



Metal Oxides as Catalyst/Supporter for CO₂ Capture and Conversion, Review

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Abstract: Various carbon dioxide (CO₂) capture materials and processes have been developed in recent years. The absorption-based capturing process is the most significant among other processes, which is widely recognized because of its effectiveness. CO₂ can be used as a feedstock for the production of valuable chemicals, which will assist in alleviating the issues caused by excessive CO₂ levels in the atmosphere. However, the interaction of carbon dioxide with other substances is laborious because carbon dioxide is dynamically relatively stable. Therefore, there is a need to develop types of catalysts that can break the bond in CO₂ and thus be used as feedstock to produce materials of economic value. Metal oxide-based processes that convert carbon dioxide into other compounds have recently attracted attention. Metal oxides play a pivotal role in CO₂ hydrogenation, as they provide additional advantages, such as selectivity and energy efficiency. This review provides an overview of the types of metal oxides and their use for carbon dioxide adsorption and conversion applications, allowing researchers to take advantage of this information in order to develop new catalysts or methods for preparing catalysts to obtain materials of economic value.

Keywords: CO₂; capturing; conversion; carbon dioxide capture technologies; metal oxide

1. Introduction

 CO_2 levels in the atmosphere are rising primarily due to fossil fuels and their derivatives such as gasoline and diesel. Because of the country's economic growth (GDP), avoiding development, such as industrialization, urbanization, and transportation, for CO_2 emission reduction is complicated. There were approximately 32.8 billion tons of CO_2 emissions from the combustion of fuels around the world [1]. In addition, as a result of overpopulation, there has been a dramatic increase in the use of private vehicles.

The economy of this century depends mainly on energy supplies, including fossil fuels that contain high levels of carbon, which harm the environment and the global climate due to harmful emissions from the combustion process [2]. At the United Nations 2015 Climate Change Conference, the members agreed to establish an international framework for avoiding severe climate change by keeping global warming far below 2 °C and pursuing attempts to maintain it below 1.5 °C [3]. To reach this goal, essential measures must be taken, including the sequestration and conversion of carbon dioxide, which is the most critical factor in the climate equation.

Recently there has been a high interest in CCUS (CO_2 capture, storage, and utilization) to reduce levels of CO_2 in the atmosphere [4]. However, is it possible to reduce and eliminate carbon dioxide emissions in the atmosphere from a "green" perspective? The carbon economic circle, which allows us to store, use, and remove CO_2 , is a viable solution to this problem [1,5]. However, carbon dioxide's high thermodynamic stability was one of the significant impediments that prevented its utilization. This thermodynamic problem can be solved using high-energy co-reactants, such as hydrogen and epoxides [6].



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Metal oxides are essential in determining the overpotential and product selectivity in the CO_2 reduction reactions (CO_2 RR) [7]. In contrast, developing efficient and stable metal oxides is a significant challenge that must be achieved to lower the production cost of fuels in the practical implementation of CO_2 RR technologies [8]. Earlier, several efforts have been made to develop metal oxides to convert CO_2 into value-added chemicals and fuels [9].

The carbon capture and storage strategy are also considered solutions that reduce the inevitable emissions of carbon dioxide [10]. It is divided into three categories: precombustion technology, oxygen-fuel combustion, and post-combustion technology [11].

Post-combustion processes have been developed, including membrane separation, cryogenic fractionation, solvent absorption, and adsorption using solid sorbent [12]. In addition, post-combustion carbon dioxide-based adsorption is one of the most cost-effective processes, whether by physical or chemical methods [13].

A fundamental necessity for reducing emissions is the conversion of carbon dioxide into economically valuable and environmentally benign products. Usually, this conversion process is carried out using various catalysts. This review will discuss the properties of metal oxides for CO_2 conversion, product selectivity, and reaction conditions. In addition, various types of carbon dioxide uptake processes using metal oxides and applications based on the conversion of carbon dioxide using metal oxides are also traded.

2. Background

Factories, transportation, and power plants produce thousands of tons of carbon dioxide annually [14]. Carbon dioxide is a raw material from which many materials of economic value can be produced. For the purpose of capturing and introducing carbon dioxide, we need to develop catalysts with certain specifications, through which the stability of the carbon dioxide molecule can be overcome and introduced into chemical reactions. In this context, some metal oxides are promising catalysts with good results.

Several specifications, such as high adsorption capacity, low cost, low regeneration requirements, long-term stability, and fast kinetics, must be achieved by selective sorbents to capture and convert carbon dioxide from gaseous effluents. It's been shown that some materials, such as zeolites and activated carbons, have a moderate affinity for CO₂ uptake; however, at high temperatures, these materials' sorption capacities are reduced. SBA-15 and MCM-41, for example, have been reported to have good adsorption capabilities and cyclical stabilities when used at low temperatures, but they have also been found to be ineffective at high temperatures [15]. Hydrotalcites have been reported to be excellent CO₂ adsorbents but lack the sorption capacity to be used in large-scale industrial applications [16]. Due to their superb sportive properties at high temperatures, calcium-based adsorbents for dual-function materials (DMFs) appear most promising [17].

In 2017, there was a noticeable increase in research studies focusing on converting carbon dioxide into chemicals (methane, methanol, formic acid, etc.). However, converting carbon dioxide to other products needs high energy, as CO₂ is highly stable and relatively inert, which is reflected by its bond dissociation energy (393.5 kJ/mol) [18,19]. Several carbon dioxide conversion processes have been developed, including photocatalysis [20], plasma catalysis [21], and electrochemical catalysis [22]. Therefore, there was a boost in interest in employing catalysts in conversion processes. These catalysts are characterized by high product selectivity and increased activity. Solid catalysts are classified as conductors, semiconductors, and insulators [23]. Among the catalysts and catalytic reactions accomplished industrially, metal oxides are considered essential candidates in different fields. Metal oxide catalysts gained prominence in the mid-1950s, when they were successfully employed for a broad range of oxidation reactions, especially hydrocarbon processing [24].

3. Carbon Dioxide Capturing Processes

The processes of capturing carbon dioxide are mainly divided into three categories: pre-combustion technology; extracting carbon dioxide from fossil fuels before combustion.

Combustion of fuel with oxygen; is a process in which inert gases are removed from the combustion of flue gases: post-combustion technology; extracting carbon dioxide after the combustion of fossil fuels [25,26].

Post-combustion is the most suitable method harnessed for capturing CO_2 because it involves the ready retrofitting of existing infrastructure. Researchers have developed four different CO_2 capture techniques for post-combustion (Figure 1).



Figure 1. Post-combustion carbon dioxide capture processes.

4. Carbon Dioxide Absorption

The absorption phenomenon occurs when the particles of a substance are distributed evenly over all parts of the substance (Figure 2A), whether liquid or solid. The difference in the adsorption of gas or liquid molecules and their adherence to solid material surface is diagrammatically represented (Figure 2B). In some reactions, absorption and adsorption coincide as the particles are absorbed, then the substance is removed. Subsequently, particles get adsorbed on the surface of the material, and this phenomenon is called sorption (Figure 2C) [27]. The absorption method is one of the most suitable methods for trapping CO₂ because it has a high CO₂ loading capacity, reasonable absorption rate, and low cost. Table 1 exhibits the chemical and physical absorption and the difference between chemical and physical absorption in terms of the occurrence of the reaction, solvents used, and most critical disadvantages and advantages.

Figure 2. (A) Absorption process, (B) adsorption process, (C) sorption process.

Particularity	Physical Absorption	Chemical Absorption
The Reaction Occurs	Absorption occurs at high CO ₂ partial pressure and low temperature	Absorption occurs between CO ₂ and chemical solvent, and a weakly-bonded intermediate compound is formed, which is dissociated by heat, after which CO ₂
Solvent Used	Dimethyl ether, polyethylene glycol, and cold methanol	Monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA)
Features	Low energy and less solvent sensitivity to feed impurities	Requires high energy
Disadvantages	Low carbon dioxide absorption capacity	High carbon dioxide adsorption capacity

Table 1. Physical and absorption chemical [6,14].

5. Metal Oxides for CO₂ Uptake

Many sorbent materials have been used to increase the efficiency of capturing and absorbing carbon dioxide, including zeolite, activated carbon, and silica. Zeolite contains compounds of crystalline aluminosilicates that are characterized by chemical and physical properties, such as selectivity and high thermal stability [28]. Zeolite 13X (a bench-mark zeolite) showed absorption of up to 7.4 mmolg⁻¹ and higher selectivity than activated carbon. However, zeolite consumes higher temperatures for regeneration [29]. Metal oxides were the most cost-effective and had lesser toxicity than zeolites and MOFs among the absorbents. In addition, the oxide-based sorbents can trap carbon dioxide with high selectivity when exposed to high temperatures [30]. Usually, alkaline earth metal oxide sorbents, e.g., magnesium oxide (MgO) and calcium oxide (CaO), are utilized in the absorption CO_2 process. However, these methods offer a few disadvantages [31]. The main drawbacks associated with the application of solid absorbents are the fast saturation and consuming energy for activation after several cycles [32]. Magnesium oxide was an excellent candidate for CO_2 absorption performance [33,34] because it had a suitable surface morphology for oxygen generation that improved absorption performance and low regeneration energy consumption [35,36]. The incorporation of MgO-activated carbon nanofibers (ACNFs) for CO₂ absorption was successfully integrated by electrospun activated carbon nanofibers (ACNFs) using the simple volumetric method. The fusion of thermally stable metal oxides contributes to the absorption of CO₂ at its lowest temperature. The addition of ACNFs increases the production fusion of thermally stable, contributing to the absorption of CO_2 at its lowest temperature. The incorporation of MgO-ACNFs showed a higher CO₂ absorption capacity of 2.72 mmolg $^{-1}$ [37,38]. Another study investigated magnesium oxide (MgO) nanoparticles (NPs) and MgO nanoparticles supporting activated carbon-based bamboo (BAC) for CO₂ adsorption. The MgO nanoparticles that supported BAC had surface areas of 297.1 m² g⁻¹. The study shows that the physical adsorption of CO₂ on MgO(NPs)-BAC was improved by 112% (39.8 mg g^{-1}), compared to activated carbon-BAC (18.8 mg g^{-1}) or MgO nanoparticles (12.8 mg g^{-1}) [39].

MgO with fibrous silica was utilized to improve the performance of CO_2 absorption via ultrasound-assisted impregnation [40]. MgO-fibrous silica showed the highest absorption of 9.77 mmolg⁻¹, while fibrous silica without MgO showed an absorbance of 0.52 mmolg⁻¹.

One of the most extensively utilized is calcium oxide for its distinguishing features for CO_2 as a solid adsorbent. However, it has limited drawbacks, including excessive sintering and mechanical failure. The carbonation process and interaction between CaO and CO_2 slow down once the initial layer of calcium carbonate is created [41]. Several studies have attempted to improve the stability and reusability of CaO as an adsorbent by employing various strategies. CaO derived from nanosized CaCO₃ was studied by Florin et al. [42]. For the carbonation of CaO derived from nanosized CaCO₃, the sorbent material was subjected to five carbonation cycles (24 h per cycle). They concluded that there was no morphological impediment when given enough time. After 100 CO_2 capture-and-release cycles of 20 min, they found that the residual conversion capacity was 20% higher than previously reported for bulk CaO, demonstrating the potential of nanosized CaO. The increase of the reactivity of the adsorbent was investigated by Li et al. using an ethanol/water mixture to hydrate

CaO. They found that the spent catalyst's sorption capacity increased by two times as much as initially, and the sorption capacity of CaO could be improved by changing the synthesis method [43]. Belova et al. [44] used the strategy of dispersing CaO on an inert support, such as γ -Al₂O₃, to improve the sorption capabilities of CaO and minimize sintering. A layer of carbonate restricts the diffusion of CO_2 and slows down the initial carbonation reaction, as previously stated. Increased dispersion reduces the possibility of sintering by increasing the surface area of the CaO particles. CaO dispersed on high surface area γ -Al₂O₃ resulted in a stable sorbent that could overcome the difficulties associated with limited long-term stability, slow uptake kinetics, and energy intensive regeneration [45]. Thermal gravimetric analysis (TGA) was used to investigate CO_2 uptake kinetics and capacities, while multicycle experiments evaluated long-term stability. In comparison to bulk CaO powder, they found that dispersed CaO was a more effective low-temperature sorbent, with up to 1.7 times the capacity to bind CO₂. It was found that CaO dispersed on γ -Al₂O₃ had better long-term stability than bulk CaO, which was tested for 84 CO₂ capture-and-release cycles at 650 °C. While the bulk CaO's adsorption capacity dropped below 50% after 20 cycles, the CaO/ γ -Al₂O₃ adsorbent maintained 90% of its efficiency, with no sintering after the same number of cycles [46].

Currently, most studies have focused on improving the performance of CO_2 uptake using metal oxides at low-temperature levels; some of these studies are shown in Table 2.

Adding metal oxides to an amino acid, such as lysine, for CO_2 capturing is a promising process. Some groups had studied the catalytic effect of metal oxides on the salts of amino acids, which have many advantages that make them suitable alternative absorbers for carbon dioxide [47] Some of these advantages are their high cyclic loading and good oxygen stability. It also allows the salt formation in potassium or lithium hydroxide, which makes the amino acid salt non-volatile in a stripper. The metal oxide catalytic activity depends on the defect sites present on the metal oxide surface [48] This metal oxide surface is exposed to water, which generates metallic hydroxides, suggesting that the metal oxides can enhance the carbon dioxide absorption kinetics of the lysine salt absorbent liquid, as shown in Figure 3.

Figure 3. Structure of potassium salt of lysine (Adapted with permission from Ref. [47]. Copyright 2018 Elsevier).

Sivanesan et al. studied the effect of the absorption rate of carbon dioxide from the potassium salt of lysine-HCl solution; they found that, while adding MnO₂, the absorption rate increased from 0.192 kPa/s to 0.220 kPa/s, indicating that the addition of a heterogeneous catalyst enhanced the absorption rate [47]. On the other hand, when CuO was tried, it showed the highest carbon dioxide absorption rate. This is maybe due to the presence of the square-level engineering centers of CuO, which make the coordination sites available and assist in increasing the absorption rate of carbon dioxide. On the other hand, the dependence may be greater on the defect sites present on the surface of metal oxides of the octahedral mineral centres [49,50].

Nanoparticles, such as zinc and cobalt, have been used to increase the absorption rate of carbon dioxide, which helps reduce operating costs [51,52]. The catalytic performance of Ni (NPs), as additives to optimize CO_2 absorption in an MEA under different mixing conditions (limited- and high-mixing), was examined using two microfluidic platforms that effectively control polyphase flows. NPs (Ni) can increase CO_2 absorption by 34% and

54% in limited- and high-mixing conditions, respectively. In addition, Ni (NPs) can reduce the amount of MEA needed in the system by speeding the lengthening time to achieve equilibrium with carbon dioxide absorption. The study found that Ni (NPs) could still perform its function for more than 140 h [53,54].

The addition of TiO₂, ZnO, and ZrO₂ (NPs) were also tested with diethanolamine solution to investigate the effect on the absorption of carbon dioxide in a continuously stirred system using a stirrer bubble column, the influence of TiO₂, ZnO, and ZrO₂ nanoparticles, in aqueous piperazine solution, on the hydrodynamic and CO₂ absorption rate was examined experimentally. The absorption performance of TiO₂ and ZrO₂ nanoparticles improves with solid-loading, up to a maximum value, then declines, and the TiO₂, ZnO, and ZrO₂ nanoparticles had optimal values of 0.05, 0.1, and 0.05 (wt%), respectively. The inclusion of ZrO₂ nanoparticles had the minimum effect on the performance, compared to TiO₂ and ZnO nanoparticles, and the maximum absorption rates of TiO₂, ZnO, and ZrO₂ were 14.7%, 16.6%, and 3.7%, respectively [55].

Adsorbent Material	Method	Temperature (K)	Uptake CO ₂ mmolg ⁻¹	Ref.
TiO ₂ /GO	Volumetric analysis	298	1.88	[56]
Mixed metal oxides (MMOs)	TGA/PB	298	2.27	[57]
Diethanolamine (DEA)/CuO-MgO	Facile hydrothermal	298	21.2	[58]
CaO-loaded charcoal	sol-gel	298	15.1	[59]
MgO-FS	sol-gel	298	3.43	[40]
CaO-FS	sol-gel	298	3.11	[40]
CeO ₂ -FS	impregnation	298	7.85	[40]
MgO/C	thermaldecomposition	300	32	[35]

Table 2. Summary of CO_2 absorption studies, using different metal oxides at low temperatures.

A nanocomposite of metal-organic–silica (MOS) was synthesized and functionalized, with propyl-ethylenediamine as a metal linker, for chemically attaching Cu^{2+} and Ag^{1+} to Cu and Ag nanoparticles for CO_2 uptake. The diameter of Cu and Ag nanoparticles ranged from 5–20 nm. The study showed that the composite gradually absorbed the carbon dioxide, with a saturation peak after 25 min, and incorporated metal nanoparticles with modified silica increased CO_2 uptake from 20 to 100%. In addition, silica decorated with Cu nanoparticles showed the maximum CO_2 uptake compared to Ag, Au, and Fe [60]. The study, also notice that the effect of nanoparticles is superior to that of metal oxide nanoparticles, especially in the case of copper.

In a more specific study, the effect of the morphology and surface area of two types of mesoporous silica, rod and spherical shapes, functionalized with amine and decorated with Cu nanoparticles, were investigated (Figure 4). The study illustrated that the spherical shape, functionalized with amine and decorated with Cu nanoparticles, showed a high absorption capacity of 0.58 mmol g⁻¹, which is higher than the batch with Cu ions, instead of Cu nanoparticles [61]. Furthermore, the rod-shaped mesoporous silica particles have a greater surface area than the spherical ones (1300 m²g⁻¹), and copper nanoparticles with an average diameter of 6.0 nm were uniformly incorporated into the structure. Moreover, Cu-loaded mesoporous silica exhibits up to 40% higher CO₂ adsorption capacity than the amine-modified mesoporous silica [62]. These results confirm that the presence of metallic nanoparticles provides additional activity sites for carbon dioxide absorption.

Figure 4. TEM of images: (**a**) mesoporous silica (rod shape), (**b**) mesoporous silica rod -Cu (NPs), (**c**) mesoporous silica (spherical shape), and (**d**) mesoporous silica spherical-Cu (NPs) and the insets show the electron diffraction pattern (Adapted with permission from Ref. [62]. Copyright 2018 Elsevier).

To effectively trap carbon dioxide, the surface of silica particles was chemically modified with the amine. The particles were implanted on the membranes of polyvinylidene fluoride–hexafluoropropylene (PVDF–HFP). The results demonstrated that adding amino– silica particles improved the properties of the membrane and increased the CO₂ uptake (0.8 mmol g⁻¹) compared to the pane membrane [63].

The method of using a catalyst to capture and convert carbon dioxide is an important topic. In this context, work has been done utilizing a ZnO catalyst, integrated with Ru, with amine as a novel catalyst for CO_2 capture and conversion to methanol. The ZnO catalyst assisted the reaction in a moderate condition, due to forming a ZnO–amide bond on its surface. As a result, a 30% yield has been achieved [64].

6. CO₂ Conversion

6.1. CO₂ Conversion Using Catalyst-Supporting Materials

Metal oxide interactions are widely used to improve catalytic capabilities, but they are frequently limited to instances where only one component is assisted by the other. The surface of metal oxides is a crucial factor for effective interaction with target molecules. It can be engineered to improve activity and sensitive properties. Thanks to recent breakthroughs in nanotechnology, metal oxides can now be used in novel ways [65]. Several transition metal oxides have electrical conductivity, a broad bandgap, and stability under reaction circumstances, making outstanding catalysts for turning carbon dioxide into valuable compounds using diverse processes [66,67]. Many factors affect carbon conversion reaction using metal oxides, including the catalyst surface reaction conditions and supporting material. The CO₂ conversion process and conversion rate are greatly influenced by the catalyst, catalyst carrier, and integration strategies. Through the study of the influence of the carrier material, it is clear that the distance between the sites of the active metal oxide and carrier can be engineered to improve the interaction of the surface metal support by adapting the support integration method [68]. In this context, Bachar Alrafei et al. studied the conversion of CO₂ to methane using Ni and (Ni-Co) catalysts supported on alumina in different ratios of nickel from 5% to 20 wt% and cobalt from 3% to 10 wt%. The optimum ratio was Ni 20 wt% and Co 10 wt%. These catalysts showed high activity at low temperatures. In addition, the selectivity was 100%, and it showed a high rate of methane production and carbon dioxide hydrogenation compared to other catalysts. In another perspective, nickel oxide, supported by titanium, showed more activity in CO oxidation than the catalysts of alumina and silica [69,70].

From another viewpoint, a study on increasing the conversion rate of CO_2 and methane through Co–Pt/MgO–Al₂O₃ bimetallic aerogel catalysts found that it had significant activity and improvement compared to Co/Pt. The conversion rate of carbon dioxide reached 40%, while Co/Pt was less than 1%. Furthermore, the addition of Pt enhanced the ability to reduce CO, due to the electron transfer process between the active sites of metals [71].

For CO₂ reduction into syngas, the Pt/TiO₂ was utilized with photoelectrochemical assistance. The solar-to-syngas efficiency was 0.87%, and the stability was 10 h. The role of the metal/oxide catalyst in this process is to activate CO₂ molecules and stabilise the primary chemical intermediates, whereas the function of the supporting surface is electronic induction [72]. Silver nanoparticles on MOFs, Ag@MIL-100(Fe), and Ag@UIO-66(Zr) have been tested to capture and convert CO_2 into carboxylic acids. The Ag@MOF, under mild conditions, showed excellent activity and reusability for CO_2 capture and conversion [73]. Pd/Ce-MOF have been developed for CO oxidation and CO₂ uptake. The combination of Pd nanoparticles within Ce-MOF results in a unique catalyst capable of both CO oxidation at modest temperatures (370 K) and efficient uptake of the CO₂ (at 273 K) [74]. A thin film of iron oxide has been employed as a supporter, and the conversion of CO_2 to hydrocarbon has been achieved using copper tetramers (Cu₄) on a thin film of iron oxide (Fe₂O₃) at atmospheric pressure, as the Cu_4 on Fe_2O_3 could enhance methanol synthesis at low temperatures and has a selectivity of 63%. However, at temperatures above 325 °C, the reaction pathway shifted from methanol to methane ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$), and methanol production deteriorated, whereas when the reaction was performed at 425 °C, the selectivity for methane reached 98% [75].

The interaction and activation of CO₂ on the Bi₂O₃-TiO₂ was examined. The results showed that the properties of bismuth-containing oxides could be utilized to adsorb and excite carbon dioxide, which is the crucial first step in the reductive conversion of CO_2 to valuable molecules. This combination of Bi³⁺ in TiO₂ species offers a fascinating composite that can stimulate CO_2 by strong adsorption and alteration or electron transfer to produce a carboxylate or by direct breaking of the C-O bond [76]. The use of metal oxides to load the noble elements in carbon dioxide conversion reactions was carried out using different oxides (TiO₂, SiO₂, γ -Al₂O₃, ZrO₂, and CeO₂). The noble metals (Ru, Rh, and Pd) are effective catalysts in converting carbon dioxide [77]. Under moderate reaction conditions, the alkaline metal oxide (MgO) supported by (Pd) has been investigated. Pd/MgO was examined with commercial noble metal catalysts to verify its efficacy in converting carbon dioxide to methanol, using 5% wt of the metal, at 150 °C and 70 bars for 15 h, by adding K₃PO₄. The addition of K₃PO₄ to Pd/MgO showed a negative effect on converting carbon dioxide to methanol, as it was 0.3%, while, in the absence of K_3PO_4 , it was 4.63% [78]. The productivity of the Pd/MgO catalyst is low compared to the Pd-Z1FO catalyst, which gave a 14% conversion rate to CO_2 . However, the linear association between methanol and the amount of PdZn shows that the PdZn increased the active sites, and the selectivity was 52% [79].

Among the metals, nickel is a promising metal due to its high activity and the fact that it is relatively cheaper than noble metals. However, Ni-based catalysts tend to be deactivated during the methanation reaction due to coke formation and sintering of Ni particles at high temperatures [80]. It has been suggested that the addition of ceria can enhance the catalyst performance and coke resistance; therefore, as shown in Figure 5, Ceria (CeO₂) can work as a structural and electronic promoter in order to promote the dispersion of Ni on the support and change the properties of Ni via metal-support interactions, due to the oxygen vacancies of ceria [81], where it acts as a structure promoter to improve the dispersion of Ni species on the supporter, as well as electron promoter to accelerate [82]. For the samples without Ce modification [83], the results show that the CO₂ conversion rate using Ni/RGO was 63.1% at 400 °C and 78.4% at 350 °C, respectively, while, with Ce modification, the CO₂ conversion increased, compared to the samples without Ce. Both the experimental and theoretical investigations confirm that the excellent catalytic performance of Ni-Ce/RGO reaches the highest activity at 350 °C, with a CO₂ conversion of 84.5% and 78.7% (400 °C) [84].

Figure 5. Conversion of CO₂ using Ni/RGO both with and without modification Ce and Ce. (Adapted with permission from Ref. [84]. Copyright 2019 Elsevier).

6.2. CO₂ Conversion Using Single Metal Oxide

Several studies have been conducted to separately evaluate the effect of metal oxides on the conversion process. For instance, five metal oxides (ZnO, SnO₂, Fe₂O₃, La₂O₃, and CeO₂) were synthesized using the sol–gel process in polyvinyl alcohol, and their catalytic activity was tested in direct carbonization of glycerol with CO₂. The results showed that the best reaction condition was 180 °C, 150 bar, and 12 h of reaction time, and zinc oxide showed the best performance among other oxides, with a yield of 8.1% of glycerol carbonate [7]. Highly active $Co_x(CoO)^{1-x}$ catalysts are used as catalysts for CO₂ hydrogenation reaction. The association between catalytic reactivities and metal/metal oxide ratios and the functions of catalytic activities were examined. Metal ratios of x = 0.2, 0.5, and 0.8 were applied in the samples. The reaction was studied using a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) chamber, from a low temperature of 25 to a high temperature of 350 °C. The result demonstrated that the C–O bond could be easily broken on the cobalt catalyst to produce hydrocarbons. The maximum conversion was obtained at 350 °C, with a conversion rate of 98, 99, and 93% on Co(0.2), Co(0.5), and Co(0.8) samples, respectively [85].

6.3. Binary Metal Oxides for CO₂ Conversion

Binary metal oxides (BMOs) contain two metal ions that are either electrochemically active or inactive. BTMOs are characterized by their high conductivity and abundant active sites, making them more stable. BMOs are synthesized in several ways, including the template, electrodeposition, microwave-assisted, and solvothermal methods [86]. Zhou et al. used $Fe_3O_6H_6/Cu$ (111) as an analogue model for CuFe electrocatalyst by taking a CO_2 aqueous environment, and a clear improvement was observed, compared to iron and copper separately because of a more suitable for electron-hole reinforcement than a copper catalyst, in addition to providing active centers to enhance kinetic properties [87]. Calculations of Density Functional Theory (DFT) revealed that the copper-iron binary system could operate in synergy to distort the linear formation of carbon dioxide, resulting in a significant reduction in activation energy and, thus, aiding in methanolic synthesis, with a 51% faradaic efficiency and more than twice that of 20% Cu and 0% Fe.

On the other hand, a two-metal, Zn–Cu electric catalyst introduced selectivity and high-efficiency activity to convert CO₂ to CO, where DFT calculations demonstrated that the fusion of copper on the zinc surface reduced the activation capacity from 0.44 to 0.15 volts, increasing the selectivity of Zn–Cu to be 97% faradaic efficiency. In contrast, zinc selectivity was only 30% faradaic efficiency, indicating that incorporating copper into zinc generates a synergistic effect that improves the conversion of CO_2 [88]. The highly cooperative win-win metal-oxide interaction that enables unprecedented catalytic functionalities for electrochemical CO₂ reduction reactions has been investigated in a single SnOx/Ag catalyst. In the CO production mode, the oxide promotes the metal. In the HCOOH production mode, the metal promotes the oxide, resulting in potential-dependent bifunctional CO_2 conversion to fuels and chemicals, with H₂ evolution repressed throughout the potential window. The electron transfer from Ag to SnOx and dual-site cooperative binding for reaction intermediates at the SnOx/Ag interface are responsible for stabilizing the key intermediate in the CO pathway, changing the potential-limiting step in the HCOOH pathway and increasing the kinetic barrier in the H₂ evolution pathway, all of which lead to highly synergistic CO₂ electroreduction, as per spectroscopic studies and computational simulations [89].

Mixtures of two or more metal oxides, or with heterogeneous materials, may enhance the effectiveness of the catalyst in converting carbon dioxide to other materials because they contain oxygen in varying proportions, where can be divalent, trivalent, or tetravalent, which leads to the synergistic effect. For instance, studying the hydrogenation of carbon dioxide to methanol while adding graphene oxide to CuO-ZnO-ZrO2 catalysts significantly enhanced the methanol selectivity and production rate of the catalysts. There are more active sites for CO_2 and H_2 adsorption when added 0.5–2.5 wt% (GO). When graphene oxide content exceeded 2.5 wt%, the size of the CuO particles grew significantly, resulting in a lower rate of methanol production. The graphene oxide-free CuO–ZnO–ZrO2 catalyst was compared to the graphene oxide-coated CuO–ZnO–ZrO₂ catalyst at different temperatures [90], as shown in Figure 6a,b. In order to facilitate the hydrogenation and other intermediate species on the copper surface, the GO nanosheet acts as a catalyst bridge between the copper surface and other oxides. With GO-free catalysts, on the other hand, the active sites are more effective when the metal oxides are not in direct contact with the Cu surface. At 200 °C and 20 bar, GO-prepared catalysts outperform GO-free catalysts to obtain the maximum selectivity of 75.9%.

 MoO_3 / SiO₂ solid acid catalyst was employed to transesterify diethyl oxalate with phenol to generate diphenyl oxalate. The high selectivity was obtained (100%). The variety of MoO_3 /SiO₂ ratios of Mo was (1–20 wt%) with the conversion of 80.9, and 100% respectively obtained [91].

6.4. Metal Oxide Nanoparticles for CO₂ Conversion

Nanoparticles (NPs) are a broad class of materials that include particulate substances, with one dimension less than 100 nm. This broadly divided NPs into various categories, depending on their morphology, size, and chemical and physical properties [92,93]. Copper nanoparticles (NPs) were able to selectively transform C2–C3 products (ethylene, ethanol, and propanol) with low redundant capacities. Some researchers found that, when making copper NPs at high temperatures, the copper NPs transformed into cubic-like particles mixed with smaller nanoparticles, as shown in Figure 7. These nanoparticles (NPs) can convert carbon dioxide into polycarbonate products with high selectivity, capable of forming ethylene, ethanol, and n-propanol, as they are formed during electrolysis by the structural transformation of the copper NP group.

Selectivity (CZZ) with Go and Go oxide-free (CZZ) at different temperatures.

Figure 6. Selectivity (CZZ) with GO and GO oxide-free (CZZ) by different temperatures (**a**), and graphene oxide nanosheet as a bridge, promoting hydrogen spillover from the surface of copper to the surface of other metal oxides (**b**) (Adapted with permission from Ref. [90]. Copyright 2018 Elsevier).

Figure 7. Schematic diagram of the transformation of Cu NP ensembles. (Adapted with permission from Ref. [94]. Copyright PNAS).

These structures can selectively generate C2 and C3 products together, C2–C3 faradaic efficiency (FE), reaching 50%, at only -0.75 V, illustrating the importance of on-site structural evolution. In contrast, it was concluded that catalyst support plays an essential role in the high selectivity of the multiple carbons. Furthermore, they found that the structural transformation can occur not only under low bias conditions but is controlled by the initial arrangement of NPs. Thus, the catalytic behaviour can be significantly improved [94].

7. Various Techniques for the Conversion of Carbon Dioxide

CO₂ conversion techniques based on metal oxide as catalysts have shown promising solutions [95,96], including photocatalytic electrochemical, plasma etc. [97,98]. Figure 8 depicts the products that can be obtained by converting carbon dioxide using various techniques and metal oxides.

Figure 8. Conversion of CO₂ to value-added products by metal oxides.

7.1. Photocatalytic Applications of Carbon Dioxide Conversion

Among the various ways to reduce carbon dioxide is photocatalysis, which uses sunlight in the conversion processes of CO_2 [99].

The photocatalysis process, by semiconductors, can generally be divided into; general phases, the generation of charge carriers, separation and migration of charge carriers, and redox reaction [100].

TiO₂-based catalysts are a standard for studying photocatalysis due to their simple preparation, low cost, and high stability. However, TiO₂-based catalysts still do not effectively absorb visible light due to the large bandgap, making it of minor importance for solar energy harvesting [101,102]. Figure 9 shows that TiO₂ acts as a photocatalyst under light radiation, where the incident photons are absorbed with energy higher or equal to that of the bandgap conductor. Then, the pair charges, electrons, and holes are generated, reducing the carbon dioxide into value-added products [103].

Figure 9. Schematic illustration of photoreduction of CO₂ into fuels on the photocatalyst.

Research has been conducted to convert carbon dioxide using visible light catalysis to methane; this was carried out in the presence of H_2O over various mesoporous materials, using (TiO₂ and SnO₂) and compound semiconductors (ZnS and ZnSe). The pore system and metal oxides of SnO₂ and TiO₂, as well as the composite semiconductors from CdS, CdSe, ZnS, and ZnSe, were fabricated using the nano replication pathway. In addition, they compared the catalytic CO₂ conversion performance of porous metal oxides and semiconductors composite under visible light irradiance [104,105]. The results showed that the productivity of porous metal oxides (TiO₂ and SnO₂) was 9–10 times higher than that of methane, with 2–3 times higher yields of CO, owing to their high surface area [106,107].

Furthermore, the mesoporous CdSe produces the highest CO yield rate (5.884 μ mol gcat⁻¹h⁻¹). The cause may be attributed to the bandgap's smallness over other materials with medium pores, which allows for the photoconversion of carbon dioxide with visible light.

ZnS mesoporous showed the highest yield (5.884 μ mol gcat⁻¹h⁻¹) for CH₄. Moreover, the rates of porous composite semiconductors offer higher yields of CH₄ and CO than porous metal oxides due to the band gaps of ZnSe, CdSe, and CdS being much smaller than porous minerals oxides [104].

One of the essential features of a promising photocatalyst is its low bandgap and high surface area. The modified ZnO/ZIF-8 catalyst is used in the presence of water by employing the mercury vapour lamp to produce methanol through the carbon dioxide conversion process [108]; the activity was higher than the Cu-TiO₂/ZIF-8 [109] and ZnO [110] catalysts.

Using the sol-gel method to convert carbon dioxide into methanol by fabricating a ZnFe₂O₄/TiO₂ photocatalyst in visible light was investigated [111]. A 3% increase in methanol production was observed when using the halogen tungsten lamp, where the maximum yield was 527.4 µmol gcat⁻¹, as opposed to CeF₃/TiO₂ [112] and Cu₂O/SiC [113]. Currently, researchers are seeking to develop photocatalysts through bandgap modulation, especially for TiO₂. In recent years, MXene materials have been discovered, which are used as photocatalysts for semiconductors, as they enhance and activate CO₂ absorption by reducing photocorrosion and accelerating charge separation [20]. This novel 2D nanostructure material (MXenes), synthesized by selectively etching X element from ternary metal carbides, was used as a helper, with the Pd50-Ru50 catalyst, to convert CO₂ to CH₃OH, where Pd50-Ru50/MXene demonstrated a 78% conversion efficiency of CO₂ with a 76% methanol crop [114].

7.2. Carbon Dioxide Conversion by Plasma Catalysis

Interest has increased recently in the combination of heterogeneous catalysis and plasma [115,116], known as plasma catalysis [117,118], due to its use to fix greenhouse gases improve conversion rates, and reduce the activation barrier for various reactions [115]. The conversion of carbon dioxide using plasma catalysis has a great potential to increase the efficiency of the reaction due to the synergistic effects between the plasma and the catalysts.

However, this technology requires a paradigm shift in process design to improve the catalytic performance of the plasma [119]. The high temperature is usually used in the conversion processes of carbon dioxide due to the high stability of the CO_2 molecule, which results in low efficiency and high energy consumption. Therefore, non-thermal plasma (NTP) processes have been used as an alternative to conventional thermal catalytic processes [120,121].

One of the essential advantages of non-thermal plasma is integrating with energy sources, such as solar energy and wind. The speed of shutdown and operation can also be controlled. However, non-thermal plasma needs a qualitative leap in improving the catalytic performance of the plasma in terms of energy efficiency and conversion because it is an obstacle to its use at the industrial level [119,122]. As demonstrated in Table 3, the researchers increased the conversion and selectivity of metal oxides, resulting in improved catalytic performance in thermal plasma processes.

Catalyst	Conversion CO ₂ (%)	Selectivity	Ref.
Ni/CeO ₂ -SGM	80.5%	96%	[123]
CuO/Al_2O_3	15.7%	48%	[124]
BaTiO ₃	28.0%	96%	[125]
5% ZnO + g-C ₃ N ₄	12.0%	70%	[126]

Table 3. Results of some studies in thermal plasma processes to improve CO_2 conversion and selectivity by metal oxides.

Thermal reactors find difficulty in the repair processes, not to mention the need for higher degrees of heat that cause an adverse reaction, resulting in a decrease in conversions [127].

Cold or non-thermal plasma was an appropriate alternative, providing the required energy through active electrons at room temperature [128].

Ce metal was considered good in plasma catalytic conversion processes in CO_2 to CO; however, it was costly, leading researchers to collect it with abundant and inexpensive metals, such as iron. The highest rate of CO_2 conversion, using Fe/Ce, was (24.5%). However, Ce showed better performance with CO_2 conversion by 28.2%.

Although the Ce conversion rate was slightly higher than that of Fe/Ce, the Fe/Ce catalyst would reduce operating costs while decreasing conversion [129].

Some studies have shown that the presence of water with calcium oxide can help improve the conversion of carbon dioxide in the non-thermal plasma process from 11.3% to 14.7% at room temperature. The selectivity of methanol, ethanol, acetaldehyde, and acetone increased from 1.0%, 0.3%, 0.3%, 0.4% to 1.4%, 0.5%, 1.1%, and 0.7%, respectively [130].

Di Li Group developed a catalytic plasma reactor, called DBD, with SiO₂ air-gel catalysts to convert carbon dioxide and methane into liquid chemicals using Co and Fe. Plasma experiments were conducted on carbon dioxide and methane without catalysts. The conversion rates of methane were 28.6% and, for carbon dioxide, 15.2%. In contrast, in the presence of catalysts, the conversion ratio increased by 2:1, respectively, increasing the selectivity of liquid chemicals by about 40% [21].

Experimental studies have been done to improve the barrier discharge (DBD) plasma reactor performance in non-thermal plasma, using polyurethane foam to provide high air insulation stability [131,132]. For further improvement, Taghvaei and others coated different metallic oxides on top of the foam to measure their effect on the efficiency and conversion of carbon dioxide into carbon monoxide. BaTiO₃, coated on foam, provided the highest conversion rate of 27.4% [133]. It can be deduced from previous research that the low energy efficiency of the DBD reactor was one of the most notable drawbacks. In contrast, the conversion of CO₂ using plasma needs additional improvement [134].

7.3. Electrocatalyst Applications in Converting Carbon Dioxide

Electrocatalysis can be defined as the catalytic processes of redox reactions that directly transfer electrons [135]. The electrolysis of carbon dioxide has attracted wide attention due to the moderate operating conditions, where the reaction rate and requirements of the reaction process can be controlled, and the use of simple equipment and energy; additionally, the catalyst is recyclable [136]. Electrical stimulation generally occurs when an electron is transferred from cathode to anode. A membrane is placed in between to prevent mixing, and a salt bridge is placed to maintain electroneutrality [137].

The majority of the carbon dioxide reduction reactions depend on operating conditions and electrical stimuli.

However, CRR electrocatalysts are subject to many obstacles, such as high production cost, high activation barrier (or excessive overvoltage), and poor control of product selectivity [138]. Currently, the copper oxide electrodes are characterized by high faradaic efficiencies of methanol, in a study conducted by M. Le Group to examine the composition and behaviour of methanol using multiple electrical catalysts with surface sites [139]. It was found that the types of copper oxides have a significant role in raising the efficiency of faradaic, as the electrodeposited cuprous oxide electrodes were higher than the copper oxide by air with a faradaic efficiency of (38%), as shown in Figure 10, for methanol production using catalysts based on CuO, Cu₂O/ZnO₂ mPy [140], and Cu₂O/ZnO [141]. Through these studies, the researchers developed modified nanoparticles of graphene oxide reduced carbon with a heterocyclic compound containing an N ring and imidazole, known as (NB), with copper nanoparticles (CuNPs @ rGO-NB) [142,143]. RGO (rGO-NB) is widely used in electrical catalysis processes due to its high activity and selectivity and has long-term stability when used as a catalyst [144]. In comparison, nanoparticle symmetric copper electrodes are used to produce a mixture of hydrocarbon products [145].

Figure 10. CH₃OH production using copper oxide-based catalysts.

The main intention of applying this nanocomposite is to enhance the electroactivity of rGO and increase the efficiency of CO_2 conversion. As a result, the total products produced from the conversion of carbon dioxide by modified electrocatalyst reached 86%. Furthermore, the results showed that the main CO and CH₄ products in the gaseous phase were higher than the liquid phase because the rate of electron transfer/hydrogenation was incompatible with the rate of interaction between the adjacent carbon dioxide molecules; once carbon dioxide reaches the level of the catalyst, the electron is moved immediately, resulting in lower production of more complex molecules [146].

Recent studies have shown that the conversion efficiency of reduction processes can be enhanced by modifying electrical catalysts [147].

8. Conclusions

This review provides a thorough discussion of the subject of CO_2 uptake and conversion, using metal oxides as a catalyst or supporter, as well as the recent developments in carbon capture and conversion processes using metal oxides. Capturing and converting carbon dioxide can reduce the environmental problems caused by the increasing consumption of fossil resources. The absorption processes are considered one of the most effective methods of capturing CO_2 . Different catalytic methods are briefly probed to reduce the content of carbon dioxide. However, low yield, energy consumption, and low conversion efficiency still exist problems and thus make the method and catalysts need continuous development.

Consequently, there has been a surge in research on finding catalysts that improve product selectivity. The most notable catalytic materials developed so far in the absorption and conversion processes contain noble metals that work well at high and low temperatures. However, due to their high cost, cheap alternative materials are highly desirable. Metal oxides have long been used as alternative catalysts instead of expensive rare metals, although they offer little activity at lower temperatures compared to noble metals. However, at high temperatures, activity is quite comparable. It is evident from the above that some metal oxides have high thermal stability and high catalytic performance, making them suitable candidates for many applications, such as photocatalysis, plasma catalysis, and electrical stimulation. Although metal oxides are functional in many applications, some challenges related to the thermodynamics of carbon dioxide and its capturing and conversion still need more research and studies in the coming future, especially in the field of materials engineering.

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