



Review

# Metal oxides and their roles in heterogeneous catalysis: special emphasis on synthesis protocols, intrinsic properties, and their influence in transfer hydrogenation reactions

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Received: 28 February 2023 / Accepted: 14 June 2023

Published online: 21 June 2023

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## Abstract

This review emphasizes La-based metal oxides of the perovskite form and their application in heterogeneous catalytic transfer hydrogenation (CTH) reactions from year 2013. Perovskites are potential alternatives to noble metals. The possibility of induced-synergy between two cations in the  $ABO_3$  or multicationic perovskites makes them attractive for hydrogenation reactions. Herein, we look at recent developments in their synthesis protocols, and how the various physicochemical properties derived from the individual synthesis protocols affect the catalytic performances of perovskite oxides in transfer hydrogenation reactions. Furthermore, we review different type of perovskite-based catalysts and the mechanisms of the surface catalyzed transfer hydrogenation reactions.

**Keywords** Perovskites · Transfer hydrogenation · Synergistic effect · Heterogeneous catalysis

## 1 Introduction

Numerous catalysts with various mechanisms of action have been developed to optimise and catalyze the rapid development of the chemical industry in the twenty-first century. This review focuses on heterogeneous surface catalysis, mainly with the use of metal-oxides, with emphasis on La-based perovskites, due to their relevance in heterogeneous catalytic transfer hydrogenation reactions. Generally, hydrogenation reactions are carried out using platinum group metals (PGMs) such as iridium, ruthenium, platinum, palladium, osmium and rhodium. It is important to mention that noble metals have their own limitations too. These limitations include scarcity that leads to high cost, and susceptibility to sulphur poisoning. Therefore, it

is vital to explore alternative noble-metal free catalysts to circumvent these challenges.

We focus mostly on catalytic transfer hydrogenation reaction due to its widespread application in modern catalytic technologies. This chemical conversion route is based on the reduction of unsaturated organic compounds in the presence of catalysts and hydrogen donors that generate hydrogen in-situ [8–10]. The in-situ production of hydrogen solves the handling, safety, and diffusion issues associated with molecular hydrogen. The reaction is also atom efficient because the sacrificial alcohol acts as both the solvent and the hydrogen donor. Overall, the catalytic transfer hydrogenation reactions are cheaper and easy to handle with reduced cost of transportation and storage. However, there are minor challenges that are often encountered in the transfer hydrogenation process. The

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most formidable obstacle in carrying out transfer hydrogenation processes is achieving high product yields without forming any pollutants or by-products and without using toxic solvents that are harmful to the environment.

The byproducts produced in catalytic hydrogenation reactions include partially hydrogenated substrates, esters, acetyls, chlorinated organic compounds, such as HCl, volatile organic compounds common with the hydrogenation of aldehydes, nitrous oxides and generation of heavy metal containing waste [1, 23, 99, 105]. As such, the development of sustainable, green, cost- and time-effective chemical reactions that significantly contribute to reducing contaminants of the environment is imperative. The green chemical principles accomplished by CTH reactions include atom economy as the hydrogen utilized comes from a donor molecule that is then converted to a value-added chemical, use of catalytic systems that can be recovered when the reaction is complete and reduce the need for excessive agents, and renewable and non-toxic solvents are usually utilized [99, 173]. Simultaneously, developments to establish synthetic routes that convert produced pollutants into less hazardous compounds or vaporizing the by-products are progressing [150, 151]. These involve converting abundant pollutants (such as CO<sub>2</sub>) into value-added chemicals and utilisation of bio-derived materials as starting materials instead of potentially hazardous substances.

There are numerous catalysts that have been utilised to make catalytic reactions faster and more atom efficient. These include palladium on carbon, Raney catalysts, ruthenium, rhodium and platinum on carbon. These diverse catalysts have diverse benefits for different substrates offering varying reactivity and selectivity under different conditions [71, 103, 187]. For the purposes of this review, only mixed metal oxides and perovskites will be discussed further as viable substitutes of noble and expensive metal catalysts. Various mixed metal-oxides such as perovskites, cobalt-, ferrous- and ferric oxide catalysts are currently used in chemical industry. This is attributed to their controllable physicochemical properties which offer the ability to evaluate and deduce the relationship between the surface and bulk properties of the catalyst with its activity [123]. Perovskites found relevance in many reactions and different studies due to their tuneable structures. Since the evolution of nanoscience, several approaches to improve catalytic reactions were developed, driving perovskite materials into a new golden age [128, 160]. Various noble and non-noble metals are incorporated into the structures of perovskites, giving versatile perovskite-based catalysts [122]. Perovskites have unique properties that potentially enhance the performance and selectivity of the catalysts. Physical properties such as electric, magnetic, and optical characteristics, and the effect of the electronic properties

and electronic substitutions on catalysis with perovskites will be discussed in this review.

There are many types of perovskites discussed in literature for various applications, such as, BaMO<sub>3</sub>; (M = Ti, Zr, and Cu), bismuth-based perovskites, alkaline metal halide oxide perovskites and organic metal halide perovskites [11, 27, 61, 119]. These show remarkable advantages in catalysis and other fields. However, we will establish emphasis on La-based perovskites and their derivatives. La-based perovskites are the most used perovskites because they demonstrate remarkable catalytic performances in different reactions [66, 133, 184]. Recent advances in La-based perovskite catalytic systems will be discussed for reactions involved in the catalytic transfer hydrogenations of unsaturated organic compounds.

Overall, this literature review aims to provide a comprehensive overview of the significance of metal oxide catalysis, with focus on transition metal oxides, porous metal oxides and mostly perovskites. The subsequent discussions will emphasize more on the applications of the perovskites in catalysis, particularly in catalytic transfer hydrogenations. Furthermore, a sections will explore the other catalysts capable of catalyzing CTH reactions. This will all be done with the goal of enhancing the understanding of their roles and potential in advancing chemical reactions.

## 1.1 Metal-oxide catalysts

Metal-oxides are chemical species with metal-oxygen bonds as the building blocks of repeating units. They are of transition metal- or main group-oxides, depending on the type of metals used. Suitable surface, morphological, and solid-state properties of the metal oxides catalysts drive necessities and prerequisites in completing complex heterogeneous catalytic reactions [123]. Therefore, it is important to cautiously study the associations and links between the structural properties and the activity of the metal oxide catalysts to develop vastly "green", stable, active, and selective catalysts. There are various types of metal oxides and all of them have different structural makeup and properties.

### 1.1.1 Transition metal-oxides

Transition metal oxides (TMO) are used extensively as heterogeneous catalysts and grouped according to their physicochemical traits. The most important property is the stability, which is governed by the integrity of the metal oxidation states. For this reason, chromium (Cr), titanium (Ti), manganese (Mn), vanadium (V), zinc (Zn), and aluminium (Al) oxides with stable high oxidation states as well as those derived from metals such as iron (Fe), nickel (Ni), cobalt (Co) and lead (Pb) which produce oxides possessing

intermediate stability, are the most used in catalysis. On the other hand, unstable oxides are used mostly as nanoparticles or other forms as they do not perform as stable bulk oxides under moderate temperatures. These include ruthenium (Ru), platinum (Pt), silver (Ag), palladium (Pd) and gold (Au) oxides [125].

It is known that noble metal catalysts have better activity than metal-oxides counterparts. Metal-oxides have been applied vastly in catalysis because they are more resistant to poisoning. Electrical conductivity distinguish metal-oxides since non-conducting materials have less freedom of electron movement, hence their poor catalytic capabilities. A compelling example of these is the n-type oxides that are not catalytically active in oxidation reactions. Some of the less conducting oxides are used as supports for the fabrication of other noble metal containing catalysts [125]. Metal oxides may be classified into single or mixed oxides, based on the number of metal cations in their structure.

**1.1.1.1 Classification of transition metal-oxides** Single metal oxides are referred to as binary oxides because they constitute one cation, for example transition metal and oxygen anion bonded together to form an oxide compound. They are the simplest form of oxides. Binary oxides that have a ratio of different cations of the same atom with different oxidation states in their structures are called spinel oxides [20]. Some of these are used as catalysts in oxidation, ammoxidation, and reduction reactions [109]. Single metal-oxides containing a transition metal have numerous catalytic applications because of their multiple valence states and flexibility in redox reactions [163]. Additionally, they are inexpensive and readily available, making them economically friendly and viable substitutes in a number of applications than their precious metal counterparts.

Apart from the general positive traits of the oxide materials, single metal-oxides do have limitations when utilised in catalysis. These include the low catalytic activity as compared to precious metals [163]. The other limitation arise when metal oxides are in their non-porous form because they only interact with molecules only at their exterior surface and not making use of the interior atoms. This served as a motivation to rather use porous oxides that can utilise the materials' interior surfaces increasing the collision frequency of the molecules within the porous network and hence, improved activity.

**1.1.1.2 Porous metal-oxides** Porous metal oxides can be classified into three categories, that is, microporous (pore diameter less than 2 nm), mesoporous (diameter between 2 and 50 nm), and macroporous materials (diameter above 50 nm) [163]. Most heterogeneous reactions

depend on the availability of exposed active sites on the surface of the catalytic material. Therefore, micro- and mesopores increase the material surface area while the macropores are important for transporting molecules [95, 159]. The study of porous oxides can be traced back to the mid-twentieth century. However, full characterization of these materials was not possible at the time due to lack of effective techniques, leading to some of their physical and chemical properties not being fully explored. Consequently, the development of the porous materials has recently caught the attention of scientists in order to utilize them to their full potential, especially in catalysis.

Most of the porous oxide materials synthesized at the time of their discovery had mass transfer limitations and disordered porous network. For example, Corma et al. reported that microporous and mesoporous sieves limited the transfer of reactants through the pillared clays as they had rectangular and incompletely opened pores [31]. Studies were then conducted to resolve these limitations and optimise the use of porous oxide catalytic materials [38, 79, 135]. In the year 1992, the use of mesoporous structured oxides was launched, discovering Mobil Composition of Matter No. 41 (MCM-41) at Mobil company [144]. This is an ordered mesoporous silica material composed of hexagonal-ordered cylindrical pores [15]. Three years later, Santa Barbara Amorphous material (SBA-15), a three-dimensional porous material, was synthesized [60, 182]. SBA-15 has since been used extensively in catalysis as either a catalyst supports or a templating agent for the synthesis of other metal-oxide catalysts.

**1.1.1.3 Mesoporous metal-oxides** The attention towards mesoporous materials with periodic and ordered pore arrangements has increased, especially in heterogeneous catalysis, owing to their unique properties. These materials are effective as catalysts and catalyst supports in many catalytic reactions due to their robust thermal stability, high surface areas, and large pore volumes [163]. A number of studies on the use of porous oxide materials in different applications, especially catalysis have been reported [98, 120, 124, 167]. For instance, Wang et al. reported the combustion of toluene using mesoporous spherical and cubic  $\text{LaMnO}_3$ . The cubic perovskites were more active obtaining 90% conversion at a minimal temperature of 110 °C [167]. This is complemented by the ordered porous materials' ability to implore exceptional mass diffusion properties, solid-gas exchange if it possesses small pores and high flow rates if with larger pores, especially with porous oxides in the meso-range. High product selectivity is also an important advantage offered by use of porous oxides as catalysts. This is achieved by either control-

ling the contact and progression of the reactants or regulating the reaction molecules' contact time.

Ordered and periodic porosity in metal oxide materials is introduced into catalysts using different synthetic strategies. The most frequently used methods are the template synthetic methods. The soft templating strategy makes use of templates such as surfactants, while the hard templating method involves the use of pre-synthesised mesoporous materials such as polymers, silica, and well-ordered carbon [77, 139, 148, 177]. Biological materials are also used as soft templating agents for the synthesis of metal oxide materials. Amongst the mesoporous materials, Shen et al. [139] proved KIT-6 to be the best template compared to SBA-15, FDU-12 and SBA-16. For instance, KIT-6 templated-CeO<sub>2</sub> catalyst displayed superior activity for the oxidation of CO compared to CeO<sub>2</sub> templated by other mesoporous silica materials. Additionally, KIT-6 templated-CeO<sub>2</sub> catalyst was determined to have a large surface area as compared to SBA-15 [77, 148], FDU-12 and SBA-16-templated CeO<sub>2</sub> [177]. The average surface area of the oxide catalyst prepared using KIT-6 as a template was found to have a surface area of 852 m<sup>2</sup>/g, while an average surface area of 50–140 m<sup>2</sup>/g was measured for the SBA-15 templated oxide catalyst.

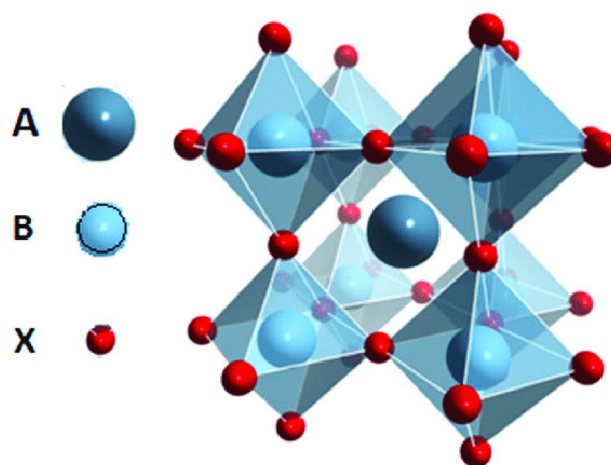
**1.1.1.4 Mesoporous mixed-metal oxides** On the other hand, mixed-metal oxides have advanced properties due to the presence of more than one metal cation in their structure. These mixed-metal oxides include spinel structures based on 3d transition metals that have robust thermal stability and that are effective in catalytic reactions. Due to their versatile properties, they are utilized in a wide range of applications in various scientific disciplines. These have a general formula given by AB<sub>2</sub>O<sub>4</sub>, where the A site is for bivalent cations and the B site for trivalent cations [25]. This review, however, will focus not on these types of mixed oxides with the formula AB<sub>2</sub>O<sub>4</sub>, but rather on the perovskite structures with the ABO<sub>3</sub> formula. The addition of cations to the oxide structure affects the oxides' electronic structure, directly impacting its catalytic efficiency. An example that portrays this, is the study that was recently conducted, where different cations were tuned for perovskites to increase their electronic and physical properties. The A site cations were varied between methyl ammonium, formamidinium and cesium ions, whereas, the B-site cations were tailored between Sn<sup>2+</sup>, Ge<sup>2+</sup> and Pb<sup>2+</sup> [72]. These metals showed remarkable effects that were suitable for different reactions, showing the versatility and adaptability of perovskites.

## 1.2 Perovskite oxides catalysts

Perovskites are mixed-metal oxide catalysts with the general formula ABO<sub>3</sub>, a cubic lattice structure when ideal from the *Pm3m* space group and a tolerance factor of 1 [133]. The ideal cubic structure has the A cations located in the edges, whilst the B cations are at the center and oxygen anions in the middle of the edges [133]. Calcium titanate (CaTiO<sub>3</sub>) was the first combined oxide to be discovered with the ABO<sub>3</sub> formula and was named a perovskite, derived from the name of the discoverer, Lev Perovski in the nineteenth century [65]. The A site cation is usually rare earth metals; however, these can be modified to make the catalyst more efficient by partial substitutions [100, 176]. The B sites are usually transition metal cations with alternating oxidation states [22]. The general structure of the perovskite consists of A and B cations and X anions arranged in an octahedral, corner sharing arrangement. The general formula of the most studied perovskite is ABX<sub>3</sub> with a lattice occupying the corner of the lattice. The B cation is usually at the center of the octahedral cage and the X anion is usually on the face centered positions of the lattice (see Fig. 1). There are different ways of arrangement of the lattice structures which then results in a variety of perovskites with different chemical properties. The various oxidation states of the transition metals make perovskites to possess interesting properties.

### 1.2.1 Properties of perovskites

The ability of various materials to catalyze reactions is dependent on the properties the materials possess. These are properties such as electronic, steric, and magnetic properties. The multiplicity of oxidation states in the



**Fig. 1** Diagrammatic representation of the structure of perovskites [171]



perovskite structures is the major property responsible for their catalytic activity [78, 169, 170]. However, the contribution of other important characteristics such as redox, acid–base, electron mobility, magnetic properties, and superconductivity to the catalytic activity of perovskites cannot be ignored [123, 130, 133]. Moreover, their pyro-, ferro-, thermo- and *piezo*-electricity give them vast applications [169]. Additionally, they have the *pseudo* capacity for anion intercalation and oxygen ion diffusion in devices like fuel cells that are oxide-based [65]. For these reasons, there are over a thousand papers in the literature that discuss synthesis, applications, modifications, mechanisms of action and structure clarifications of these materials.

### 1.2.2 Synthesis of perovskites

Synthesis procedures involving low temperatures often result in lower surface areas of the as-synthesised materials compared to those prepared at higher temperatures. For this reason, chemical synthetic methods such as the sol–gel synthesis [80], polymerizable complexations [153], co-spraying, freeze-drying [90], and spray-drying [67], are often preferred more recently as compared to the solid-state reactions used in the twentieth century that produced materials possessing small surface area of approximately  $30 \text{ m}^2\text{-g}^{-1}$  [78]. Later in the twentieth century, an improved solid reaction route that produce perovskites with higher surface area was developed. However, the limitations of this improved solid state method is that it was time-consuming [140]. Moreover, this method was not as “green” as the solution chemistry methods used for perovskites’ synthesis. As a result, the majority of twenty-first-century studies still use solution chemistry methods for the synthesis of the perovskites. However, it was necessary to note that the ratios of solvents and parameters used in the synthesis were crucial for the synthesised material’s catalytic properties as discussed in the next section.

**1.2.2.1 Solid state synthesis route** Compounds with different crystalline symmetries but having the same chemical formulations may be formed depending on the procedure followed to synthesise them. The ceramic route, solid-state synthesis, was the first developed technique for the synthesis of perovskites where oxides or carbonates were subjected to heat treatments. These materials, however, had poor properties, for example, the low surface area and grain growth, which negatively affected their activity in catalysis and left room for improvement [134]. As a result, in the 1980s, solution-mediated methods were developed, such as coprecipitation, sol–gel, and complexation synthesis.

These methods involve dissolving precursors in a liquid media, followed by drying and calcination. These generally

reduced the temperature required for the synthesis, thus reducing the surface area and grain growth. Homogeneity is one of the advantages offered by the solution mediated methods used for perovskite synthesis. Another method used is mechano-synthesis, where high energy milling is employed at room temperature for the synthesis of perovskite and perovskite-like materials. This method has been patented by Kiliaguine et al. [133].

One of the first perovskites synthesized by the high-energy milling method is  $\text{LaMnO}_3$  [181]. The milling method is energy-saving and allows material sizes to be kept in the nano-size range. However, high-energy milling requires a longer reaction time and is, therefore, time-consuming. The use of additives was also incorporated into this technique to increase surface area. However, the time required for the milling process was still long. In addition, leaching challenges reduced its chances of being commercialised [133]. To eliminate the leaching process associated with mechano-synthetic method and increase the final product’s surface area, Alamdari et al. [2] proposed a modified mechano-synthesis method for the preparation of perovskites. The process involved both the ceramic and milling routes. The modified route has since received a lot of attention as it reduced the many milling hours to 2 h.

**1.2.2.2 Solution state synthesis routes** On the other hand, perovskites were synthesized from rare earth hexagonal (*h*) mixed oxides, such as  $\text{RMnO}_3$  using high-pressure systems. However, for some *h* systems, it was not possible to achieve the desired perovskites [183]. Furthermore, with an increase in perovskites’ applications over the years, the coprecipitation and sol–gel methods for synthesising perovskites were developed and extensively applied. These methods are discussed in the next sections.

**1.2.2.3 Coprecipitation and Sol–gel methods for perovskite synthesis** Coprecipitation involves more than one compound precipitating out of the solution. One of the compounds is usually soluble under the conditions of the reaction, but is carried down by the precipitate, that is, soluble materials may be coprecipitated by being carried together with the insoluble substance. Different parameters and precursors are used for the synthesis of perovskite as stated in the literature. Subsequently, with coprecipitation, the sintering challenge associated with distorted tetragonal perovskites was solved [39, 184]. Coprecipitation gives highly sinterable lead titanate powders of different composition using the coprecipitation of oxalates of different cations in ethanol solution. The metal precursors used are oxides and carbonates of lead, manganese, cobalt and tungsten for the B site cations. For the A site cations precursors of Ca, La, Nd, Sm and Gd nitrates are utilised. The first step to the coprecipitation method

involves the blending of the B-site precursors with oxalic acid and dilute ethanol. Thereafter, the A site precursors are dissolved in ethanol together with tertiary butoxide. The A site cation would react with the formed precipitate to form metal hydroxides which then react with oxalic acid to form basic oxalate. The coprecipitation is achieved by adding ammonia to the solution. Thereafter, calcination and sintering would give the desired products.

On the other hand, the sol–gel method has gained popularity in literature not only for perovskites but also for the synthesis of other various solid materials. For perovskites, the cation stoichiometric ratios should be regulated, specifically depending on the target structure. Different calcination temperatures play a role on the outcome of the final materials [51, 149]. The calcination step is carried out to remove residual carbonates from the obtained final product [145]. The citrate sol–gel process has been investigated for the synthesis of porous perovskites. The citric acid allows for the formation of acid complexes that aid with the dispersion of the metal, forming amorphous metallic organates with an extensive variability of composition. This was demonstrated in a recent study by Nzuzo et al. where high surface area perovskites where a chelating agent, citric acid and precursor solution made up of water and metal nitrates, were mixed together prior to adding ethylene glycol. The gel was then acquired through heating cycles at 120 °C and calcination at 180 to 680 °C. Perovskites of up to 28.5 m<sup>2</sup>/g were made. The perovskites had orthorhombic, cubic and hexagonal crystal systems depending on the type of A and B cation used [116].

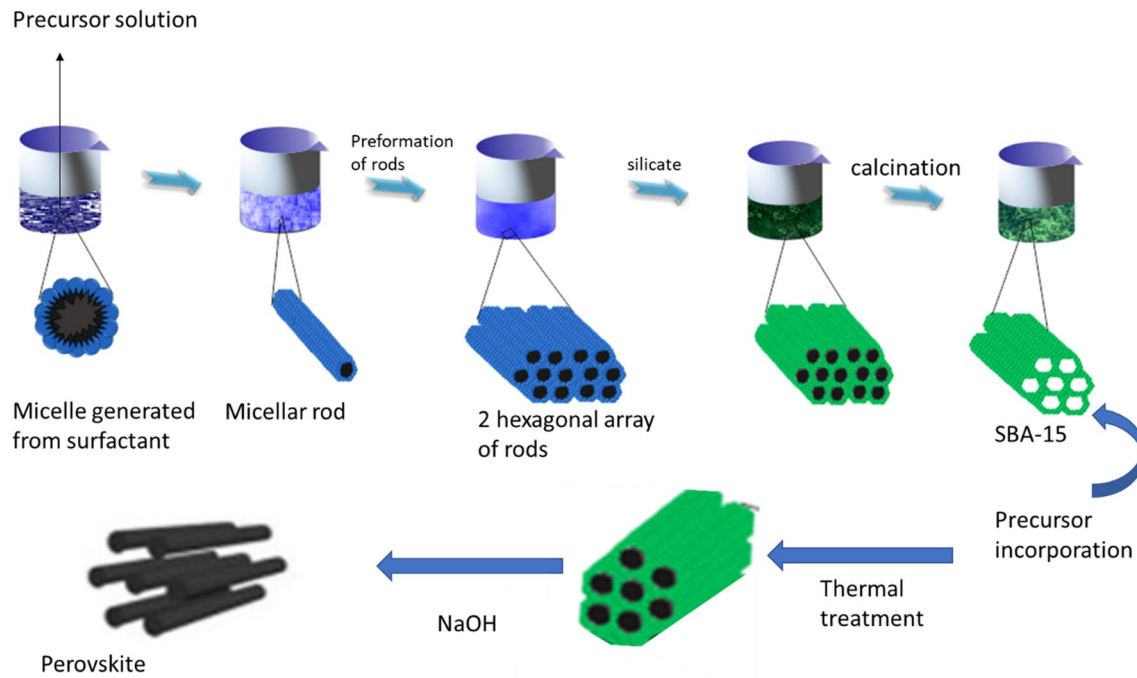
Highly ordered and homogenous metal-oxides such as perovskites are achieved from organates through thermal decomposition at low calcination temperatures [184]. The process renders the surface areas of these materials to be high, hence more favourable [73]. In some studies, low calcination temperatures are preferred when using the co-precipitation method. In contrast, solvent evaporation is increased using the freeze-drying process [89]. Recently, the in-situ carbon templating method has been developed to synthesise perovskites with high surface areas compared to those obtained from the sol–gel method. For instance, Ping et al. discovered the novel in-situ carbon templating method to prepare porous LaFeO<sub>3</sub> catalysts with high surface areas than those obtained when using the traditional methods [173]. Colloidal crystal templating is another potential method that aids in synthesising perovskites with high surface areas [166].

**1.2.2.4 The nanocasting route to mesoporous perovskites** Nanocasting is one of the procedures used to synthesise mesoporous catalysts because it results in well-defined porous structures. Over the last decades, nanocasting has been used in different applications [37,

39]. This motivated the urge to explore the synthesis of mesostructured perovskites using the nanocasting method. Because materials obtained using the nanocasting method have ordered and systemized porosity in the meso-range, nanocasting is perceived as one of the powerful synthetic routes for various metal oxide materials. Different templates, such as porous silica, graphene, and carbon are used in nanocasting. However, mesostructured silica materials such as Vinyl silica [168], or KIT-6 [164], are mostly preferred because of their remarkable properties, such as high surface area and large pore sizes. The final perovskite or metal oxide structure is a replica of the pores of the template, thus producing perovskites or metal oxides of rod-like nature that are interconnected, see Scheme 1. Wang et al. are the first group to utilise mesostructured silica as hard-templates to synthesise LaFe<sub>x</sub>Co<sub>1-x</sub>O<sub>3</sub> and LaCoO<sub>3</sub> perovskites with mesoporous pores for methane combustion [168]. To date, a few studies have been published on the use of nanocasting technique [16, 112, 165].

The procedure involves the synthesis of the template itself before permeating the precursors previously complexed with citric acid into its pores, as shown in Scheme 1. Subsequently, the composite is subjected to heat treatments to crystallize the perovskite. An alkaline solution (such as NaOH or KOH) of high concentration is used to remove the silica template, leaving imprinted new pores on the perovskite material. Materials exceeding a surface area of 100 m<sup>2</sup>/g and reaching 270 m<sup>2</sup>/g are obtained when low-temperature heat treatments are used. The stability of nanocasted materials is exceptional [16, 111, 112]. However, the hard-template process is exceedingly expensive due to the use of a silica template and requires careful considerations with issues regarding waste and environment management. Consequently, nanocasting method is ideal for highly valued products if economic factors are to be considered.

The nanocasting method's effectiveness is portrayed in a catalytic study done using LaCoO<sub>3</sub> by Wang et al. [168]. The nanocasted material has high thermal stability, thus effective in the combustion of natural gas. The nanocasted materials had high BET surface areas of greater than 96.7 m<sup>2</sup>/g, contributing to high catalytic activity than the LaCoO<sub>3</sub> counterparts synthesized using the standard citrate method. However, a significant reduction of surface area (from 96.7 to 27.2 m<sup>2</sup>/g) was observed after one reaction cycle. This was attributed to the restructuring of the perovskite physical structure. In a different study by Nair et al. three different perovskites were synthesized using the hard-template method using ordered mesoporous silica (KIT-6) as a templating agent [111]. The obtained final materials had high surface areas (110–155 m<sup>2</sup>/g) than those reported by Wang et al. These materials displayed



**Scheme 1** Nanocasting of perovskites using SBA-15 as a template [99]

higher conversions, which reinforces that the material's surface area is one of the factors that governs nanocasted perovskites' catalytic activity. In addition, there was a minimal reduction of the surface area of the materials during recyclability tests by at most 15 m<sup>2</sup>/g. Table 1 summarizes the widely applied synthesis conditions for each protocol used in fabrication of metal oxides of the perovskite form. The table also gives surface areas and set-back associated with the reported synthesis protocols.

### 1.2.3 Lanthanum-based perovskites and mode of catalysis

Lanthanum based perovskites have attracted a lot of attention in the literature [7, 117, 133]. La in perovskite lattice is

usually located at the A site of the material with transition metals at the B-sites. The B-sites can either induce oxygen vacancies through partial substitution, thus making the resultant perovskite suitable for oxidation reactions or precursors for nanosized catalyst preparation suitable for hydrogenation reactions. The interest in La-based perovskites is attributed to the fact that the perovskite is constantly reduced or oxidised under controlled conditions in redox reactions. The structural integrity of the catalysts depends on the metal on the A site. This is because the B metal will remain dispersed on a matrix of the A<sub>2</sub>O<sub>3</sub> oxides. La has proven to be the most stable compared to other A site cations such as Sr, Ca, Pr, Nd, Sm, and Gd. Due to their high catalytic activities, Mn, Fe, Co, and Ni have been

**Table 1** Summary of synthesis procedures, surface areas, and conditions of synthesis of metal oxides of the perovskite form

Synthesis procedure	Surface area (m <sup>2</sup> /g)	Conditions of synthesis	Setback	References
Energy milling	–	Room temperature milling Calcination at 500–700 for 8 h	Time-consuming	[179]
Hydrothermal	32.5	Heating at 160 for 15 h	Low surface area, time-consuming	[93]
Co-precipitation	14.6	Calcination at 700 for 3 h	Low surface area	[129]
Sol-gel	14	Calcination at 500–700 for 4–6 h	Low surface area	[81]
	15			[141]
Carbon templating	179	Calcination at 700 for 4 h	Adds extra cost	[173]
Nanocasting	135	Calcination at 500–700 for 4 h	The template adds extra costs Sometimes difficult to fully remove	[16]

extensively used at the B site [122]. The Mn and Co have been proven to be the best transition metals for carbon monoxide and hydrocarbons' oxidation reactions catalyzed by La-containing perovskites [78]. Some precious metals like Pd and Pt are also used in small quantities [16]. The incorporation of these metals is done to bring unique catalytic properties to the La-containing perovskites that are not observed when cheaper and abundant transition metal cations are used.

Like all the other perovskites, La-based perovskites have the B site cations having primary roles towards catalytic activity whilst the A site is secondary. The reduction profiles of the La-containing perovskites are mostly due to the B cation, proving that it governs the material's redox catalytic properties [32, 47]. The B cations bind to oxygen in two ways; either in bulk or on the surface. Hence desorption studies ( $O_2$ -TPD) have been used to investigate the movement of oxygen in their lattice structures. The surface oxygen is usually weakly bound, and as such, it easily desorbs at a lower temperature, whereas the bulk-bound oxygen requires higher temperatures [184]. This are some of the indicators of the stability and properties of the La-based perovskites.

The interlink comprehension between solid-state and catalytic properties is essential to acquiring the most effective perovskite for any catalytic reaction. Fiero et al. has emphasized the surface structure effects on catalytic activity [42]. However, it is important to note that the exterior structure also depends on its composition, therefore, affecting its absorption properties and catalytic efficiencies. It is also important to note that perovskites tend to experience saturation in gas reactions because of loss of coordination and symmetry of the A and B sites which mask the adsorption of reactants on the surface of the

catalyst, thus affecting catalytic properties of the La-based perovskite materials [42]. Therefore, for easy determination of the interlink between the two factors, stated above, knowledge about the material's reaction mechanism is important.

#### 1.2.4 General application and mechanism of action of perovskites in catalysis

The perovskites' catalytic mechanism can interlink the solid-state and catalytic properties. The B site metals are placed at relatively large distances from each other; therefore, the substrate can only interact with one site at a time. The perovskites either catalyse the reaction intra-facially or supra-facially. In the intra-facial processes, the catalyst is used up partially in the reaction as a reagent and regenerated at the end, whereas supra-facial mode involves the reaction of the substrates on the surface of the catalyst (Fig. 2).

For the supra-facial processes to occur, there must be vacant d-orbitals of correct symmetry in the perovskite catalyst. This is the reason why more often than not, transition metals occupy the catalytically active B-site [22, 24, 174]. Overall, perovskites' catalytic mechanism is demonstrated to be governed by the electron occupancy on the  $e_g$  orbital. When close to unity, the intrinsic oxygen reduction or evolution reaction activity for  $LaBO_3$  (where B = transition metals) are optimized. However, the full mechanism has not been fully understood.

Overall, perovskite materials can undergo both A and B site substitutions without altering their crystal structures. However, they encounter some structural defects such as anionic or cationic vacancies which are due to lower valence substitutions on the A site. The electroneutrality

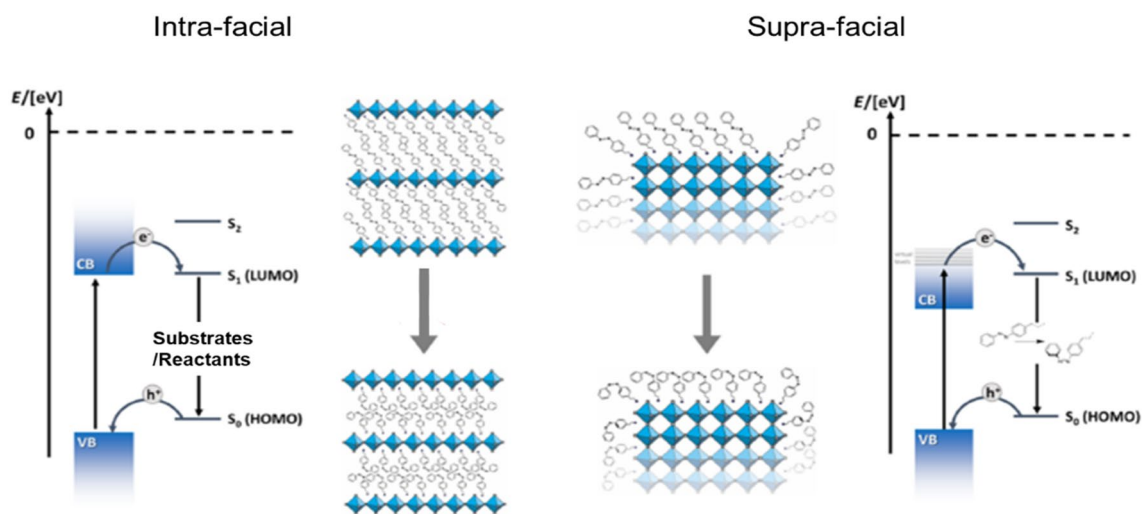


Fig. 2 The (a) supra-facial and (b) intra-facial catalysis by perovskites [43]



of the compound is preserved by adjusting the B cation's oxidation state [117]. It has been proven that vast amounts of accessible oxygens are generated by the redox process and at minimal temperatures when the oxidation states of the B cation are higher. Furthermore, the perovskite becomes more catalytically active in oxidation reactions due to increased oxygen mobility.

Concisely, perovskites are considered potential candidates for substituting noble metal-based catalysts for extensive research in the catalysis field. Up to 90% of the metal elements in the periodic table may be used to substitute either the A or the B site of the perovskites. Thus, perovskites are tailored to meet the requirements of different reactions. However, various opportunities are explored for the development of hybrid catalysts by using the associations between various noble metals and perovskites in small quantities. This aids in reducing the costs of different reactions catalysed by perovskites, making them economically viable. This was emphasised clearly in one of the publications by Misino [107]. Therefore, these advancements in perovskite developments are in line with the requirements sustainable and green technologies.

**1.2.4.1 Stability of perovskite oxides** Perovskites are extremely stable, thermally and chemically, which makes them suitable candidates for heterogeneous catalytic reactions. By simply varying the methods in which perovskites are prepared, numerous crystal phase symmetries are acquired. This includes structures such as tetrahedral, orthorhombic, monoclinic, and triclinic [78]. The stability of the perovskite is determined by the Goldschmidt's tolerance factor. It is noteworthy to mention that, irrespective of the chosen method, the Goldschmidt tolerance factor should lie between 0.75 and 1 for the perovskite structure to be stable [52]. The Goldschmidt tolerance factor is given by Eq. 1

$$t = \frac{r_A - r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

where  $r_A$ ,  $r_B$ , and  $r_O$  are the radii of A, B cations and  $O^{2-}$  anion, respectively. Perovskites are potential catalysts for a number of reactions because they are reused in different cycles and reduce the amounts of precious elements from the catalysts without altering their activity and stability. In other words, for perovskites to be stable and active as well as characterized as perovskites, they should meet the required ionic radius determined by the tolerance factor calculations. This property defines the perovskite's symmetry, which in turn affects the dielectric properties associated with the material. When the tolerance factor is greater than 1, the B cation is smaller than A and has free space to move flexibly which reduces the activity and

stability perovskite [110]. Furthermore, Royer et al. state that a hexagonal ilmenite structure is adopted by the perovskites when the  $t$  value goes below 0.75. However, if above 1, a hexagonal symmetry is obtained instead [133].

**1.2.4.2 Overall charge distribution in perovskite oxides** Another condition to be fulfilled for the stability of the perovskites is electroneutrality. Variations of the perovskite's crystal's stability depend on the oxygen content. For example, the A sites are usually coordinated to about 12 oxygen anions, whilst the smaller B sites form octahedral environment with oxygen atoms [78]. The valence state and non-stoichiometry of the cationic sites (A and B) and both anionic and cationic sites, respectively can be controlled using the modifications of the A and B sites based on the electroneutrality factor [170]. Overall, the A site's main function is to induce stability, whereas the B site is considered the primary active site in the perovskite structure [154]. The perovskite's electroneutrality is explained in terms of the cations' total charges in the structure (A and B metal charges) and is equal to that of oxygen anions. For example, the charge arrangement probabilities are  $A^{3+}B^{3+}O_3$ ,  $A^{2+}B^{4+}O_3$  and  $A^{1+}B^{5+}O_3$ .

The electroneutrality allows for partial substitutions at either the A or the B site whilst maintaining the material's overall structure. However, this may result in deformed perovskites due to deficiencies of the oxygen anions and cationic sites. The former case has been reported to be more common. This deficiency is termed the non-stoichiometry in perovskites and is discussed in numerous studies in the literature [143]. To account for the partial substitutions, oxygen excess and deficiency, a more general formula for perovskites is given, that is,  $A_{1-x}A'_x B_{1-x}B'_x O_\delta$ . The  $Ca_2Fe_2O_5$  is one example of defected oxides with one-sixth of oxygen vacancies [143]. For instance, Sayagués et al. [136] published a study where an oxygen anion deficient mixed metal oxide,  $La_2Ni_2O_5$ , was successfully characterized, showing that the integrity of the perovskites is maintained, and its catalytic properties were conserved.

The presence of excess amount of oxygen, than required, in the perovskite structure is not common as the addition of oxygen interstitially into the framework is not thermodynamically prohibited. Nonetheless, some structures exhibit oxygen in excess, especially those that have cation non-stoichiometry. This could be due to A or B site vacancies, though not common. An example of perovskite with cation non-stoichiometry is  $Cu_{0.5}TaO_3$  [123]. Most physical properties linked to the perovskite structure are usually for the non-defected crystal lattices. In most cases, these properties are maintained even with the defected perovskites. Small variations of these physical properties, however, may be observed. Overall, when the electroneutrality and ionic radii requirements have been

met, the synthesized material had a higher probability of being a stable perovskite.

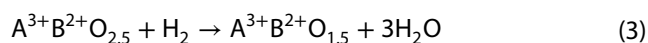
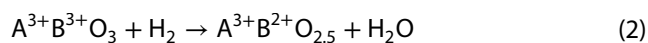
**1.2.4.3 Electron arrangement in perovskite structures** The initial use of perovskites is dated to be in the mid-twentieth century by Parravano et al. [121]. During that time, numerous ferroelectrics were evaluated for carbon monoxide reduction as the reaction involves electron transfer between the gas and solid phases of the catalysts. There was an evaluation to determine if the electron arrangement contributed to this transfer. Results obtained proved this hypothesis true for sodium, potassium niobates and lanthanum ferrites (perovskites), because they had active transition points for the reaction [121]. The vitality of the electronic arrangement and properties of the perovskite in catalysis was further cemented thirteen years later by the study done by Dickens and Whittingham about the use of perovskites in the form of alkali metal tungsten bronzes [36]. In the study, the recombination of oxygen atoms on the surfaces of these bronzes was studied. The perovskites' electronic properties contributed vastly to the catalytic process. In 1970 and 1971, cobalt-based perovskites were found to be perfect substitutes in electrocatalysis processes. While manganate perovskites were found to be excellent candidates for carbon monoxide oxidation [155]. Since then, perovskites have been assessed in different reactions such as oxidation and reduction of hydrocarbons both partially or fully [133], photocatalytic processes [162], hydrogenolysis of hydrocarbons, NO removal [185], electrocatalytic processes [183], and steam reforming of bio-oil [24], all of which are accessible in the literature.

**1.2.4.4 Limitations of perovskites** Despite the versatility of the perovskites, their long-term stability has not been achieved yet, which leaves room for improvement by further exploring the materials. They can be considered as viable substitutes for platinum group metals because they are easy to synthesize, cheap and can be tailored to enhance catalytic capabilities [133]. Although they have not been commercialised in most industrial applications, they are tipped to be potential candidates, especially in automobile exhaust controls [156]. It is, however, noteworthy to mention that these materials are sensitive to sulphur poisoning, which poses limitations to their potential catalytic application in automobile sector. Therefore, studies aimed at understanding the perovskite structure's mechanism are vital because they are the key to unlocking many possibilities in the field of catalysis.

**1.2.4.5 Acid–base properties of perovskite oxides** The evaluation of perovskites' applications indicated a few other properties and parameters that stood out and con-

tributed to the catalytic activity in various reactions. One of these is the redox property of the perovskites. It was noted that the B site of the perovskite is the main contributor to the catalytic activity observed in perovskite materials [78]. Therefore, its nature is crucial depending on the conditions required by the reaction it is intended to catalyze. The A site, on the other hand, does not bring significant changes to the outcomes of the reaction with one exception. When the partial substitution of the A site occurs, it causes a great change in the valency that influences the oxidation state of the B site, which in turn affects the catalytic properties of the overall perovskite material [157]. An example of this is the La-based perovskite, LaFeO<sub>3</sub>, where La and its oxidation state's basicity affects the B site Fe from Fe<sup>4+</sup> to Fe<sup>3+</sup>, resulting in high catalytic conversions.

Redox properties for perovskites can be evaluated using hydrogen temperature-programmed reductions (H<sub>2</sub>-TPR). A number of studies reviewing the redox properties for perovskites have been reported so far. For instance, Futai et al. [47] and Crespin et al. [32] produced similar results explaining the perovskite materials' reduction profile to be in two steps instead of the one step of their normal oxide counterparts. In these studies, it was shown that low-temperature TPR profiles were associated with the formation of an oxygen-deficient perovskite structure, whereas the high-temperature profiles indicated the complete reduction of the B cation to a zero-valent metal nanoparticle. These reduction processes are represented by Eqs. 2 and 3. The equations justify the capabilities of the perovskites to catalyze redox reactions. The position of the reduction peaks vary with calcination temperatures the material is subjected to due to the sintering process, which consequently reduces the average surface area. Similar results were also obtained for Fe-based [127], and Mn-based perovskites with small variations depending on the A site cation associated with the perovskite [127]. The Sr substitution on the A cation site was found to promote reducibility of manganese in Mn-based perovskites [68].



In contrast, perovskites' acid–base properties play a crucial role in numerous catalytic reactions such as hydrogenation reactions. The acid–base properties of perovskites are usually evaluated using desorption or adsorption studies of ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>) [186]. Kuhn et al. reported a study that proved the perovskite material surfaces to exhibit both Lewis acidic and basic sites [83]. The A site's changeover results in a charge balance variation that produce acidic sites. Contrarily,

properties associated with basic sites dependent on the B cation. This deduction differed from that of Natile et al. [113] who showed that either of the two cations (A or/and B) contributes to the material's acidic properties. It was also proven in a study reported by Hammami et al. [59] that the perovskites' surface is not homogenous, leading to different acid/base strengths as shown by their ability to adsorb CO<sub>2</sub>. This adsorption possibility is made possible by oxygen-deficient sites and surface oxygen, while weak basic sites are from either the A or B cation. These parameters are dependent on the synthesis procedure used in the perovskites' preparation and affect the morphology, crystal structure, and texture of the catalytic materials. The higher the specific surface area of the perovskite, the better its catalytic performance. This is attributed to the fact that, as the surface area is increased, there are many redox binding sites for the substrates.

Overall, the acid–base properties of perovskites have not been as vastly explored as their redox properties. However, Lewis acid–base theory allows the application of the metal cations and oxygen anions in the perovskite as acidic and basic centers respectively. This is confirmed by a study done Xiao et al., and is complimented by reviews of other studies conducted [45, 99, 126, 172, 173]. These have proven that acidity of the catalysts plays a crucial role in the conversion and selectivity of the reaction, which is a field worth exploring.

### 1.3 Heterogeneous catalyst supports

Immobilisation of a catalyst increases catalyst's surface area and the catalyst's lifetime and these are the main roles of metal oxides catalytic supports. In addition, immobilization of catalytic species enhance hydrophobicity and lessen the extent of catalyst deactivation associated with sintering process. In that way, the stability of the catalyst is enhanced chemically, thermally, and hydrolytically [104]. Catalytic supports may act as co-catalysts depending on the nature of catalysed reaction, resulting in enhanced catalytic activity. The study carried out by Cooper et al. where the support improved the transportation of oxidant into the solution is a suitable example of how supports play a dual role during the catalytic reaction [30]. Porosity of the support and a reduction in the supported metal catalyst size increase the exposed active surface area of the atoms of the catalyst material. In a study by Chambers et al. it was found that the different pore sizes of silica gave varying selectivities towards cinnamyl alcohol, hydrocinnamaldehyde and phenyl propanol [19]. For instance, the overall catalysts, catalytic species and the support, with average pore sizes of 20 nm had higher selectivity toward cinnamyl alcohol than the 10 nm bimodal pore structure Cu/SiO<sub>2</sub> materials. Therefore, it is prudent to conclude

that the support's textural properties govern a material's chemo-selectivity.

Perovskites are supported on numerous supports such as metal-oxides (alumina, titania, silica to name a few) [13, 21, 54, 131], monoliths [115], zeolites [88], fibers [88], ceramic materials, pillared clay [85], red mud [97], polymers [63] and carbon black for different applications. However, this review focuses mainly on the metal-oxide supports. Silica materials are used in the immobilisation of organometallic complex catalyst [44]. These are thermally stable, porous and have high surface areas. In contrast, zeolites are hydrous aluminium silicate materials that have been used extensively in oxidation and hydrogenation reactions of numerous halogenated organics [96]. These usually confine positively charged ions of sodium (Na<sup>+</sup>), calcium (Ca<sup>2+</sup>), potassium (K<sup>+</sup>), barium (Ba) and strontium (Sr) or consequent synthetic compounds. However, both the zeolites and silica are used less extensively than the metal-oxides supports because their synthesis is time consuming and require expensive reagents to synthesize as compared to other oxides [125]. The different catalysts that the perovskites are supported on will be discussed in the next sections to highlight their physical and chemical synergies to the activity of the catalyst.

#### 1.3.1 Metal-oxides as heterogeneous catalysts supports

For the improved catalytic performance of metal-oxides, modification of their surface by base or noble metal nanoparticles is necessary. These may be on the oxide's external surface or acting as promoters embedded within the oxides' pores [34]. In essence, metal-oxides are often utilised as supports for a noble metal catalyst, especially nanoparticles. Some of the transition metals (non-noble metal) catalysts have limitations such as low activity due to low metal-support interaction and high light-off temperatures (temperatures at which conversion reaches 50%) in catalytic reactions despite their availability and low cost. As a result, modifying their surfaces with noble metals is important in trying to overcome these setbacks.

Most industries have adopted the use of metal oxide support materials, especially in the automotive industry as gas purifiers. Within this instance, the size of the metal oxide-supported noble metal play a crucial role. For example, methane combustion using alumina and zirconia supported-palladium and platinum-based catalysts was investigated by Robert et al. [62] to evaluate the structure sensitivity of the overall catalysts. The materials' size was the governing factor for the turnover frequency (TOF) and activation energy. In a different approach, Yang et al. investigated the performance of Ag, Pd, and Pt nanoparticles supported on three-dimensionally ordered mesoporous (3DOM) ceria and alumina (3DOM CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) for toluene

oxidation. They found that smaller Au particles with homogenous dispersion and uniform porosity of 3DOM  $\text{CeO}_2\text{-Al}_2\text{O}_3$ -support led to the lower activation energy for the toluene oxidation. These observations further confirmed that, indeed catalyst support materials play a major role during a catalytic reaction. Similar observation was reported by Arandiyana et al. [6] during methane combustion catalysed by three-dimensionally ordered macroporous  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  supported-Ag nanoparticles ( $\text{Ag}/3\text{DOM } \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ). It was proven that the diffusion of the substrate was slow on the 3DOM  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  support, which enhanced the contact between the substrate and the  $\text{Ag}/3\text{DOM } \text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  catalyst, hence increasing the catalytic activity. Therefore, it is safe to assume, based on these literature reports, that the promotion of metal-support interaction is one of the key factors for enhanced catalytic performance in metal oxides-supported catalytic species.

Metal-oxide supports show greater metal-support interactions than any other support. This is better revealed in the study conducted by Kwangjin et al. [5], compared to the catalytic performance concerning metal-support interactions using mesoporous  $\text{Co}_3\text{O}_4$ , NiO,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CeO}_2$  as supports for platinum (Pt) nanoparticles in a CO oxidation reaction against mesoporous silica supports. It was found that the metal-oxides supported Pt catalysts were more catalytically active than when supported on mesoporous silica. Furthermore, the  $\text{Co}_3\text{O}_4$  supported catalysts were substantially more catalytically active than the other metal-oxides catalysts because of the oxidation stabilisation and oxygen content of  $\text{Co}^{2+}$  as shown in Fig. 3.

### 1.3.2 Alloying strategy on metal-oxides supports

Periodic and ordered pores in an oxide structure provide stability to the nanoparticles deposited onto its surface and make the accessibility of the active atom sites to the reactants easy [94]. In various reduction and oxidation reactions, porous oxides are used extensively to support noble metal catalysts. The wide use of porous metal oxides is attributed to the confinement of the active site and control of alternative attack pathways which subsequently promote higher selectivity [147]. Supported bimetallic noble metal alloys have better selectivity and activity than mono-metallic counterparts [94]. The alloying strategy is used vastly to produce hybrid-like catalysts on oxide supports, therefore, providing the catalytic material's unique properties.

The alloying strategy is utilized to alter the electronic structure and properties of transition metals (such as Ag, Au, and Cu) catalysts with filled d-orbitals that are not willing to form bonds and are catalytically inactive, making them more catalytically active [101]. The first bimetallic

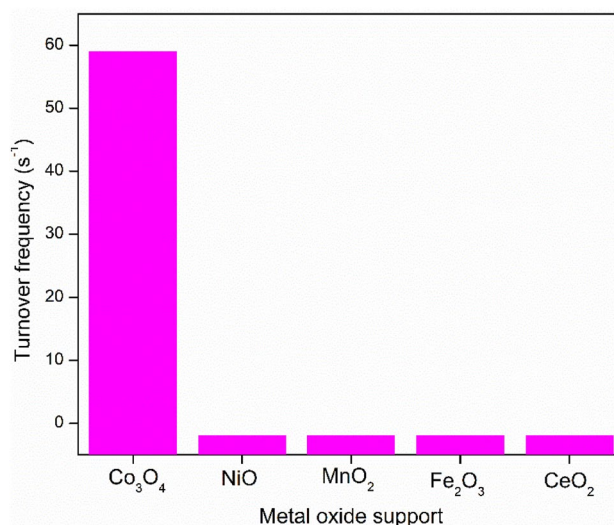


Fig. 3 Approximations of different activities of various metal support as reported by An et al. [5]

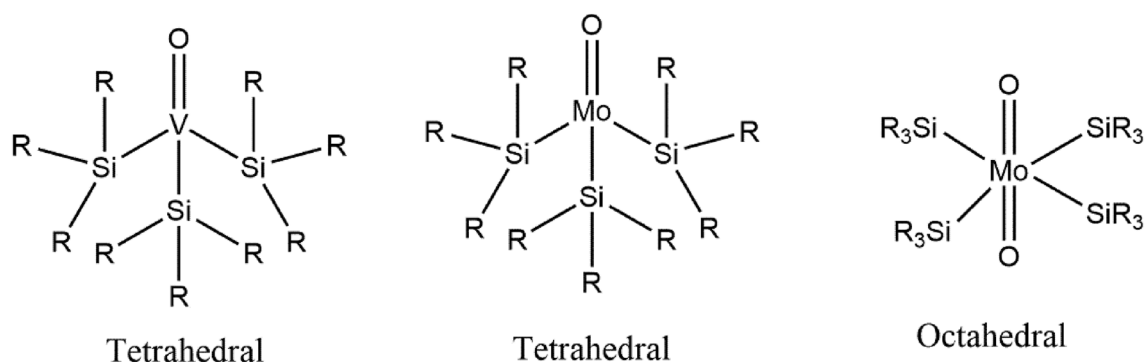
noble metal alloy reported was comprised of Au and Pd catalysts in 1980 which was utilised in hydrogen fuel cells, pollution control, [161] and other various applications [152]. Thereafter, the study on acetoxylation of ethylene to vinyl acetate conducted by Chen et al. over palladium-gold alloy (Pd-Au alloy) catalysts in the year 2005 validated the alloying strategy proof that the formation rate of vinyl acetate was enhanced for non-contiguous and suitable spaced monomer Pd sites than for just single Pd atoms [26]. To date, numerous studies have been reported on bimetallic catalysts supported on metal-oxides with ordered pores and large surface area, thus promoting effective dispersion of the metal alloys on the oxide support's surface.

### 1.3.3 Metal oxides as supports for other metal oxides

Just like metallic nanoparticle catalysts, metal-oxides may too be supported on solid supports. The metal-oxides and the support are bonded via surface hydroxyl groups to form M–O–S bonds [132]. This, however, varies vastly depending on the metal-oxides used. For instance, molybdenum species offer Mo=O on their terminal side and four bridging oxygen to the support while the vanadium species offers three bridging instead, see Fig. 4. In aqueous conditions, the M–O–S bond can be hydrolysed, forming aqueous solutions of the supported oxides. However, some dehydrated species have been used in other studies, and it was found that the structure is conserved during catalytic reactions [14].

Species spread out on dehydrated supported oxides are stabilized through surface functional group interactions such as hydroxyl groups, which control the oxide's





**Fig. 4** Proposed environment of vanadium (V) oxide and manganese on silica supports [33]

monolayer coverage on the support [14]. These are usually isolated or bi-dimensional polymeric species. As Wachs reported, the monolayer coverage of many oxides has been determined to be more than that of silica supports [158]. The interactions amongst the supported oxide materials are directly proportional to the monolayer loading resulting in the formation of M–O–M bonds for polymeric species less pronounced in silica supports. For this reason, supported metal oxides have vast applications in many catalytic reactions [14].

#### 1.4 Immobilised perovskite type oxides catalysts on metal oxide supports

Despite the advantages stated about perovskites as catalysts such as their ability to be tailored, high absorption coefficient, excellency as transport materials, robust stability, and low cost, they are limited by small surface areas, more especially if their porous structures collapse due to harsh reaction conditions [28, 74, 76]. To counteract this problem, the use of supports with large surface areas that expose the perovskites' active sites has been explored [180, 184]. It is, however, still challenging to model an ideal perovskite/support hybrid type catalysts.

Achieving the ideal hybrid catalyst that conserves the perovskite structure upon immobilisation on a support and maximising the perovskite's uniform dispersion is the main goal driving many researchers to explore the preparation and application of these types of catalysts. For this reason, there are numerous studies carried out on metal oxide-supported perovskites catalysts [3, 4]. Attempts are made to immobilize perovskites on silica and alumina by coating the perovskites onto the supports. However, non-active silicate and aluminate materials were formed, therefore, these materials were found to display poor catalytic activity as supported perovskites [108]. Despite the inactivity of silicate and aluminates, silica- and alumina-centred supports are frequently used because they ensure

well-defined perovskites due to the inert characteristics of the supports. According to the discoveries made by Kaliaguine et al. MCM-41 mesopores are highly advantageous for supporting  $\text{LaCoO}_3$  with 10–50 wt% of the perovskites within the pores [114]. When analysing the supported perovskites' physicochemical properties such as surface areas and pore diameters, they are far improved than their unsupported counterparts [102]. However, the supported perovskite materials suffered from the reduction of the MCM-41 support weight ratio of the catalyst. Therefore, ceria and zirconia oxides counterparts are more ideal candidates for this purpose. This is due to the oxygen storing properties associated with the low reduction potential amongst  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  [46, 184]. This was proven when  $\text{LaCoO}_3$  and  $\text{LaFeO}_3$  showed high conversions in the CO oxidation when supported on  $\text{ZrO}_2$  [29]. Even better conversions were obtained when  $\text{LaCoO}_3$  was supported on mixed oxides support,  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ , via wet impregnation method. Overall, it suggested that enhanced oxygen mobility and high active surface area govern the catalytic performance of supported perovskite. The next sections place emphasis on the use of supported and unsupported perovskites as catalysts in catalytic transfer hydrogenations. To do so, catalytic transfer hydrogenation in general will be discussed prior to explaining the advances of perovskites with this type of chemical transformations.

#### 1.5 Catalytic transfer hydrogenations

Hydrogenation reactions involving organic compounds play a crucial role to play both small-scale laboratories and industries. Reduction reactions can be classified into (i) hydrogen addition to unsaturated compounds and (ii) addition of hydrogen across single bonds leading to bond cleavage, known as hydrogenolysis. It can also be the removal of oxygen from organic compounds [75]. This review, however, will solely focus on the hydrogenation reaction aspects of reduction, especially catalytic transfer

hydrogenations (CTH). During the twentieth century, CTH reactions were under-utilized. However, with the progress of research in the twenty-first century, there are advances to explore their use. For example, Braude et al. [17] conducted one of the first CTH reactions using cyclohexane and similar hydroaromatic compounds as hydrogen donors for the reduction of ethylenic and acetylenic bonds in hydrocarbons and carboxylic acids in the year 1954 although it was overlooked due to long reaction times and poor product yields. However, with advances in the modern techniques, the yield and the reaction times are significantly improved and shortened, respectively.

The advantages of CTH reactions are vast as compared using molecular hydrogen. Molecular hydrogen is an easily diffusible gas with low molecular weight, which contacts the catalyst-solvent mixture easily. However, it is easily ignitable and presents hazards, especially in large-scale processes. Moreover, it has low solubility in many solvents. Therefore, high pressures are often required in order to achieve optimum yields and selectivity. This consequently increases the costs associated with the reaction processes, especially when considering large-scale production in industrial setups [49]. The use of bioderived hydrogen-containing molecules as sources of hydrogen for hydrogenation reactions helps reduce these drawbacks and opens an opportunity to control the reaction's selectivity using the hydrogen donor's properties [75].

Consequently, the best hydrogen donors are made of hydrogen-bonded to compounds, groups or elements with similar electronegativities, such as hydrogen itself. Therefore, alcohols, formic acids, hydrazine, hydrides of boron, and hydrocarbons can be utilised as hydrogen donors [49]. The transfer of hydrogen can be through different pathways, for example, the intermolecular hydride transfer which can be swayed in favour of better selectivity control. However, the intermolecular hydrides were overshadowed by the use of molecular hydrogen until a few decades ago. Low yields and reaction rates are also some of the major drawbacks but vast progress has been made in reducing various functional groups such as alkenes, alkynes, carbonyls, nitrous, cyano, and N=N bonds through the CTH reactions.

There were concerns about the use of bio-derived materials as hydrogen donors for catalytic transfer hydrogenation reactions because the process increase the steps of separation and recycling processes. This concerns both the alcohol that remains untransformed, which act as internal hydrogen donor and aldehydes produced, which can subsequently be separated and utilised as substrates in Aldol condensation reactions to make value-added chemicals [27, 49]. Therefore, this serves as one of the major setbacks of catalytic transfer hydrogenations. To add to the setback, the identification of active sites on solid catalysts

in catalytic transfer hydrogenations poses a challenge because the catalyst's surface is usually unstable.

Extremely effective method for the catalytic generation of 2,5-di-methylfuran from 5-(hydroxymethyl)furfural was reported by Thananattananachon et al. [146], using formic acid as an internal hydrogen donor and as an acid catalyst together with Pd/C. High conversions of up to 95% were obtained. One vital aspect to note from the conclusions drawn from this study was that formic acid as a hydrogen donor in catalytic transfer hydrogenations reduces handling and transport issues posed by hydrogen but presents difficulties in maintaining the material and durability of the catalyst. This is due to the corrosive nature of the acid. Because of their non-corrosiveness, alcohols are extensively studied for catalytic transfer hydrogenations. For example, in another related study, the same reaction was investigated using 2-propanol as a hydrogen donor. A lower yield of 80% was achieved, compared to when formic acid is used [70].

Armstrong et al. conducted a study on transfer hydrogenolysis of aromatic alcohols using Raney Co catalysts and 2-propanol as a sacrificial alcohol [53]. The dehydromethylation was found in the hydrogenolysis of primary alcohols, and Raney Co in refluxing 2-propanol is an effective system for deoxygenating  $\alpha$ -substituted alcohols only. A study was conducted by Scholz et al. that initially focused on the catalytic transfer hydrogenation of furfural and 5-hydroxymethylfurfural to 2-methylfuran and 2, 5-dimethylfuran, respectively over in-situ reduced, Fe<sub>2</sub>O<sub>3</sub>-supported Cu, Ni, and Pd catalysts using 2-propanol as an internal hydrogen donor [137]. The expected primary product in this reaction was furfural alcohol. However, successive hydrogenolysis and decarbonylating of the furfural were secondary reactions. Therefore, it was necessary for further studies to be conducted to circumvent these secondary reactions. Further investigations towards the development of selective perovskites and other potential catalytic candidates were conducted. Remarkably, the studies validated that 2-propanol acted as a hydrogen donor by monitoring the produced acetone concentration, a ketone by-product.

### 1.5.1 Donor capabilities of alcohols in CTH

In terms of the hydrogen donor capabilities of alcohols, secondary alcohols display a better donor potential than primary alcohols [35, 50, 64, 86]. The strong donor capabilities of secondary alcohols is attributed to the stabilisation of the secondary carbocation that forms upon donation of hydrogen. Scholz et al. [137] upon transfer hydrogenation of furfural and 5-hydroxymethylfurfural to 2-methylfuran and 2, 5-dimethylfuran, respectively over in-situ reduced Fe<sub>2</sub>O<sub>3</sub>-supported Cu, Ni, and Pd catalysts also reported that the substitution of the alcohol plays a part

in its donor capabilities. Therefore, a decrease in carbon chain length results in a decrease in the donor capabilities. Of the studied alcohols such as 2-butanol, ethanol, pentanol and 2-propanol, the best hydrogen donor capability was displayed by 2-propanol. Similarly, Johnstone et al. reported that alcohols could be used as both donors and solvents in the catalytic transfer hydrogenation reactions of aromatic compounds [75]. Tertiary alcohols, although stabilised, cannot serve as donors because they lack the  $\alpha$ -hydrogen (hydrogen on the carbon next to the hydroxyl group).

The effect of the structure of alcohols in catalytic transfer hydrogenations was reported by Vlachos et al. who discovered that secondary alcohols were superior to primary counterparts in converting furfural to 2-methylfuran utilising a carbon supported-Ru based catalyst [118]. Furthermore, they proved that whether in primary or secondary alcohols, the length of the alkyl chain affected the reaction. The longer the chain, the better the donor capabilities resulting in higher catalytic activity. However, there was one challenge encountered when the side chain (alkyl group) had more than two carbon atoms, the donor became weak. This could be attributed to steric hindrance or a stronger C-H bond. The study's findings further proved that the alcohols' activity was in the order 2-pentanol, 2-butanol, 2-propanol, 1-butanol, 1-propanol, and lastly, ethanol.

Unsaturated alcohols have numerous applications in industry, for example in fragrances and drug synthesis. It is, therefore, important for cheaper, greener, and sustainable procedures to be established in this endeavour. Acquiring desirable selectivity during these CTH reactions has proven to be challenging for unsaturated carbonyl compounds, especially if the target site is the carbonyl site because it is less thermodynamically favoured than the C=C [142]. The use of homogenous catalysis for the synthesis of these alcohols is possible. However, heterogeneous counterparts are more environmentally friendly as they are easy to recycle and separate from the products [100]. The catalysts' ability to activate the C=C and C=O bond of the unsaturated aldehydes is the key towards CTH reactions of unsaturated aldehydes.

Hydrogen generation from liquid sources has gained so much interest because it is known in organic synthesis. Methanol, ethanol, propanol, and formic acid are promising hydrogen donors produced in vast amounts from fossil-based feed. Base-free catalytic transfer hydrogenations of aldehydes and ketones using 2-propanol as a hydrogen source were evaluated by Dubey et al. [37]. In the study, Pd, Ru and Rh complexes were used as catalysts stabilized by organochalcogen ligand. They were successfully characterised using NMR, HR-MS and single-crystal X-ray diffraction. The base free hydrogenation was done upon

optimum loading of the catalyst (0.2–0.5 mol %) at ambient conditions. The reaction was proven to be a homogeneous reaction with the alkoxides, and M-H bond formation proposed in an uncertain proposed mechanism based on the  $^1\text{H}$  NMR and ESI-MS at reaction times of 1–2 h.

Most CTH reactions use biomass-derived chemicals with high oxygen moieties and high boiling points and molecules that decompose easily. Therefore, the use of alcohols as donors proves advantageous because they serve as hydrogen donors and solvents at the same time. Self-etherification of alcohols is a challenge because it is a side reaction in catalytic transfer hydrogenations, especially in the presence of Lewis acid sites on the catalyst surface. However, these side reactions have not received much attention in literature because their yields are negligible. Supported metal nanoparticles such as Pd, Ru, Au, and Pt are the most frequently employed catalysts for catalytic transfer hydrogenations and the supports of choice include activated carbon,  $\text{Al}_2\text{O}_3$ , zeolites, and porous metal-oxides.

### 1.5.2 Catalysts for catalytic transfer hydrogenation reactions

Zeolites are effective catalysts in catalytic transfer hydrogenations, especially tetrahedrally coordinated  $d^0$  or  $d^{10}$  metal centres. This is attributed to their Lewis acid character [69]. Little is known about long-term stability and the deactivation of zeolites in transfer hydrogenations. During zeolite catalysed CTH reactions, the synthesis of diether is favourable but challenging as it requires carbonyl group hydrogenation before etherification in unsaturated aldehydes [92]. There are numerous catalysts that are utilised for this reaction. Noble metal catalysts like palladium, rhodium and platinum have also been used in CTH reactions, however, they are expensive which increases the cost of the research. Therefore, perovskites serve as viable counterparts which are cheaper and can be tailored to suit the properties essential for the catalytic transformation [41]. This review will focus on the use of mixed oxides, in particular, perovskites oxides. Table 2 compares the activity and selectivity of different catalysts on the CTH reaction of cinnamaldehyde.

### 1.6 Perovskites metal oxides as catalysts for catalytic transfer hydrogenation reactions

The selection of metals to use during heterogeneous catalytic transfer reactions can prove complex because of the need to evaluate their geometric and electronic properties. Firstly, metals exist in different crystal phases, influencing the catalytic properties. The face centered cubic metals with Miller indices (111) have

**Table 2** Comparison of different catalysts in the catalytic transfer hydrogenation of cinnamaldehyde

Catalyst	Conversion (%)	Selectivity (%)	References
LaFeO <sub>3</sub>	99	82.0	[99]
Pd/LaFeO <sub>3</sub>	88.0	100	[16]
Pt zeolites	87.0	55.0	[48]
Ru /C <sub>60</sub>	20.0	71.0	[91]
Ru/SWCNT	80.0	92.0	[91]
Pd/ LaCoO <sub>3</sub>	80.0	100	[16]
Pt nanoparticles	94.0	92.6	[175]

lower adsorption steps as compared to (100) [101]. It is imperative to perform an X-ray diffraction analysis of the as-synthesized materials to estimate the reaction pathway that the reaction will follow. Secondly, the metal's electronic properties are crucial in selecting the catalyst because they determine the reactivity and adsorption of substrates onto the catalysts' surface.

Hydrogenation transformations of various compounds into value-added chemicals using perovskites as heterogeneous catalysts have been a success. Bewana et al. studied the selective catalysis of cinnamaldehyde to cinnamyl alcohol using selective nanoparticles embedded in perovskite materials [16]. In extremely short reaction times, conversions of approximately 25% were achieved when pure perovskites were used, owing to the materials' porous nature and their remarkable electronic properties. Moreover, the catalyst was recyclable, achieving up to 100% selectivity towards hydrocinnamaldehyde. The perovskite materials had been synthesized using the nanocasting method and induced a synergistic effect on Pd nanoparticles to obtain conversions greater than 80%.

Similarly, perovskites in catalytic transfer hydrogenation reaction are advantageous in terms of the ease of separation upon completion of the reaction and show robust activity during the reduction of nitro compounds to the desired amines. This was shown in a study of selective transfer hydrogenation of aromatic nitro compounds into aromatic amines under microwave heating by Farhadi et al. where ferromagnetic BiFeO<sub>3</sub> nano-powdered catalysts were synthesized from the Bi[Fe(CN)<sub>6</sub>]<sub>5</sub>·5H<sub>2</sub>O complex through thermal decomposition [40]. Particles of up to 20 nm and with surface areas of 48.5 m<sup>2</sup>/g produced yields and selectivities of up to 96% using propanol as a hydrogen donor under microwave radiation. The perovskite catalysts were magnetically recoverable and recyclable, and this proved faster and more suitable for large scale anilines production. The catalytic transfer hydrogenation of these compounds is cheap, regio- and chemo-selective, and compatible with the reducible substrates.

Conversely, Pt, Pd, Ru and Raney Ni are classical catalysts employed in catalytic transfer hydrogenation reactions [40]. This provides a promising method for generating pure nanosized perovskite materials with relatively high surface areas for catalysis. This method is the thermal decomposition of heteronuclear complexes and provides high circumvention of strong acidic media superior to its noble metal catalyst counterparts. The strong acidic media must be circumvented to prevent corrosion and to give better control of the outcomes of the reaction.

This method validates the findings made by Kulkarni et al. who used microwave radiation to synthesize La-based perovskites, LaMO<sub>3</sub>, (where M = Mn, Fe, Co, Cr or Al) [84]. Just like with Farhadi et al. the method was found to be exceedingly fast and cost-effective for the synthesis of specifically tailor-made perovskites. The perovskites were synthesized in just 15 min and were successfully used to reduce aromatic nitro compounds using isopropanol, in this instance, with potassium hydroxide as a promoter. High conversions and selectivities were obtained. This was further validated by the study published a year later, where the influence of substitutions at A sites in the perovskite structure was evaluated in the nitrobenzene reduction, using the same conditions and a series of La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> (x = 0.0–1.0) oxides as catalysts [84]. There have been numerous other reports on the catalytic transfer hydrogenation of nitro compounds using different hydrogen donors over the past two decades [58, 138].

### 1.6.1 Metal oxides as heterogeneous catalyst supports for CTH

The use of metal-oxides supports is studied in catalytic hydrogenation reactions because its nature affects different catalysts' motion during the catalysts' pre-treatment. The acidic supports favour side reactions [82], whilst basic supports favour unsaturated alcohols due to their ability to present properties that are electron-rich to the active metal. Due to its ability to enhance chemoselectivity in carbonyl compounds' hydrogenation, iron oxide (Fe<sub>2</sub>O<sub>3</sub>) has been used extensively as supports [101]. In the studies done by Milone et al. the purpose of introduction of ferric sites was to enhance the electronic properties of the Au NPs [106]. Therefore, catalysts support plays a vital role in governing the electronic and adsorption properties of the catalytic material, enhancing conversions and selectivities in CTH reactions. Therefore, the addition of inexpensive metals often reduces the occurrence of side reactions. Similarly, in a study done by Scholz et al. it was found that the hydrogenation of furfural using Pd/FeO<sub>3</sub> as a catalyst was attributed to strong metal-support interactions, whilst the selectivity has been shown to depend strongly on Pd loading.



### 1.6.2 Heterogeneous metal oxide catalysts pre-treatment for CTH reactions

Considering the origins of the metals intensively, catalysts need to undergo pre-treatment as they might not be active as metal precursors. There are many reasons for pre-treatment, these include changing the material's size, increasing activity and selectivity [87, 178], removing residual chlorides and influencing alloy formation [101]. Furthermore, it reduces the reducibility and increase oxygen sites depending on the treatment [12]. Depending on the material's origins, it is important to calcine the material in pre-treatment [54, 55]. Catalytic metal dispersion of the metal is one of the attributes of pre-treated material. Other techniques that may be utilized for the enhancement of catalytic material are ageing and the use of modifiers [56, 57].

### 1.6.3 Effect of acidity and basicity of metal oxide catalysts in CTH reactions

The transformation of furfural to a value-added chemicals such as furfural alcohol using CTH requires the carbonyl and alkene functional groups' activation. This is like sugar hydrogenation, in which many catalysts have proved to be selective and highly active. Metal–acid or base pairs are remarkable with CTH reactions [73]. Catalytic activity in terms of turnover frequencies of  $60 \text{ h}^{-1}$  has been obtained for Ru and Pd catalysts with high

selectivities. However, this does not exclude non-noble metals like Ni, Cu, Co and Fe, especially when infused in the perovskite structure. It has been proven that the Lewis acidity outpaces the basicity when it comes to methyl furan during the CTH of furfural. This is true for all the other unsaturated carbonyl compounds. The formation of the side products requires further investigations. Therefore, it is vital to note that morphology and metal support interactions are crucial for CTH reactions, with the acid/base-H bond determining the intrinsic kinetics for C–O cleavage.

Acid–Base catalysts accelerate catalytic hydrogenation reactions mostly through direct hydrogen transfer between a donor and substrate molecule. This is attributed to the fact that hydrides' formation is not thermodynamically favoured on these acid–base pairs and it is extremely difficult. Both the acid and the base sites are crucial for the reaction, although they are unlikely to be on the same catalysts. The electron-deficient metal centre of the Lewis acid bonds to the carbonyl and hydroxyl oxygen of both the substrate and the donor, respectively. On the other hand, the base attracts the H of the O–H bond, weakening it. Therefore, the acidity depends on the Lewis acid's strength and the hydroxyl interaction, facilitating the proton's base abstraction. If the base is too strong, it initiates a hydride transfer mechanism as it abstracts the proton leaving an alkoxide [49]. This mechanism is similar to the one described by Xiao et al. as illustrated in Fig. 5.

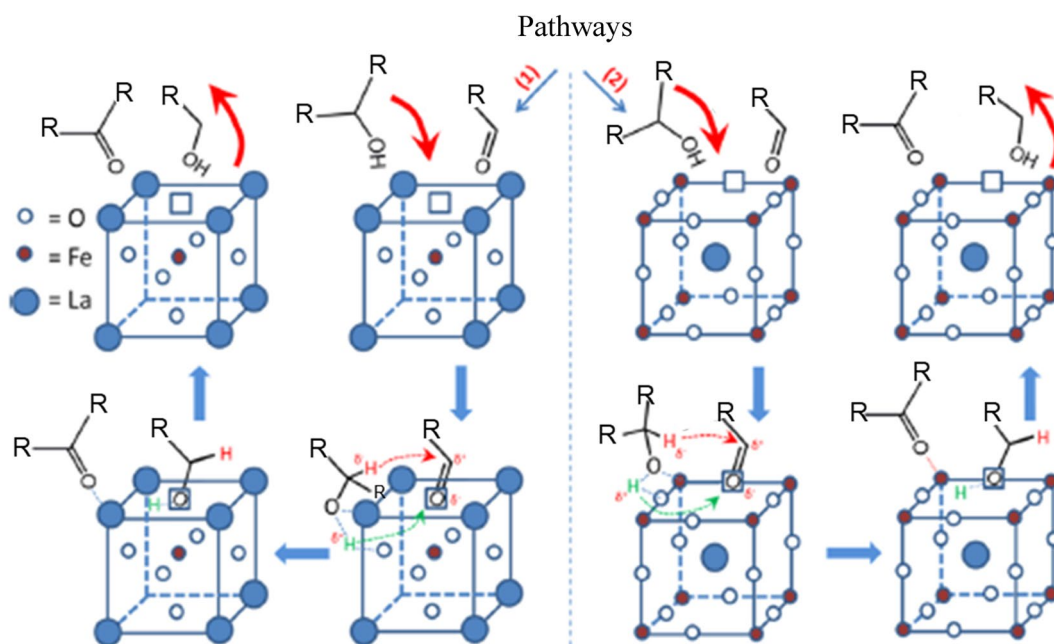
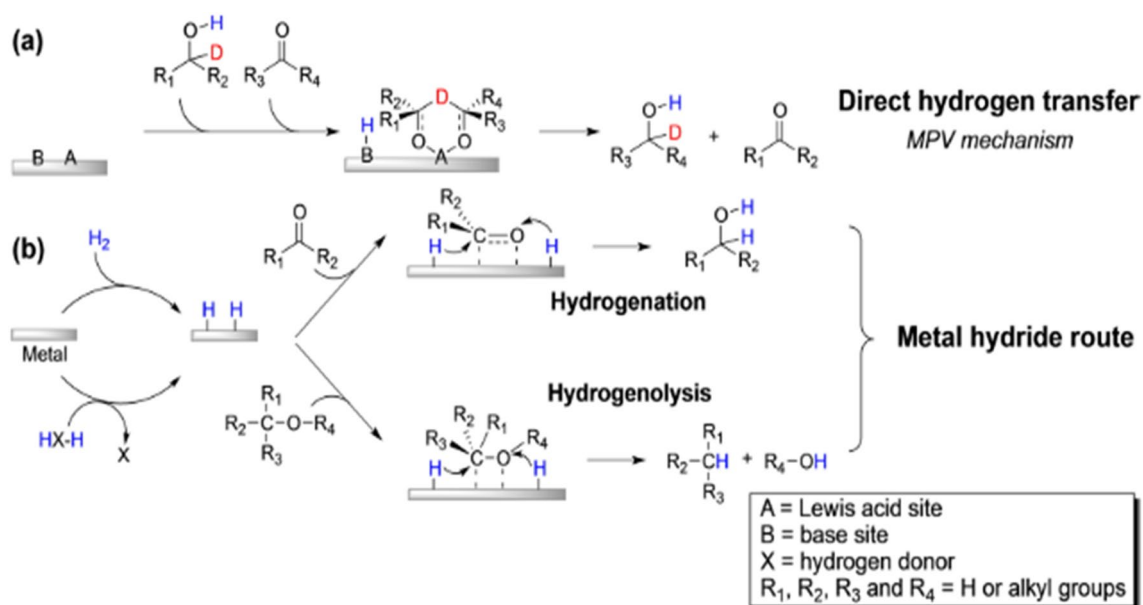


Fig. 5 Catalytic transfer hydrogenation mechanism as proposed by Ping et al. [173]



**Scheme 2** Direct hydrogen transfer and metal hydride route of catalytic transfer hydrogenation [49]

### 1.6.4 Carbon-doped perovskites in CTH reactions

Carbon composites improve perovskites' performance when prepared in-situ as far as CTH reactions are concerned. Xiao et al. studied the design of perovskites to improve the activity and selectivity of LaFeO<sub>3</sub> perovskites towards the CTH reaction of furfural-to-furfuryl alcohol [172]. The basic notion is to ensure the timely delivery of the reactants onto catalysts' active sites for the reaction to occur at its optimum, manipulating the holes made between the catalyst particles. The perovskites with the carbon material have an enhanced reaction rate, six times faster than that of perovskites without the carbon material, of 5.17 mmol g<sup>-1</sup> h<sup>-1</sup>. Thus, from the results of this study, it is evident that carbon's absorptive characteristics increase the migration of reactants from the solution onto the catalyst's active sites. In addition, the area of the material seemed to be positively affected by the presence of carbon. This opens the channels for improving perovskites and all other low surface area catalysts, providing a better future for these types of catalytic materials. Moreover, the mechanism of the reaction was fully explored. This mechanism was similar to the discoveries they made the previous year, as illustrated in Fig. 4 [173]. Proposed mechanism of catalytic transfer hydrogenation reactions on metal oxides.

Xiao et al. described the catalytic hydrogen transfer mechanism of furfural and cinnamaldehyde over perovskites to be an acid–base rather than the redox mechanism [173]. The isopropanol binds to the perovskite's metal cations, either the A or B cations, using the oxygen atom on the hydroxyl group. The hydrogen atom of the hydroxyl

group, in turn, interacts with the adjacent oxygen anion. The carbonyl oxygen of the substrate binds to the oxygen vacancy on the perovskite, from which the reducing electron comes. This makes the acyl carbon susceptible to nucleophilic attack, initiating enolization. This way, the catalyst acts as an interface for the hydrogen donor and the substrate. Enolization occurs with this arrangement, resulting in the transfer of two hydrogen atoms from the hydrogen donor to the carbonyl compound (Fig. 4).

Catalytic transfer hydrogenation reactions described by Gilkey et al. have two main mechanisms: direct hydrogen transfer or the metal hydride route in the homogeneous systems [49]. These use deuterated hydrogens as tracking atoms. Upon utilising alcohols as hydrogen donors, the direct hydrogen pathway is employed where the –H is transferred from the –carbon of the donor to that of the substrate without forming the metal hydride. The mechanism is believed to go through a concerted step involving forming a six-membered ring intermediate: the Meerwein-Ponndorf-Verley (MPV) mechanisms. The presence of a base enhances reactivity. The MPV mechanism has also been proven to apply to heterogeneous catalysts. With solid catalysts, the possibility of the MPV mechanism is brought by a Lewis acid site that has a deficit of electrons and a neighbouring base site.

However, some heterogeneous catalysts undergo the metal hydride route, split into two: the monohydride and dihydride mechanisms, as shown in Scheme 2. The difference between the two lies in whether the hydrogen atoms in either the hydroxyl or C–H are preserved in the product. Thus, when alcohols and formic acid lose the

hydrogen from the  $\gamma$ -carbon to the metal, the mechanism is referred to as the monohydride process. If both the hydrogen from the  $\gamma$ -carbon and the hydroxyl group are transferred, it is called the dihydride mechanism [49]. Nevertheless, the study of the mechanisms of catalytic transfer hydrogenation reactions has proven to be complex when using heterogeneous catalysts. As a result, more studies are conducted to try and rectify this challenge. However, it is believed that the mechanism with perovskites is an acid–base catalysed reaction.

Overall, it is vital to note that despite all the benefits of CTH reactions, there is a gap in the fundamental and systematic studies on the hydrogen generation's kinetics on bimetallic and metal acid–base pair catalysts. Furthermore, the changes that occur to the catalyst surface during the reaction are not yet fully understood. However, postulations have been made on vital parameters such as hydrogen spill-over, hydrogen donor efficiency, and uptake capabilities. This may be attributed to the fact that most studies concentrated on catalyst composition and performance instead of the nanostructures and interfacial characteristics. Therefore, there is a need for more research to be conducted in this regard.

## 1.7 Synopsis and outlook

Due to the reliability of heterogeneous and electro-chemical catalysis on the exposure of metal cations to electrons to accommodate the reactants and intermediates, metal oxides, more especially perovskites have been proven by different sources to be suitable candidates to replace noble metals. This is due to their tunable unique structural properties. In attaining purity and suitable textural properties for catalysis, the metal oxides' synthesis protocol is vital. The sol–gel citrate and nanocasting methods gained the popularity among the reported protocols. The use of perovskite structured oxide in heterogeneous catalysis is progressing, especially in applications involving high temperatures and oxygen steam atmospheres where their stability comes to play.

However, there are challenges that emanate when synthesizing metal-oxides. These include high coordination numbers of transition metal ions, which pose challenges in terms of control during the assembly with surfactants and destruction of the micropores by heat treatment required for template removal or structure crystallization. Therefore, there is a need to either use easily removable templates or less coordinated oxides. The costs of the synthesis of perovskites is high due to expensive templates such as biopolymers [18, 163]. Ideally, natural sources like wood and porous minerals would be used to substitute expensive templates, improving the synthesis steps economically. The

template removal step would be eliminated in terms of structure retainment, although they minimise architectural control. Perovskites require high temperatures and long calcination times during their synthesis, especially when comprising two or more metals. This challenge makes them thermally stable with extremely high boiling points; however, it results in low surface areas, limiting their surface reactions. Sintering, poisoning, and leaching are the main causes of catalyst deactivation on heterogeneous catalysis. However, these can be controlled using catalytic supports. Perovskites on catalyst supports are promising alternatives that sort the surface area problem associated with heterogeneous catalysts. Perovskites with high surface areas need to be synthesized by focusing on improving synthesis methods by advancing porous structures or nanomaterials. This should be done considering the associations between the physical and chemical properties and catalytic activity. Secondly, due to their diverse, interconnected channels that maximise contact with substrates, there is a need to synthesise 3D perovskites. Lastly, there must be an extensive improvement of perovskites' electronic conductivity before implementing them on catalysis.

Catalytic transfer hydrogenation reactions are sophisticated processes that entail the complex design of interfacial structures for controllable kinetics. Numerous research efforts have concentrated on the composition of the catalysts for reactions other than interfacial characteristics and nanostructures. Therefore, future research is recommended to focus on enhancing the atom efficiency of catalytic transfer hydrogenations and understanding electrons' reconfigurations due to morphological changes and structural manipulation. Furthermore, understanding the characterization of substrate interactions with in-situ hydrogen is vital for unsaturated aldehydes hydrogenation on the catalyst's surface. Therefore, intrinsic properties need to be considered for complete optimisation, such as metal hydrogen bonding and activation barriers.

Overall, catalytic transfer hydrogenation reactions are among the green and cheaper reactions that make chemical synthesis more sustainable. This reaction eliminates the need for precious metal catalysts and the use of hazardous molecular hydrogen. This decreases costs as the need for high-pressure reactors is eliminated. Moreover, sustainable development is achieved as these readily available bioderived hydrogen donors replace their non-renewable counterparts, reducing the carbon footprint. There are limitations with this reaction, including the price of external alcohols, hence reducing this reaction's applicability compared to hydrogen-based hydrogenations. Incidentally, cheap primary and secondary alcohols have been utilized as hydrogen donors and solvents.

**Acknowledgements** This work is supported by the National Research Foundation of South Africa (Grant UID: 138186) and the Research Center for Synthesis and Catalysis hosted by the University of Johannesburg.

**Author contributions** N.B. and M.M. did conceptualization T.P.M., N.P.M., and S.N. gathered the data T.P.M. wrote and formatted the manuscript. All authors proof-read the manuscript. N.B. secured funding.

## Declarations

**Competing interests** The authors declare no competing interests.

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