

# Mechanochemistry: A Green and Fast Method to Prepare a New Generation of Metal Supported Catalysts

## Rational design leads to novel properties

### Maila Danielis, Sara Colussi

Dipartimento Politecnico, Università degli Studi di Udine, Via del Cottonificio 108, 33100 Udine, Italy

### Núria J. Divins, Lluís Soler

Departament d'Enginyeria Química, Institut de Tècniques Energètiques, Centre de Recerca de Ciència i Enginyeria Multiescala de Barcelona, Universitat Politècnica de Catalunya, EEBE, Eduard Maristany 10–14, 08019 Barcelona, Spain

### Alessandro Trovarelli\*

Dipartimento Politecnico, Università degli Studi di Udine, Via del Cottonificio 108, 33100 Udine, Italy

### Jordi Llorca<sup>§</sup>

Departament d'Enginyeria Química, Institut de Tècniques Energètiques, Centre de Recerca de Ciència i Enginyeria Multiescala de Barcelona, Universitat Politècnica de Catalunya, EEBE, Eduard Maristany 10–14, 08019 Barcelona, Spain

**Email:** \*alessandro.trovarelli@uniud.it;  
<sup>§</sup>jordi.llerca@upc.edu

## PEER REVIEWED

Received 29th June 2023; Revised 23rd August 2023;  
Accepted 29th August 2023; Online 30th August 2023

In this review, we report on recent advances in the use of mechanochemistry to synthesise

new catalytic materials. We report recent results obtained by our groups where a rational design of the milling parameters led to the synthesis of advanced materials with novel properties such as unconventional arrangements of metals on the surface of oxide support materials, highly dispersed metals or the stabilisation of species in particular oxidation states. These properties resulted in superior catalytic performances of the mechanochemically-synthesised catalysts compared to their counterparts prepared by traditional impregnation methods. To illustrate these advances, we review the progress made in two important fields of catalysis where noble metals are used: (i) emission control catalysis using palladium-based materials; (ii) the development of photocatalysts to produce hydrogen based on gold and palladium materials.

## 1. The Mechanochemical Approach

Milling is an ancient art and the use of mechanical forces to promote chemical reactions has been used since prehistory; however, a systematic approach to the so-called 'mechanochemistry' is quite recent (1, 2). In recent decades, the use of solid-state synthesis methods for the preparation of advanced functional materials and novel catalytic formulations has attracted a great deal of attention due to its potential to stabilise metastable phases which would be otherwise challenging to obtain (3–5), considering the chemical and thermal equilibria limitations involved in conventional solution-based synthesis methods. Recently, the environmental benefits guaranteed by replacing conventional wet-based synthesis approaches with

solvent-free mechanical processes have further rekindled research efforts in the application of mechanochemistry to the preparation of catalytic materials (6–8). Several reviews have highlighted successful results obtained in the use of mechanical energy to improve the performance of complex oxides (4, 9–12), energy-storage materials (13, 14), zeolites (15) and metal-organic frameworks (16, 17), among others. Gas-phase reactions promoted by mechanochemistry have also been investigated (18–21). The development of a dedicated apparatus in the form of a single-screw device for a continuous process was reported for pharmaceutical applications (22), showing the promising translation of the mechanical method at the industrial scale. Indeed, screw extruders have been recently developed and successfully applied for larger scale mechanochemical processes involving the synthesis of metal organic frameworks and organic molecules in general, showing excellent sustainability and a great potential for industrial application (23, 24).

In addition to the abovementioned environmental advantages, the success of the mechanochemical synthesis process also lies in its simplicity of operation. In the milling synthesis method, the precursor materials are simply mixed in a milling vial where the milling media (often grinding balls) move and transfer their kinetic energy through impacts, attrition and shear stresses to the powders, as schematically represented in **Figure 1**. The movement of the milling media is characteristic of the type of mill, among which shaker mills, planetary mills, vibration mills and attritors (stirring ball mill) can be distinguished. Media other than grinding balls can also be employed, such as in the

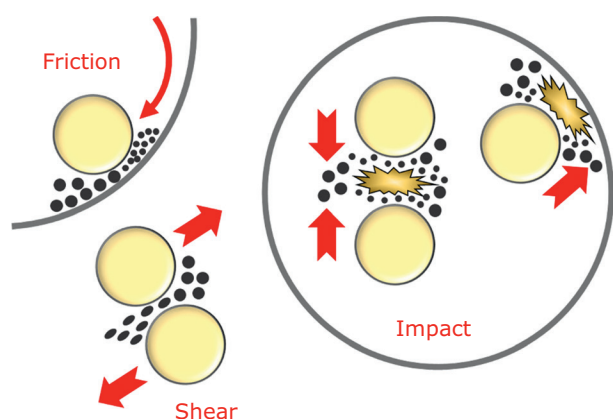


Fig. 1. Main forces acting on powder particles during milling. (Reproduced with permission from (25))

case of mortars, pin mills and rolling mills (2). The impacts and stresses generated during milling lead to alterations in the pristine powder structure, such as comminution and fracturing of large particles, agglomeration of finer nanoparticles, stabilisation of metastable phases such as supersaturated solid-solutions and amorphisation due to accumulation of structural defects (25).

However, the application of milling for the dry synthesis of metal-supported catalytic materials has been scarcely investigated in the past years (26, 27), as the mechanically induced metal-support interaction was often reported as negligible or less effective compared to other conventional synthesis methods such as wet impregnation, coprecipitation, solution combustion synthesis, or atomic layer deposition. Some recent works exploit the comminution and anchoring mechanisms occurring during milling for the preparation of supported metal catalysts (21, 28), while examples of mechanically induced metal-support interaction have only recently been reported for redox support oxides such as ceria (26) and titania (29). Possibly, the difficulties arise from the intrinsic complexity of the many, often interconnected, process parameters involved in the milling process (30–32), which hinder a straightforward tuning of the specific metal-support interplay and, consequently, the engineering of metal-supported catalytic materials. In addition, the dry milling process is known to induce uncontrolled contamination from the equipment's materials (vial and balls), especially if carried out at high energy conditions (33, 34). Features achieved during milling might also be lost due to particle agglomeration, for example, by hiding the metal active phase (35), or by further thermal treatments, hence leading to unsuccessful or inconclusive results (36). Lastly, without a comprehensive theoretical background most studies have to rely on trial-and-error approaches, partially explaining the contradictory results reported in the literature. In fact, in metal-supported catalysis a successful theoretical prediction would need to include both mechanical stresses at the mesoscale and microscale, generated by the physical milling apparatus and sustained by the catalyst components respectively, as well as the subsequent effect on the chemical and electronic structure of the catalytic materials.

Nonetheless, optimising the metal dispersion and mass efficiency of metal-supported catalytic materials is paramount for the fields where the use of a noble metal active phase is imperative, such as air pollution control of mobile sources, where

legislation limits require elevated activity standards and prolonged stability under harsh conditions (up to 200,000 km and ten years of age in the new Euro 7 proposal for light duty vehicles) (37–39). Several approaches have been attempted to address this issue, starting from improved recycling of noble metals (40) up to pushing research towards their partial substitution by metal-free alternatives (41). In addition, the entire catalyst life cycle, including the whole preparation route, has to be considered in order to assess and improve the sustainability of the chosen catalytic materials (42). In this respect, mechanochemistry has been increasingly investigated for the preparation of metal-supported catalysts following the sustainable development goals and green assessment of material production (6, 7), offering environmental advantages compared to the solvent-based counterparts. Also, wet and dry milling processes are generally employed at the industrial scale to reach the desired particle size distribution or morphological characteristics which are needed for catalyst powders processing into structured ones (pellets, extrudates, coatings, among others) (43, 44). Integrating the synthesis process directly into a single milling step could possibly reduce the number of such operations, further contributing to the energy consumption reduction (i.e. fuel use and CO<sub>2</sub> generation) of the whole catalyst industrial life.

One of the best examples of mass efficiency maximisation is the deposition of noble metals as sub-nanometric particles or single atoms, the latter representing the maximum mass efficiency, provided that the induced metal-support interaction does not negatively affect reactivity (37). In fact, some works report that the surface energy of the single atom noble metal might be insufficient for gas reactions, where metal-metal interactions are needed (45, 46). In this case, the single atom configuration might be exploited as a starting point to grow sub-nanometric metal clusters *via* appropriately tuned thermal treatments and under reaction conditions that lead to maximisation of catalytic activity and mass efficiency (47, 48). Within this framework, some recent works report successful efforts in the application of dry milling processes for the preparation of single atom catalysts (49–51). Remarkably, such an approach led to the generation of palladium on zinc oxide single atom catalysts for selective hydrogenation reactions (51), where the developed solvent-free milling method was also easily scaled up to the kilogram-scale, corroborating the more

facile implementation of dry mechanochemistry synthesis methods compared to other wet-based deposition methods or chemical vapour deposition techniques (49). In another approach, single atoms of iron, cobalt, nickel and copper were dispersed over nitrogen-doped graphite by appropriately tuned abrasion of the metal from the milling media to the carbon support in nitrogen atmosphere (50).

Alternatively, an increase in mass efficiency of the catalyst can be achieved by promoting metal-support interaction, synergistically enhancing the mass activity per metal atom. In this respect, our group reported several noble metal-reducible oxide compositions where, by means of a simple dry-milling method, the metal-support interaction and the metal surface state were altered as to lead to enhanced activity and stability of three-way catalysts for unburnt methane abatement (26, 52) and in the photocatalytic production of hydrogen (27, 53). In the following sections, the characteristics of metal-supported catalysts prepared by dry mechanical methods will be covered in depth, revealing the improved activity and structure-reactivity findings over novel catalytic materials for air pollution control and green hydrogen production, highlighting the potential of the mechanochemical synthesis route in the preparation of novel metal-based catalytic formulations.

## 2. Dry Milling of Palladium and Platinum on Ceria for Air Pollution Control

It is well known that increasing the intimate contact between the supported noble metal and the support oxide leads to enhanced activity and prolonged stability over time, through synergistic interaction among metals and metal oxides. Both parameters (absolute activity and long-term stability) are key for new, sustainable catalytic materials (37). Therefore, optimising platinum group metal (pgm) loading and deactivation resistance is of utmost importance, particularly in aftertreatment catalytic systems. Often, the most critical points are related to: steam resistance, cold start (i.e. low-temperature activity), hot spots (i.e. high-temperature stability) and stability over repeated reduction-oxidation cycles (37, 54). A close interaction between the redox support oxide (ceria or ceria-zirconia) and the noble metal (palladium or platinum) was obtained by solution combustion synthesis and was reported as significantly improving the performance of the materials for pgm applications, both in terms of

abatement activity (55, 56) and resistance to steam deactivation and cycling stability (57). However, the proposed synthesis method, based on controlled combustion of the catalyst precursors, was not sustainable at industrial scale. As the strong interaction was obtained by the extreme local energies released during combustion, mechanical stresses could represent an alternative method to achieve a similar intimate contact with the noble metal embedded in the outermost ceria surface. Hence, mechanochemistry was applied to the same class of materials, proving to be remarkably successful in the preparation of palladium on ceria based catalysts for methane abatement (26, 52). An example of the milling apparatus employed is reported in **Figure 2**, showing on the left a picture of the Fritsch Pulverisette P23 vibratory Mini-Mill and, on the right, a scheme of the main parameters which should be considered for synthesis.

An appropriate tuning of the milling parameters and precursor salts was necessary to obtain active materials (35), showing how different the optimal conditions can be compared to the state-of-the-art reached for other mechanochemical synthesised materials and alloys (58). In fact, a mild intensity mechanochemical procedure was found necessary to ensure the optimal dispersion of palladium on a ceria support, resulting in a peculiar amorphous shell-core structure with enhanced metal-support interaction and improved catalytic performance (26). Conversely, high intensity milling conditions usually employed for the alloying of functional materials resulted detrimental to the metal dispersion and the integrity of the support particle structure (35). The unique nature of the catalytic materials

prepared by the mild energy, dry milling route is reflected in the peculiar morphology observed by high-resolution transmission electron microscopy (HRTEM) images, reported in **Figure 3** for samples milled with metallic palladium (**Figure 3(a) and 3(b)**), palladium acetate (**Figure 3(c)**), metallic palladium and platinum (**Figure 3(d)**) and their counterparts prepared *via* conventional incipient wetness (IW) impregnation method (**Figure 3(e) and 3(f)**). Most remarkably, the palladium species over the milled ceria catalysts are not distinguished clearly, such as metallic palladium nanoparticles, but are well dispersed over ceria in an amorphous-shell-like structure surrounding ceria crystallites.

The unprecedented catalyst morphology is reflected in outstanding catalytic activity for methane abatement in mobile exhausts application, where a series of catalysts prepared by dry milling (including monometallic and bimetallic palladium and palladium-platinum on ceria samples) were tested under the most representative abatement conditions, such as lean oxidation (26, 52), stoichiometric operation (59), dry and wet reaction feed (60, 61), in transient and in stability experiments (62). In all conditions the milled samples outperformed the conventionally prepared counterpart, displaying higher activity (see **Table I**) and higher stability over time. Moreover, palladium on ceria milled catalysts showed also enhanced high temperature resistance particularly when palladium acetate was milled onto ceria (52, 63). **Figure 4** shows the suppression of the activity loss due to the high temperature palladium oxide-palladium-palladium oxide transition on PdAcCe M compared to a conventional impregnated sample. The unique

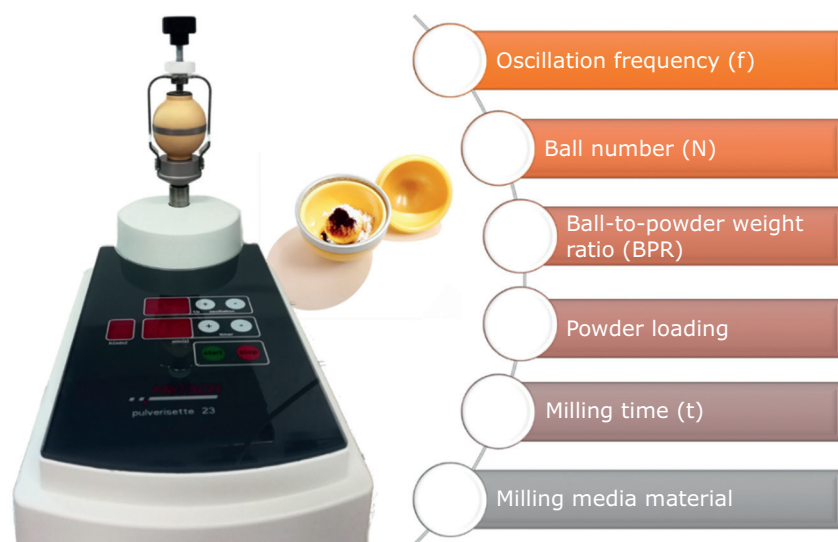


Fig. 2. The Fritsch Pulverisette P23 Mini-mill employed for the mechanochemical synthesis of catalysts with some key parameters

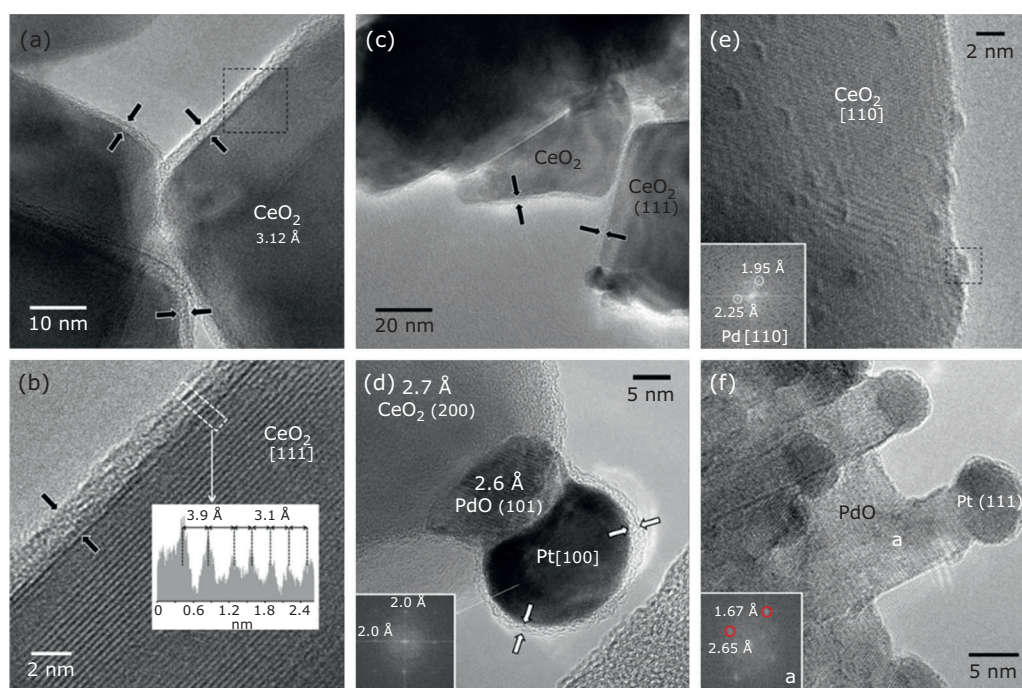


Fig. 3. HRTEM images of ceria-based samples milled with: (a) and (b) metallic palladium; (c) palladium acetate; (d) metallic palladium and platinum and their counterparts prepared *via* conventional incipient wetness impregnation method; (e) PdCeIW; and (f) PtPdCeIW (26, 52, 60). Reprinted from (26) with permission from Wiley. Reprinted from (60) under Creative Commons Attribution license 4.0 (CC BY 4.0 DEED)

**Table I Catalytic Activity Data<sup>a</sup>**

Sample	Reaction feed <sup>b</sup>	Temperature, K	Reaction rate, $\mu\text{mol}_{\text{CH}_4} \text{g}_\text{M}^{-1} \text{s}^{-1}$	Ref.	
<b>PdCeM</b>	dry, lean	520	14.1	(52)	
	wet, lean	613	12.8		
<b>PdAcCeM</b>	dry, lean	520	25.1		
	wet, lean	613	17.2		
<b>PdCeIW</b>	dry, lean	520	6.4		
	wet, lean	613	5.4		
<b>PtPdCeM</b>	dry, lean	580	22.1		(60)
	wet, lean	680	28.4		
<b>PtPdCeIW</b>	dry, lean	580	18.2		
	wet, lean	680	13.6		
<b>4PdAcCeM</b>	dry, lean	520	8.8	(52)	
	wet, lean	580	5.2		
	dry, stoich.	563	13.5	(59)	
wet, stoich.	613	14.9			
<b>4PdCeIW</b>	dry, lean	520	3.3	(52)	
	wet, lean	580	1.3		
	dry, stoich.	563	4.8	(59)	
	wet, stoich.	613	4.2		

<sup>a</sup>Reaction rates were calculated from the second heating ramp in light-off experiments, ensuring kinetic conditions (methane conversion below 5%) and are reported per mass of active metal

<sup>b</sup>Wet: 10 vol% water added to the gas feed. Lean: 0.5% methane, 2% oxygen in helium. Stoichiometric: 0.5% methane, 1% oxygen in helium

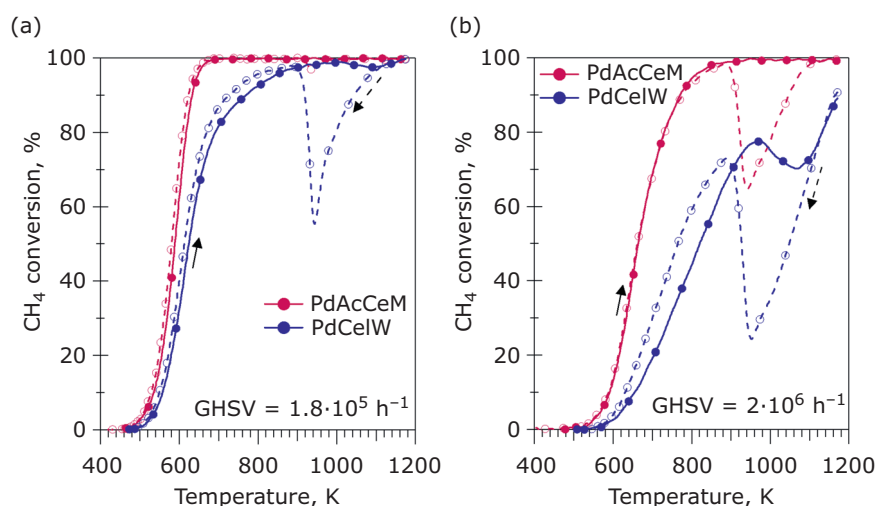


Fig. 4. Suppression of the activity loss due to the high temperature PdO–Pd–PdO transition on 4wt% PdAcCeM compared to conventional PdCeIW impregnated sample, as exhibited during methane oxidation tests at different gas hourly space velocities (GHSV): at (a) GHSV  $\approx 180,000 \text{ h}^{-1}$ ; and (b) GHSV  $\approx 2,000,000 \text{ h}^{-1}$ . Gas feed: 0.5% methane, 2% oxygen, helium to balance

results obtained by milling metallic palladium and palladium acetate over ceria with respect to other precursors such as palladium oxide (26) and palladium nitrate (63) could be ascribed, on the one hand, to the physical properties of the precursors, whereby softer powders are more easily spread over the support oxide and on the other hand, to the presence of reduced Pd<sup>0</sup>, either in the precursor composition (metallic palladium black) or obtained after decomposition (for palladium acetate). Conversely, fully oxidised Pd<sup>2+</sup> species, either in palladium oxide, palladium(II) nitrate or obtained through subsequent thermal treatment, proved to be ineffective in the promotion of strong palladium-ceria interaction (63).

The results obtained from these studies showed not only the viability of the methodology for the preparation of metal-supported catalysts but also allowed to disclose new nanoscale catalyst arrangements inaccessible by conventional wet methods. As briefly anticipated, the unique catalytic and morphological properties of this class of materials were maintained also when a bimetallic palladium-platinum formulation was investigated and appeared to be stable under more complex reaction atmospheres (60, 61), highlighting the potential of the proposed solvent-free mild milling process for further industrial development. Indeed, preliminary scale-up tests carried out in a planetary ball-mill have demonstrated the feasibility of the synthesis at the 10–100 g scale, while maintaining catalytic performance comparable to the state-of-the-art three-way catalyst (TWC) formulations (62). Alternatively, a large mortar mill with appropriate downward force might be a viable method for the synthesis of palladium on ceria catalytic materials, replicating the movement

of the small-scale vibrational mill at low energy. However, experimental attempts have been so far focused on palladium on ceria-only materials and the inclusion of other metals and metal oxides for the preparation of fully formulated TWCs has not yet been explored.

One of the most challenging issues when dealing with these pgm on ceria catalysts was the characterisation of their nanoscale structure and chemistry. To unveil the details of the metal-ceria interaction at the outermost surface of the materials prepared by dry milling and to correlate it with the enhancement in catalytic performance, an array of *in situ* and *ex situ* characterisation techniques was used to follow the evolution of their peculiar shell morphology, redox interplay and surface properties. As expected, the novel synthesis method led to unique behaviour both in terms of surface and bulk structural evolution during reaction and in terms of chemical affinity towards adsorbed intermediates *via* ambient pressure X-ray photoelectron spectroscopy (AP-XPS), *in situ* X-ray diffraction, X-ray absorption spectroscopy and HRTEM analyses. Not only the milled catalysts were revealed to maintain higher dispersion of the noble metal on the ceria surface, but also the intimate nanoscale interaction between the support surface lattice and the metal phase proved to be able to maintain the noble metal in a combination of oxidation states (0, 2+,  $\delta+$ ) throughout reaction (52, 59), which is indicated both by experimental and theoretical studies as the most active configuration for the C–H bond activation (64–66). These results further corroborate the importance of the metal precursor properties in determining the efficiency of the milling synthesis.

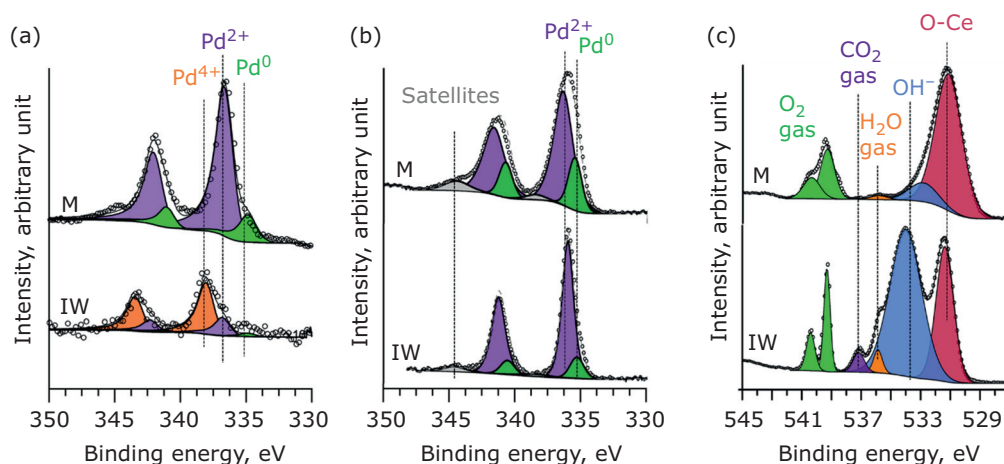


Fig. 5. Representative AP-XPS spectra collected: (a) in the palladium 3d region under lean methane oxidation atmosphere (0.0133 mbar methane, 0.0533 mbar oxygen, 373 K); (b) in the palladium 3d region under stoichiometric methane oxidation atmosphere (0.6 mbar methane, 1.4 mbar oxygen, 673 K); and (c) in the carbon 1s region on a 4 wt% palladium on ceria milled sample (M) and its conventional incipient wetness counterpart (IW) under stoichiometric methane oxidation atmosphere (0.6 mbar methane, 1.4 mbar oxygen, 673 K) (52, 59). Reprinted from (59) under Creative Commons Attribution License 4.0 (CC BY-NC 4.0 DEED)

**Figure 5(a)** and **5(b)** reports some representative XPS spectra collected under *in situ* methane oxidation conditions, showing the stability of the Pd<sup>2+</sup>/Pd<sup>0</sup> mixed configuration over the milled catalyst compared to the IW counterpart. In addition, spectroscopic techniques such as Raman and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were used to further investigate the effect of the peculiar metal-support configuration in the reactivity of the milled materials, following the evolution of reaction intermediates and probe adsorbates on the pgm on ceria M catalysts. The enhanced stability over time displayed by the materials prepared *via* mechanochemical synthesis (52, 59, 60) is due to a lower affinity towards OH adsorbates (**Figure 5(c)**), whose presence on the palladium surface is reported as one of the main factors inducing deactivation of TWCs by formation of palladium hydroxide (67, 68) or inhibition of the PdO<sub>x</sub>-CeO<sub>x</sub> oxygen exchange (57, 69).

The unique behaviour of the mechanically induced palladium–cerium interaction is not limited to methane activation. As a matter of fact, several additional relevant reactions in air pollution control were also evaluated, such as dry reforming of methane (DRM) (70), carbon dioxide methanation (71) and low temperature NO<sub>x</sub> adsorption (72). For example, PdCeO<sub>2</sub> milled materials exhibited a more facile C–H bond activation and peculiar CO<sub>2</sub> activation routes under oxygen poor conditions, such as in dry reforming of methane and under reducing conditions (70, 71),

suggesting that the unique palladium–cerium configuration, extensively observed under oxidative conditions (52), is generated during the milling process and then maintained after pretreatment, regardless of the reaction atmosphere, hence becoming an intrinsic property of the milled material. Moreover, the reaction pathways observed on milled catalysts were strikingly different from those detected over the conventional impregnated counterparts. Remarkably, only by using isotope labelled diffuse reflectance infrared Fourier transform spectroscopy it was possible to disclose the transient mechanisms involved in the selective hydrogenation of CO<sub>2</sub>, dominated by the direct oxidation of CH<sub>x</sub> to carbon monoxide and by the presence of carbon modified Pd<sup>0</sup> (71). The same carbon-doped palladium surface structure was also unravelled in the presence of CO<sub>2</sub> and methane under dry reforming conditions (70), where standard and isotope labelled DRIFTS showed opposite reaction mechanisms compared to the metallic Pd<sup>0</sup> phase, preferentially activating either methane or CO<sub>2</sub>, respectively. Remarkably, the insertion of carbon atoms into the strained palladium lattice of the milled palladium on ceria M sample also inhibited coke deactivation, which usually plagues DRM catalysts, enabling higher activity, hydrogen production and stability over time.

A completely different scenario was considered when applying palladium on ceria M materials for the passive adsorption of NO<sub>x</sub> (72), a process that is investigated for the improvement of the

performances of catalysts for the selective catalytic reduction of NO<sub>x</sub>. In this case the behaviour of milled materials was also found to be significantly different compared to that of impregnated samples and again the differences involved the reaction mechanism. The milled materials in fact showed a different NO<sub>x</sub> desorption profile, where most of the NO<sub>x</sub> desorbed as nitrogen dioxide at higher temperature compared to PdCeIW. This was ascribed to the easier oxidation of nitric oxide to more stable nitrates observed on PdCeM, which, in turn, was related to the stronger palladium-ceria interaction leading to higher oxygen mobility.

For all these reactions, the mild intensity conditions, rarely reported in the literature as successful for the preparation of functional materials, proved to be key to obtain a high dispersion of metallic phase over a metal oxide support, without damaging the lattice structure of the latter and a unique metal-ceria interaction leading to high activity, stability and different reaction mechanisms.

### 3. Mechanochemical Synthesis of Supported Metal-Oxide Photocatalysts

In spite of the remarkable and rapid progress achieved in photocatalysis (73–77), there are still obstacles to overcome in the quest for effective photocatalysts that can operate under solar light, as well as selective co-catalysts and more efficient mechanisms for hydrogen photoproduction. Anticipating the near future, we envision that the collaboration between nanotechnological tools for fabrication and photoreaction engineering will assume a crucial role. In this regard, the mechanochemical approach has recently emerged as one of the most interesting synthetic protocols to produce novel photocatalysts with advanced functionalities. Mechanochemistry has been proven as an efficient approach to prepare active photocatalysts such as N-doped and S-doped titania (78–82), photoactive semiconductor mixtures of ferric oxide-titania and molybdenum sulfide-titania (83–85) and magnetically separable titania (86). Recently, the preparation of gold on titania for hydrogen photoproduction from gold complexes and manual grinding has been reported (87, 88).

Decreasing the size of metal entities supported onto the surface of semiconductor particles from a few nanometres down to homogeneously dispersed clusters or single atoms has been proven to be an effective strategy to enhance the photocatalytic

efficiency. Nevertheless, designing a simple and scalable manufacture process has consistently been a challenge. The mechanochemical synthesis of ultra-small noble metal clusters anchored over inorganic oxide supports has proved to be an interesting approach to synthesise photocatalysts, not only by providing a facile method to obtain well-dispersed sub-nanometric metal clusters, but also because the photocatalytic properties of the resulting materials are significantly improved in terms of both photoactivity and long-term operational stability. For instance, a facile one-step ball milling protocol to synthesise gold clusters dispersed over the surface of titania P90 nanoparticles has been developed (89). Gold(III) acetate was added as a solid precursor and was ball-milled with titania P90 powder, obtaining anchored sub-nanometric gold clusters (see **Figure 6**). All the ball-milling parameters were optimised to achieve the highest hydrogen production and, in a similar way as described for the palladium on ceria system, the best photocatalytic performances were obtained at low milling energy (15 Hz for 10 min with a ball-to-powder ratio of 45). The obtained gold clusters present a particular interaction with titania, which was demonstrated by XPS analysis showing a strong signal at 83.6 eV that can be ascribed to activated gold clusters Au<sup>0\*</sup>. The resultant gold on titania mechanochemically activated photocatalysts exhibited a photoactivity that doubled the photoproduction of hydrogen under ultraviolet (UV) light compared with a conventional gold on titania photocatalyst containing gold nanoparticles prepared by incipient wetness impregnation methodologies. A further photocurrent and electronic impedance spectroscopic analyses of gold on titania samples pointed out that the mechanochemically-prepared photocatalysts possessed a lower resistance than a gold on titania sample conventionally produced by impregnation, which indicated that milled metal-oxide samples achieved better electron transfer processes and allow more efficient electron-hole charge separation phenomena. Additionally, the specific architecture reached by mechanochemical milling between gold and titania not only leads to a higher photoactivity under UV light, but also to a significant increase in the use of visible light in the photocatalytic production of hydrogen, which certainly represents a remarkable milestone.

The mechanochemical approach has also been successfully employed for the preparation of titania-based photocatalysts with co-catalysts other than gold. Nanoshaped titania materials



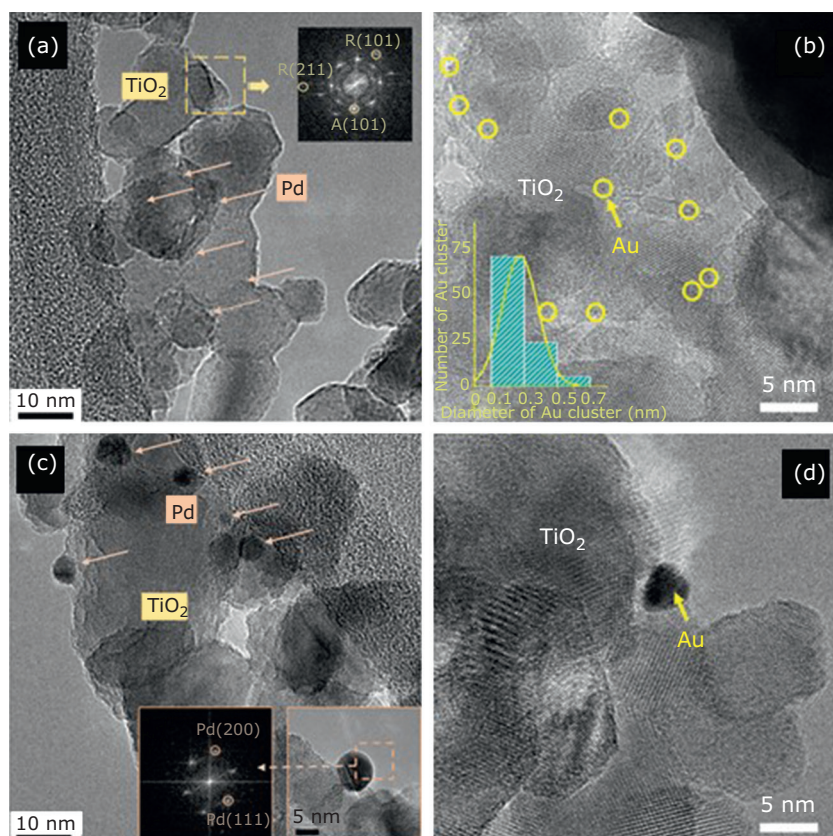


Fig. 6. HRTEM images of titania-based samples freshly obtained by milling titania with: (a) palladium (II) acetate; (b) gold (III) acetate; (c) and (d) the same samples after a photocatalytic hydrogen generation reaction (27, 53). Reprinted from (53) under Creative Commons Attribution License 4.0 (CC BY-NC-ND 4.0 DEED)

enriched with graphene, which are linked to a reduced recombination of electron-hole pairs, have been modified with platinum and copper precursors in a mechanochemical process to obtain enhanced photocatalysts for continuous hydrogen production (80). The preparation of the desired shapes of titania (nanotubes, nanobelts and nanowires) was carried out by a hydrothermal method varying the experimental conditions (temperature, time, potassium hydroxide or sodium hydroxide concentration). Biomass-derived reduced graphene oxide (rGO) was synthesised from calcination of grinded and sifted orange peels, followed by a reduction with hydrazine. The ball milled metal precursors were platinum(II) chloride and hydrated copper(II) nitrate. The experimental results showed that a combination of 0.5% platinum-0.5% copper-2% rGO-TiO<sub>2</sub> nanotubes photocatalyst resulted in an effective hydrogen photogeneration with an advantageous synergistic effect of copper-platinum decorating the rGO-TiO<sub>2</sub> support compared to the monometallic counterparts.

A photocatalyst prepared by mechanochemistry with highly dispersed palladium clusters onto commercial titania P90 nanoparticles has also been

recently reported (53). The mechanochemically-synthesised catalyst reported involved the use of a palladium(II) acetate precursor that was ball-milled with titania powder. To assess the photocatalytic behaviour of palladium species anchored over titania, a series of comparative experiments were conducted using samples prepared through ball milling with different titania and palladium precursors (titania P90, titania P25, palladium(II) acetate, palladium(II) chloride and palladium(II) nitrate). Considering the support materials, titania P90 exhibited superior photocatalytic performance compared to titania P25. This can be attributed to its larger surface area, which promotes better dispersion of palladium co-catalyst species, leading to enhanced contact with gaseous reactants and active sites during the photocatalytic hydrogen production process. Additionally, the photocatalyst synthesised from palladium(II) acetate demonstrated better photocatalytic performance when compared to samples prepared from palladium(II) nitrate or palladium(II) chloride. The impact of various milling parameters on hydrogen production was examined. Again, the photocatalytic performance exhibited a notable dependence on the milling

energy, where a higher frequency corresponded to a lower rate of hydrogen production. This observation implied that lower impact velocities promote a more effective interaction between the metal and the support material. Importantly, following the photoreaction, it was observed that the palladium clusters in the palladium on titania M sample exhibited a higher tendency to agglomerate, as shown in **Figure 6**. Consequently, the palladium clusters underwent a transformation during the photocatalytic hydrogen production, forming nanoparticles with sizes ranging from approximately 2.5 nm to 4 nm. To delve deeper into the interaction between palladium species and the titania support, XPS was employed. The deconvoluted palladium 3d signal unambiguously showed the different oxidation states of palladium existing on the surface of the different photocatalysts. In the sample palladium on titania M, palladium 3d<sub>5/2</sub> peaks with binding energies at around 335.0 eV, 336.0 eV and 337.2 eV can be ascribed to metallic palladium (Pd<sup>0</sup>), Pd<sup>2+</sup> and superoxidised Pd<sup>δ+</sup> species, respectively, where the metallic palladium was the dominant species (51.1%). In contrast, in conventional palladium on titania samples prepared by impregnation methods or palladium on titania M samples with calcination treatment, palladium was mostly in oxidised form. In the fresh ball-milled palladium on titania samples, the presence of metallic palladium exhibited a remarkable influence on the separation of electron-hole pairs generated during photocatalysis. Notably, a unique interaction effect between palladium clusters and the titania support was observed in the palladium on titania M photocatalysts during UV illumination. This interaction effect can be effectively elucidated through the surface variations detected in the XP titanium 2p and oxygen 1s spectra, as well as the comprehensive analysis of the palladium K-edge X-ray absorption near-edge structure spectra (91).

Therefore, the utilisation of mechanochemical strategies presents promising prospects for producing stable metal clusters supported on oxides, serving as enhanced photocatalysts without the need for organic ligands to stabilise the active sites. As depicted in **Figure 7**, mechanochemical synthesis can serve to obtain different features in the photocatalytic materials, including but not limited to: (i) anchoring ultra-small active sites onto semiconductor surfaces; (ii) improving visible light absorption using plasmonic materials; (iii) boosting charge separation and transport reducing

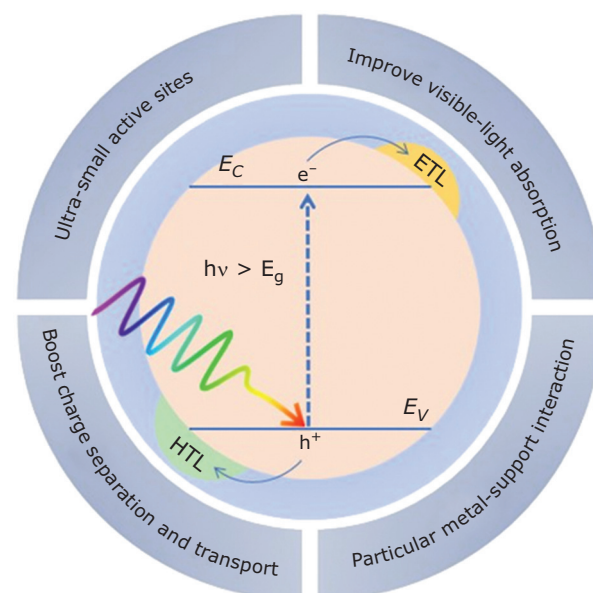


Fig. 7. Summary of features that can be achieved *via* mechanochemically synthesising photocatalysts. The central scheme depicts a composite semiconductor and two selective contacts, an ETL and a HTL formed by milling two different cocatalysts with the semiconductor. e<sup>-</sup> and h<sup>+</sup> are the photogenerated electrons and holes, respectively. E<sub>C</sub> is the energy of the conduction band, E<sub>V</sub> is the energy of the valence band, E<sub>g</sub> is the band gap energy, hν is the incident light energy

the electrical resistance of the resultant material and creating effective hole transport layers (HTL) and electron transport layers (ETL); and (iv) obtaining a particular metal-support interaction that results in specific electronic properties and oxidation states that improve the overall photocatalytic performance.

#### 4. Summary and Outlook

Mechanochemistry offers tremendous potential in catalyst preparation, presenting opportunities for innovative and sustainable catalyst development. The synthesis of supported metal catalysts through mechanochemical methods has minimal environmental impact compared to traditional wet preparation techniques and can be easily scaled up for industrial production. The simplicity of the equipment and absence of complex setups make mechanochemistry an attractive choice for large-scale catalyst synthesis.

While the results reported in this account focus mainly on the palladium (platinum) on ceria, gold on titania and palladium on titania systems, their implications can be extended to a variety of

metal/support combinations, thus leading to the development of novel classes of materials. For instance, recent studies have explored the use of gold on ceria prepared *via* mechanochemistry for carbon monoxide oxidation and selective preferential oxidation of carbon monoxide in hydrogen-rich streams for fuel cell applications (91). Bimetallic formulations prepared using mechanochemical methods have also shown promise, where the order of metal addition and milling conditions can imprint unique characteristics. Notably, this has been observed in the low-temperature partial oxidation of methane to produce syngas over palladium-nickel on ceria, palladium-ruthenium on ceria and nickel-ruthenium on ceria (92–94), as well as in the steam reforming of methane over iron-nickel on ceria (95).

Mechanochemistry facilitates the integration of multiple components and structures, such as metal nanoparticles, semiconductors and co-catalysts, for the development of highly efficient photocatalysts. By correlating synthesis parameters with the resulting structure, mechanochemistry allows tuning the supported metal particle morphology, ranging from nanometric ensembles to sub-nanometric clusters and single-atom catalysts. The unique architectures of catalytic active sites achieved through mechanochemistry set them apart from conventional catalysts, leading to improved catalytic activity, selectivity and stability.

Undoubtedly, further research is needed to fully explore the potential of mechanochemistry in designing catalysts and photocatalysts with tailored properties. This emerging area of research in catalysis and surface science requires a better understanding of the resulting active sites and the establishment of a theoretical foundation for comprehending structure-activity relationships, optimising catalyst design and predicting surface architectures based on milling conditions. Addressing this challenge is crucial since the architectures resulting from mechanochemistry are likely to be out of equilibrium. Theoretical modelling can provide insights into the influence of surface structures, defects and surface energetics on the catalytic activity and selectivity of mechanochemically prepared catalysts. Additionally, the use of *in situ* and *operando* advanced characterisation methods is imperative for identifying these unique active sites and their potential evolution into more stable structures under reaction conditions, as demonstrated in this review.

## Acknowledgements

This work has been funded by MICINN/FEDER PID2021–124572OB–C31 and GC 2021 SGR 01061 grants and by Ford Motor Company under 2014–2195R University Research Program Award. M.D. acknowledges funding from Regione Friuli Venezia Giulia under Operating Program of the European Social Fund 2014/2020 and from REACT EU Italian PON 2014–2020 Program – Action IV.4 – Innovation (DM 1062, 10/08/2021). M.D. and S.C. are grateful to Fondazione CRUI for Go for IT Project CUP G29C20000830001. N.J.D. acknowledges the funding received from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 897197. L.S. is grateful to the MICINN Ramon y Cajal program for individual fellowship grant agreement RYC2019–026704–I. J.L. is a Serra Hünter Fellow and is grateful to the ICREA Academia programme.

## References

1. L. Takacs, *Chem. Soc. Rev.*, 2013, **42**, (18), 7649
2. P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J. M. Criado, F. Delogu, E. Dutková, E. Gaffet, F. J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii, K. Wieczorek-Ciurowa, *Chem. Soc. Rev.*, 2013, **42**, (18), 7571
3. M. G. Rinaudo, A. M. Beltrán, M. A. Fernández, L. E. Cadús, M. R. Morales, *Mater. Today Chem.*, 2020, **17**, 100340
4. M. H. Enayati, F. A. Mohamed, *Int. Mater. Rev.*, 2014, **59**, (7), 394
5. V. Šepelák, A. Düvel, M. Wilkening, K.-D. Becker, P. Heitjans, *Chem. Soc. Rev.*, 2013, **42**, (18), 7507
6. K. J. Ardila-Fierro, J. G. Hernández, *ChemSusChem*, 2021, **14**, (10), 2145
7. T. Iwasaki, *KONA Powder Part. J.*, 2022, **40**, 186
8. A. P. Amrute, J. De Bellis, M. Felderhoff, F. Schüth, *Chem. Eur. J.*, 2021, **27**, (23), 6819
9. B. Szczęśniak, J. Choma, M. Jaroniec, *Mater. Adv.*, 2021, **2**, (8), 2510
10. J.-L. Do, T. Friščić, *ACS Cent. Sci.*, 2017, **3**, (1), 13
11. R. A. Buyanov, V. V. Molchanov, V. V. Boldyrev, *Catal. Today*, 2009, **144**, (3–4), 212
12. X. Jiang, M. A. Trunov, M. Schoenitz, R. N. Dave, E. L. Dreizin, *J. Alloys Compd.*, 2009, **478**, (1–2), 246
13. M. J. Muñoz-Batista, D. Rodríguez-Padron, A. R. Puente-Santiago, R. Luque, *ACS Sustain. Chem. Eng.*, 2018, **6**, (8), 9530

14. R. Schlem, C. F. Burmeister, P. Michalowski, S. Ohno, G. F. Dewald, A. Kwade, W. G. Zeier, *Adv. Energy Mater.*, 2021, **11**, (30), 2101022
15. D. N. Rainer, R. E. Morris, *Dalton Trans.*, 2021, **50**, (26), 8995
16. S. Główniak, B. Szczeńniak, J. Choma, M. Jaroniec, *Mater. Today*, 2021, **46**, 109
17. M. F. Thorne, M. L. R. Gómez, A. M. Bumstead, S. Li, T. D. Bennett, *Green Chem.*, 2020, **22**, (8), 2505
18. O. Lapshin, O. Ivanova, *Adv. Powder Technol.*, 2022, **33**, (12), 103852
19. G.-F. Han, F. Li, Z.-W. Chen, C. Coppex, S.-J. Kim, H.-J. Noh, Z. Fu, Y. Lu, C. V. Singh, S. Siahrostami, Q. Jiang, J.-B. Baek, *Nat. Nanotechnol.*, 2021, **16**, (3), 325
20. C. Bolm, J. G. Hernández, *Angew. Chem. Int. Ed.*, 2019, **58**, (11), 3285
21. H. Schreyer, R. Eckert, S. Immohr, J. de Bellis, M. Felderhoff, F. Schüth, *Angew. Chem. Int. Ed.*, 2019, **58**, (33), 11262
22. C. Gomes, C. S. Vinagreiro, L. Damas, G. Aquino, J. Quaresma, C. Chaves, J. Pimenta, J. Campos, M. Pereira, M. Pineiro, *ACS Omega*, 2020, **5**, (19), 10868
23. R. R. A. Bolt, J. A. Leitch, A. C. Jones, W. I. Nicholson, D. L. Browne, *Chem. Soc. Rev.*, 2022, **51**, (11), 4243
24. J. Casaban, Y. Zhang, R. Pacheco, C. Coney, C. Holmes, E. Sutherland, C. Hamill, J. Breen, S. L. James, D. Tufano, D. Wong, E. Stavarakakis, H. Annath, A. Moore, *Faraday Discuss.*, 2021, **231**, 312
25. A. F. Fuentes, L. Takacs, *J. Mater. Sci.*, 2013, **48**, (2), 598
26. M. Danielis, S. Colussi, C. de Leitenburg, L. Soler, J. Llorca, A. Trovarelli, *Angew. Chem. Int. Ed.*, 2018, **57**, (32), 10212
27. Y. Chen, L. Soler, C. Xie, X. Vendrell, J. Serafin, D. Crespo, J. Llorca, *Appl. Mater. Today*, 2020, **21**, 100873
28. Q. Liu, Y. Xu, Y. Zhao, K. Wang, C. Liang, S. Zhao, X. Wang, X. Guo, N. Xue, W. Ding, *Adv. Mater. Technol.*, 2023, **8**, (10), 2202007
29. M. Li, T. Zhang, S.-Z. Yang, Y. Sun, J. Zhang, F. Polo-Garzon, K. M. Siniard, X. Yu, Z. Wu, D. M. Driscoll, A. S. Ivanov, H. Chen, Z. Yang, S. Dai, *ACS Catal.*, 2023, **13**, (9), 6114
30. L. F. Orozco, D.-H. Nguyen, J.-Y. Delenne, P. Sornay, F. Radjai, *Powder Technol.*, 2020, **362**, 157
31. Y. T. Feng, K. Han, D. R. J. Owen, *Mater. Sci. Eng.: A*, 2004, **375–377**, 815
32. W. Chen, R. N. Dave, R. Pfeffer, O. Walton, *Powder Technol.*, 2004, **146**, (1–2), 121
33. C. Suryanarayana, *Prog. Mater. Sci.*, 2001, **46**, (1–2), 1
34. E. Aneggi, V. Rico-Perez, C. de Leitenburg, S. Maschio, L. Soler, J. Llorca, A. Trovarelli, *Angew. Chem. Int. Ed.*, 2015, **54**, (47), 14040
35. M. Danielis, S. Colussi, C. de Leitenburg, L. Soler, J. Llorca, A. Trovarelli, *Catal. Sci. Technol.*, 2019, **9**, (16), 4232
36. M. G. Rinaudo, G. Pecchi, L. E. Cadús, M. R. Morales, *Ceram. Int.*, 2023, **49**, (11B), 18614
37. A. K. Datye, M. Votsmeier, *Nat. Mater.*, 2021, **20**, (8), 1049
38. R. J. Farrauto, M. Deeba, S. Alerasool, *Nat. Catal.*, 2019, **2**, (7), 603
39. C. Morgan, J. Goodwin, *Johnson Matthey Technol. Rev.*, 2023, **67**, (2), 239
40. C. Hagelüken, J. U. Lee-Shin, A. Carpentier, C. Heron, *Recycling*, 2016, **1**, (2), 242
41. M. Monai, T. Montini, R. J. Gorte, P. Fornasiero, *Eur. J. Inorg. Chem.*, 2018, (25), 2884
42. P. T. Benavides, D. C. Cronauer, F. Adom, Z. Wang, J. B. Dunn, *Sust. Mater. Technol.*, 2017, **11**, 53
43. N. Kotake, M. Kuboki, S. Kiya, Y. Kanda, *Adv. Powder Technol.*, 2011, **22**, (1), 86
44. D. Chen, B. Liu, W. Xu, C. Zhang, E. Guo, J. Lu, G. Sun, Y. Pan, J. Zhang, X. Lu, *Adv. Powder Technol.*, 2022, **33**, (11), 103803
45. E. D. Goodman, A. C. Johnston-Peck, E. M. Dietze, C. J. Wrasman, A. S. Hoffman, F. Abild-Pedersen, S. R. Bare, P. N. Plessow, M. Cargnello, *Nat. Catal.*, 2019, **2**, (9), 748
46. A. M. Gänzler, M. Casapu, P. Vernoux, S. Loidant, F. J. C. S. Aires, T. Epicier, B. Betz, R. Hoyer, J.-D. Grunwaldt, *Angew. Chem. Int. Ed.*, 2017, **56**, (42), 13078
47. H. Jeong, O. Kwon, B.-S. Kim, J. Bae, S. Shin, H.-E. Kim, J. Kim, H. Lee, *Nat. Catal.*, 2020, **3**, (4), 368
48. H. Wang, J.-X. Liu, L. F. Allard, S. Lee, J. Liu, H. Li, J. Wang, J. Wang, S. H. Oh, W. Li, M. Flytzani-Stephanopoulos, M. Shen, B. R. Goldsmith, M. Yang, *Nat. Commun.*, 2019, **10**, 3808
49. Y. Hu, B. Li, C. Yu, H. Fang, Z. Li, *Mater. Today*, 2023, **63**, 288
50. G.-F. Han, F. Li, A. I. Rykov, Y.-K. Im, S.-Y. Yu, J.-P. Jeon, S.-J. Kim, W. Zhou, R. Ge, Z. Ao, T. J. Shin, J. Wang, H. Y. Jeong, J.-B. Baek, *Nat. Nanotechnol.*, 2022, **17**, (4), 403
51. X. He, Y. Deng, Y. Zhang, Q. He, D. Xiao, M. Peng, Y. Zhao, H. Zhang, R. Luo, T. Gan, H. Ji, D. Ma, *Cell Rep. Phys. Sci.*, 2020, **1**, (1), 100004
52. M. Danielis, L. E. Betancourt, I. Orozco, N. J. Divins,

- J. Llorca, J. A. Rodríguez, S. D. Senanayake, S. Colussi, A. Trovarelli, *Appl. Catal. B: Environ.*, 2021, **282**, 119567
53. Y. Chen, L. Soler, M. Armengol-Profítos, C. Xie, D. Crespo, J. Llorca, *Appl. Catal. B: Environ.*, 2022, **309**, 121275
54. A. Raj, *Johnson Matthey Technol. Rev.*, 2016, **60**, (4), 228
55. S. Colussi, A. Gayen, J. Llorca, C. de Leitenburg, G. Dolcetti, A. Trovarelli, *Ind. Eng. Chem. Res.*, 2012, **51**, (22), 7510
56. S. Colussi, A. Gayen, M. F. Camellone, M. Boaro, J. Llorca, S. Fabris, A. Trovarelli, *Angew. Chem. Int. Ed.*, 2009, **48**, (45), 8481
57. A. Toso, S. Colussi, S. Padigapaty, C. de Leitenburg, A. Trovarelli, *Appl. Catal. B: Environ.*, 2018, **230**, 237
58. A. Trovarelli, F. Zamar, J. Llorca, C. de Leitenburg, G. Dolcetti, J. T. Kiss, *J. Catal.*, 1997, **169**, (2), 490
59. M. Danielis, N. J. Divins, J. Llorca, L. Soler, X. Garcia, I. Serrano, L. E. Betancourt, W. Xu, J. A. Rodríguez, S. D. Senanayake, S. Colussi, A. Trovarelli, *EES. Catal.*, 2023, **1**, (1), 144
60. A. Mussio, M. Danielis, N. J. Divins, J. Llorca, S. Colussi, A. Trovarelli, *ACS Appl. Mater. Interfaces*, 2021, **13**, (27), 31614
61. N. J. Divins, A. Braga, X. Vendrell, I. Serrano, X. Garcia, L. Soler, I. Lucentini, M. Danielis, A. Mussio, S. Colussi, I. J. Villar-Garcia, C. Escudero, A. Trovarelli, J. Llorca, *Nat. Commun.*, 2022, **13**, 5080
62. M. Danielis, S. Colussi, J. Llorca, R. H. Dolan, G. Cavataio, A. Trovarelli, *Ind. Eng. Chem. Res.*, 2021, **60**, (18), 6435
63. M. Danielis, S. Colussi, C. de Leitenburg, A. Trovarelli, *Catal. Commun.*, 2020, **135**, 105899
64. A. Hellman, A. Resta, N. M. Martin, J. Gustafson, A. Trincherio, P.-A. Carlsson, O. Balmes, R. Felici, R. van Rijn, J. W. M. Frenken, J. N. Andersen, E. Lundgren, H. Grönbeck, *J. Phys. Chem. Lett.*, 2012, **3**, (6), 678
65. S. Colussi, P. Fornasiero, A. Trovarelli, *Chin. J. Catal.*, 2020, **41**, (6), 938
66. T. Franken, M. Roger, A. W. Petrov, A. H. Clark, M. Agote-Arán, F. Krumeich, O. Kröcher, D. Ferri, *ACS Catal.*, 2021, **11**, (8), 4870
67. W. Huang, E. D. Goodman, P. Losch, M. Cargnello, *Ind. Eng. Chem. Res.*, 2018, **57**, (31), 10261
68. M. Cargnello, J. J. D. Jaen, J. C. H. Garrido, K. Bakhmutsky, T. Montini, J. J. C. Gamez, R. J. Gorte, P. Fornasiero, *Science*, 2012, **337**, (6095), 713
69. R. Gholami, M. Alyani, K. Smith, *Catalysts*, 2015, **5**, (2), 561
70. J. D. Jiménez, L. E. Betancourt, M. Danielis, H. Zhang, F. Zhang, I. Orozco, W. Xu, J. Llorca, P. Liu, A. Trovarelli, J. A. Rodríguez, S. Colussi, S. D. Senanayake, *ACS Catal.*, 2022, **12**, (20), 12809
71. M. Danielis, J. D. Jiménez, N. Rui, J. Moncada, L. E. Betancourt, A. Trovarelli, J. A. Rodriguez, S. D. Senanayake, S. Colussi, *Appl. Catal. A: Gen.*, 2023, **660**, 119185
72. A. Toso, M. Danielis, C. de Leitenburg, M. Boaro, A. Trovarelli, S. Colussi, *Ind. Eng. Chem. Res.*, 2022, **61**, (9), 3329
73. Y. M. Alsalik, K. Katsiev, H. Idriss, *J. Phys. Chem. C*, 2022, **126**, (36), 15184
74. R. Yang, Y. Fan, Y. Zhang, L. Mei, R. Zhu, J. Qin, J. Hu, Z. Chen, Y. H. Ng, D. Voiry, S. Li, Q. Lu, Q. Wang, J. C. Yu, Z. Zeng, *Angew. Chem. Int. Ed.*, 2023, **62**, (13), e202218016
75. Z. Wang, C. Li, K. Domen, *Chem. Soc. Rev.*, 2019, **48**, (7), 2109
76. J. Ma, T. J. Miao, J. Tang, *Chem. Soc. Rev.*, 2022, **51**, (14), 5777
77. F. Matter, M. Niederberger, *Adv. Sci.*, 2022, **9**, (13), 2105363
78. S. Yin, H. Yamaki, M. Komatsu, Q. Zhang, J. Wang, Q. Tang, F. Saito, T. Sato, *Solid State Sci.*, 2005, **7**, (12), 1479
79. Q. Zhang, J. Wang, S. Yin, T. Sato, F. Saito, *J. Am. Ceram. Soc.*, 2004, **87**, (6), 1161
80. Z. Zhou, X. Zhang, Z. Wu, L. Dong, *Chin. Sci. Bull.*, 2005, **50**, (23), 2691
81. T. Umabayashi, T. Yamaki, S. Tanaka, K. Asai, *Chem. Lett.*, 2003, **32**, (4), 330
82. Y. C. Tang, X.-H. Huang, H.-Q. Yu, L.-H. Tang, *Int. J. Photoenergy*, 2012, 960726
83. T. K. Ghorai, M. Chakraborty, P. Pramanik, *J. Alloys Compd.*, 2011, **509**, (32), 8158
84. W. Subramonian, T. Y. Wu, S.-P. Chai, *J. Alloys Compd.*, 2017, **695**, 496
85. Y. Zhu, Q. Ling, Y. Liu, H. Wang, Y. Zhu, *Phys. Chem. Chem. Phys.*, 2015, **17**, (2), 933
86. W. Ouyang, E. Kuna, A. Yopez, A. M. Balu, A. A. Romero, J. C. Colmenares, R. Luque, *Nanomaterials*, 2016, **6**, (5), 93
87. C. Marchal, M. Behr, F. Vigneron, V. Caps, V. Keller, *New J. Chem.*, 2016, **40**, (5), 4428
88. C. Marchal, A. Piquet, M. Behr, T. Cottineau, V. Papaefthimiou, V. Keller, V. Caps, *J. Catal.*, 2017, **352**, 22
89. Y. Chen, L. Soler, C. Xie, X. Vendrell, J. Serafin, D. Crespo, J. Llorca, *Appl. Mater. Today*, 2020, **21**, 100873

90. A. Pollap, J. Serafin, I. Serrano, J. Srenscek-Nazzal, J. Llorca, *J. Env. Chem. Eng.*, 2022, **10**, (6), 108877
91. Y. Chen, L. Soler, M. Armengol-Profítos, C. Xie, D. Crespo, J. Llorca, *Appl. Catal. B: Environ.*, 2022, **309**, 121275
92. S. Ge, Y. Chen, Y. Guo, J. Llorca, L. Soler, *Appl. Mater. Today*, 2023, **33**, 101857
93. S. Fazlikeshteli, X. Vendrell, J. Llorca, *Int. J. Hydrogen Energy*, 2023, **48**, (32), 12024
94. S. Fazlikeshteli, X. Vendrell, J. Llorca, *Fuel*, 2023, **334**, (2), 126799
95. S. Fazlikeshteli, X. Vendrell, J. Llorca, *Int. J. Hydrogen Energy*, 2023, **51**, (A), 1494
96. A. Braga, M. Armengol-Profítos, L. Pascua-Solé, X. Vendrell, L. Soler, I. Serrano, I. J. Villar-Garcia, V. Pérez-Dieste, N. J. Divins, J. Llorca, *ACS Appl. Nano Mater.*, 2023, **6**, (9), 7173

## The Authors



Maila Danielis earned her PhD in 2020 from the University of Udine, Italy. As a graduate student, she focused on novel methane abatement catalysts prepared by mechanical methods, working closely with several industrial partners and the Catalysis: Reactivity and Structure (CRS) Group of Brookhaven National Laboratory (BNL) in Upton, New York, where she spent three months of her PhD. Her research interests lie in developing novel catalysts through mechanochemistry for the valorisation of small waste molecules into higher value feedstock, coupling the analysis of the peculiar reactivity with structural characterisation methods.



Professor Sara Colussi earned her Master's degree in Chemical Engineering at the University of Trieste in 2002 and her PhD in Chemical and Energetic Technologies at the University of Udine in 2006. With more than 40 international papers in the field of heterogeneous catalysis and a strong experience in presenting at national and international conferences, she is currently Associate Professor at the Polytechnic Department of the University of Udine, Italy. Her research interests involve palladium-based catalysts, particularly on ceria-containing supports, for the abatement of methane and volatile organic compounds emissions from natural gas fuelled vehicles and metal-based catalysts for CO<sub>2</sub> valorisation.



Núria J. Divins earned her PhD from the Technical University of Catalonia–BarcelonaTech (UPC) in 2015. After graduating, she served as a postdoctoral researcher at the Ruhr–University Bochum, Germany. Currently, she is a Marie-Sklodowska Curie postdoctoral fellow at UPC. Her research focuses on the development of catalysts for energy and environmental applications, such as hydrogen production. In particular, she gives special emphasis to the investigation of catalysts under reaction conditions (*operando* characterisation) to derive structure-activity correlations, mainly using X-ray photoelectron and absorption spectroscopies.



Lluís Soler received his PhD in chemistry from the Autonomous University of Barcelona (UAB) in 2010. He has worked as a senior postdoctoral researcher at the Technical University of Catalonia–BarcelonaTech (UPC) since autumn 2014. From 2012–2014, he joined the IFW Dresden and the Max-Planck-Institute for Intelligent Systems in Stuttgart, Germany, in a postdoctoral position. With over 60 scholarly articles, three book chapters and four patents, his current research lines span from heterogeneous catalysis and photocatalysis for green hydrogen production to engineered nanomaterials for enhanced sunlight harvesting.



Professor Alessandro Trovarelli is Professor of Industrial Chemistry at the University of Udine from 2003 where he is the coordinator of the Catalysis for energy and environment group. He is currently on the Editorial Board for *Applied Catalysis B: Environmental* and the *Journal of Rare Earths*. He is the 2015 Recipient of the Ford Motor Company University Research Program Award and the 2022 recipient of the Giacomo Levi Medal award of the Division of Industrial Chemistry of the Italian Chemical Society. He is author or coauthor of ca. 200 articles and seven international patents. He is presently Prorector for Research at University of Udine, Italy.



Professor Jordi Llorca earned his PhD in Chemistry from the University of Barcelona. He joined the Technical University of Catalonia–BarcelonaTech (UPC) in 2005 and later became Full Professor as a Serra Húnter Fellow in 2014. He has been awarded with the Distinction of Generalitat de Catalunya for University Research Promotion, the Humbert Torres Prize and the ICREA Academia. With over 450 scholarly articles, ten patents and two spin-offs, his work focuses on developing efficient catalysts for energy and environmental applications. Currently, he serves as the Vice-rector for Research at UPC. Asteroid 2013 WD1 has been named in his honour by the International Astronomical Union.