



Review

Meta-analysis of CO₂ conversion, energy efficiency, and other performance data of plasma-catalysis reactors with the open access PIONEER database

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ARTICLE INFO

Article history:

Received 21 May 2023

Revised 28 June 2023

Accepted 4 July 2023

Available online 9 August 2023

Keywords:

Open-access database on plasma-catalysis experiment

CO₂ conversion

Plasma-catalysis

Carbon capture and utilisation (CCU)

Energy efficiency

Specific energy input

Dielectric barrier discharge

Packed bed reactor

Methanation

Dry reforming of methane

ABSTRACT

This paper brings the comparison of performances of CO₂ conversion by plasma and plasma-assisted catalysis based on the data collected from literature in this field, organised in an open access online database. This tool is open to all users to carry out their own analyses, but also to contributors who wish to add their data to the database in order to improve the relevance of the comparisons made, and ultimately to improve the efficiency of CO₂ conversion by plasma-catalysis. The creation of this database and database user interface is motivated by the fact that plasma-catalysis is a fast-growing field for all CO₂ conversion processes, be it methanation, dry reforming of methane, methanolisation, or others. As a result of this rapid increase, there is a need for a set of standard procedures to rigorously compare performances of different systems. However, this is currently not possible because the fundamental mechanisms of plasma-catalysis are still too poorly understood to define these standard procedures. Fortunately however, the accumulated data within the CO₂ plasma-catalysis community has become large enough to warrant so-called “big data” studies more familiar in the fields of medicine and the social sciences. To enable comparisons between multiple data sets and make future research more effective, this work proposes the first database on CO₂ conversion performances by plasma-catalysis open to the whole community. This database has been initiated in the framework of a H2020 European project and is called the “PIONEER DataBase”. The database gathers a large amount of CO₂ conversion performance data such as conversion rate, energy efficiency, and selectivity for numerous plasma sources coupled with or without a catalyst. Each data set is associated with metadata describing the gas mixture, the plasma source, the nature of the catalyst, and the form of coupling with the plasma. Beyond the database itself, a data extraction tool with

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direct visualisation features or advanced filtering functionalities has been developed and is available online to the public. The simple and fast visualisation of the state of the art puts new results into context, identifies literal gaps in data, and consequently points towards promising research routes. More advanced data extraction illustrates the impact that the database can have in the understanding of plasma-catalyst coupling. Lessons learned from the review of a large amount of literature during the setup of the database lead to best practice advice to increase comparability between future CO₂ plasma-catalytic studies. Finally, the community is strongly encouraged to contribute to the database not only to increase the visibility of their data but also the relevance of the comparisons allowed by this tool.

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action with complex materials, catalytic or not. In particular, he makes extensive use of infrared absorption spectroscopy in the gas phase or on solid surfaces.

1. Introduction

Although the first article mentioning the association of a non-thermal plasma source with catalysts dates back to 1921 [1], studies on this subject have increased dramatically since the 1990s, see for instance [2–21] and references therein. An overview of the growth of the number of plasma-catalysis publications per year obtained from different popular search engines is shown in Fig. 1. The plasma-catalysis coupling can be used either to decontaminate a gas (indoor air treatment, NO_x destruction, etc.) or to realise the synthesis of a molecule (NH₃ synthesis, CO₂ conversion into CO, hydrocarbons and alcohols, etc.). In the particular case of CO₂ conversion, a plasma-catalyst coupling can increase the yield of different molecules (e.g. methane, methanol, ethanol, and other hydrocarbons) compared to plasma-only conversion depending on the gas mixture and the catalysts used. All these processes, whether methanation, dry reforming, or others, are also studied in thermal catalysis. However, the reaction pathways and the performances obtained are fundamentally different in plasma-catalysis. In thermal catalysis, the reactant molecules in their ground state adsorb on the catalyst, then react only on the surface, and finally desorb, possibly after several steps. In plasma-catalysis, excited species and radicals are created in the gas phase by the plasma, which can then reach the catalyst surface and alter the

kinetics, promoting different reaction pathways compared to thermal catalysis. In addition, the interaction between the plasma and the catalyst may open up new reaction pathways, which are not available in thermal catalysis. For example, the strong electric fields induced by the plasma can affect the adsorption energies and the mobilities on the catalyst surface [23]. Alongside this, the presence of charged species and high-energy photons results in reactions that are occasionally compared to photo-catalysis or electro-catalysis [24]. However, as will be explained later, the reaction pathways within plasma-catalysis cannot be simply categorised as either thermal-catalytic, electro-catalytic, or photo-catalytic. Instead, the unique combination of reaction pathways within plasma-catalysis may constitute a new form of non-equilibrium catalysis worthy of a separate category of its own.

The fast-increasing number of plasma-catalysis publications, as shown in Fig. 1, puts pressure on the development of tools for benchmarking and performance comparison. However, plasma-catalysis is still lacking in standardised tools and benchmarks to allow relevant performance comparison for different catalytic materials. Appropriate examples may be model reactors, systematic characterisation methods, or fully-characterised reference materials, openly available to the community as being done for conventional catalysis [25]. The complexity of plasma-catalysis is such that systematic procedures are yet to be established. To do

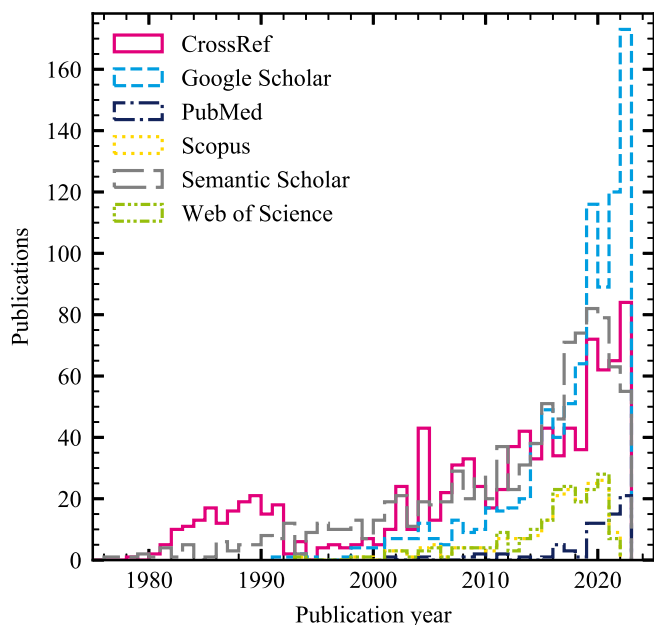


Fig. 1. Number of publications on plasma-catalysis per year obtained from different popular search engines for maximum objectivity using the Publish or Perish software [22].

so, two approaches, complementary to each other, have to be developed in parallel.

1. in situ and time-resolved measurements in combination with modelling to get a deeper, fundamental understanding of plasma-catalyst interactions.
2. developing meta-analysis tools and approaches to capture key parameters for performance improvement from existing conversion studies, even if the experiments were not conducted under standardised conditions.

The first approach generally imposes the use of specific reactor geometries that are dedicated to the study of a particular phenomenon and are thus not focusing on high CO₂ conversion. On the contrary, reactors designed for high conversion performance have more complex geometries and are typically not well-suited for advanced in situ diagnostics, making comparisons between different reactors more challenging. To compensate for this and make the second approach listed above more effective, a detailed description of the experimental conditions must be provided to ease the comparison. Thus, this work proposes a meta-analysis tool, suitable for CO₂ plasma-catalysis, with the aim of facilitating the identification of key parameters and trends for performance improvement. The proposed tool is an open access database collecting all the relevant performance data from the literature. The database is the result of a joint effort between 13 PhD students (first authors of this work), part of the European PIONEER project [26], and is therefore called the PIONEER database (abbreviated as CO₂-PDB from now on). In addition, an online user interface, allowing the extraction, filtering and plotting of the data from the database has been developed and is accessible via <http://db.co2pioneer.eu> (and aliases <http://pdb.co2pioneer.eu> or <http://database.co2pioneer.eu> or <http://pioneer.database.co2pioneer.eu>). More details, e.g., practical information to get started, using and referencing the CO₂-PDB, can be found in the online documentation: <https://docs.co2pioneer.eu>. The CO₂-PDB is exclusively limited to plasma-(catalysis) CO₂ conversion results. This is motivated by the specificity of plasma-catalysis for CO₂ conversion, as will be discussed in Section 2. CO₂ capture and storage technolo-

gies can also sometimes rely on the use of catalysts (or adsorbents), which are sometimes even produced using plasma processes [27], but these technologies, although certainly useful in the context of reducing CO₂ emissions, are not included in the database proposed here. The positioning compared to other existing databases, the graphical interface and the type of data set to be provided to the CO₂-PDB are described in Section 3. One of the ambitions of this work is to propose a minimal set of parameters that should be reported in any work dedicated to plasma-catalysis coupling for CO₂ conversion. This minimal set of parameters must include enough information/parameters to characterise the experiments and enable a comparison with other experimental works. This set can be divided into four main subsets, namely, (i) the plasma source, (ii) the catalytic material, (iii) the type of coupling configuration, and (iv) the gas mixture. The selection criteria of these subsets and the parameters therein included will be explained in Section 3.2, together with general information about the data set already included in the CO₂-PDB at the time of publication. The main features of the CO₂-PDB and the graphical interface developed to extract data will be presented in Section 3.3. The explanation of how to use the basic and more advanced features of the CO₂-PDB will be explained in Sections 3.3.1 and 3.3.2, respectively. Section 4 provides first examples of data extraction from the CO₂-PDB. A comparison with figures from previously published review papers in the field of plasma-catalysis is first shown in Section 4.1. Section 4.2 explains in a broad manner the use of the CO₂-PDB web interface. The caveats and disclaimers are explained in details in Section 4.3. To illustrate the possibilities offered by the numerous input parameters of the database, Sections 4.4 and 4.5 highlight the role of the support vs. the role of the active phase for CO₂ conversion performances and also the behaviour of C_xH_y molecules in various plasma-catalytic reactor configurations. The graphs that will be discussed in these data extraction examples are obtained from the data set already included in the CO₂-PDB at the time of submission of this paper. It is important to reiterate that this data set is intended to be developed by contributions from the whole community. The trends observed will therefore need to be confirmed against a larger and perhaps better defined data set when future publications in the field provide more complete information on the experimental conditions and characterisation of the materials used. Currently many publications suffer from a lack of characterisation of either the plasma source or the catalytic material used. This is an important obstacle to more detailed comparisons of the results obtained in different research groups. Section 5 will therefore propose some ways to enrich future work with minimal parameter sets (which can be included in the CO₂-PDB) that seem important to gain more understanding from cross comparison of results of different works.

2. Specificity of plasma-catalysis for CO₂ recycling

2.1. Plasma sources used for CO₂ conversion

As stated in the introduction, the practical applications of plasma-catalysis are predominantly gas decontamination and molecular synthesis. Despite their different end goals, these applications frequently share a common aspect, which is the use of a dielectric barrier discharge (DBD) as the plasma source and, more specifically, a “packed bed DBD” in coaxial geometry. The extensive use of packed bed DBDs is because they are easy to implement, relatively cheap, and provide simple catalyst coupling. However, in the context of CO₂ conversion, DBDs often have the drawback of being unable to exploit the more efficient vibrationally excited dissociation. This is due to the high electric field induced by the

plasma filament favouring direct electron-impact dissociation over vibrational excitation [28]. As a result, other plasma sources have been studied with or without catalyst coupling. They can be discharges often used at atmospheric pressure such as gliding arc (GDA), or nanosecond repetitive pulsed (NRP) plasma, but discharges such as microwave (MW), radio frequency (RF), or glow discharge (Glow) can operate at reduced and atmospheric pressure. These plasma sources generate conditions different from DBDs in terms of electric field, charge density, vibrational excitation, gas temperature, radical densities, etc. For example, the high gas temperature involved in GDA and MW plasma sources means that direct coupling with catalysts is not feasible. However, it is possible to place a catalyst downstream of the plasma where the gas temperature is low enough to not cause any degradation. It should be noted however that if the catalyst is positioned too far from the plasma, only molecules stable in their fundamental state will be likely to reach the surface of the catalyst and the surface reactivity which can then be obtained will not be different from what can be observed in conventional catalysis with the same molecules. Nevertheless, the benefits of adding a catalyst often outweigh the difficulty of coupling it with the plasma, and as such, increasing amounts of research are being conducted on plasma-catalysis reactors rather than pure plasma reactors. Using low (or reduced) pressure is often disregarded in conventional catalysis because catalytic phenomena, typically described by Langmuir-Hinshelwood equations, are less efficient as a result of the lowering of adsorbed species concentration. However in plasma-catalysis, this effect could be compensated in some cases for instance because of a stronger vibrational excitation at reduced pressure enhancing the efficiency of surface reaction.

The diversity of the considered plasma sources raises questions on the relevance of the operating parameters that can be compared between them, for instance, power, flow rate, pressure, etc. As such, we have included Section 3.2 dedicated to the types of parameters included in the database so that sensible comparisons can be made between the different plasma sources. In all cases though, the reactivity of these plasma sources combines the effects of charged species, excited electronic and vibrational states, strong electric fields, and often strong spatio-temporal gradients, resulting in chemical reactivity fundamentally different from that obtained in thermal catalysis.

To be able to compare different plasma sources ideally, it would be necessary to know the energy distribution function of the electrons, or at least the electric field and the electron density. It would also be necessary to characterise the spatial inhomogeneity of the energy deposited. However, these quantities are in general difficult to determine, especially when the plasma is in direct contact with a catalyst. Alternatively, more macroscopic parameters such as power or specific energy input (SEI) and gas temperature should at least be known so that one can study the conversion performances collected in the database.

2.2. Catalytic materials in contact with a plasma

A catalyst is a substance that increases the rate of a chemical reaction without modifying the overall standard Gibbs energy change in the reaction. The structure of a catalyst often consists of a support with a large specific surface area to improve exchanges with the gas phase, and an active phase dispersed on its surface. Additionally, there may be a promoter to improve the performance of the active phase. Despite containing typically three components, each of them has many parameters that can influence the efficiency of the resulting catalytic material for a given reaction. For example, there is the adsorption capacity of the material towards the reactants, the accessibility of the surface to the reac-

tants by diffusion, or the potential poisoning of the surface during the reaction.

In thermal catalysis, good practices to ensure relevant comparison of performances between catalysts require that the measured quantities are really “intrinsic” rates and selectivities [25]. This necessitates the use of “ideal” reactors, such as a “plug flow”, “batch”, or “continuously stirred tank” reactor. These “ideal” reactors also need the determination of well-defined parameters such as turnover frequency, site-normalised catalytic reaction rates, turnover numbers, or site-normalised catalytic productivities. Limitations of mass and heat transfer within the catalyst bed must also be ensured to not affect the conversion or the selectivity results.

All these thermal catalysis “good practices” impose constraints on the reactor geometries and the type of catalytic bed that can be used to determine fundamental parameters. Predominantly though, these “ideal” catalyst bed configurations are not suitable for plasma-catalysis. As plasma cannot develop on lengths smaller than the Debye length, which is in general larger than a few microns, reactors are therefore constrained by this length scale. Therefore the important parameter in thermal-catalysis of macro-, meso-, micro-, or nanoporosity (all defined at nanometric scales) is not the only surface parameter to be considered in plasma-catalysis. Specifically, the length of the pores is just as important as their diameter, as the length will determine which species reach the active sites present on the catalyst. This is a situation typical to plasma-catalysis, where the lifetime of the plasma species results in different processes. Thus, one can have a situation rather different from thermal catalysis, where the modification of the porosity at the nanometric scale can greatly improve the efficiency of a catalyst but could be irrelevant for certain cases in plasma-catalysis. Nevertheless, macroscopic structure at the scale of a few hundred microns or even millimeters can affect the way that the plasma develops along the catalyst surface, and consequently improve the access of short-lived species to the catalytic surface.

Furthermore, the very definition of certain parameters considered as intrinsic properties of a given catalytic material in thermal catalysis must be reconsidered when this material is under direct exposure to a plasma. Specifically, this is the case for the density of “active sites”. The nature and number of which can be modified according to the properties of the plasma used, and therefore can no longer be treated as a characteristic property of a given material. Even an *a priori* chemically inert surface like SiO₂ can gain new adsorption sites under plasma exposure. As an example, oxygen atoms chemisorbed on a SiO₂ surface exposed to a glow discharge can then convert NO to NO₂ [29]. The number and nature of the active sites present on a given material can thus depend on the properties of the plasma to which it is exposed, and a material usually considered as a simple support can act as a catalyst with reactive species created in the plasma.

Even a notion like the yield, *Y*, can be misleading within plasma-catalysis. *Y* is defined as the mole fraction of initial limiting reactant that is transformed into a given product. In plasma-catalysis however, the limiting reactant of a reaction happening on the catalyst surface is not necessarily one of the gases introduced into the reactor, it can also be a product of a reaction occurring in the plasma which is not necessarily known.

The complexity of the mutual interaction mechanisms between a plasma source and a catalyst was recently described in a review article [10]. This work makes it clear that to enable data comparison from different plasma-catalysis works, it is essential to consider other parameters than those used in thermal catalysis. If the pre-existing tools in thermal catalysis are insufficient to derive information from plasma-catalysis measurements, the question arises whether techniques used for other non-conventional heterogeneous catalysis processes, such as electro-catalysis and photocatalysis, could be suitable for plasma-catalysis instead.

2.3. Differences and similarities between plasma-catalysis and electro-photo-catalysis

Despite being a unique technique, plasma-catalysis shows similarities with other types of catalysis. For example, photo-catalysis relies on the transfer of charges caused by the absorption of photons of suitable energy by a catalyst, creating electron-hole pairs [30,31]. The catalyst can then participate in the reactions of interest by transferring these charges to reagents and/or intermediates. The obvious similarity with plasma-catalysis is that plasmas emit light and such light could, at least theoretically, induce photo-catalytic processes as previously reported [32]. However, this potential application requires further study, since it is generally accepted that the photon flux in plasma-catalysis reactors is too low to significantly activate photo-catalysts as seen in previous reports [33,34].

Nevertheless, this does not necessarily mean that there are no other intersections between the two types of catalysis. For instance, it was proposed that electron impact on the catalyst may induce electron-hole pairs as well, particularly in the case of DBD plasmas where the electron energy is similar to photon energies used in photo-catalytic processes (around 3 eV to 4 eV) [35]. Furthermore, it has been shown in some cases that plasma can create oxygen vacancies in the catalysts and electrons can be trapped in those vacancies, which in turn would favour photo-catalytic processes. In that sense, plasma- and photo-catalysis are not only similar, but can potentially exhibit synergy [36].

In the same way as in photo-catalysis, electron transfer is at the core of electro-catalysis, and potentially plays a role in plasma-catalysis. For example, it is possible that the electrons deposited by the plasma on a catalyst surface can result in charge being transferred to molecules such as CO₂. Indeed, it has been observed that this effect substantially impacts the ability of the material to perform reduction reactions [37] and it can be assumed to work in a similar way as in electro-catalysis. Nevertheless, it is worth highlighting that both photo-catalytic and electro-catalytic reduction of CO₂ are performed more frequently in aqueous media, being water (or aqueous species) oxidised either by the holes generated in the photo-catalysts or at the anode in the electro-catalysis. However, so far few studies reported on the plasma reduction of CO₂ in aqueous media, owing to the fact that H₂O-derived species in plasma, especially reactive oxygen species, are usually taken as detrimental. This happens because there is still no established strategy to properly separate them from the products and they tend to hinder the production of larger molecules [38]. Comparatively, in photo-catalysis this separation is usually performed by strategies like heterojunctions that can effectively separate holes from electrons, while, in electro-catalysis, this is done by separating the anode and cathode within the electrochemical cell.

Additionally, a drawback of reducing CO₂ in aqueous media is the low solubility of CO₂ in water [39], limiting the efficiency. From an operational point of view, plasma-catalysis and electro-catalysis can be switched on and off much more quickly than thermal catalysis. As such, both represent an opportunity to use intermittent electricity from renewable sources, creating an energy buffer that stabilises the electricity grid by peak shaving.

Unlike the other methods, photo-catalysis enables the direct use of solar irradiation for CO₂ conversion, reducing the amount of steps involved in energy conversion. That being said, it is not necessary to limit a chemical process to one type of catalysis. For instance, some catalysts may be suitable for both photo-catalysis and plasma-catalysis, which could allow for hybrid reactors that perform photo-catalysis in the day and plasma-catalysis at night. In this regard, oxides or a mixture of oxides are commonly used as photo-catalysts, provided their bandgap is suitable for absorbing light at the appropriate wavelengths [40]. However, as mentioned

before, electron-hole separation is one of the crucial points of development for photo-catalysis. A common strategy to tackle this problem includes the addition of a conductive material (e.g. metallic nanoparticles) on the surface of the metal oxides to “drain” the generated electrons, creating the so-called Schottky junction [41]. In that sense, the resulting material can be a metal oxide acting as a catalyst for photo-catalysis and as a “support” for plasma-catalysis, and a metal working as an electron drainer in photo-catalysis and as an active phase in plasma.

Therefore, all three techniques can be complementary and useful under different conditions, but in no way they are interchangeable. The relevant parameters to analyse the performances of electro- and photo-catalysis may sometimes overlap with the ones for plasma-catalysis (electrical current, photon flux, etc.), but plasma-catalysis remains a separate field, characterised by the high reactivity of the gas phase to which the catalyst is being exposed. In plasma-catalysis, the flux of species to the catalyst surface is a complex mixture of excited states and radicals, whereas, in the other forms of catalysis, the flux of species reaching the surface is composed of stable molecules in their ground states. As a result, the tools developed for analysing performances and comparing results in thermal, electro- and photo-catalysis cannot be easily used on a plasma-catalytic system. From the great uniqueness and complexity of plasma-catalysis processes for CO₂ conversion comes the motivation to develop the CO₂-PDB, which is presented in this publication.

3. The PIONEER database: positioning, graphical interface and type of data set

3.1. Motivation for the creation of the CO₂-PDB and positioning

The usefulness of creating a database dedicated to plasma-catalysis for CO₂ conversion arises from two main points. Firstly, the complexity of plasma-catalyst interactions discussed in previous sections necessitates large amounts of data in order to identify trends which indicate fundamental mechanisms. Secondly, the number of works in the field is becoming large and, without comparison tools, potentially useful information can be missed. Therefore, the CO₂-PDB is a first attempt to fulfil these two objectives by filling a gap with respect to existing tools in other scientific communities.

The performance data on plasma-catalysis experiments gathered in the CO₂-PDB represent a valuable contribution to the research field as no comparable database exists. Even in conventional catalysis, we are unaware of a global performance database for given catalysts. The list of catalysis databases available online includes: the Open Materials Database [42], the Materials Project [43], AFLOW [44], the Open Quantum Materials Database [45], Aiiida [46], the Catalysis-Hub [47], the Open Crystallography Database [48], NoMaD CoE [49], and the Computational Materials Repository [50]. They come with high-quality interfaces, Python modules for data handling and access, and extensive data compared to the CO₂-PDB. Nevertheless, these databases focus on data derived from computational methods (e.g. density functional theory) with the goal of discovering new materials, particularly catalysts. Comparatively, the CO₂-PDB focuses on experimental performance data from plasma(-catalytic) CO₂ conversion.

On the plasma side, databases are even more scarce. A popular example is the LXCat database for electron and ion scattering cross sections and swarm parameters [51], which provides valuable input for plasma kinetic simulations. The extension to plasma-catalysis is however not straightforward. In this regard, it is worth mentioning the Korean data center for plasma properties that provides data for the plasma-wall interaction, and other aspects [52].

Likewise the LXCat database, this database is meant to serve as input for modelling, and no performance data is included.

Therefore, the CO₂-PDB bridges the gap between large-scale/big-data studies and well-controlled, ideal, comparable, small-scale studies. In fact, all the catalysis databases presented above follow the “big-data” approach and usually come with some machine learning utility [42–44,47,49,50]. However, when it comes to plasma-catalysis performance, machine learning approaches become much more delicate. This is because results obtained by so-called machine learning techniques will never be valid if the data sets used are not complete, balanced, and well-distributed. In order to build such a data-set, a better definition of the parameters controlling the performance in plasma-catalysis is required. For example, there is significant progress in using machine learning for materials discovery in the fields of adsorbents [53], superionic conductors [54], electro- and photocatalysis [55], perovskite materials [56], etc. However, in these cases, the performance parameters or the expected properties are much better understood. Also, given the broad characteristic of plasma experiments in CO₂ conversion, using different gas compositions, catalytic materials, reactor designs, and plasma sources, the spatial coverage of possible target variables is also very broad, which machine learning models usually have trouble dealing with. For example, a catalyst can perform well for the dry reforming of methane in a microwave plasma. Still, its performance may be completely different in a DBD, which has a lower working temperature, or for another reaction, such as CO₂ hydrogenation. In its current form, it is quite challenging to compartmentalise

the available data to have its coverage referring to similar cases while still maintaining a training data-set that is large enough to drive materials design or discovery. While the comparability between different experiments and reactors is currently limited, small-scale studies isolate certain fundamental parameters, enabling a comparison with other small-scale studies, but are intrinsically limited in parameter space. The CO₂-PDB therefore connects disparate experimental studies in literature, and thus creates an environment for more systematic studies on the most promising directions. Over time, the practices used to study plasma catalysis will become more comparable because the database will make it easier for everyone to be aware of the critical parameters needed to cross-check data from one system to another. New contributions from the entire community will improve the quality and completeness of the data sets in the database. Ultimately, this will make it possible to identify the physico-chemical properties that are really beneficial to plasma-catalyst coupling, in order to define new materials, probably quite different from the catalysts usually used in thermal catalysis, that are really capable of improving the performance of the plasma itself as well as taking advantage of the short-lived species generated by the plasma.

3.2. Scope of the database

The research fields of plasma and catalysis feature an enormous versatility of characterisation that only expands when the two merge. Thus, any attempt to cover everything in one plasma-catalysis database is unlikely to succeed. For that reason, we

Table 1

Overview of some metrics of data contained in the database (as of April 2023). For more elaboration on nomenclature and calculations, reference the [Supplementary Material](#).

Metric	Value	Comment
Papers in the database	193	Based on DOI codes, as of April 2023
Combinations of y vs x parameters	181	
Total files/datasets included in database	4477	Including datasets (re)calculated from metadata
Total (x,y) pairs	18503	Including datasets (re)calculated from metadata
Total original files/datasets	3041	Data without recalculation applied
Total original (x,y) pairs	11312	Data without recalculation applied
Total files/datasets (re)calculated from metadata	1436	Data with some form of recalculation applied from metadata
Total (re)calculated (x,y) pairs	7191	Data with some form of recalculation applied from metadata
Datasets of experiments with catalysts	2012	Incl. (re)calculated data
Total (x,y) pairs of experiments with catalysts	7184	Incl. (re)calculated data
Reported unique catalyst compositions	99	Unique notations for composition
Different catalyst supports	37	
Different catalyst active phases	19	
Most common active phase	Ni	2609 (x,y) pairs
Most common catalyst support	Al ₂ O ₃	2430 (x,y) pairs
Most common catalyst complex	Ni-/C	811 (x,y) pairs
Reported temperature range of data	100 K to 8400 K	
Reported pressure range of data	0.14 mbar to 5080 mbar	
Reported volume range of data	$4.7 \times 10^{-6} \text{ cm}^3$ to $2.01 \times 10^3 \text{ cm}^3$	

Table 2

Overview of process parameters in the database, i.e. the x-axis values, discussed in more detail in the [Supplementary Material](#).

Process parameter	Unit	Comment
SEI	JL ⁻¹ \ eV molecule ⁻¹	
concentration in initial mixture	%	for CO ₂
GHSV	h ⁻¹	gas hourly space velocity
gas flow rate	scmm \ mL min ⁻¹	
pressure	mbar	
temperature	K	
t _{on}	s	plasma pulse duration
process treatment time	min	
residence time	s	
power	W	Converted to SEI (JL ⁻¹) where possible

prioritise comparability and importance of included data over quantity, leading to a manageable set of data for each measurement series. An in-depth discussion of included data is given in the [Supplementary Material](#) while this section gives a brief overview and focuses on some selected metrics. [Table 1](#) gives an overview of the amount and diversity of the data included in the CO₂-PDB at the time of submission of this manuscript. In short, the CO₂-PDB reports on so-called “process parameters”, i.e. *x*-values in [Table 2](#), against so-called “performance parameters”, i.e. *y*-values in [Table 3](#), which are backed up by metadata to facilitate the interpretation and comparison of trends. Note that all data sets in the CO₂-PDB report on plasma experiments on CO₂ conversion, of which 2012 are plasma-catalytic experiments. No data of conventional thermal catalysis is included. Insights obtained in this section are used in [Section 5](#) to give some best practice advice.

The data collected in the CO₂-PDB must have been previously published in a peer-reviewed journal in English. As such, the validity of the measurements is ensured by the classical peer reviewing process and is in no way the responsibility of the CO₂-PDB authors. Beyond the simple identification of the article in which the data were published, the CO₂-PDB metadata allows the characterisation of the gas mixture studied, the plasma source, the nature of the catalyst, and the way in which the catalyst is coupled to the plasma. Each data set (i.e. set of (*x*, *y*) pairs that comprise a measurement, line, or equivalent) in the CO₂-PDB is associated to all these parameters when the information is available in the published article.

[Fig. 2](#) shows the fraction of data sets in the CO₂-PDB providing certain information focusing on the plasma in [Fig. 2\(a\)](#) and on the catalyst in [Fig. 2\(b\)](#). Hence, each bar in the chart corresponds to one column in the database. For [Fig. 2\(a\)](#), all data sets in the CO₂-PDB are considered as all studies include a plasma (i.e. 3041 data sets at the date of submission of this paper, see [Table 1](#)), while [Fig. 2\(b\)](#) includes only plasma-catalytic studies (i.e. 2012 data sets). All data are considered important such that the closer a bar is to 100%, the better. Note that only a selection of all data columns in the CO₂-PDB is shown, namely, those data columns that are crucial to each and every data set. For instance, power always has to be deposited to ignite the plasma. Conversely, MW discharges do not rely on an applied voltage, which is not included in [Fig. 2](#).

From the comparison of [Fig. 2 \(a and b\)](#), it becomes apparent that in the general perspective of the database, the plasma is more exhaustively characterised than the catalyst. In fact, the average fraction of provided data for plasma is 89%, while it is only 45% for the catalyst. A possible rationale is that the field of plasma-catalysis is still relatively young, needs significant interdisciplinary efforts, and is still being led mostly by the plasma community, which has less experience in catalyst characterisation. Therefore, the characterisations provided for the catalysts are still not in the standard of other more established fields of catalysis. From [Fig. 2 \(a\)](#), it can be seen that parameters that are best documented mainly concern what is put into a reactor and in what quantity, for example, gas composition, and flow rate. Conversely, the physical properties of the plasma studied are limited except for power

Table 3

Overview of performance parameters in the database, i.e. the *y*-axis values, discussed in more detail in the [Supplementary Material](#).

Performance parameter	Unit	Species
Conversion	%	CO ₂ , CH ₄
Selectivity	%	CO, H ₂ , CH ₄ , CH ₃ OH, CH ₃ COOH, C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ , C ₂ H ₅ OH
Yield	%	CO, H ₂ , CH ₄ , CH ₃ OH, CH ₃ COOH, C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ , C ₂ H ₅ OH
Carbon balance	%	
Energy efficiency	molecule J ⁻¹	CO ₂ , CH ₄
Energy efficiency ratio $\frac{H_2}{CO}$	-	CO ₂ , CH ₄

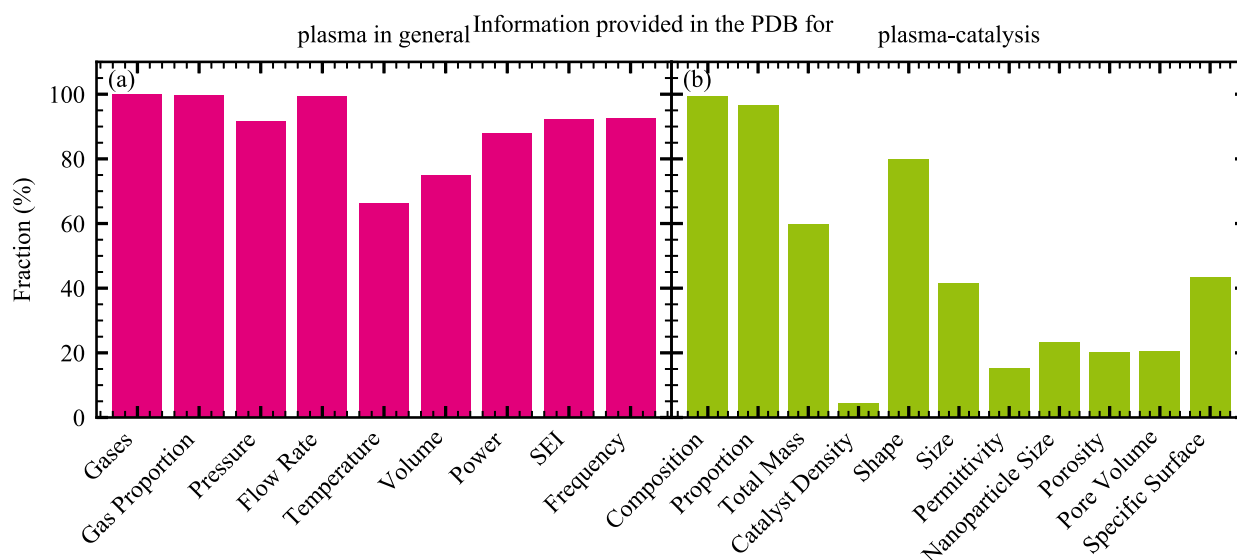


Fig. 2. The fraction of data sets that provide information about individual plasma parameters with respect to the total number of sets in the CO₂-PDB in (a). The fraction of data sets that provide information on catalyst parameters with respect to the total number of data sets including a catalyst in (b).

and SEI. Parameters such as electron densities, electric fields, or vibrational temperatures would provide great value, but unfortunately these parameters are unknown in the vast majority of cases and therefore are not included as CO₂-PDB metadata for the moment. However, as previously mentioned, plasma-catalysis is an interdisciplinary field, and drawing reliable conclusions requires a complete and comprehensive characterisation of both the plasma and the catalyst. Unfortunately, many crucial parameters are underreported. For example, only 65% of papers report the gas temperature T_g in the plasma despite its importance for assessing residence time, non-equilibrium characteristics [57], and the role of thermal versus plasma-catalysis [2]. Even when a temperature value is given, the various methods used to measure this temperature can lead to inconsistencies when comparing studies, see also the discussion of Fig. 15 in Section 5.1.

It is interesting to note that the SEI, calculated as the ratio of power over flow rate, is one of the most popular process parameters, i.e. the most frequent x -coordinate, as it allows for maximum comparability across different plasma sources. However, the total fraction of data sets reporting the SEI is only around 90%, which is probably because studies on fundamental mechanisms tend not to document the SEI, whereas those on process optimisation do. For the sake of comparability, we recommend always reporting it.

In panel Fig. 2(b), we see that the catalyst composition and its proportions are usually reported. However, information on the remaining fields is scarce and the bulk density of the catalyst material is almost never reported. To a lesser extent the data scarcity also concerns the size and surface area of the particles, which are crucial parameters in all fields of catalysis but were reported in less than half of the papers. More generally, the macroscopic characteristics of the catalyst bed (dimensions greater than typically a hundred microns) are not sufficiently described despite their impact on plasma initiation.

It is worth emphasising that following the definition used here, the catalyst data do not include any process parameters. Process parameters are regarded as the “control knobs” of the experiment

that are tuned to optimise the performance. There is no doubt that advanced catalyst design is a key element in the further development of plasma-catalytic CO₂ conversion. However, the design of the catalyst and reactor occurs before CO₂ processing, while the plasma process parameters can be adjusted in real time. Nonetheless, no data is lost. Literature data reporting performance parameters against catalyst properties are rearranged: the catalyst properties end up in the catalyst metadata and a new (x,y) pair is created, with x preferably being the SEI, see also the [Supplementary Material](#).

The database also foresees developments in the separation of the plasma reaction products. Few publications have dealt with separation of products, specifically oxygen atoms as they can participate in the back reaction to CO₂ [58,59]. At the time of publication, it is hard to estimate which possible input data would be interesting for the database. So far, separation type and position are the only parameters included but this can change and extend according to future developments. More is discussed in the [Supplementary Material](#).

To summarise, the CO₂-PDB comprises data extracted from a large and wide-ranging collection of peer-reviewed publications arranged into an easy-to-use format (Table 1). However, we have not included all possible items from the reported data. Instead, we only included data that we deemed important and comparable. This means that vital parameters that only appear in a small number of studies will not be included. Therefore, the data selected for the CO₂-PDB are proposed as a minimum parameter set for comparing CO₂ plasma-catalysis performance results. We chose a minimum collection so that the CO₂-PDB can evolve over time with the addition of new parameters proposed by the plasma-catalysis community.

3.3. The PIONEER database web interface

The PIONEER database contains a wealth of useful data on plasma and plasma-catalytic CO₂ conversion. To make the information within the database accessible and provide a platform for the



Fig. 3. Screenshot of the main user interface, showcasing the main view port and sidebar containing tabs to access plot setup, normalisation and filter options. Version: May 2023.

community to compare results, an online front-end point providing access to the database can be found at <https://db.co2pioneer.eu>. This tool provides capabilities for visualising data from the database, as well as selecting, filtering, and exporting data and/or graphs from the database. It is also possible to overlay user data on top of the main visualisation. In the following subsections a brief overview of the interface and some of its features are highlighted. These subsections also serve as a primer for basic operation of the database, which are complemented by the [Supplementary Material](#) and the online documentation. The ambition is to continue adding new data to this online platform and contributions of (newly) published scientific results are strongly encouraged. The only conditions for proposing new data to be included in the CO₂-PDB are that the results have first been published in a peer-reviewed journal, and that the authors provide (i) the metadata in the template provided here, and (ii) the corresponding data sets as two-columns (x,y) ASCII files formatted as described in detail in the online documentation. The CO₂-PDB app (shown in [Fig. 3](#)) provides two main modes of interacting with the database. The first is the main visualisation section, which allows users to explore performance ([Table 3](#)) versus process parameters ([Table 2](#)) for plasma-catalytic conversion. The second is the advanced database inspection interface, which provides features for more advanced data interaction, such as selection, inspection, and export. However, we have developed the main visualisation section so that there are sufficient features to effectively analyse the data in a visual manner both within the app and offline via a vector quality export of the graphs in *.svg format.

Nevertheless, if more granular control, or an export of the underlying data is desired, the advanced inspection interface can be used. These two modes of interacting with the database are discussed in more detail below, with further information also provided via the online documentation.

3.3.1. The main interface for graphing performance versus process data

The main user interface consists of two regions: A central viewport with widgets for filtering the database and an Y vs. X graph of the selected data, and a sidebar containing controls for the plot appearance and normalisation applied to the selected data, see [Fig. 3](#).

The main viewport The “Main UI” tab in the main viewport constitutes what will be called the main interface, which consists of three parts. The top row consists of a set of widgets that allow the desired parameters of the Y vs. X graph to be selected, which are tabulated in [Tables 2 and 3](#) respectively. It also includes indicators for the number of data points, data sets and papers that are either shown or contained in the database. Since the core feature of the tool is to create Y vs. X plots, these widgets are always shown in the main user interface.

The second part provides more granular filtering options. These options are located in several “contextual” tabs and contain filter widgets related to the same context, for instance, plasma metadata. An overview of how these filters are structured can be found in [Table 4](#). Most of these filters are inclusive categorical filters, i.e. they serve to restrict the data in the graph to a particular subset or category. Data exclusion is performed by clicking on a legend label in the graph, which will toggle the visibility of the corresponding data. The exception to this are filters for the gas composition, gas flow, pressure, catalyst specific surface and relative permittivity, and catalyst active phase or support containing element, which behave differently, see [Table 4](#). Whenever a filter widget is set to NA (shorthand for Not Applicable), no filtering will occur on that particular category. Note that this is distinct from the “None” option, which can be the absence of a property, for instance, the absence of an active phase. Finally, the third part contains the graph element that displays the data that have been selected by the various filtering widgets.

The visibility of individual or groups of lines in the plot can be controlled by clicking on the corresponding legend entry, as stated. A toolbar to the right of the figure provides access to various tools related to the plot and its underlying data, for instance, data inspection, zooming and panning. Although *.png images can be exported from here as well, their use is discouraged in favour of annotated *.svg exports (see below). Further control over the graph and displayed data can be exercised via the assorted widgets in the sidebar, which are discussed next.

The sidebar menu The collapsible sidebar contains buttons for opening the documentation, updating the loaded database model, plotting the data, and exporting the current plot view in vector format, or a BibTeX of included references in the plot. This vector export is the intended way of exporting graphs, since it contains

Table 4
Overview of filter criteria supported in the tool grouped by their thematic panel (or tab) in the main interface, discussed in more detail in the [Supplementary Material](#).

Panel	Filter criterion	Comment
Plasma	Source type	
	Plasma main diagnostic	
	Plasma power diagnostic	Relevant diagnostic used to determine power
	Plasma/gas temperature diagnostic	Relevant diagnostic used to determine plasma or gas temperature
Catalysts	Catalyst used	True/False
	Coupling	how catalyst is introduced in the plasma/reactor/effluent
	Catalyst support material class	Filtering on classes like Perovskites
	Catalyst active phase	
	Catalyst support	
	Catalyst promoter	
Catalyst properties	Catalyst active phase search by element	Allow filtering materials based on custom string
	Catalyst support search by element	Allow filtering materials based on custom string
	Surface area (m ² g ⁻¹)	Numeric setting of upper/lower threshold (based on secondary widget)
	Permittivity	Numeric setting of upper/lower threshold (based on secondary widget)
Gas	Gas species	Select which elements to in/exclude, if ‘None’ is chosen, does not filter
	Gas combinatoric operator	Controls how to filter the selected gas species
	Gas pressure (mbar)	Numeric slider to control the pressure range
	Gas flow (sccm)	Upper (if negative) or lower (if positive) bound for flow rate
Misc.	Author	Last name of the listed first author of a publication
	Goal	The outcome of the process under investigation, e.g. CO ₂ splitting, methanation, etc.
	Separation type	Method of output product separation such as a carbon bed or membrane
	Separation position	The position where the separation is applied
	Calculated	Whether some form of calculation has been applied to the data