

Review

Electron Traps in Thermal Heterogeneous Catalysis: Fundamentals, Detection, and Applications of CO₂ Hydrogenation

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Abstract

The field of developing effective catalysts for heterogeneous catalysis has recently focused on controlling the structures of catalysts themselves to optimise the density and energy of crystal lattice defects. This can significantly influence catalytic activity in terms of both reaction rates and reaction mechanisms, and thus the selective production of desired substances as well. In many cases, these crystal lattice defects manifest themselves as so-called electron traps (ETs) and thus significantly influence charge transfer between the catalyst and reactants. ETs provide the missing electronic link between atomic-scale defects and macroscopic performance in heterogeneous catalysis. Therefore, the importance of ETs for catalysis is particularly evident in areas where charge transfer plays a fundamental role in the reaction mechanism, such as photocatalysis and electrocatalysis. In the field of thermally initiated reactions, the importance of ETs in heterogeneous catalysis has not yet been fully appreciated. However, several studies have already addressed the importance of ETs for this type of reaction. This review consolidates and extends the concept of ETs to purely thermal-initiated reactions, with a focus on CO₂ hydrogenation using typical transition metal catalysts. Firstly, in this review, ETs are defined as band gap states associated with internal and external defects, and their depth, density, spatial location, and dynamics are then coupled with key steps in thermocatalytic cycles, including charge storage/release, reactant activation, intermediate stabilisation, and redox turnover. Secondly, electron trap detection is reviewed based on advanced spectroscopic techniques, including reversed double-beam photoacoustic spectroscopy (RDB-PAS), thermally stimulated current (TSC), deep-level transient spectroscopy (DLTS), thermoluminescence (TL), electron paramagnetic resonance (EPR), and photoluminescence (PL), highlighting how each method describes trap energetics and populations under realistic operating conditions. Finally, case studies on the application of metal oxides and supported metals are discussed, as these are typical catalysts for the reaction mentioned above. This review highlights how oxygen vacancies (OVs), polarons, and metal–support interfacial sites act as robust electron reservoirs, lowering the barriers for CO₂ activation and hydrogenation. By reframing thermocatalysts through the lens of ET chemistry, this review identifies ETs as actionable targets for the rational design of next-generation materials for CO₂ hydrogenation and related high-temperature transformations.



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1. Introduction

Current trends in the development of efficient heterogeneous catalysts focus on defect engineering, as defects play an essential role in modulating catalytic activity [1–3]. Lattice imperfections reshape the electronic structure, and in turn affect adsorption, charge transfer, and reaction pathways [4,5]. Within the spectrum of defect-related electronic states, electron traps (ETs) are well-documented in photocatalysis and electrocatalysis, where their application in the reaction mechanism is crucial; however, their roles in thermal heterogeneous catalysis are insufficiently appraised [1,6,7]. Even in purely thermally driven reactions, many key steps involve electron transfer processes (oxidation, reduction, hydrogenation, etc.); thus, ETs are inherently embedded in the reaction mechanism [5,8]. ETs govern how catalysts store, release, and shuttle charge under operating conditions, thereby directly influencing adsorption energetics, the stabilisation of intermediates, and the kinetics of redox-limited steps [6,9]. Because trap states differ in depth, density, spatial location, and dynamics, no single characterisation technique can capture the complete trap landscape. The band structure of the material determines which traps form, thereby determining their density, depth, and interactions with charge carriers [10]. An ET is an electronic state within the band gap that localises electrons momentarily (shallow) or persistently (deep); its energy position, capture cross-section, and de-trapping kinetics govern carrier lifetimes, recombination pathways, and thermally induced redox chemistry [11]. Structural defects, vacancies, interstitials, antisites, dislocations, grain boundaries, and local coordination mismatches are departures from an ideal lattice; some introduce band gap levels that function as ETs, whereas others do not. A multi-technique approach provides the information about trap states [12–14]. This review critically examines electron trap detection using advanced spectroscopies, including reversed double-beam photoacoustic spectroscopy (RDB-PAS) [14,15], deep-level transient spectroscopy (DLTS) [16], thermally stimulated current (TSC) [17], thermoluminescence (TL) [18], electron paramagnetic resonance (EPR) [19], and photoluminescence (PL) [20]. Beyond the dedicated methods used to probe electron traps, X-ray absorption spectroscopy (XAS) provides complementary, element-resolved insight into the local environment of the catalytic system [21]. An X-ray absorption near-edge structure (XANES) can be used to follow changes in oxidation state and electronic structure, while an extended X-ray absorption fine structure (EXAFS) reports short-range coordination geometry [22]. Under in situ/operando conditions, XAS is particularly valuable for tracking the dynamic structural and redox evolution, which helps contextualise trap-related signatures and trends in catalytic performance [21]. As the primary objective of this review is to establish an integrated interconnection between ETs and thermally initiated catalytic processes, the existing gap in the study of ETs in thermocatalysis is addressed by surveying the fundamentals, detection, and catalytic implications of ETs under thermal conditions. This review is organised around three main objectives. First, we establish the conceptual link between ETs, lattice defects, and the kinetics of thermocatalytic reactions, paying particular attention to how trap characteristics (depth, density, localisation, and dynamics) influence adsorption energetics, charge transfer barriers, intermediate stabilisation, and rate-limiting redox events. Second, we systematically evaluate advanced spectroscopic techniques capable of resolving trap states. Third, we present case studies on defect engineering in the design of metal oxides and supported metal-based catalysts, focusing on the influence of ETs on thermally driven reactions.

2. Fundamentals of Electron Traps (ETs)

Scientists often categorise ETs by their energy depth relative to the band edges. Electronic and catalytic behaviours are controlled by two main types of traps: shallow and deep [23]. Shallow traps are near the conduction band minimum (CBM). They temporarily hold electrons, which they release into the conduction band when heated or illuminated, thereby affecting conductivity, recombination, and carrier lifetimes [24]. Deep traps reside further within the band gap (often in the mid-gap); they strongly localise charge, act as efficient recombination centres, and typically reduce carrier mobility due to long de-trapping times and higher activation energies for release [25].

“Trap” denotes an electronic role, while “defect” denotes its structural origin. In thermocatalysis, trap states mediate charge storage/transfer, stabilise intermediates, and couple to small-polaron transport. Intrinsic and extrinsic processes examine the mechanisms of ET formation. Intrinsic ET formation mechanisms depend on structural disorders in amorphous materials [24], coordination defects [26], and crystalline defects [27]. Amorphous materials exhibit irregularities in bond length, coordination numbers, and bond angles. These variations lead to the formation of localised states within the band gap that do not disrupt chemical bonds and act as intrinsic ETs [28]. In the case of coordination defects, an atom has one more under- or over-coordinated neighbouring atom than in an ideal crystal. Under-coordinated atoms that form dangling bonds create localised energy states within the band gap, functioning as intrinsic ETs [26]. Intrinsic ET over-coordinated atoms cause distortions in bond lengths and angles, producing trap states indirectly by modifying the local electronic structure [29]. In crystalline defects, intrinsic ETs are formed by point defects such as interstitials and vacancies. These create localised states within the band gap that can act as ETs [27]. Extrinsic ETs form when foreign-atom dopants (impurities) are added to a material, generating localised energy states in the band gap that can capture electrons [30]. During fabrication processes such as crystal growth, thin-film deposition, and thermal treatments, defects, such as vacancies, can form, creating trap levels in the band gap that act as ETs. These traps are also considered extrinsic traps in nature [31]. The energy levels of ETs originate from intrinsic defects, such as vacancies, and extrinsic sources, including impurities [32]. In reducible oxides, oxygen vacancies (OVs) commonly generate reduced cations and defect-derived mid-gap states. For TiO_2 , removing lattice oxygen produces Ti^{3+} centres with associated gap levels; for CeO_2 , oxygen deficiency shifts the $\text{Ce}^{4+}/\text{Ce}^{3+}$ balance and creates vacancy-related states that enhance visible-light absorption and can modulate catalytic activity [33]. Additionally, on reducible oxides such as anatase TiO_2 and CeO_2 , OVs and their reduced cations can directly assist CO_2 activation [34]. The same structural motif can be beneficial or detrimental depending on the depth and density of the induced traps’ states on the surface. OVs typically improve interfacial charge separation/transport and enhance reactivity. In contrast, bulk-embedded defects more often act as non-radiative recombination centres that impede transport, as reported, for example, for $\alpha\text{-Fe}_2\text{O}_3$ (hematite) [35].

3. Detection of ETs Based on Spectroscopic Methods

To understand the movement of charge carriers in catalytic and semiconducting materials, it is essential to detect and comprehensively characterise ETs precisely [20]. A variety of spectroscopic techniques are commonly employed to identify, quantify, and analyse these trap states. Each method possesses distinct advantages based on the material’s characteristics and the type of traps [36].

ETs are key not only to understanding photocatalytic or electrocatalytic reactions but also some thermal-driven catalytic processes. This is because they influence charge localisation, shift redox potentials, and affect surface reactivity, which directly impact

the catalyst's speed and selectivity [37,38]. Therefore, techniques for locating, counting, and measuring the energy of trap states in solid materials are crucial for interpreting the influence of ETs on catalytic reactions. The following overview outlines the principles and applications of several established techniques for investigating ETs [36]. Key methods discussed include RDB-PAS [14], TSC [39], DLTS [40], TL [13], and EPR [41]. Table 1 briefly compares their core observables, typical measurement conditions, main limitations, and key outputs, which form the methodological framework for analysing ETs across photocatalyst, electrocatalyst, and thermally induced catalytic systems.

Table 1. Basic comparison of trap characterisation techniques (RDB-PAS, TSC, DLTS, TL, EPR, PL), summarising core observables, practical applications, main limitations, and key quantitative outputs for electron trap analysis in heterogeneous catalysts.

Technique	Measures (Essentials)	Best Use	Limits	Outputs (Key Symbols)
RDB-PAS [14,15,42,43]	Energy-resolved trap distribution (shallow vs. deep)	Powders/films; no electrodes	Relative unless calibrated; optical background	ERDT vs. energy (eV), VBT-referenced
TSC [44–47]	Thermal emptying trap depth and amount	Electrodes pellets/films; dark/thermal	Needs good contacts; peak overlap	Trap depth E_t (eV); peak T; released charge (area)
DLTS [48–50]	Deep levels and kinetics	Device/junction (Schottky/capacitor)	Requires device; not for loose powders	E_t (eV); capture σ ; time constant τ ; trap concentration N_t
TL [51–53]	Radiative de-trapping depth and population	Contact-free thermal readout	Only radiative channels; deconvolution	E_t (eV); peak T; integrated intensity
EPR [54–56]	Paramagnetic traps (identity/environment)	Verifying trapped e^- /defect type; in situ possible	Diamagnetic traps are invisible; artefact risk	g-tensor; hyperfine; relative spin count
PL [20,57,58]	Recombination pathways and lifetimes	Fast screen of trap-mediated losses	Mainly radiative; depth needs other methods	Emission spectra; lifetimes (ns– μ s)

3.1. Reversed Double-Beam Photoacoustic Spectroscopy (RDB-PAS)

Reversed double-beam photoacoustic spectroscopy (RDB-PAS) is an emerging spectroscopic analysis technique that enables the detailed identification and characterisation of semiconducting materials, including photocatalysts [14], electrocatalysts [15], and thermal catalysts [42]. It provides a unique range of semiconductor fingerprints, including metal oxides, which provide essential information about their electrical architectures [43,59].

The intensity of the sound waves produced in RDB-PAS is typically proportional to the concentration of the absorbing species within the sample [59]. Upon illumination with light of a particular wavelength, the sample is heated in certain areas, producing sound waves. The study of these waves has revealed helpful information regarding the electronic structure and trap dynamics of semiconducting materials [60]. A simplified RDB-PAS setup is shown in Figure 1a. A light source with a variable wavelength fills trap states, while a modulated LED light source generates the photoacoustic response in a sealed cell. The acoustic signal recorded with a microphone is demodulated with a lock-in amplifier to isolate the trap-specific contribution [61].

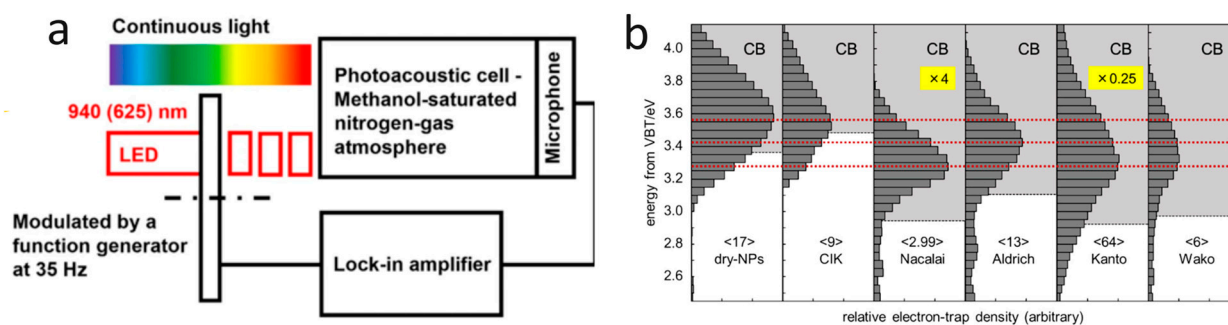


Figure 1. (a) Schematic of the RDB-PAS setup, adapted with permission from ref. [61] under the terms of the CC-BY licence. (b) ET density distributions (ERDT spectra) and conduction band edge positions for sol-gel-derived and commercial SnO_2 samples, adapted with permission from ref. [62].

In brief, the RDB-PAS method can be described as follows: Electrons in the valence band are photoexcited directly into empty electronic-state ETs within the band gap via wavelength-selective continuous monochromatic light irradiation [63]. This energy-resolved excitation, scanning from longer (lower energy) to shorter (higher energy) wavelengths, gradually fills trap states, allowing their distribution to be characterised. Photoacoustic spectroscopy utilises modulated LED light to detect increases in light absorption resulting from the accumulation of electrons in ETs [59]. Scanning across wavelengths generates the energy-resolved distribution of ETs (ERDTs), which represents the density of empty electronic states within the band gap. This is achieved by distinguishing signals from lower-energy (longer-wavelength) and higher-energy (shorter-wavelength) light [59]. Quantitative analysis is realized by calibrating the observed trap density (initially in arbitrary units) against known values from chemical titration data, enabling conversion to absolute units ($\mu\text{mol g}^{-1}$) [64]. The energy of each ET's level, corresponding to the excitation wavelength, is referenced from the top of the valence band (VBT) specific to each sample. Compared to commonly used methods, this new spectroscopy method can better describe surface-state disturbances by resolving ETs with higher resolution [43,65]. As shown in Figure 1b, RDB-PAS can resolve, for example, distinct ERDT profiles for SnO_2 nanoparticles prepared using the sol-gel method and commercial SnO_2 . Monodispersed nanoparticles exhibit a markedly reduced density of deep surface traps and display efficient photocatalytic H_2 evolution, whereas the trap-rich commercial material is essentially inactive. This case illustrates how RDB-PAS can quantitatively relate trap distributions to catalytic performance in practical SnO_2 -based systems [62]. The same approach has been used to characterise the catalytic activity of titanium dioxide (TiO_2), zinc oxide (ZnO), and their composites for photocatalytic [66,67] or electrochemical [59] applications. Several recent studies have utilised RDB-PAS to measure ERDT in C_3N_4 -based photocatalysts [68,69]. These applications demonstrate the method's versatility in evaluating the electronic properties of various catalytic families, establishing ERDT as a practical descriptor that complements conventional spectroscopies and electrochemical probes.

More recently, RDB-PAS has also been deployed on thermally induced heterogeneous catalysts, demonstrating utility beyond photo-driven systems. As an example, Kajabová et al. (2024) showed that RDB-PAS can probe trap energies and densities of FeO_x catalysts under CO_2 hydrogenation conditions and relate these parameters to catalytic performance [42,43]. The key point of this study lies in the link between the stability of catalytic activity and the density and energy distribution of ETs in a particular catalyst.

One significant advantage of RDB-PAS is that it can describe ETs in situ during catalytic reactions. Most of the time, conventional techniques face limitations in providing real-time insights, as they typically require post-reaction analysis or extensive sample preparation [43]. In contrast, RDB-PAS enables in situ observation of the electrical envi-

ronment around ETs during catalytic reactions. This real-time capability is crucial for better understanding the role of ETs and supporting the development of more efficient catalysts [9]. Beyond photo-driven systems, RDB-PAS has now been validated on thermally operated heterogeneous catalysts, where in situ ERDT measurements can be directly correlated with catalytic performance under realistic conditions [9,15,62].

3.2. Thermally Stimulated Current Spectroscopy (TSC)

TSC is one of the few photoelectrical techniques that can directly probe electron and hole trap states in solids [44]. It is particularly suitable for thermally induced heterogeneous catalysis because the experiment itself is based on a controlled temperature ramp, which mirrors how such catalysts are commonly operated. In this context, TSC quantifies electronically active defect states that govern charge availability and redox balance at elevated temperatures, without requiring optical transparency or specialised optical access. The method is therefore helpful for powders, pressed pellets, and supported films, providing a route to characterise materials in forms close to those of practical catalysts [44]. In a typical TSC experiment, traps are first filled at low temperature, usually through optical or electrical excitation, and the sample is then heated at a constant rate. This sequence is illustrated in Figure 2a,b, which depicts trap filling at low temperature, followed by a linear heating ramp and the acquisition of the TSC spectrum [44]. As the temperature increases, trapped charge carriers are thermally released into the conduction or valence band, resulting in a transient current peak. From the shape and position of these peaks, important trap parameters can be extracted, including trap depth (activation energy), trap density, and, in favourable cases, the capture cross-section [45]. Figure 2c,d illustrate this analysis, where systematic shifts in the TSC peak with heating rate are plotted in Arrhenius form to extract the activation energy and capture cross-section of the dominant trap level, demonstrating how TSC can quantitatively resolve deep traps [70]. For reproducibility, precisely controlling the trap-filling conditions (illumination/bias, duration, filling temperature) and the exact linear heating rate is necessary, since both peak temperature and area determine which activation-energy analysis (initial-rise or peak-shape) is appropriate. Peak deconvolution or fractional emptying strategies can separate overlapping parts, while the areas under peaks provide quantitative measures of released charge. This makes TSC a robust method for characterising ETs in solids. TSC has been applied across various inorganic catalyst-relevant families (e.g., TiO_2 , ZnO , SiO_2 , Fe_2O_3 , WO_3) and selected organics (e.g., polyimides), typically revealing trap energies ranging from a few tenths of an eV to ~ 1 eV [39,46,71–74]. Device-oriented and thin-film studies further illustrate the generality without delving into material details (e.g., ZnO devices, GaN/AlGaN heterostructures, and $\beta\text{-Ga}_2\text{O}_3$ films) [47,72,75]. TSC has also been demonstrated in molecular solids (e.g., C_{60}), underscoring its methodological breadth [76]. Reliable TSC measurements require attention to contacts, environment, and leakage currents. Because TSC is typically recorded under an applied bias, a parasitic current is inevitably present and grows quickly with temperature. If left unchecked, this background can obscure defect-related TSC peaks and reduce sensitivity. Accurate baseline acquisition and subtraction, together with suitable contact design and atmosphere control, are necessary to recover the accurate trap signal [77]. A same-day blank ramp (without prior ET filling) and an internal reference sample help verify that leakage and contact resistance remain stable across the ramp window. Ohmic contacts are preferred to avoid barrier artefacts; the choice of contact metal can strongly affect fidelity. With these precautions, peak positions and areas are reproducible under identical heating programs [78–80]. Within a catalysis characterisation suite, TSC complements optical/electron-spin methods by supplying an integral, temperature-programmed electrical signature of trap release. Systematic shifts in peak temperature and peak area

across pretreatments (e.g., redox cycling, doping, and support changes) provide quantitative evidence for changes in trap depth and trap population, enabling correlations to macroscopic activity without specifying particular materials here. Practically, TSC-derived trap descriptors function as actionable parameters for defect engineering in thermally driven heterogeneous catalysis [47,77,81].

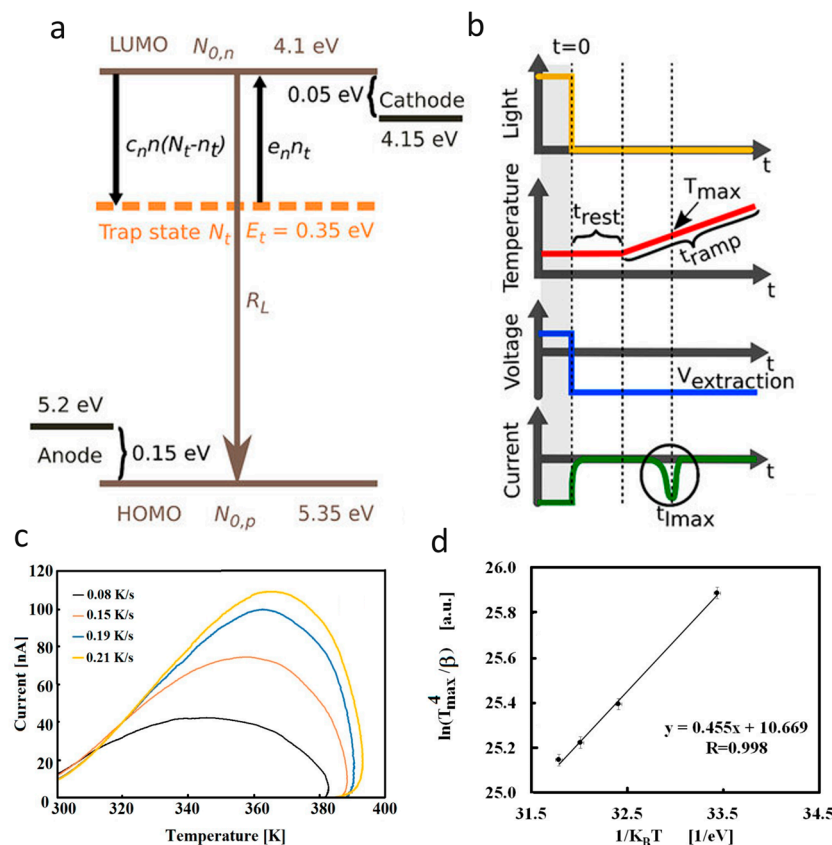


Figure 2. (a) Energy-level scheme with HOMO, LUMO, and trap states used in the TSC model, adapted from ref. [44] under the terms of the CC-BY licence. (b) TSC transient protocol with light excitation, temperature ramp, extraction bias, and corresponding current response, adapted from ref. [44] under the terms of the CC-BY licence. (c) TSC spectra between 300 and 400 K at different heating rates after LED priming, reproduced with permission from ref. [70] under the terms of the CC-BY licence. (d) An Arrhenius plot is used to extract the trap energy and capture cross-section, reproduced with permission from ref. [70] under the terms of the CC-BY licence.

3.3. Deep-Level Transient Spectroscopy (DLTS)

Deep-level transient spectroscopy (DLTS) was first introduced by D.V. Lang in 1974 [82]; it is a capacitance transient method used to detect and measure deep-level impurities and defects in semiconductor materials. The basic isothermal DLTS pulse scheme used to generate these capacitance transients is illustrated in Figure 3a [70]. DLTS provides detailed insight into the types of ETs, their energetic positions relative to the band edge, capture cross-sections, and concentrations [48,49,83]. This method is based on thermally activated carrier emission from deep-level states, described by the electron-emission rate equation for transitions to the conduction band. DLTS detects ETs by examining changes in capacitance within space-charge structures after excitation pulses as the temperature varies [50]. The method shows trap spectra as positive and negative peaks on a flat baseline that change with temperature. The sign of the peak indicates how close traps are to the conduction or valence bands, the peak height indicates the number of traps, and the peak position indicates how thermal emission works [84]. In standard DLTS measurements, ETs typically appear as negative peaks, indicating a connection to the conduction band.

DLTS is performed as a capacitance-transient thermal-scanning measurement, typically operating at megahertz frequencies [83]. With varying temperature and applied electric fields, trap energies can be determined from transient capacitance changes as carriers are released [85]. DLTS has become a central tool for characterising defect levels in electronic materials, enabling the accurate identification of deep-level traps that influence the electrical behaviour of semiconductors and insulators [82]. Such traps are also crucial in thermally driven heterogeneous catalysis, where they can significantly impact charge carrier transport and reactivity [5,83,86]. A significant advancement to the DLTS method brings the inverse Laplace transform of capacitance transients, which enhances spectral resolution and the ability to distinguish energy levels that are too closely spaced to be resolved with conventional DLTS [87]. Optical DLTS, which employs light pulses to probe photoactive traps, and isothermal DLTS, which monitors trap kinetics at a constant temperature, further enhance the technique's versatility [88]. These improvements enable the detection of small defect states in nanostructured materials. For instance, DLTS results for different ZnO morphologies (e.g., nanorods and nanoribbons) indicate that each morphology has a distinctive trap distribution [89]. This is illustrated in Figure 3b,c, which compares DLTS spectra for different ZnO morphologies and directly visualises how morphology tunes deep-level trap populations [89]. DLTS can detect deep traps that form when hydrogen is present in Pt/mesoporous TiO₂ hydrogen sensors, indicating high sensitivity to defects that are important for catalysis [90]. When combined with complementary techniques such as optical absorption spectroscopy, DLTS provides deeper insights into defect behaviour and energy levels, surpassing the limitations of purely electrical methods applied individually [91].

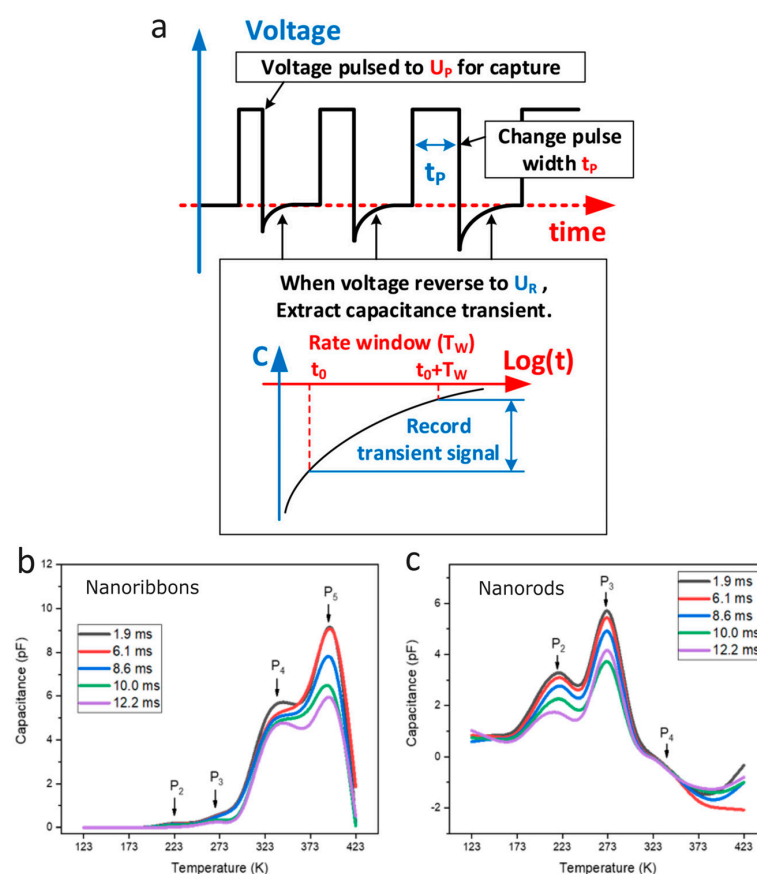


Figure 3. (a) Schematic of the isothermal DLTS measurement, adapted under the terms of the CC-BY licence from ref. [70]. (b,c) DLTS spectra of ZnO/p-Si heterojunctions based on nanoribbon and nanorod ZnO, reproduced under the terms of the CC-BY licence from ref. [89].

DLTS has been applied across catalyst-relevant semiconductor families (e.g., GaN, AlGaIn/GaN, ZnO, CdS) and device platforms (e.g., Schottky diodes, heterostructure channels, mesoporous sensor architectures), typically resolving trap energies ranging from sub-eV to ~1 eV with device-appropriate concentrations [40,89,92]. DLTS has also been paired with optical probes to corroborate defect assignments, underscoring methodological breadth [91]. These examples demonstrate that DLTS can effectively probe different trap energies, densities, and spatial locations in semiconductors, which are crucial for catalysis.

3.4. Thermoluminescence (TL) Spectroscopy

Thermoluminescence (TL) spectroscopy approaches the problem of detecting and characterising ETs from an optical perspective. When trapped charge carriers are thermally released, a transition occurs from higher-energy localised states to lower-energy states within the material [13]. This mechanism is schematically illustrated in Figure 4i. Under excitation, electron–hole pairs are generated (a), with electrons captured in trap levels (Tr) and holes (or recombination sites) in centres R (b). Upon heating, trapped electrons are thermally promoted to the conduction band over an activation barrier E (c) and subsequently recombine at R, giving rise to the TL glow peak (d). Trap depth E sets the glow-peak temperature and thus reflects the thermal stability of the trapped carriers [52].

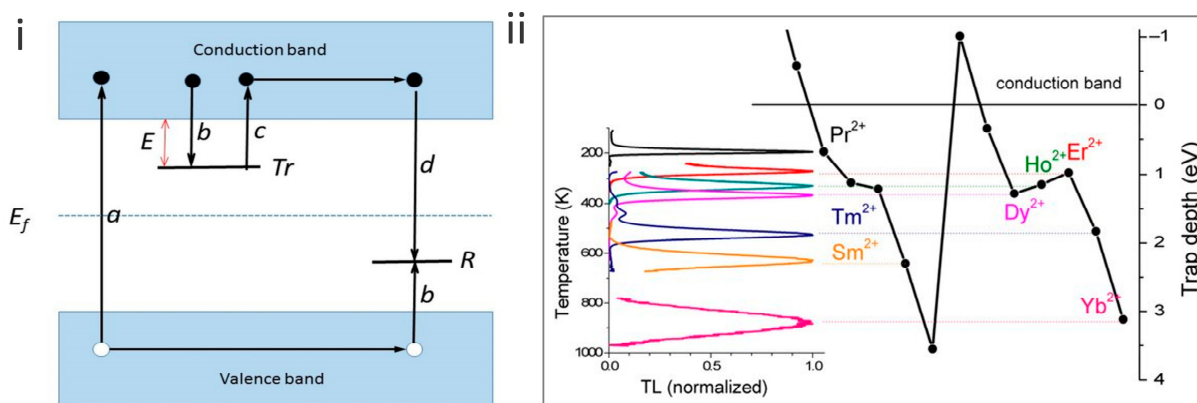


Figure 4. (i) Simplified schematic of the thermoluminescence mechanism adapted under the terms of CC-BY licence from ref. [52]. (ii) Comparison of predicted trap depths from the zigzag energy-level scheme with experimentally measured TL glow-peak maxima for YPO₄: Ce³⁺, Ln³⁺, adapted under the terms of the CC-BY licence from ref. [52].

Therefore, some part of the stored energy is emitted as photons (light) rather than being entirely dissipated as heat. These photons form the thermoluminescence signal, and their intensity at any given temperature reflects the number of carriers recombining at luminescent centres at that moment. The temperature at which this emission occurs is directly related to the trap's activation energy [51]. In practice, activation energies are obtained using standard treatments, initial-rise, peak-shape, and variable-heating-rate analyses, each exploiting the established temperature dependence of TL intensity for traps that thermally empty into recombination centres [51,52]. The position of each peak indicates the trap's thermal stability: shallow traps release carriers at lower temperatures, while deeper traps release carriers at higher temperatures [52]. Peak shape encodes kinetic order and re-trapping. Near-first-order peaks are typically more asymmetric, whereas general-order kinetics and substantial re-trapping produce broader, more symmetric profiles. These features are routinely exploited to deconvolute overlapping contributions [52,53]. The height and area of a peak indicate how many traps were occupied, while the shape of the curve reflects the way carriers are freed and whether they are captured again before recombining. Because the heating rate (β) shifts TL peak temperatures, comparing glow curves

at multiple β values helps decouple trap depth from re-trapping effects and constrains the pre-exponential factor (attempt-to-escape frequency, s) in standard TL formalisms [52,53]. In catalytic materials, several types of traps are often present simultaneously, resulting in complex glow curves. Separating these curves into their individual components enables us to identify traps associated with specific features, such as surface defects, bulk vacancies, dopant atoms, or grain boundaries [53]. Deconvolving complex spectra into a minimal set of component peaks, each characterised by trap depth (E), frequency factor (s), and kinetic order (b), enables the semi-quantitative mapping of shallow versus deep trap populations. This capability is illustrated in Figure 4ii, where the linear correlation between calculated trap depths and TL glow-peak maxima for $\text{YPO}_4\text{:Ce}^{3+}$, Ln^{3+} (where Ln^{3+} denotes trivalent lanthanide co-dopants such as Dy^{3+} and Sm^{3+}) shows that TL can quantitatively resolve discrete defect levels, providing a practical basis for engineering and assessing trap states in functional materials [52]. These populations can then be tracked across pretreatment, atmosphere, and temperature histories relevant to catalysis [53]. Therefore, TL further confirms that traps exist; it offers a detailed picture of their depth, concentration, and release dynamics, making it a valuable tool for understanding how defects influence the performance of thermally driven catalysts. In this context, shallow traps are linked to rapid charge availability and surface-mediated processes. In contrast, deeper traps serve as longer-lived reservoirs that stabilise charge over extended timescales; both regimes are quantifiable from glow-curve metrics [52,53]. In the spirit of a method-focused overview, only brief examples are provided here to indicate scope without material-specific detail: (i) Oxides (e.g., TiO_2 , ZnO) consistently exhibit the shallow vs. deep trend noted above: low-T TL peaks ($\sim 120\text{--}200^\circ\text{C}$) associated with surface-related traps and higher-T peaks ($>300^\circ\text{C}$) attributed to bulk defects, supporting the use of TL peak position/area/shape as practical descriptors of trap depth and population in catalysis-relevant oxides [93,94]. (ii) Chalcogenides (e.g., CdS nanoclusters in zeolite-Y) show distinct low-temperature glow features absent in the host, indicating that numerous ETs are tied to cluster surface states and demonstrating TL sensitivity to size and confinement (representative peak near $\sim 315\text{ K}$) [95]. These concise examples emphasise that TL outputs (peak temperature, integrated intensity, and kinetic order) can be used as comparative descriptors across materials libraries or processing conditions, aiding data-driven screening for catalytic performance [53]. TL has long been used as a technique in radiation dosimetry [96], archaeological dating [18], and defect physics [97]. In recent times, it has become a key research tool for studying semiconductors, insulators, and catalytic materials. Cross-field maturity in dosimetry, geochronology, and defect physics provides tested protocols for uncertainty estimation, calibration, and reproducibility that can be directly adopted in catalyst studies, thereby improving confidence in trap-depth assignments and inter-study comparability [18,96,97]. Pairing TL with absorption or electrical measurements then sharpens shallow/deep assignments and connects trap energetics to activity/selectivity under thermal conditions [52,53].

3.5. Electron Paramagnetic Resonance (EPR)

EPR, also known as Electron Spin Resonance (ESR), is a powerful magnetic resonance technique for detecting and characterising species with unpaired electrons, such as trapped charge carriers, paramagnetic defects, and transition metal ions [54,98]. Since the early 1960s, it has been applied to surface chemistry and heterogeneous catalysis [55]. Its principle is based on the Zeeman effect: when a sample containing unpaired electrons is placed in an external magnetic field and irradiated with microwaves of an appropriate frequency, resonance absorption occurs when the microwave energy matches the energy difference between the electron spin states [56]. The resonance parameters (e.g., g -tensor or g -factor, hyperfine structure) are sensitive to the local magnetic environment, allowing the

identification of defect types and symmetry. A schematic of a basic EPR spectrometer is shown in Figure 5a, highlighting the key components used to detect these paramagnetic trap states [55].

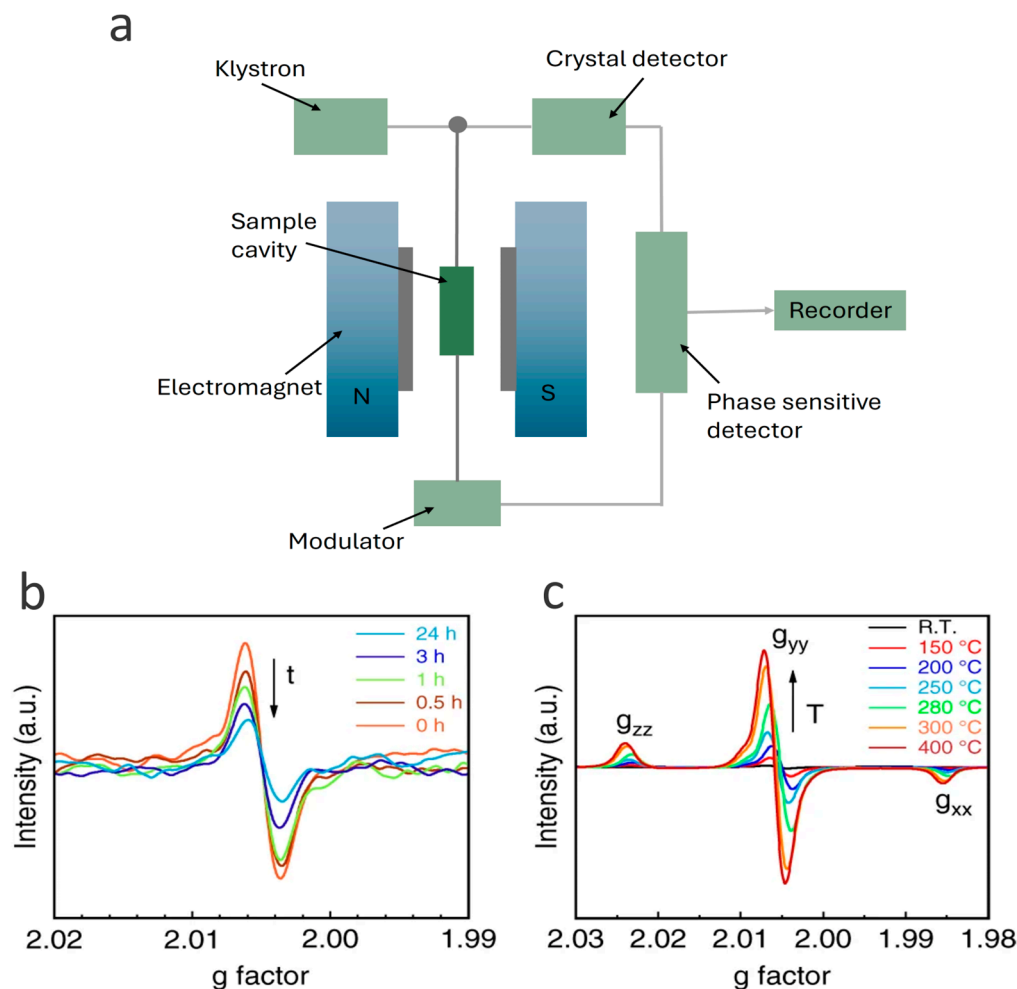


Figure 5. (a) Schematic of a basic EPR spectrometer. (b) Time-dependent evolution of the $g \approx 2.01$ –1.99 signal and (c) temperature-dependent spectra showing the thermally activated depopulation of traps, adapted under the terms of the CC-BY licence from ref. [99].

EPR is particularly valuable because it provides direct evidence of the presence, nature, and local environment of paramagnetic trap states in catalytic and semiconducting materials. Because diamagnetic backgrounds are silent, EPR can detect very low concentrations of trapped electrons/holes even in complex systems, and it can help quantify their populations and environments. As an early example relevant to catalysts, in 1985, Howe and Grätzel demonstrated the direct detection of ETs in colloidal TiO₂ using EPR spectroscopy [100]. Under UV irradiation in the presence of hole scavengers, photogenerated electrons were captured by Ti⁴⁺ centres, forming paramagnetic Ti³⁺ species at interior or surface defect sites. The g-factor is a dimensionless EPR parameter that characterises the spectral position of a paramagnetic resonance and reflects the electronic environment of the unpaired electron. Consequently, variations in g are often used to differentiate distinct paramagnetic species and defect states. More generally, the g-factor can be treated as a second-rank g-tensor (anisotropic in solids), whose principal components and orientation encode the symmetry and local coordination of the paramagnetic system. Accordingly, distinct g-tensor fingerprints for each environment enable the quantification and assessment of thermal stability, establishing EPR as a tool for locating and characterising ETs in

heterogeneous catalysts. Building on this, Morra et al. showed that integrating continuous-wave (CW), pulsed, and in situ EPR provides precise characterisation of Ti^{3+} electron trap centres under realistic conditions, distinguishing between bulk and surface trapping environments and linking structure to catalytic function [101]. For example, Figure 5b,c show how continuous-wave EPR can be used to construct “electron trap plots” for thermocatalysts. The anisotropic resonance at $g \approx 2.01\text{--}1.99$ is characteristic of electrons localised at defect sites (e.g., oxygen-deficient centres or reduced cations). Variable-temperature spectra reveal that the particular centre is progressively quenched on heating, which is consistent with the thermally activated release of electrons from the trap into the conduction band or neighbouring redox sites [99]. In 2021, Bonke et al. demonstrated the application of in situ EPR for the direct monitoring of paramagnetic species, including trapped electrons, during catalytic reactions [102]. More recently, in 2024, Seif-Eddine et al. introduced operando film-electrochemical EPR (FE-EPR) to track paramagnetic species in real time during electrochemical reactions [19]. By combining thin-film electrodes with continuous-flow EPR measurements, they detected and quantified trapped electrons and radical intermediates under working conditions. When unpaired electrons are too short-lived to be seen directly by EPR, spin trapping is a helpful alternative [103]. Spin trap is a diamagnetic molecule that quickly reacts with the transient radical or trapped electron species to form a more stable paramagnetic adduct. The resulting adduct has a longer lifetime and a unique EPR signature, which enables its identification and characterisation. Particularly in thermally driven heterogeneous catalysis, EPR cannot directly detect many reactive intermediates due to their short lifetimes [104]. This issue can be addressed via spin trapping, which involves adding a reactive spin trap molecule to the catalytic system. This approach is advantageous during redox stages or surface-activation processes, when short-lived intermediates break down rapidly at higher temperatures [20]. EPR is highly sensitive to paramagnetic centres; it cannot detect diamagnetic traps (fully paired electrons), which limits its universality. Additionally, interpretation requires careful control of the sample environment to avoid spurious signals from adsorbed species or impurities. Nevertheless, when combined with complementary techniques such as TSC or RDB-PAS, EPR offers unique and direct insight into the electronic structure of active sites and ETs in catalytic systems.

3.6. Photoluminescence (PL)

Photoluminescence (PL) spectroscopy is based on radiative recombination following optical excitation and is sensitive to trap-mediated Shockley–Read–Hall (SRH) pathways [57]. A schematic of a basic PL spectrometer is shown in Figure 6a. Spectral position and bandwidth distinguish band edge from sub-gap (trap) emission, while time-resolved PL (TRPL) separates fast band-to-band from slower trap-assisted channels [58]. Power-dependent PL adds a useful discriminator: sublinear intensity–fluence slopes typically signify defect-assisted (SRH) loss, whereas near-linear and super-linear behaviour reflect radiative and higher-order channels, respectively [105]. Excitation wavelength dependence further separates state filling from distinct defect manifolds when lifetimes and spectra covary with pump energy, enabling the fingerprinting of trap families without invoking material-specific details [106]. Temperature-dependent PL (TDPL) distinguishes between shallow and deep traps.

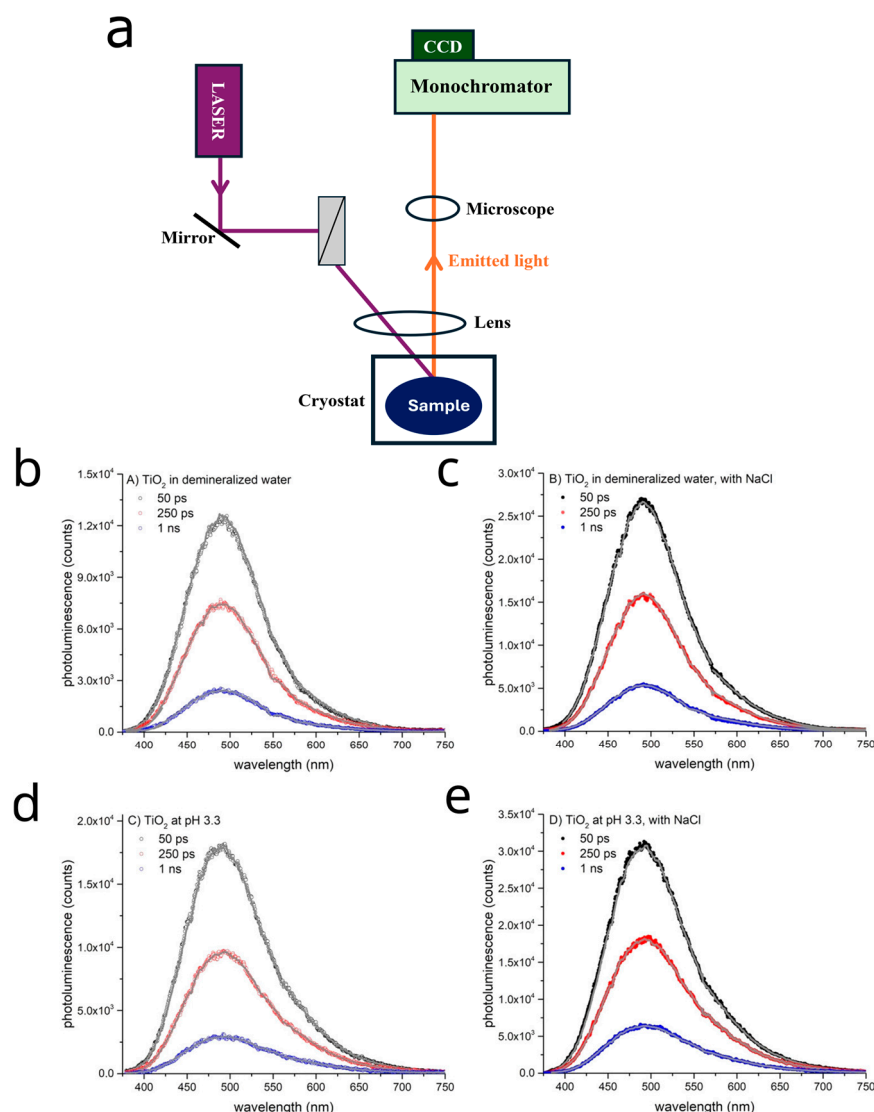


Figure 6. Schematic of a steady-state photoluminescence (PL) setup (a). PL spectra recorded at 50 ps, 250 ps, and 1 ns after 267 nm excitation for TiO₂ films in (b) demineralised water, (c) 0.6 M NaCl, (d) pH 3.3 solution, and (e) pH 3.3 + 0.6 M NaCl. Solid lines show global fits using a three-component parallel-decay model, reproduced under the terms of the CC-BY licence from ref. [58].

Shallow traps give near-band edge emission with strong thermal quenching, whereas deep traps produce broader, red-shifted bands with thermally activated kinetics [107]. Analyses of lifetime distributions and fluence-dependent decay accelerations have been used to identify defect families and their capture kinetics in semiconductors relevant to catalysis and photo(electro)chemistry [108]. For catalysis-relevant measurements, in situ/operando PL couples optical readout with reactors that control gas composition, humidity, and temperature; recent reviews and studies describe cell designs and data-quality practices (optical access, flow geometry, thermal management) and show how operando luminescence tracks recombination pathways and local reaction conditions in real time [109]. In oxide catalysts (e.g., TiO₂, Fe₂O₃, CeO₂), PL trends often parallel synthesis-induced changes in trap populations and may correlate with catalytic performance or interfacial charge dynamics [110]. In Figure 6b–e, the TRPL spectra of nanostructured TiO₂ films (50 ps, 250 ps, and 1 ns) demonstrate how the aqueous environment tunes defect-related emission. In demineralised water (b), the broad band provides the reference response of intrinsic surface/defect states. Adding 0.6 M NaCl at neutral pH (c) leaves the spectral shape

essentially unchanged, indicating that ionic strength alone has only a minor influence on the trap landscape. At pH 3.3 (d), the defect band becomes more pronounced, evidencing protonation-induced modification of surface trap populations. Under combined acidic and saline conditions (e), the low-energy emission is further enhanced and persists longer, indicating that realistic electrolyte/acid conditions stabilise trap-mediated recombination [58]. Temperature-programmed PL delimits trap energetics via Arrhenius-type quenching and thermally activated de-trapping, enabling the assignment of depth classes from peak shifts and lifetime evolution across controlled heating ramps; recent reviews synthesise these strategies for oxide photocatalysts and highlight how synthesis-controlled defect populations (OVs, surface states, dopants) modulate PL yield and kinetics [111]. Because PL is selectively sensitive to radiatively active states, it is most powerful when paired with defect-quantifying techniques that report absolute trap depths and densities. Reviews on TiO_2 and related oxides recommend combining steady-state PL, TRPL, and TDPL measurements with complementary methods to avoid overinterpreting any single metric as a universal activity predictor [111]. For quantitative benchmarking, absolute PL quantum yield (PLQY) measured with integrating-sphere methods is recommended. Recent interlaboratory and methodological studies provide validated procedures and uncertainty budgets directly applicable to catalytic materials [112]. In summary, a PL workflow (i) uses model recombination with SRH-based rate expressions, (ii) applies power-dependent PL and TDPL to diagnose dominant channels and trap activation, (iii) uses TRPL to separate fast band edge from slower defect-assisted decays, and (iv) implements acquisition under controlled atmospheres, which yields mechanism-level insight into recombination routes that govern charge availability for catalysis while remaining material-agnostic [57,109]. PL primarily identifies radiatively active states; non-radiative traps manifest indirectly as quenching or reduced lifetimes [113]. Accordingly, PL is best suited for the rapid assignment of recombination pathways, whereas TL/TSC/DLTS/RDB-PAS provide quantitative measurements of trap depths and densities [114]. To avoid surface chemistry artefacts, maintaining acquisition conditions is fundamental, including excitation energy, atmosphere, and temperature. Additionally, corrections for reabsorption/inner-filter effects, as well as the control of laser-induced heating at higher fluences, are necessary to prevent artificial quenching or peak shifts in powders, films, and other scattering media, thereby ensuring precise data [115].

4. ETs in Heterogeneous Catalysis

The way catalysts store, shuttle, and release charge is regulated by ETs, which are frequently linked to surface/subsurface defects and aliovalent dopants. ETs affect the fundamental processes that determine catalytic activity, selectivity, and stability by stabilising redox-active intermediates and reducing activation barriers. Therefore, the standard methods for surface modification, defect engineering, and doping are overviewed in the following text. Initially, a brief description of the role of ETs in charge transfer and reactant activation in photocatalysis and electrocatalysis is provided. The primary focus will be on the catalytic hydrogenation of CO_2 , as this reaction has been widely studied in the context of global warming (Figure 7).

4.1. Methods for ET Production in Metal Oxide Catalysts

In the preceding section, standard methods used to characterise ETs in metal oxide catalysts were outlined, including energy-resolved optical tools (RDB-PAS/ERDT), thermal release techniques (TSC, TL, DLTS), photoluminescence (PL), and EPR. These methods collectively describe trap depth, density, location, and dynamics. This section dis-

cusses standard ET production methods, such as surface modification, defect engineering, and doping.

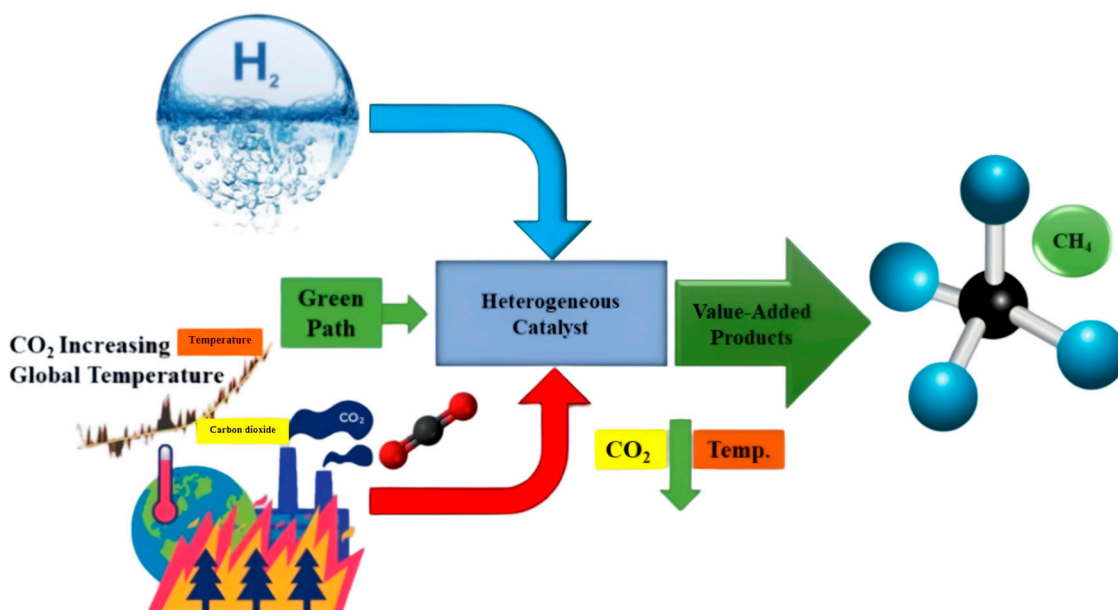


Figure 7. Conceptual schema of CO₂ hydrogenation over heterogeneous catalysts, reproduced under the terms of the CC-BY licence from ref. [116].

Doping Strategies

Doping reconfigures the electronic structure and oxygen-vacancy density of oxide catalysts, thereby determining the properties of ET states. Aliovalent dopants introduce charge imbalance, stabilise OVs, and tune trap energies, thereby lowering barriers to CO₂ activation [117–119]. In an iron-based catalytic system, alkali promoters such as potassium (K) and caesium (Cs) support Fe²⁺/Fe³⁺ redox cycling and improve reaction selectivity by altering adsorption energy [120,121]. Experiments further demonstrate that alkali dopants influence the formation energies of vacancies and product distributions in iron molybdate and related oxides [122]. These findings suggest that doping is an effective strategy for enhancing trap density and enhancing thermocatalytic performance [123].

Defect Engineering

Defect engineering deliberately controls the ET population and enhances the efficacy of metal oxide catalysts. Thermal treatments and redox cycling are prevalent methods for forming OVs, which trap electrons and enhance CO₂ activation [117]. Reducing atmospheres (e.g., H₂ pretreatment) enriches the vacancy population on Fe₂O₃, promoting polaron hopping and faster redox cycling, yielding direct gains in turnover [124]. Recent direct real-space imaging has confirmed the dynamic role of polarons and localised trap states in hematite, affirming defect engineering as a method to enhance thermal reactivity [125]. These studies collectively illustrate that the deliberate insertion and stabilisation of defects provide an effective way to enhance ET's positive effect on thermocatalysis.

Surface Modification Techniques

Surface modification targets the near-surface electronic structure and metal–support interface to tune the energetics, density, and accessibility of ETs. By reshaping interfacial charge transfer and stabilising vacancy populations, these treatments can accelerate redox turnover and bias product pathways under typical thermocatalytic reaction temperatures. Strong metal–support interactions (SMSIs) are a prominent example: they can stabilise OVs, modulate spillover processes, and enhance cross-interface electron flow, thereby elevating thermocatalytic rates [126,127]. Promoter overlayers (e.g., alkali coatings) on iron oxides

adjust surface basicity and adsorption energetics, thereby improving CO₂ activation and steering selectivity [128]. Conformal overcoats via atomic layer deposition (ALD) are used to correct surface imperfections and make ETs more accessible, thereby enhancing catalytic performance over a range of temperatures [129,130]. Altogether, surface engineering provides a precise means with which to control ET dynamics at active interfaces and to translate that control into reliable thermocatalytic performance.

4.2. Basic Principles of ET's Role in Heterogeneous Catalysis

ETs act as transient electron donors/acceptors that stabilise key anionic intermediates (e.g., CO₂[−], O₂[−]) during bond activation steps in thermocatalysis [42]. On iron oxides, OV_s, and reduced Fe²⁺ provide electron-rich sites that strengthen CO₂ adsorption and facilitate activation by stabilising CO₂-derived intermediates such as activated CO₂δ[−], carbonate/bicarbonate, and formate species, as discussed by Etim et al. [131]. On Fe₂O₃, Kajabová et al. showed that small changes in synthesis conditions modify the energy and density of ETs measured via RDB-PAS and that the catalyst with the lowest trap density achieves the most stable CH₄ production during CO₂ hydrogenation [42]. Furthermore, the presence of OV_s in iron oxides lowers the energy barrier for CO₂ activation, as indicated in both computational and experimental research [132]. A recently published review highlights oxygen-vacancy engineering as a general approach to enhancing the efficiency of CO₂ hydrogenation across oxide catalysts [133].

ETs regulate intra- and interfacial charge flow by donating or capturing electrons during the catalytic process. In iron oxides, Fe²⁺/Fe³⁺ trap states support thermally activated small-polaron hopping, which sustains rapid redox cycling and improves overall rates [41]. At metal–oxide interfaces, OV_s enhance synergistic reactivity by facilitating electron exchange between the metal particles and the support [134]. The density, energetic depth, and accessibility of ETs correlate with the efficiency of charge transfer, as trap-mediated electron flux lowers barriers for processes such as CO₂ reduction and H₂ activation [131]. Optimising these properties is therefore a central design technique for thermocatalysts.

4.3. Comparative Roles of ETs in Photocatalysis, Electrocatalysis, and Thermally Induced Heterogeneous Catalysis

ETs localise excess electrons and thereby gate the time and location of reduction steps in CO₂ conversion. Their role depends on the energy input from photons (photocatalysis), electrical bias (electrocatalysis), or heat (thermocatalysis). Altogether, published studies indicate that catalyst design should focus on tuning trap depth, density, spatial location, and stability, as well as on calculating physically meaningful quantities such as oxygen-vacancy formation energies and trap energies, which can be correlated with CO₂ activation and hydrogenation rates [135]. In photocatalysis, ETs are helpful only when they prolong electron lifetimes without acting as Shockley–Read–Hall recombination centres. Shallow intermediate traps near the conduction band edge can mediate electron transfer to form intermediate OCHO in the initial step of CO₂ hydrogenation, thereby lowering the barrier to carboxylate (−COOH) formation. In contrast, deep traps typically accelerate e[−]–h⁺ recombination and reduce photocatalysis efficiency [136,137]. In electrocatalytic CO₂ reduction on Cu, metal–oxide interfaces, and doped sites can accumulate charge and stabilise key intermediates such as CO₂[−] and −COOH, thereby lowering overpotentials and shifting the balance toward C₁ and C₂₊ products [138]. Because the electric double layer and applied potential continuously reshape these energetics, theoretical quantitative modelling should use constant-potential (grand-canonical) DFT with explicit PCET and solvation [139]. Oxide-derived or oxide-modified Cu surfaces are therefore tuned such that CO binds strongly enough for further reduction or C–C coupling, but not so strongly that it poisons active sites [140,141]. In thermally induced catalysis, OV_s, polarons, and metal–

support perimeter sites act as robust electron reservoirs that persist and re-equilibrate under operating conditions of temperature and pressure, thereby lowering barriers for CO₂ activation and H-assisted steps. To describe and design such defect-mediated reservoirs on a theoretical level, it is helpful to calculate defect formation energies under realistic oxygen and hydrogen partial pressures and to evaluate polaron formation and hopping barriers. These quantities can then be compared with the reaction barriers for the key CO₂ hydrogenation steps (CO₂ → COOH → CO → HCO → CH₃OH) on defective versus ideal surfaces, as well as with the stability of vacancy-rich perimeter sites and atomically dispersed metal centres against migration and coarsening during reaction [142,143]. A canonical exemplar is Cu/ZnO/Al₂O₃, where Zn is decorated with Cu steps, stabilised with bulk and surface defects, which correlate with high methanol activity, thus illustrating trap-fed, perimeter-controlled kinetics under industrial conditions [144]. More broadly, in thermally driven catalysis, well-positioned ETs can serve as robust, regenerable electron reservoirs. In contrast, in photocatalyst and electrocatalysis, deep traps mainly act as recombination centres and must be suppressed. This difference implies different design targets: stabilising beneficial traps at interfaces for thermocatalysts, and minimising detrimental traps for photocatalysts and electrocatalytic systems [139].

To summarise the aforementioned facts, Table 2 contrasts the operating conditions, dominant trap roles, characteristic defect motifs, key kinetic limitations, and preferred computational descriptors for ETs in photocatalytic, electrocatalytic, and thermally induced CO₂ conversion.

Table 2. Comparison of the roles of ETs in photocatalytic, electrocatalytic, and thermally induced heterogeneous CO₂ conversion.

Aspect	Photocatalysis [145]	Electrocatalysis [139]	Thermal Catalysis [144]
Energy input	Light from e [−] /h ⁺ pairs	Applied potential injected e [−]	Heat thermally activated carriers
Dominant trap roles	Extend e [−] lifetime; mediate e [−] → CO ₂ transfer; balance shallow vs. deep traps	Accumulate/stabilise charge at interfaces; lower η; steer selectivity via intermediate stabilisation	Vacancies/polarons + metal–support sites localise e [−] ; lower barriers for H-assisted steps; sustain activity at elevated reaction temperatures
Typical trap motifs	Surface/bulk shallow deep states in semiconductors (e.g., defective In ₂ O ₃ , doped g-C ₃ N ₄)	Interface traps at metal–oxide junctions; dopant-induced states	OV, polarons, single-atom/metal–support traps (e.g., Cu/ZnO/Al ₂ O ₃ , TiO ₂ , WO ₃)
Key kinetic pain point	e [−] –h ⁺ recombination	Overpotential and mass transport	Defect dynamics (formation/migration) and sintering
Design-relevant descriptors	Excited-state lifetimes, trap depths, e [−] transfer barriers to CO ₂	Grand-canonical DFT of charged surfaces, PCET barriers, double-layer effects	Defect formation energies, polaron binding/hopping barriers, CO ₂ /H activation at defective sites
Typical reactions	CO ₂ photoreduction to fuels/chemicals	CO ₂ electroreduction (C ₁ /C ₂₊)	CO ₂ hydrogenation, methanol synthesis

ETs couple tightly to oxygen-vacancy dynamics in Mars–van Krevelen (MvK) cycles, where vacancy formation/annihilation can control reaction kinetics [146]. Ultrafast XUV reflection absorption spectroscopy in hematite (α-Fe₂O₃) reveals a consistent connection between surface electron trapping, Fe³⁺ reduction, and the creation of a tiny polaron, linking trap states, electron localization, and redox turnover in iron oxides [124]. Recent real-space observations of polarons in hematite confirmed that these localised trap states

actively participate in electron transport, thereby validating their critical role in thermally driven catalytic pathways [125].

5. Case Studies: ETs in Selected Thermocatalytic Reactions

The literature identifies three primary types of inorganic materials utilised in heterogeneous catalysis: metal oxides, supported metals, and porous frameworks. The first two are discussed in this section; however, porous frameworks are beyond the scope of this review. As in the previous section, cases related to CO₂ hydrogenation are discussed here as well. Alam et al. reviewed thermally driven CO₂ conversion methods (methanation, RWGS, and methanol synthesis), highlighting the formate, carboxyl, and RWGS pathways as a conceptual bridge to the subsequent case studies. OVs and similar electron-rich defect states are often not referred to as “ETs”, but they do act as electron donors that stabilise important anionic intermediates (CO₂[−], HCOO[−], COOH), which lowers kinetic barriers. This viewpoint inherently links traditional thermocatalytic mechanisms with the increasing acknowledgement of ETs as indicators of catalytic efficacy [147].

5.1. Metal Oxides

Metal oxides are ubiquitous thermocatalysts owing to their stability, tunable redox chemistry, and defect tolerance. In these materials, OVs and associated ETs often govern activity by stabilising anionic intermediates, steering charge transport, and reducing activation barriers.

A representative example is Fe₂O₃. Kajabová et al. tuned the defect and ET density in Fe₂O₃ by varying precipitation conditions and quantified the trap landscape using RDB-PAS. Catalysts with very high ET density, generated by fast precipitation, exhibited unstable CH₄ production and rapid deactivation. In contrast, the sample with the lowest ET density and the lowest trap-tail energy showed the most stable methane productivity during CO₂ hydrogenation, demonstrating that ETs’ energy and density are useful criteria for selecting Fe oxide catalysts [42]. Defect engineering in In₂O₃ further illustrates ETs’ control of catalytic reactions. Liu et al. demonstrated that introducing small amounts of Al³⁺ into In₂O₃ enhances the concentration of OVs, thereby increasing methanol production during CO₂ hydrogenation. With 5 mol% Al doping, the catalyst achieved a methanol space–time yield approximately 60% higher than that of undoped In₂O₃. XPS confirmed the results: OV densities were higher than in undoped In₂O₃, and CO₂-TPD showed that CO₂ was adsorbed more strongly at trap sites. High levels of doping (>10%) led to the formation of additional Al₂O₃ domains on the In₂O₃ surface, which blocked active sites and reduced the observed activity [148]. Beyond substitutional metal doping, transition metal promoters can also modulate trap states in oxides. Zhu et al. demonstrated that introducing small amounts of Ni into In₂O₃ creates Ni–In interfacial synergy, which significantly accelerates the synthesis of methanol from CO₂. At an optimal NiO loading of 6 wt%, the CH₃OH formation rate was nearly four times higher than that observed for undoped In₂O₃. However, higher Ni contents shifted selectivity toward undesired products, CO and CH₄. Characterisation via H₂-TPR and O1s XPS confirmed an increase in oxygen vacancy density, while in situ EPR revealed that electrons were trapped in these anion vacancies during the reaction. DFT calculations revealed that low-valence Ni species (single atoms or small clusters) markedly reduce the H₂ dissociation barrier, thereby facilitating the hydrogenation of CO₂ adsorbed at OVs [149].

Another useful example is defective molybdenum oxides. Kuwahara and Yamashita demonstrated that Pt/H_xMoO_{3-γ} yields superior methanol production in CO₂ hydrogenation, with OVs functioning as dynamic charge reservoirs through reversible Mo redox cycling (studied using in situ XANES). For Ru/H_xMoO_{3-γ}, defect-rich overlayers

altered the selectivity of the CO vs. CH₄ reaction. These findings underscore the capacity of non-stoichiometric oxides to utilise OV-associated ETs to modulate both activity and selectivity [150]. Ceria (CeO₂) serves as a prototypical model, wherein Ce³⁺/Ce⁴⁺ cycling is intricately linked to vacancy formation. Huang et al. concluded that facet-dependent vacancy formation energies are directly connected to selectivity in alcohol oxidation, indicating that CeO₂ is an effective model for understanding how trap states control catalytic performance. These results clarify how vacancy-associated trap states control charge transfer and activity in ceria-based thermocatalysts [151]. Subsurface traps are also essential in In₂O₃. Wei et al. showed that incorporating metallic indium into In₂O₃ nanoflakes enhanced subsurface OVs, which act as ETs that transfer charge to surface sites. Operando ESR and CO₂ temperature-programmed desorption (CO₂-TPD) determined that these defects caused CO₂ adsorption to be more stable, C–O bond stretching, and an increase in the activation of the CO₂ molecule. The modified catalyst exhibited turnover frequencies approximately three orders of magnitude higher than those of pure In₂O₃. This study highlights the role of OVs' engineering in maintaining electron mobility and redox cycling under thermal conditions [132].

At TiO₂ and ZnO, band bending and surface states create electronic levels in the gap, which act as ETs. Zhang and Yates (2012) describe the formation of electronic states within the band gap due to dangling bonds and OVs, which act as traps, stabilising the Fermi level and causing band bending [152]. These defect states have been confirmed with spectroscopic evidence, such as trap-assisted photoluminescence recombination (the Shockley–Read–Hall mechanism). Adsorption studies have revealed that electron-acceptor molecules (e.g., O₂) enhance upward band bending and fill traps, whereas donor molecules (e.g., alkenes, H₂) decrease band bending. These trap-mediated charge reservoirs affect the strength of adsorption, charge transfer, and reactivity in thermal catalysis on oxides. K-modified Fe₂O₃ in RWGS is an example of how promoters can change the populations of ETs. Tian et al. demonstrated that on bare Fe₂O₃, CO₂ activation primarily occurs through a redox mechanism, wherein OVs and Fe³⁺/Fe²⁺ trap states facilitate electron transfer to generate CO [132]. Potassium enhances surface basicity, stabilises associative intermediates, and redirects the mechanism towards a formate-mediated pathway. Operando XPS, Mössbauer, and CO₂-TPD described the electronic environments, whereas DFT demonstrated that K reduces vacancy formation energies and modifies trap occupancy. Studies on Fe oxide systems demonstrate how ETs alter system function. Jiang et al. stated that in Fe₂O₃/Fe₃O₄, OVs and Fe³⁺/Fe²⁺ redox pairs act as charge reservoirs, allowing CO₂ activation through redox vacancy cycling or associative formate intermediates. Under reaction conditions, partial conversion to Fe carbides facilitates Fischer–Tropsch (F-T)-type C–C coupling. Promoters (K, Na, Mn, Ce) change vacancy density and electron availability, thereby altering selectivity. For example, alkalis make the material more basic, slow CO₂ adsorption, and favour olefins. Conversely, Ce or Zr facilitates the movement of oxygen more easily and helps vacancies regenerate. Spectroscopic and kinetic data collectively identify electron transfer sites (OVs, Fe²⁺ centres) as the switchboard between the RWGS and F-T routes [153]. High OV densities in oxides like CeO₂, TiO₂, and In₂O₃ create localised reduced cations (Ce³⁺, Ti³⁺, In²⁺) that charge adsorbates, lengthening C–O bonds and stabilising CO₂-derived intermediates (CO₂[−], formate). Operando EPR/XPS experiments demonstrate that OVs do not remain static; instead, they continuously regenerate under H₂/CO₂ feed conditions, linking vacancy dynamics to sustained redox activity. By adjusting the vacancy levels, oxides can switch between redox and associative CO₂ activation pathways. This is a clear example of how ETs control the reaction mechanism in thermally activated hydrogenation [133]. In CO₂-assisted ethane dehydrogenation (CO₂-EDH) at 650 °C, Tasioula et al. illustrated that iron oxides function as dynamic electron reservoirs:

$\text{Fe}^{3+}/\text{Fe}^{2+}$ redox pairs and coordinated OV's stabilise charge transfer steps that link ethane dehydrogenation with CO_2 reduction [123]. XPS, EXAFS, and XRS recorded changes in Fe oxidation states, linking ET dynamics to high ethylene selectivity (~90%). These findings illustrate how intrinsic ETs in Fe oxides co-regulate activity and selectivity by associating hydrocarbon activation with CO_2 utilisation in thermocatalytic tandem reactions.

In addition, Figure 8 summarises the distribution of trap-state activation energies (E_t) reported between 2019 and 2025 for catalyst-relevant materials, extracted from DLTS, TSC, and TL studies, with the corresponding numerical data compiled in Tables 3–5. These techniques were selected because they provide direct or quantitatively interpretable access to trap energies, populations, and recombination pathways.

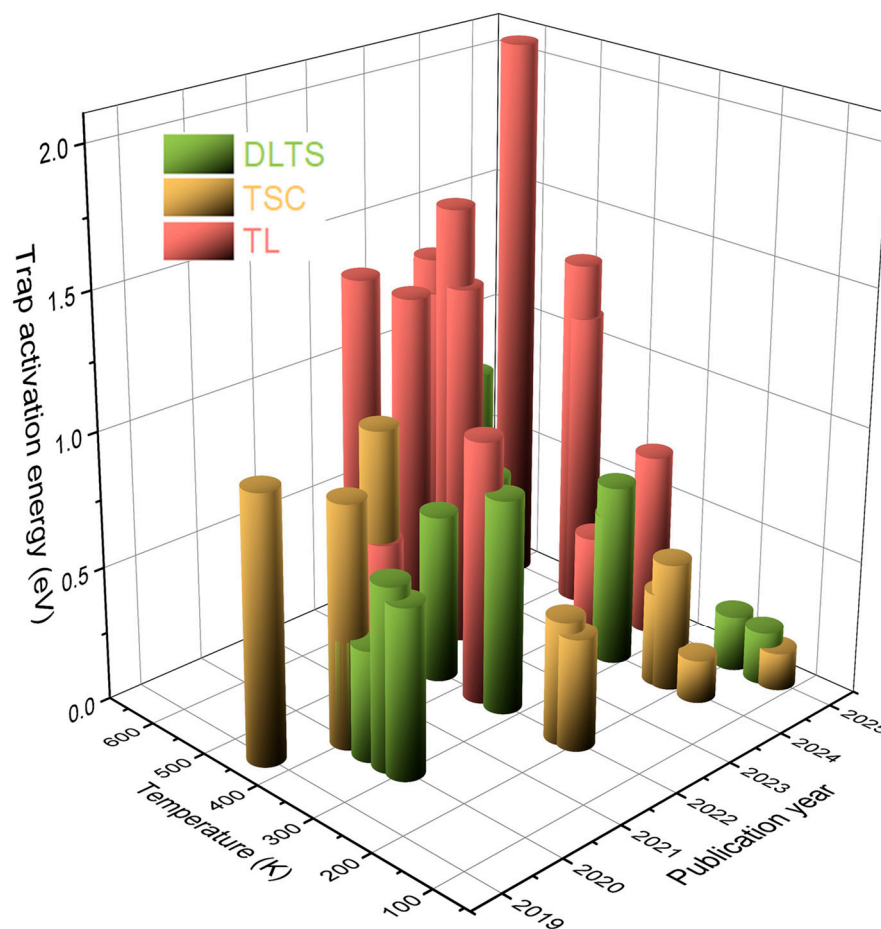


Figure 8. Research landscape of trap-state activation energies (E_t) reported between 2019 and 2025 for catalyst-relevant materials, extracted from DLTS, TSC, and TL. The corresponding numerical data are provided in Tables 3–5.

Table 3. Dataset corresponding to Figure 8: trap-state activation energies (E_t), temperatures, and publication years extracted from deep-level transient spectroscopy (DLTS) studies on catalyst-relevant materials reported between 2019 and 2025.

No.	Materials	E_t (eV)	Temp. (K)	Year	Ref.
1	$\beta\text{-Ga}_2\text{O}_3$	0.209	200 K	2025	[154]
2	$\beta\text{-Ga}_2\text{O}_3$	0.196	150 K	2025	[154]
3	$\beta\text{-Ga}_2\text{O}_3$	0.68	450 K	2024	[155]
4	AlGaIn/GaN	0.56	325 K	2024	[156]
5	$\beta\text{-Ga}_2\text{O}_3$	0.89	580 K	2024	[155]

Table 3. *Cont.*

No.	Materials	E _t (eV)	Temp. (K)	Year	Ref.
6	MoS ₂	0.632	300 K	2023	[157]
7	β-Ga ₂ O ₃	0.8	330 K	2023	[158]
8	AlGa _{0.5} N _{0.5} /Ga _{0.5} N _{0.5}	0.63	446 K	2022	[159]
9	Sb ₂ S ₃	0.69	500 K	2021	[160]
10	n-GaAsBi	0.41	360 K	2021	[161]
11	Sb ₂ S ₃	0.64	475 K	2021	[160]
12	β-Ga ₂ O ₃	0.68	325 K	2020	[162]
13	MoS ₂	0.4	400 K	2020	[163]
14	4H-SiC	0.68	322 K	2020	[164]
15	Mo _{0.3} W _{0.7} S ₂	0.47	400 K	2020	[163]

Table 4. Dataset corresponding to Figure 8: trap-state activation energies (E_t), temperatures, and publication years extracted from thermally stimulated current (TSC) measurements on relevant materials reported between 2019 and 2025.

No.	Materials	E _t (eV)	Temp. (K)	Year	Ref.
1	NaBi(MoO ₄) ₂	0.14	127.5 K	2025	[165]
2	CsPbBr ₃	0.48	225 K	2024	[166]
3	PbWO ₄	0.35	237.5 K	2024	[39]
4	PbWO ₄	0.16	178.1 K	2024	[39]
5	MAPbI ₃	0.459	225 K	2022	[167]
6	MAPbI ₃	0.414	205 K	2022	[167]
7	CdZnTe	0.56	450 K	2021	[78]
8	CdZnTe	0.6	475 K	2021	[78]
9	β-Ag ₂ O	1.03	450 K	2021	[47]
10	InGaZnO	0.9	400 K	2020	[168]
11	β-Ga ₂ O ₃	0.99	441 K	2019	[169]

Table 5. Dataset corresponding to Figure 8: trap-state activation energies (E_t), temperatures, and publication years extracted from thermoluminescence (TL) measurements on relevant phosphors and oxides reported between 2019 and 2025.

No.	Materials	E _t (eV)	Temp. (K)	Year	Ref.
1	K ₂ Y _{0.9} Eu _{0.1} F ₅	1.32	478 K	2025	[170]
2	SrAl ₂ O ₄ :Eu ²⁺ , Dy ³⁺	0.69	345 K	2025	[171]
3	Ca ₅ (PO ₄) ₃ OH	1.12	473 K	2025	[172]
4	K ₂ Y _{0.9} Eu _{0.1} F ₅	2.07	600 K	2025	[170]
5	Ca(Sr)ZnOS	0.45	359 K	2024	[173]
6	GdAl ₃ (BO ₃) ₄	1.63	518.08 K	2023	[174]
7	GdAl ₃ (BO ₃) ₄	1.42	559.32 K	2023	[174]
8	SrMoO ₄	1.03	560 K	2023	[175]
9	SrMoO ₄	1.3	550 K	2023	[175]

Table 5. Cont.

No.	Materials	E _t (eV)	Temp. (K)	Year	Ref.
10	BaTi ₅ O ₁₁	1.35	502 K	2023	[176]
11	BaTi ₅ O ₁₁	1.4	560 K	2023	[176]
12	BeO:Na,Yb,Dy	1.39	496 K	2022	[177]
13	SrGa ₂ O ₄ :Cu ²⁺	0.98	367 K	2022	[178]
14	MgO:Tb,Gd,Li	0.62	443 K	2021	[179]

5.2. Supported Metal Catalysts

In supported catalysts, OV sites are significant for controlling ETs and changing how well the catalyst works. Huang et al. reported that Au/CeO₂ and Pd/CeO₂ catalysts benefit from OV sites that stabilise cationic metal centres and decrease the activation barriers for C–H bond breakage. Single-atom Au anchored on CeO₂ exhibits even better activity because it makes more traps at the metal oxide interface [151].

In 2016, Sun et al. reviewed the morphology-controlled ZnO systems across various catalytic applications. This review focuses primarily on photocatalysis (e.g., dye degradation) and, in some cases, on specific thermal reactions in which ETs play a crucial role in reactivity. For example, Cu/ZnO nanoplates with exposed (002) facets improved the conversion of CO₂ to methanol by stabilising intermediates through vacancies [180]. Pd/ZnO nanoballs improved the selectivity of H₂ production in methanol steam reforming by having more vacancies [181]. Au/ZnO twin-brush mesocrystals had better CO oxidation performance by taking advantage of strong metal–support interactions caused by vacancies [182]. Many other examples demonstrate how the shape of ZnO and the chemistry of its defects directly affect the density of ETs, which in turn controls the activity and selectivity of supported metal catalysts in thermal-initiated reactions [183].

Ni/Ca–ZrO₂ catalysts demonstrate that the aliovalent doping of oxide supports can alter the density of trap states and enhance the thermocatalytic activity of supported metals. Everett et al. showed that replacing Ca²⁺ in ZrO₂ results in paired OVs and coordinatively unsaturated sites, as demonstrated by EPR and XPS. These ETs effectively stabilised CO₂ activation intermediates at the Ni/ZrO₂ interface, leading to an almost threefold increase in methanation activity compared to undoped Ni/ZrO₂. This work demonstrates the importance of defect engineering in altering the behaviour of ETs, thereby enhancing the interaction between the metal and the support and improving catalytic performance [184]. Similarly, Ru species supported on Al₂O₃ were shown to change dynamically during CO₂ hydrogenation, going from single atoms to clusters depending on the reaction conditions. The trap states in the support altered the electron density of Ru, thereby directly affecting the adsorption and hydrogenation of CO₂ [185]. Another extensively researched example is Au supported on ceria (CeO₂), where ETs linked to OVs are crucial in regulating metal–support charge transfer. According to Liu and Corma, single-atom Au on CeO₂ has much higher CO oxidation activity than Au nanoparticles as the vacancy-associated traps stabilise cationic Au species and make it easier for O₂ to activate at the Au–CeO₂ interface. The dynamic interaction between Ce³⁺/Ce⁴⁺ redox cycling and the Au charge state has been demonstrated to influence reaction pathways, thus establishing a direct connection between trap-state density and catalytic turnover. These insights underscore that the efficacy of supported noble metals is fundamentally linked to the electron trap chemistry of reducible oxide supports [185].

Pr-doped Ru/CeO₂ offers a distinct thermal scenario in which ETs at the metal–support interface control catalytic turnover. López Rodríguez et al. examined CO₂ methanation, a representative thermally driven reaction and showed that adding 3 wt% Pr increased the

concentration and mobility of OV in CeO_2 . These vacancies functioned as ETs, stabilising CO_2^- intermediates and facilitating hydrogenation at the Ru– CeO_2 interface. In situ Raman spectroscopy confirmed the increased vacancy density, and DRIFTS spectra showed that the addition of Pr halted the buildup of unreactive carbonate species. The catalyst with the best doping produced more CH_4 at lower temperatures; however, excessive Pr weakened metal–support interactions, thereby lowering the activity. This case study demonstrates how aliovalent doping can be utilised to fine-tune the populations of trap states in reducible oxides, thereby directly improving the performance of thermal CO_2 methanation [186]. OVs have a unique function at the interface between support and metal: they control the electron density of the metal phase and direct catalytic pathways. Wang et al. demonstrated that Ru/ CeO_2 and Pd/ CeO_2 benefit from interfacial vacancies that facilitate charge transfer, stabilising catalytically active (often cationic) metal states, enhancing CO_2 adsorption, and reducing hydrogenation barriers. In situ XPS directly measured vacancy density in the support, which correlated with both CO_2 conversion and product selectivity. Unlike bulk oxides, where trap states can act as the active sites, interfacial ETs primarily modulate metal reactivity, functioning as “electron valves” that tune the behaviour of supported metals [133]. Supported Fe catalysts further underline the importance of interfacial ETs in thermal CO_2 hydrogenation. Jiang et al. reported that Fe nanoparticles on reducible oxides (ZrO_2 and CeO_2) generate abundant interfacial OVs that act as shallow traps, promoting CO_2 activation via charge transfer. In situ XPS again correlated conversion and selectivity with the vacancy population, emphasising that, relative to bulk Fe oxides, interfacial trap states primarily regulate the electronic structure and reactivity of the metal rather than serving as standalone active sites [153]. Support composition can actively shape these traps formed at the interface. For FeO_x supported on Ni–Mg–Zr mixed oxides operating in CO_2 -assisted ethane dehydrogenation, XRS and EXAFS showed that the interfacial oxygen coordination evolves under reaction. Mg and Zr sites moved the charge around, keeping Fe stable in mixed-valence states while keeping active OVs. This synergy prevented Fe from being over-reduced, maintained high ethylene selectivity, and improved CO_2 conversion [123]. Kots et al. showed that ETs at Ru/ TiO_2 metal–support interfaces control activity in polypropylene hydrogenolysis.

At the end of this discussion, we present two examples that illustrate the influence of ETs on reaction activity in different reaction types, such as CO_2 hydrogenation. For Ru/ TiO_2 , hydrogen spillover from Ru into the TiO_2 lattice generated Ti^{3+} shallow traps and partially filled the TiO_2 conduction band. These trap states acted as electron reservoirs, stabilising surface hydrogen and facilitating C–C scission during polypropylene hydrogenolysis. Operando ^2H MAS NMR, FTIR, Raman, and NAP-XPS confirmed the dynamic generation of Ti^{3+} under reaction conditions. Trap-rich Ru/ TiO_2 exhibited higher hydrogen coverage, faster rates, and greater liquid yields than trap-poor counterparts, underscoring the value of tuning interfacial ET populations to regulate hydrogen availability and reactivity [187].

Kitano et al. (2012) used the electride $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(\text{e}^-)_4$ (C12A7: e^-) as a support for Ru nanoparticles in catalytic ammonia synthesis, providing an extreme example of support-driven ET engineering. The electride keeps extra electrons in cage-like structures that act like stable shallow traps. In this manner, charge is transferred to Ru, thereby dramatically accelerating N_2 activation via electronic back-donation. The energy required to initiate the reaction to produce ammonia was approximately half that of conventional Ru catalysts. Simultaneously, C12A7: e^- acted as a reversible hydrogen reservoir that protected Ru from H-poisoning. The combined effects of donating electrons and buffering hydrogen led to an almost tenfold increase in activity, demonstrating that supports naturally rich in traps can alter thermocatalytic pathways [188].

6. Conclusions

In conclusion, defect engineering is crucial for all types of heterogeneous catalysts. Since a significant proportion of defects is associated with the formation of electron traps (ETs), this area is becoming essential for both understanding the mechanisms of heterogeneously catalysed reactions and developing more effective catalysts. ETs are the electronic bridge between atomic-scale defects and macroscopic catalytic performance in heterogeneous catalysis. Therefore, ETs are being intensively studied to elucidate mechanisms in photocatalysis and electrocatalysis, where charge transfer or redox processes play a fundamental role. However, currently, only a few studies have directly addressed the influence of ETs on the course of thermally initiated reactions. Thus, even in this type of reaction, the basic reaction step is also a charge transfer or redox process, and therefore, it is essential to consider the influence of ETs on its course. The ETs' depth, density, location, and release kinetics govern how charge is captured and released to active sites, thereby setting activity, selectivity, and stability across oxides, metal oxide perimeters, and porous frameworks. This review was therefore created to summarise basic knowledge about the existence of ETs, the most common methods of their study, and, in particular, significant works in the field of thermally initiated heterogeneous catalysis that address the influence of ETs on their mechanism. For brevity, the case studies were limited to reactions related to CO₂ hydrogenation, which is currently the focus of many researchers seeking to reduce the emissions of this greenhouse gas. Evidently, from these examples, quantification has certain limitations, as individual probes capture only a slice of the trap landscape. Even though trap populations evolve under realistic temperature, pressure, and gas conditions, they are often inferred from *ex situ* measurements because the applicability and fidelity of *operando* methods are limited. Researchers are also uncertain about surface physics at perimeters and subsurface domains, where vacancies and small polarons can either accelerate chemistry or act as recombination sinks, depending on the conditions. There are also limitations to design-based approaches, which can lead to defects if the appropriate trap energetics are not prescribed at the relevant sites. The above overview of selected critical complementary approaches provides an integrated description of ET properties, including the energy-resolved distribution, thermal release and kinetics, recombination, and lifetime; these properties allow the presence of a trap to be translated into quantitative, comparable descriptors that align with catalytic metrics and help realize this complex task. Studying the CO₂ hydrogenation reaction leads to the revelation of certain advantages associated with its mechanism, as typical catalysts for this reaction represent calibrated ensembles of shallow and deep traps that tune activation barriers and hydrogen-assisted steps. Future research can focus on establishing measurement standards to calibrate energy scales and determine the absolute released charge. This approach can also report depth, density, spatial distribution, and release kinetics alongside rates/selectivity. Another significant problem is the development of *operando*, interface-aware analytics, which combine time-resolved, gas-switching spectroscopies with microkinetics to track trap formation and annihilation, as well as polaron hopping. These priorities can provide a new direction for future research in the domain of controlled defect engineering and are beneficial not only for predictable improvements but also in the field of thermally initiated heterogeneous catalysis and CO₂ hydrogenation.

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