, therefore improving the photocatalytic activity [35,58].

#### Synthesis methods for Au-supported catalysts

The morphology and size of Au NPs play an important role, and once again the synthesis procedures employed are key. Under mild operating synthetic conditions, gold particles below 10 nm supported on a matrix with considerable specific surface area can be obtained with very low metal loadings [19].

Traditional wetness impregnation method has turned out as ineffective for obtaining Au-based photocatalysts, as it leads to larger Au particles (>10 nm) even when mesoporous supports are used [59].

Microwave-assisted hydrothermal reaction approach for AuNPs TiO<sub>2</sub>/SBA-15 nanocomposites, reported by Chen et al. [60], accomplishes high TiO<sub>2</sub> surface area with short rod-like morphologies and close interaction between Au and TiO<sub>2</sub>.

Colloidal chemical coreduction with chloride salts in water uses a surfactant, typically polyvinyl alcohol, NaBH<sub>4</sub> as a reducing agent and HCl solution as an acidifier. Although chloride ions are reported to improve the dispersion of Au NPs, Cl<sup>-</sup> ions must be carefully eliminated as they can cause deactivation and accelerate NP sintering [61]. With this synthesis method, well-distributed round-shaped nanoparticles with sharp size distribution can be obtained [62–64].

Photodeposition method is a simpler process, with tunable light irradiation source, so different particle sizes can be obtained. In this process, the support, in powder form, is solubilized in deionized water or a mix of deionized water/methanol and sonicated. Then, the Au precursor is added, pH adjusted to 9.5 using NH<sub>4</sub>OH and the suspension is irradiated (LED, UV lamp) at a particular wavelength, then filtered, washed, dried and calcined [65].

Currently, most of the syntheses are carried out using the deposition–precipitation technique, which uses NaOH, Na<sub>2</sub>CO<sub>3</sub> or urea as the precipitating base. Continuous control on pH, temperature, reagents concentration and washing is crucial for obtaining finely dispersed supported Au NPs (size 2–3 nm). In a typical synthesis, a solution of gold salt precursor such as HAuCl<sub>4</sub>·3H<sub>2</sub>O is prepared, in which a precipitating base solution is added until reaching pH 9. The support is added, and the resulting suspension is kept at 70 °C for several hours, keeping the pH constant. The recovered solid is washed, dried and calcined [34].

#### Concluding remarks and outlook

Promising catalysts with high photoactivity are the basis for purifying hydrogen-rich streams using solar energy

via CO preferential photo-oxidation. The development of catalysts with specific structural, textural and optical properties, as summarized above in this review, is the most effective way to understand the catalytic mechanisms in detail and to obtain high intrinsic photocatalytic activities.

In general, each of the catalyst types herein reported has an optimum operating conditions range, outside of which CO conversion is too low and/or selectivity to CO<sub>2</sub> decreases in favour of H<sub>2</sub> oxidation. Control of the undesirable hydrogen oxidation reaction that affects the CO<sub>2</sub> selectivity is a key issue for CO-PROX catalysts. Another fundamental parameter is the photoactive support, which plays a crucial role in any photocatalytic reaction. Crystalline phases, particle size and morphology of the support exert a significant influence on the CO preferential photo-oxidation reaction. Undoubtedly, the best strategy to accomplish good photocatalytic performance in the visible region is coupling titania with noble metal nanoparticles, especially Au alone or as Au/Cu binary system. Modifying the nature of the interface between the noble metals and the support and systematic variation of the size of both the gold (gold-copper) nanoparticles and the support are required for the development of more effective supported gold photocatalysts for CO-PROX.

Although some encouraging progresses have been made in the recent decade in the development of suitable photocatalysts, none of these entirely solve the issues of stability, selectivity and high CO conversion. In this sense, much has been attained but an improvement in the design and development of photo-PROX catalysts is still necessary, also taking into consideration the use of more economical and abundant materials.

#### Conflict of interest statement

Nothing declared.

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