CO2 Activation on Catalyst Surfaces

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Utilizing CO2 as a sustainable carbon source to form valuable products requires activating it by active sites on catalyst surfaces. These active sites are usually in or below the nanometer scale. Some metals and metal oxides in this scale dimension can catalyze the CO2 transformation reactions. Herein, CO2 activation on metal-based catalyst surfaces and how their structures impact the activation process are highlighted.

CO2 CO2 activation metal oxide nanoparticles

1. Introduction

 CO_2 is a chemically inert molecule due to its kinetically stable nature; thus, its conversion by reduction to economically viable products relies on its activation to kinetically vibrant species ^[1]. The stable nature of CO_2 and high activation barrier (1.9 eV) implies that its transformation in the presence of a catalyst should create a unique environment for facilitating activation pathways ^{[2][3][4][5][6]}. It is possible to apply either homogeneous or heterogeneous catalysis to transform CO_2 into value-added products, the latter through thermo-, electro-, or photocatalysis, to induce the catalytic reactions ^{[2][8]}. Each of these processes comes with its shortcomings and benefits. The electrocatalytic and photocatalytic processes have advantages in tuning the reaction products but are difficult to scale up ^[9]. Scale-up is, however, promoted in the thermocatalytic process due to its fast reaction rate and high efficiency, although thermodynamic balance is an issue. Given the intricacy of the accompanying reaction mechanisms and the dynamics of heterogeneous catalysis under reaction conditions, there is still a lack of very fundamental understanding of the chemistry of CO_2 reduction. In the presence of small but reactive molecules such as hydrogen or water, CO_2 can be transformed into stable products over heterogeneous catalysts with more favorable thermodynamics. The catalyst must possess activity for activating CO_2 in addition to enabling effective conversion reactions.

Adsorption and activation are two important steps that occur during the CO_2 reduction on catalyst surfaces. The adsorption (physisorption and chemisorption) of CO_2 on the surface of heterogeneous catalysts has become a subject of growing research interest in recent years ^[10]. The activation of CO_2 on the heterogeneous catalyst surface yields CO_2 -derived species that eventually convert to useful products. Several CO_2 -derived species, including carboxylate and carbonates, have been identified, irrespective of which approach is adopted for CO_2 conversion ^[3]. The generation of specific activated carbon species determines the kind and selectivity of the product(s). Co-reactants such as water contribute to the overall reduction reaction by promoting adsorption and subsequent activation. As with most chemical conversion technologies, the choice of catalyst is also an important factor, which must have suitable selectivity and activity for activating CO_2 under relatively mild conditions. Many

studies reported in the literature tried to understand how to promote the chemisorption and subsequent activation of CO_2 by focusing on catalysts preparation and structures. Specifically engineered or surface-modified catalysts have shown improved performance for CO_2 activation. Catalysts (metal oxides) with rich surface defects or high concentrations of oxygen vacancies have been particularly effective for CO_2 activation. Oxygen vacancies can greatly influence the interaction of CO_2 with the surface and enhance the adsorption of CO_2 molecules. Thus, oxygen vacancies play important roles in CO_2 conversion. Surface defects can be created in metal oxide catalysts either during reactions or incorporated by external methods. Understanding the nature of CO_2 in the activated form and the catalyst characteristics will be important in developing novel strategies for activating CO_2 . An appreciable understanding of the reaction of CO_2 on pure metal surfaces is well documented; however, less is known about the reactivity of CO_2 on metal oxide surfaces, e.g., how the surface defects contribute to the mechanism of CO_2 activation. A discussion on the CO_2 activation mechanism on metal oxide surfaces and the roles of surface defects in the activation process is put forward in this piece.

2. Activation of CO₂ on Heterogeneous Catalyst Surface

The interaction of CO_2 molecules with metal-based surfaces has attracted intense research attention for a long time. Reduction of CO_2 by H₂ has been studied on some transition metals (e.g., Cu, Co, and Ni) and metal oxide catalysts (e.g., TiO₂, CeO₂, and In₂O₃). The catalytic surfaces for the activation of CO_2 include metal sites, metal-oxide interfaces, and oxygen vacancies. For facile CO_2 activation and conversion, efforts should be made to know, design, and optimize functional sites in heterogeneous catalysts, which involves constructing surface sites with a charge density gradient capable of reorganizing the electronic structures of CO_2 and polarizing the adsorbed species [11].

Metal-based catalysts are capable of effectively activating CO_2 even in the absence of hydrogen ^[12]. These include pure metal surfaces, doped or promoted metal surfaces, and supported metal nanoparticles. On supported metal surfaces, CO_2 activation occurs mainly through acceptance of charge from the metal; the oxide support plays a big part in the activation process through different mechanisms such as acid sites interactions and provision of oxygen vacant sites ^[13]. The metal surface is also important in the dissociation of H₂ in CO_2 hydrogenation reactions ^[3].

2.1. CO₂ Activation on Representative Pure Metals

Metal nanoparticles sit on a metal oxide serve as active sites for the electron transfer. Transition metals such as Cu, Ni, and Fe are particularly energetic for activating CO₂. Their surfaces possess high binding abilities to CO₂. DFT calculations evidenced that on Pt, Rh, Ni, Cu, Ag, and Pd (111) surfaces, the affinity toward oxygen is different for the metals, which selects their reaction pathways for the CO₂ activation in the RWGS) reaction. Pt, Ag, and Pd tend to favor the COOH-mediated mechanism, whereas Rh, Ni, and Cu dissociate CO₂ into CO and O ^[14]. This difference underlines the variation in the CO² dissociation barrier of the different metal groups. Thus, the nature of the interaction between the adsorbed O and the surface is critical for determining the CO² dissociation barrier. In the activation of CO₂ via the charge transfer mode, which is prevalent on metal surfaces, the partial and full charge transfer leads to the formation of CO₂^{δ^-} </sup> and CO₂⁻, respectively. The degree of charge transfer can be analyzed on

metal surfaces after adsorption. Physisorption and chemisorption of CO_2 on single crystal surfaces of various metals have been studied by means of DFT calculations ^[15]. Chemisorption states are highly dependent on both the metal itself and adsorption sites. Chemisorbed CO_2 molecules often have a bent structure with O–C–O angle varying between 121 and 140° compared with the nearly linear coordination of the physisorbed CO_2 molecules, and their extent depends on the kind of metal surface. In other words, the degree of CO_2 activation varies with metal surfaces. Similar behavior can be observed for the amount of charge transferred. According to Wang et al. ^[16], who investigated CO_2 chemisorption on nine transition metal surfaces (Fe, Co, Ni, Cu, Rh, Pd, Ag, Pt, and Au), the adsorption strength is affected by both the *d*-band center of the metal surface and the charge transfer, which control the activation of the C=O bond. It is possible to promote chemisorption by adjusting the properties of the catalysts, such as the catalyst surface area, surface defects, basic sites, and the addition of promoters ^[17].

The coordination of CO_2 with metals can take different modes via the electron-deficient C atom as the electron acceptor and the C=O bonds or O atoms as the electron donor. Electron-rich metal surfaces such as Ni (110) and Cu (100) generally activate CO_2 by attaching to the carbon atom ^{[18][19]}. In the process, electrons in the d_z^2 orbital of the metal transfer to the unpopulated antibonding π^* orbital of the CO₂ molecule. Consequently, negatively charged surfaces are efficient for CO₂ activation via the charge transfer mode. Such charged surfaces can be generated through inserting strong metal-support interaction, bimetallic and ligand effects, etc. ^[11]. Electron-deficient metal surfaces, such as Ti, Cr, V, and Mn, favor the end-on coordination with CO₂ ^[20]. In this mode, the bending or distortion of the linear CO₂ molecule is difficult ^[11]. For metal centers with combined binding behavior, i.e., possessing both an electron acceptor site and an electron donor site, CO₂ adsorption generally prefers the bridge sites. More efficient activation can result through this mechanism and lead to bending of the linear CO₂ molecule from different sites ^[11].

Investigations by DFT calculations revealed the characteristic adsorption and activation of CO_2 on Rh, Pd, Pt, Ni, Fe, Cu, Re, Al, Mg, and Ag metals ^{[14][21]}. Strong evidence has been provided for the formation of CO_2^- according to spectroscopic results. Depending on the type of metal, CO_2 can also dissociate into CO and O or be transformed into $CO_3^{2^-}$ and CO. The activation of CO_2 on Pt, Rh, Ni, Cu, Ag, and Pd followed different elementary steps as a result of the different levels of interaction of the metals with adsorbed oxygen in the RWGS reaction. Metals with high affinities toward oxygen presented lower activation barriers, leading to facile hydrogenation reactions ^[14]. The presence of preadsorbed oxygen was responsible for forming carbonates of different structures ^{[14][21]}. On most metal surfaces, CO_2 activation is highly surface orientated, pressure- and particle size-dependent ^{[16][22][23][24]}. For e.g., Yu et al. ^[24] demonstrated through spin-polarized DFT calculations that adsorption and dissociation of CO_2 were dependent on the Co particle size. They showed that CO_5 nanoclusters had the highest CO_2 dissociation activity in comparison to CO_{13} and CO_{38} . However, CO_{13} activated CO_2 with the smallest O-C-O angle (123°) against 137° for both CO_{38} and CO_{55} nanoclusters.

Cu-based materials have gained much attention in the CO_2 conversion process due to their wide applicability in the different conversion processes and low cost ^{[9][25]}. Despite these and other massive studies, the activation of CO_2 on Cu catalysts is still an issue due to the poor understanding of its mechanism. Studies have shown that CO_2 interacts weakly on low-index Cu surfaces under UHV conditions ^{[26][27]}. However, a recent study found Cu (100)

surface to be more active in dissociating CO_2 than Cu (111), producing atom oxygen ^[19]. Ambient pressure X-ray photoelectron spectroscopy (APXPS) and DFT calculations revealed the activation of CO_2 on Cu surfaces. APXPS showed that CO_2 adsorbed as $CO_2^{\delta^-}$ on Cu (111) surface under a pressure of 0.01 mbar at 300 K. With an increase in pressure to 1 mbar, adsorbed $CO_2^{\delta^-}$ partially transformed into carbonate as a result of the disproportionation reaction between CO_2 molecules. Subsequent annealing at 400 K or higher temperatures led to the dissociation of $CO_2^{\delta^-}$ and carbonate and the formation of a chemisorbed oxygen-covered surface. On Cu (110) surface, the $CO_2^{\delta^-}$ gradually dissociated into CO and chemisorbed oxygen under the same CO_2 pressure at room temperature. On both surfaces, atomic oxygen was generated that catalyzed the self-deactivation of CO_2 adsorption. The DFT results, which collaborated experimental findings, further indicated that the Cu (110) surface was more active than the Cu (111) surface in breaking C–O bonds ^[23]. Comparing the adsorption of CO_2 on Cu (111), (100), and (110) surfaces, it was found that CO_2 molecules aligned parallel to Cu (111) and (100), whereas a vertical configuration was more stable for the adsorbed CO_2 on Cu (110) > Cu (110) > Cu (111) ^[16]. A decrease in the activation energies for CO_2 dissociation has been observed when Cu surfaces have step or kink defects in comparison with the flat surface. Chemisorption of CO_2 was reported on Cu stepped surfaces ^{[26][27][28][29].}

Ni-based catalysts can dissociate and convert CO_2 into value-added products, such as methane; thus, a fundamental understanding of the interaction between CO_2 and Ni surface at the atomic level is crucial to design even more efficient Ni-based catalysts. According to theoretical studies, the surface orientation of Ni influences the activation of CO_2 by altering the energetics for subsequent C–O bond cleavage ^[30]. Ab initio calculations using slab models have shown that CO_2 reactions on model Ni are surface sensitive, with reactivity in the following trend: Ni (110) > Ni (100) > Ni (111) ^{[30][31]}. Experimental investigations revealed the capability of Ni (110) surface to molecularly adsorb and subsequently dissociate CO_2 at room temperature ^[32]. By using in situ APXPS, carbonate was identified as the dominating surface intermediate at room temperature upon CO_2 adsorption on Ni (111) and Ni (110) surfaces. Carbonate, CO, and graphitic carbon were all observed on both Ni (111) and Ni (100) surfaces under a CO_2 pressure of 0.2 Torr. Ni (111) was predominantly covered with carbonate, whereas adsorbed CO^* and graphitic carbon were prevalent on the Ni (100) surface as indicated in **Figure 1**a–d ^[35]. The CO_2 adsorption and dissociation on ideal Ni (111) and stepped Ni (211) surfaces are shown in **Figure 1**a–d ^[35]. The CO_2 adsorption and dissociation is endothermic by 20 kJ·mol⁻¹ on Ni (111) surfaces, whereas it is exothermic by 40 kJ·mol⁻¹ on Ni (211) surfaces [^{36]}.



Figure 1. Ambient pressure XPS spectra of (**a**,**b**) C 1s, and (**c**,**d**) O 1s Ni (111) and Ni (100), respectively. CO_2 adsorption was performed under 0.2 Torr CO_2 at room temperature. Reproduced with permission from ^[35]. Copyright 2019 American Chemical Society; (**e**) Energy profile diagram for the CO_2 activation on Ni (111) and Ni (211) surfaces, edges of Ni₁₃ particle, and edges and terraces of the Ni₅₅ particle and the activation geometries on the Ni₁₃. Reproduced with permission from ^[36]. Copyright 2016 American Chemical Society.

Based on the experimental results of the ultrahigh vacuum (UHV), Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), and high-resolution electron energy loss spectroscopy (HREELS), it is difficult for CO₂ to adsorb on a clean Pt (111) surface between 110 and 300 K, but the dissociation capability can be improved by doping alkali metals such as potassium [37][38]. Conversely, it was reported that Pt foil treated with CO_2 in the gas phase during in situ UHVXPS experiments at 77 K formed chemisorbed CO species [39]. In collaboration with the latter assertion, on the clean Pt (111) surface, CO₂ dissociated into adsorbed CO and O at both room and elevated temperatures $\frac{[40]}{2}$. The production of adsorbed CO increased upon the introduction of H₂ (hydrogenation reaction). This observation was obvious for the CO₂ adsorption at all temperatures and led to the deoxygenation (consumption of oxygen) of the surface, cleaning the sites for further CO production and desorption from the surface at elevated temperatures. The Pt surface was active in the RWGS reaction. At low pressure, the RWGS was initiated at 300 °C; on the contrary, at high pressure (H₂:CO₂ of 150 mtorr: 15 mtorr), a low temperature (200 °C) favored the initiation of the RWGS reaction, and the conversion of CO₂ increased with increasing temperatures $\frac{[40]}{2}$. Moreover, under a pressure of 40 mtorr of pure CO₂ and at temperatures below 150 °C, graphitic carbon has been also observed as a product of the Boudouard reaction. IR spectroscopy revealed the size-dependent nature of CO_2 adsorption on Pt clusters. On small Pt clusters anions (Pt_n^- , n = 4–7), CO_2 was highly activated but remained molecularly adsorbed on Pt₄⁻. On large clusters, dissociative adsorption was observed [10].

2.2. CO₂ Activation on Bimetallic/Alloyed Catalyst Surfaces

Bimetallic surfaces are highly unique and active for a wide range of CO_2 transformation reactions due to the electronic and geometric alterations within the structure. These alterations could be observed as a change in the

morphology of metal, adsorption mode and configuration, and chemical ordering with varying composition and particle size ^{[5][41]}. This can help to control the adsorption properties to attain desired adsorption coverages. Numerous studies have discussed both activation of CO₂ and the subsequent conversion of CO₂ to fuels and chemicals on bimetallic catalysts. Ko et al. ^[15] studied the CO₂ activation and adsorption by performing DFT calculations on a range of bimetallic alloy surfaces. The dissociation energy barriers of CO₂ were screened by combining Bronsted–Evans–Polanyi (BEP) relation, scaling relation, and surface mixing rule. It was found that CO₂ dissociated into CO and O, which sum of their adsorption energies was linearly related to both the energy for CO₂ dissociation and that for CO₂^{δ^-} adsorption. The activation of CO₂ proceeded through a direct dissociation (CO₂ \rightarrow CO + O) mechanism in three successive elementary steps: physisorption of CO₂ from the gas phase on the metal surface, chemisorption of CO₂^{$\delta^-} from the physisorbed CO₂, and direct dissociation of CO₂^{<math>\delta^-} into CO and O.$ </sup></sup>

The predicted activation energies for the CO₂ dissociation on bimetallic alloy surfaces are shown in **Figure 2**, with the row and column indicating the host and solute metals of the bimetallic alloys, respectively. The alloying effect would lead to a reduction in surface reactions when the solute metals are placed in the bulk region. In the figure, the activation energy (E_a^{act}) decreases from right to left and from bottom to top, thus alloys with relatively low activation energies (~0.75 eV) are Fe-, Ru-, Co-, Ni-, Rh-, and Ir-based alloys, whereas Pd-, Pt-, and Cu-based alloys possess high activation energies (~1.51 eV). Still, some metals, including Ru-, Co-, Ni-, Rh-, Ir-, and Cu-based alloys, have activation energies in between the extremes (0.76–1.50 eV). This picture makes sense for fabricating bimetallic catalysts for CO₂ conversion reactions by manipulating the activation energies [15].



Figure 2. Screening for E_a^{act} for CO₂ dissociation on pure metals and bimetallic alloys. Gray cells indicate the bimetallic alloys which are not preferred to the surface segregation of solute atoms. E_a^{act} were estimated by combining BEP relation, scaling relation, and surface mixing rule. Reproduced with permission from the authors of ^[15]. Copyright 2016 American Chemical Society.

The mechanisms of CO₂ dissociation on bimetallic clusters (Pt_3Ni_1 , Pt_2Ni_2 , and Pt_1Ni_3) were investigated and characterized by the activation barrier ^[42]. Compared with the single metallic clusters (Pt_4 and Ni_4), results showed the activation barrier to be between those of the monometallic clusters. Increasing Ni atoms in the bimetallic clusters moderately raised the activation barrier, which means that such a bimetal combination could have a significant negative impact on the activity of Pt for CO₂ reaction ^[42].

Results from an ab initio study of chemisorption and activation of CO_2 on Pt-based transition-metal nanoalloys on 55-atom nanoclusters (Pt_nTM_{55-n}), where n = 0, 13, 42, 55, and TM = Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Au, indicated a linear correlation between the interaction energy, charge transfer from the nanoclusters toward CO_2 and the bent CO_2 angle ^[5]. It was further realized that the interaction energy was enhanced for larger angles and molecular charge. With 55 atoms for Cu, Ag and Au in the Pt alloy, a change from physisorption to chemisorption was observed, whereas the strong interaction energy of CO_2 with Os_{55} , Ru_{55} , and Fe_{55} can be decreased by alloying with Pt ^[5]. It means that certain metals (Fe, Co, and Ni) activate CO_2 more strongly as monometals than in an alloyed form due to weaker adsorption energy in the latter.

2.3. CO₂ Adsorption and Activation on Metal Oxide Surfaces

2.3.1. Metal Oxide

Various metal oxides (MO_x) or (M_xO_y) are investigated as supports or as catalysts for CO₂ conversion, including In₂O₃, CeO₂, ZnO, ZrO₂, TiO₂, and CeO₂. Metal oxide surfaces consist of both metal (Mⁿ⁺) and oxygen (O²⁻) ions, which are effective sites for CO₂ activation. The activation can occur by coordination to one or two adjacent metal sites through the terminal oxygen atoms or C atom of the CO₂ molecule, forming monodentate or bidentate carbonate species ^[43]. Interaction of the C atom is on the surface oxygen sites of the metal oxide. The CO₂ activation can also occur via the σ -bond and π -bonds activation on metal ions and oxygen ions, respectively, as observed upon chemisorption on metal oxides applied as catalyst supports ^[44]. Due to the large surface areas, switchable redox properties, and rich oxygen vacancies, metal oxides can act as adsorption and activation sites for small molecules, including O₂, H₂, and CO₂ ^[45]. The surface oxygen vacancies interact with the carbon and/or oxygen atoms of CO₂ through which electron transfer from the oxide defective site to adsorbed CO₂ becomes feasible. One example is In₂O₃, which is rich in oxygen vacancies and has shown a high activity for CO₂ activation and methanol synthesis by hydrogenation ^[45].

On oxide surfaces, generally, CO_2 interactions can vary from physisorption to chemisorption, the extent that affects the structure and reactivity of the adsorbed CO_2 , and the kinetics and mechanisms of surface catalytic reactions ^[43]. The surface structure is important for CO_2 adsorption and activation ^[46]; thus, the interaction of CO_2 with metal oxides can be structure-dependent. It was found that CO_2 adsorption on Zn_2GeO_4 (001) was higher than that on

 Zn_2GeO_4 (010) surface ^[46]. The interaction with (010) surface led to bidentate carbonate species, whereas on the (001) surface, stronger interaction with CO₂ resulted in a bridged carbonate-like species. The strongest adsorption based on calculated CO₂ adsorption energies was around the surface oxygen vacancy site on both surfaces. Analysis of the LDOS and Mulliken charge for adsorbed CO₂ on perfect Zn_2GeO_4 surfaces revealed that CO₂ formed a $CO_2^{\delta^-}$ species upon accepting electrons from the surface. CO₂ molecule was found to be activated on the CuO surfaces ((011), (111), and (-111)), with strong adsorption only on the (011) surface. The CuO (111) and CuO (-111) surfaces showed relatively weak adsorption. CO₂ activation was characterized by structural transformations and charge transfer that resulted in the formation of bent $CO_2^{\delta^-}$ species with an elongation of the C–O bonds ^[22].

The ability of metal oxides to bind and activate CO₂ depends greatly on several factors, including their preparation methods, physiochemical properties, redox properties, and electronic and geometric structures [36][43][47]. The preparation methods were found to impact the properties of CeO₂ nanostructures for the photocatalytic reduction of CO₂ [48]. A high surface area was obtained for catalysts synthesized through the sunlight-assisted combustion process, in addition to possessing a small particle size, high concentration of oxygen vacancies, and a narrow bandgap. Compared to that prepared from the conventional combustion process with a spongy-like structure, a porous network consisting of small and uniformed pores was also obtained for the sunlight-assisted process. The superior catalytic properties could be attributed to the novel properties endowed by solar irradiation during the synthesis process. As demonstrated with the CeO_x/Cu catalyst, the important roles of metal oxide ions were revealed on the catalytic cycle of H₂O and CO₂ activation. The Cu phase was reduced into Cu⁰ that promoted Ce⁴⁺ reduction into Ce^{3+} . H₂O and CO₂ activation occurred on the Ce^{3+} sites. Without the presence of Cu, Ce^{3+} would lead to oxidation into Ce⁴⁺. However, in contact with Ce⁴⁺, Cu⁰ reacted to form Cu⁺ and Ce³⁺, sustaining ceria in the more active state. The cycle is closed when Cu⁺ reduced to Cu⁰ [49]. This synergistic effect afforded the catalyst with high reactivity in the RWGS reactions. The chemisorption of CO₂ molecules on CeO₂ at RT as studied using in situ DRIFTS indicated adsorption at both the Ce³⁺ and Ce⁴⁺ sites, although adsorption was also found at the oxygen sites that resulted in carbonates and bicarbonates species $\frac{50}{2}$. In the same study, the CO₂ chemisorption on TiO₂ under similar reaction conditions and instrumentation was observed at both Ti³⁺ and Ti⁴⁺ sites, exhibiting O–C–O vibrations at 1667 and 1248 cm⁻¹ and 2339–2345 cm⁻¹, respectively ^[50]. The CO₂ molecules adsorbed at Ti³⁺ sites formed CO₂⁻ species, which concentration increased with the amount of oxygen vacancies present. Like with CeO₂, CO₂ chemisorption at the oxygen sites formed carbonates and bicarbonates species. It was observed that the interaction between TiO₂ and CO₂ molecules is somewhat weak compared with that of CeO₂. Such weak interactions can be improved by doping TiO₂ with CeO₂. CeO₂ doping can improve the interaction of TiO₂ with CO₂ as a result of the introduction of Ce^{3+} , which strengthens the bonding of CO_2 with catalyst surfaces and enhances the production of bidentate carbon species that can readily be transformed to surface CO_2^- in the presence of H₂O under solar irradiation. The formation of adsorbed species of CO2 over CeO2/TiO2 could be attributed to the binding of CO₂ species to Ti/Ce atoms that have reductive capabilities under photo-irradiation. Furthermore, the Ce³⁺ availability from CeO₂ facilitates photogenerated charge separation; thus, the CO₂ adsorption and enhanced charge separation can be tuned for increased activity of CeO2/TiO2 catalyst [51]. The surface area of materials positively correlates with their adsorption capacity. It was found that the Bi12O17Cl2 nanotubes had a higher

adsorption capacity for CO₂ (~4.3 times) than bulk $Bi_{12}O_{17}CI_2$ due to the higher BET specific surface area of the former. As a result, the effective adsorption of CO₂ on $Bi_{12}O_{17}CI_2$ nanotubes over bulk $Bi_{12}O_{17}CI_2$ favored the photocatalytic process ^[52]. In addition, the high surface area correlated with strong adsorption. Weak chemisorption of CO₂ has been reported for CeO₂ nanostructures with low exposed surface area ^[50]. Mesostructured photocatalyst displayed improved activity for CO₂ reduction into CH₄ due to the presence of high specific surface area and well-developed mesostructure that enhanced adsorption of CO₂ ^[53]. Highly mesoporous In(OH)₃ synthesized via the sol-gel hydrothermal treatment exhibited ~20-fold higher efficiency for CO₂ reduction in comparison with those lacking mesopores ^[54]. It is reported that the methanol activity of the In₂O₃ catalyst could also be improved by increasing the (111) surface area ^[55].

2.3.2. Characteristic Adsorption of Representative Metal Oxides

Ceria (CeO₂) has shown catalytic activity in the reduction of CO₂ to liquid fuels and chemicals. It has rich oxygen vacancies and high oxygen storage/release capacity. Several studies demonstrating the interaction of CO₂ with high-surface-area ceria catalysts have been reported. As noted in ref [56], CO₂ dissociates into CO and an oxygencontaining surface species on the surface Ce³⁺ ions, which are considered active sites for CO₂ activation due to the formation of carbonates or inorganic carboxylates. Graciani et al. reported a highly active CeOx/Cu nanoparticles catalyst for methanol synthesis from CO₂ $\frac{57}{2}$. The catalyst activated CO₂ as CO₂^{δ -} and exhibited a faster methanol production rate than Cu/ZnO, on which CO2 was chemisorbed as CO32-. A study on the CO2 adsorption sites of CeO₂ (110) surface using DFT was carried out by Cheng et al. [58]. Reduced and stoichiometric ceria (110) surfaces were compared. Results revealed that CO₂ adsorption on the reduced ceria (110) surface was thermodynamically favored than on the stoichiometric ceria (110) surface. Furthermore, the most stable adsorption configuration consisted of CO₂ adsorbed parallel to the reduced ceria (110) surface at the oxygen vacancy. Upon adsorption, the CO₂ molecule distorted out of the plane and formed carbonates with the remaining oxygen anion at the surface [58]. It was suggested that the structural changes in the catalyst after CO₂ adsorption were due to charge transfer between the surface and adsorbate molecule. The formation of two different adsorbate species: a carbonate and a weakly bound and linear physisorbed species, were observed upon exposure of reduced CeO_{2-x} (110) substrates to CO_2 at low temperatures. There was no evidence for the formation of $CO_2^{\delta-}$. Furthermore, based on angle-dependent C K-edge NEXAFS spectra, the most preferred orientation of the adsorbate could not be observed. The physisorbed CO₂ species and carbonate species were completely desorbed at 250 and 500 K, respectively. The authors remarked that it is most unlikely that the activation of CO_2 on the reduced CeO_{2-x} (110) surface was via breaking the C=O bond to form CO and O. However, on fully oxidized CeO₂ (110), CO₂ adsorbed as a carbonate which was completely decomposed and desorbed as CO_2 at 400 K ^[59]. CO_2 adsorbed on the CeO_2 (111) surface formed monodentate carbonate species found to be most stable on CeO₂ at low coverages $\frac{60}{2}$. Increasing the CO₂ coverage destabilized the formed species, indicating a mixed adsorption mechanism with both carbonate and linearly adsorbed CO₂ species. Although CeO₂ has been studied for CO₂ reduction reactions, the insights into CO₂ adsorption, activation, and reaction on ceria surfaces are not yet fully understood.

Titania (TiO₂) possesses good photocatalytic properties for many chemical reactions, including CO_2 reduction. Since its first demonstration in the photoelectrochemical CO_2 reduction to formic acid and formaldehyde by Inoue et al. $\frac{61}{1}$, TiO₂-based materials have attracted great research interests in CO₂ photoreduction reactions. The adsorption properties of CO_2 on both the rutile and anatase phases of TiO_2 have been widely studied using various surface science techniques $\frac{[62][63][64][65]}{[62][63][64][65]}$. Sorescu et al. $\frac{[66]}{[66]}$ investigated the adsorption and dissociation of CO₂ on an oxidized anatase (101) surface using dispersion-corrected DFT and found CO₂ to adsorbed at a fivefold coordinated Ti site in a tilted configuration. Based on in situ FTIR experiments, the CO₂ adsorption formed CO₃²⁻ and CO₂ bonded to Ti, with absorption bands at 1319, 1376, 1462, 1532, 1579, and 2361 cm⁻¹. The band at 2361 cm^{-1} was assigned to adsorbed CO₂ with Ti–O–C–O adsorption configuration [67]. The 1319 and 1579 cm^{-1} bands were assigned to bidentate carbonate, while the band at 1461 cm⁻¹ was due to monodentate or free carbonate. Under the vacuum condition, the intensities of all of the bands were reduced at 35 °C. The bidentate carbonate was the predominant species for CO₂ on TiO₂. The scanning tunneling microscopy (STM) enabled a study of the dissociation of CO_2 adsorbed at the oxygen vacancy of TiO₂ (110) at the single-molecule level ^[68]. It was found that the electrons injected from the STM tip into the adsorbed CO₂ caused its dissociation into CO and O, and the released O was observed to heal the oxygen vacancy. According to experimental analysis, ~1.4 eV above the conduction band minimum of TiO₂ is needed for the electron induction process to dissociate CO₂. The formation of a transient negative ion by the injected electron is an important step in the CO₂ dissociation, and this can only be possible above the threshold voltage. TiO2 modified with metal oxide nanoclusters possess enhanced activity to adsorb and convert CO₂ [69][70]. The Bi₂O₃-TiO₂ heterostructures obtained by modifying TiO₂ with Bi had low coordinated Bi sites in the nanoclusters and a valence band edge consisting mainly of Bi-O states due to the presence of the Bi lone pair. Upon interaction of CO2 with the reduced heterostructures, CO or CO2- were observed mainly through electron transfer to CO₂, and the Bi₂O₃-TiO₂ heterostructures became oxidized in the process with adsorbed CO_2 in carbonate form [70]. In a related study, clean or hydroxylated extended rutile and anatase TiO₂ surfaces modified with Cr nanoclusters presented an upshift valence band edge related to the existence of Cr 3d–O 2p interactions, which promoted the CO₂ activation. $\frac{[69]}{2}$. The activated CO₂ molecule reduced its O–C–O angle to 127–132° and increased the C–O bond length to 1.30 Å. It was concluded that the strong CO₂– Cr-O interaction induced the structural distortions.

Iron oxides (FeO_x) are an important component of catalysts for the conversion of CO₂ to hydrocarbons (liquid fuels). The adsorption and activation of CO₂ on FeO_x have been investigated by researchers ^[71][72][73]. It is suggested that Fe²⁺ and Fe³⁺ cations are crucial for CO₂ adsorption. Using TPD, Pavelec et al. ^[71] observed a weak interaction between CO₂ and Fe₃O₄ (001) surface. On this surface, CO₂ molecules existed in the physisorbed state as they desorbed at a low temperature (115 K). However, strong CO₂ adsorption was observed on the defects and surface Fe³⁺ sites. Weak CO₂ adsorption has also been observed on Fe₃O₄ (111) as investigated by various experimental techniques ^[74]. At different CO₂ dosages and temperatures (between 120 and 140 K), TPD experiments suggested CO₂ adsorb very weakly on a regular Fe₃O₄ (111) surface. However, CO₂ chemisorption was also observed but at relatively long CO₂ exposure times ^[74]. The formation of chemisorbed species such as carboxylates and carbonates was facilitated by surface imperfections. Conclusively, FeO_x exhibit weak interaction with CO₂ molecules, and studies are recommended in this direction to adjust its CO₂ adsorption strength.

 ZrO_2 has been demonstrated as catalyst support for the CO_2 hydrogenation reactions to a variety of products. In a study on CO_2 hydrogenation on Cu/ZrO_2 catalyst using the first-principles kinetic Monte Carlo simulations by Tang et al. [76], the authors showed that CO_2 prefers to adsorb on the bare ZrO_2 nanoparticles surface rather than at the Cu/ZrO_2 interface. This led to the bending of the CO_2 molecule with a calculated adsorption energy of 0.69 eV. The stretching of the C–O bonds and charge transfer from the ZrO_2 surface to the antibonding $2\pi_{\mu}$ orbital of CO_2 were also observed. On the bare ZrO_2 surface, bidentate bicarbonate (HCO₃) was formed upon CO_2 adsorption based on observable IR frequencies at ~1225, ~1620, and ~3615 cm⁻¹ [77].

3. Conclusion

CO2 is a kinetically stable molecule that requires high energy input for the C–O bond breaking. Its proper activation can reduce the high energy barrier substantially, easing conversion by various processes. The CO2 activation is an important step that precedes the conversion of CO2 to chemicals and fuels. It can be effected in the presence of a catalyst by altering the CO2 electronic and molecular properties. Upon accepting an extra electron from a substrate, the neutral CO2 molecule forms an anion with a full charge (CO2–) or partial charge (CO2 δ –). Some metals and metal oxides are efficient catalysts for CO2 conversion reactions; thus, they should be good for CO2 activation. In general, metal nanoparticles serve as active sites for electron transfer, with certain factors such as change in morphology of metal particles, nanoparticle size, adsorption mode and configuration, and chemical ordering as the CO2 activation marker. The interaction of CO2 with some pure metals is rather weak but can be improved by incorporating promoters (e.g., alkali metals) with low electronegativity. Metal oxide nanoparticles are utilized as supports or as catalysts for CO2 activation. Their surfaces comprise both metal (Mn+) and oxygen (O2–) ions, which can act as active sites for CO2 activation. They can activate CO2 by coordinating to one or two adjacent metal sites through the terminal oxygen atoms of the CO2 or by interaction of the carbon atom of CO2 with surface oxygen sites. A particularly interesting feature in metal oxides is the oxygen vacancies that facilitate CO2 adsorption and activation.

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