Reverse Water Gas Shift Reaction

Subjects: Engineering, Chemical | Chemistry, Applied | Nanoscience & Nanotechnology

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The catalytic conversion of CO_2 to CO by the reverse water gas shift (RWGS) reaction followed by well-established synthesis gas conversion technologies could be a practical technique to convert CO_2 to valuable chemicals and fuels in industrial settings. For catalyst developers, prevention of side reactions like methanation, low-temperature activity, and selectivity enhancements for the RWGS reaction are crucial concerns. Cerium oxide (ceria, CeO_2) has received considerable attention due to its exceptional physical and chemical properties.

Keywords: reverse water gas shift reaction ; mechanism and kinetics ; CeO2 support

1. Introduction

Carbon dioxide has been identified as the primary anthropogenic greenhouse gas that has resulted in catastrophic climate change and ocean acidification [1][2]. Various approaches have been employed to reduce the amount of CO_2 in the atmosphere. For example, power-to-liquid (PtL) sustainable aviation fuel (SAF) was recently proposed as a long-term and scalable solution to minimize aircraft CO_2 emissions. The procedure turns CO_2 into a synthetic fuel with less sulfur and fewer aromatics, which enhances local air quality and minimizes the effect of aviation at high altitudes [3]. On the other hand, since enormous amounts of low-cost, relatively pure carbon dioxide are available from carbon sequestration and storage facilities, more efforts have been made to utilize CO_2 as an alternative C1 source rather than merely considering it as waste [4]. A unique and appealing alternative to storing CO_2 through sequestration would be recycling the gas into energy-rich compounds via carbon capture, storage and utilization (CCSU) [5][6]. E-fuels, also known as electrofuels or powerfuels, are hydrocarbon fuels produced from hydrogen and CO_2 in which hydrogen is generated from water and electricity through electrolysis and CO_2 is either captured from fossil sources (such as industrial sectors) or the atmosphere [7][8][9]. E-fuels aim to directly electrify a system without the demand-side adjustments necessary for a direct electrification by substituting fossil fuels with renewable power [7]. However, the CO_2 molecule is a relatively inert and unreactive molecule with a high level of thermodynamic and chemical stability due to its linear chemical structure with double bonds connecting the carbon and oxygen atoms, so converting it to the more reactive CO is energy-intensive [10]. Among the systems currently available for CO_2 conversion, catalytic conversion to CO, commonly known as the reverse water-gas shift (RWGS) reaction (Equation (1)), is one of the most promising reversible hydrogenation methods that offer a high potential efficiency [11].

$$CO_2 + H_2 \leftrightarrow CO + H_2O \ \Delta H^0 = +41.3 \text{ kJ/mol} \quad (1)$$

RWGS reaction is recognized as an important intermediate stage in a number of key CO_2 hydrogenation reactions such as the Sabatier process [12] and methanol synthesis [13], and is hence referred to as the “building block stage” [14]. Synthesis gas ($CO + H_2$), a crucial precursor in the field of C1 chemistry, can be produced using the RWGS reaction in the presence of an appropriate catalyst. The syngas can further be used as a feedstock for the Fischer–Tropsch synthesis reaction (FTS) to produce organic compounds, such as methanol (a crucial component of synthetic fuels and polymers), hydrocarbons, or oxygenated hydrocarbons [15][16]. ExxonMobil recently revealed that its “methanol-to-jet” technology can provide SAF from methanol derived through waste, biomass, captured carbon dioxide, and low-carbon hydrogen [17]. However, further side reactions, such as CO methanation (Equation (2)) [18], could emerge under the same reaction conditions, consuming a large amount of hydrogen. The CO_2 methanation reaction is an exothermic catalytic process that normally takes place at temperatures from 150 °C to 550 °C in the presence of a catalyst [19]. The CO_2 conversion and CH_4 selectivity can almost approach 100%; however, as the temperature rises, the reaction rate increases [20], with preference for RWGS at higher temperature. Therefore, at low reaction temperatures, the highly exothermic methanation reaction is thermodynamically more preferred to the slightly endothermic RWGS reaction [21][22]; hence, reducing methanation throughout RWGS has been a challenging issue. A remaining concern seems to be either the RWGS reaction should be operated at high temperature (over 900 °C), which is thermodynamically favorable, but carbon and undesirable byproducts may also be present; or it should be performed at low temperatures (below 500 °C), in which case

it is not kinetically favored but may be made up for by extensive catalyst use [23]. Over the temperature range of 100 to 1000 °C, Kaiser et al. investigated the equilibrium composition of the gaseous products in RWGS reaction for a three-to-one molar H_2/CO_2 input ratio [24]. Based on the results, methanation was thermodynamically preferred at low temperatures (below 600 °C), while, the only product that could form at temperatures beyond 700 °C was CO and very little to no methane. However, to cut down on the energy losses and investment expenses, the temperature must be kept as low as feasible [24]. They proposed that using RWGS at greater pressures in conjunction with high temperature and high-pressure steam electrolysis might be an alternative [24]. Additionally, the FTS normally operates at 2.5 MPa, and the produced syngas or the RWGS supply gas must be compressed [25]. Kaiser et al. came to the conclusion that at this pressure (2.5 MPa), the methane curve was pushed to higher temperatures; for instance, at 900 °C, the equilibrium methane level was 4 mol% as opposed to 660 °C at 1 atm pressure [24]. When Unde et al. tested the Al_2O_3 catalyst through RWGS reaction, they discovered that the CO_2 to CO conversion equilibrium was reached at a high temperature of 900 °C. Reaction was controlled kinetically between 300 and 700 °C, and thermodynamically above this temperature range [26]. As a result, production of active RWGS catalysts operated at low-temperature with higher CO selectivity and limited CH_4 production was required. Insight into the mechanisms of CO production is also vital for rational catalyst design in such processes. Various reaction routes could lead to various kinetic parameters and selectivity variations for CO_2 hydrogenation [27].

$$CO_2 + 3H_2 \leftrightarrow CH_4 + H_2O \ \Delta H^0 = -206.5 \text{ kJ/mol} \quad (2)$$

According to the concept of microscopic reversibility and the fact that the RWGS reaction is typically carried out at equilibrium, the active catalysts in the water gas shift (WGS) process are also effective in the RWGS reaction, but may be under different reaction conditions, suggesting that similar catalysts should enhance both reactions [28]. Some typical features of WGS catalysts include the presence of oxygen vacancies, the strength at which CO can be adsorbed, and activity for dissociation of water [29]. In the earlier study, a thorough overview of the most recent advancements of catalysts utilized in low-temperature WGS reactions is presented [30]. In various CO_2 conversion processes, many types of catalysts have been used, including oxide-supported metal catalysts and oxide catalysts in which cerium oxide (CeO_2) has had a key role [30][31]. CeO_2 is a typical rare earth metal oxide with a face-centered cubic (FCC) fluorite structural pattern, and has oxygen storage capacity (OSC) and a number of intriguing features that can be exploited to improve catalytic efficiency [28][32]. In comparison to other reducible oxides, oxygen vacancies on the surface of CeO_2 are more easily formed during the reduction process owing to its unique electron arrangement [33]. Besides, the reversible redox pair Ce^{3+}/C^{4+} and the acid basic surface properties of CeO_2 are effectively leading to its broader catalytic application [34]. It was found that the reducibility of ceria had an inverse connection with the bimetallic cluster promoted local electronic band, which caused the stability of germinal OH groups and was assumed to be the reason for higher WGS activity [35]. Besides, the RWGS reaction has been reported to work well with noble metal–loaded CeO_2 catalysts [36]. In a comparative study, Castao et al. looked at the efficiency of platinum and gold catalysts on ceria supports [37]. Transition metals supported on CeO_2 also have greater RWGS activity than metals supported on non-reducible supports. Moreira et al. investigated the sorption-accelerated WGS process at low temperature (125–295 °C) over Cu-CeO_2/HTlc catalysts; Cu supported on polyhedral nanoparticle-sized ceria displayed a high conversion of 87.6% [38]. Comparing the performances of 1.7% Pt-CeO_2 and Pt-Al_2O_3 at 573 K in WGS reaction, Porosof and Chen examined the amount of CO uptake as an indicator of the dispersion of Pt metal. They found out that the amount of CO uptake using Pt-CeO_2 is ~5.7 times higher than that on Pt-Al_2O_3 [39].

2. Preparation Methods

The method of catalyst preparation determines the metal-support interaction and morphological properties of the final catalysts that considerably impact the performance of the catalysts. The impact of different preparation procedures of 1 wt.% Ni-CeO_2, e.g., co-precipitation (CP), deposition–precipitation (DP), and impregnation (IM) approaches, on the physicochemical and catalytic characteristics in the RWGS reaction was explored by Luhui et al. [40]. The Ni-CeO_2-CP catalyst achieved the highest conversion rate in the RWGS reaction when compared to the Ni-CeO_2-DP and Ni-CeO_2-IM catalysts; however, the CO selectivity followed the order: Ni-CeO_2-IM > Ni-CeO_2-CP > Ni-CeO_2-DP. As confirmed by TPR analysis, an integration of numerous oxygen vacancies and broadly dispersed small NiO particles was considered to be the reason for the outstanding performance of the Ni-CeO_2-CP catalyst in terms of high activity and good selectivity. This suggests that more nickel ions were integrated into the CeO_2 lattice to develop a solid solution. The Ni-CeO2-DP catalyst has only a limited number of oxygen vacancies in comparison to the Ni-CeO2-CP catalyst, which results in low RWGS selectivity. It was proposed that the RWGS selectivity was strongly influenced by the oxygen vacancies. It is believed that the solid solution of Ce_xNi_yO is produced when the Ni^{2+} ions are inserted into the ceria lattice to substitute certain Ce^{4+} cations [40]. Oxygen vacancies are produced by the lattice distortion and charge imbalance that occur within the CeO_2

structure [41][42]. Several reports have indicated that precipitated ceria-based catalysts have distinct properties depending on the precipitants used, which significantly influence structural properties and catalytic performance [43][44][45][46][47][48]. In other work by the same group, Luhui et al. used the CP method to make a range of Ni-CeO_2 catalysts using Na_2CO_3, NaOH, as well as a combination of precipitants (Na_2CO_3:NaOH; 1:1 ratio) in order to investigate their catalytic efficacy in the RWGS reaction [49]. According to the structural characterization findings, the catalyst developed by the mixed precipitating agents (Na_2CO_3:NaOH; 1:1 ratio) exhibited the highest oxygen vacancies along with high Ni particle dispersion, resulting in the highest catalytic activity for the corresponding catalyst, whereas the precipitants' catalytic selectivity for CO were ranked as: NaOH > Na_2CO_3 > Na_2CO_3:NaOH = 1:1 [49]. The technique used to synthesize the CeO_2 catalyst has a substantial impact on its structure, and the structure of the synthesized catalysts can greatly influence the catalytic performance in the CO_2 RWGS reaction [50]. Hard-template (HT), complex (CA), and precipitation strategies (PC) were used to synthesize CeO_2 catalysts with various structures, and their efficiency in the CO_2 RWGS reaction was examined by Dai et al. [50]. The Ce-HT catalyst had the greatest CO_2 RWGS reaction activity due to its porous structure (TEM), high specific surface area of 144.9 $m^2.g^{-1}$ (BET), and abundance of oxygen vacancies; Ce-HT > Ce-CA > Ce-PC is the temperature sequence in which the catalysts reduce in the presence of H_2 at low temperatures (H_2-TPR) [50]. Xiaodong et al. carried out the RWGS reaction over Pt-CeO_2 catalysts at temperatures between 200 and 500 °C under atmospheric pressure and various pretreatment conditions using the co-precipitated technique [51]. The samples were represented as PC-M-N, where PC stands for the co-precipitated 1%Pt-CeO_2 catalyst and M and N stand for the calcination and reduction temperatures of the samples, respectively, [51]. The catalyst prepared at a lower calcination temperature (PC-500-400) demonstrated a more favorable catalytic performance than the others due to its high Pt dispersion [51]. In another study, Ronda–Lloret et al. investigated the use of metal organic frameworks (MOFs) as precursors instead of merely using the traditional wet impregnation (WI) method in the production of CuO_x-CeO_2 catalysts [52]. After impregnating Cu-MOF using a ceria precursor, they flash-pyrolized (PF) the impregnated MOF applying distinctive conditions and procedures and compared the performances in the RWGS reaction with the WI synthesis technique finding that the MOF-derived catalyst outperformed the other catalyst [52]. Throughout the thermal decomposition procedure, the metal ions in MOFs are transformed into metallic or metal oxide nanoparticles, while the organic linkers produce carbonaceous formations which can function as supports and promote active phase distribution [53]. As Ronda–Lloret et al. concluded, by changing the pyrolysis environment, an oxidizing environment may be produced that prevents sintering and keeps copper oxidized during decomposition. Using air in the decomposition process causes the creation of copper oxide compounds that sinter with more difficultly than the metallic copper. This promotes the interaction with the ceria support, which improves its catalytic behavior. Thus, by utilizing air, highly dispersed CuO on CeO_2 can be created that is readily reducible and exhibits strong interactions with the ceria [52].

3. Shape and Crystal Face Effect

The form and exposed crystal face of catalysts have a major impact on RWGS reaction activity since they may control the adsorption and desorption energies of precursors in the reaction process [54][55][56]. Thus, the efficiency of CeO_2 supported catalysts can be modified by conducting experiments with various morphologies. The RWGS reaction was studied by Kovacevic et al. over cerium oxide catalysts of various morphologies: cubes, rods, and particles [57]. Using TPR they found that surface oxygen is less removable in the case of nanoshapes with a high concentration of oxygen vacancies and, compared to rods and particles, cerium oxide cubes had twice more activity per surface area. The stronger intrinsic reactivity of (100) crystal planes encapsulating cubes, as opposed to less intrinsically reactive (111) facets exhibited in rods and particles, results in enhanced catalytic activity of ceria cubes in RWGS [57]. In another study, Lin et al. found that under similar conditions and the same active metal, the CeO_2(110) surface has substantially more activity than the CeO_2(111) surface, indicating that the ceria support performance is facet-dependent [58]. According to their study, once Cu particles are loaded onto the CeO_2-Nanorod (NR) and CeO_2-Nanosphere (NS) surfaces, the NR sample exhibits greater RWGS reaction activity. This is mostly due to the increased feasibility of CO_2 dissociative activation and the generation of active bidentate carbonate and formate intermediates over CeO_2(110) [58]. Liu et al. used RWGS to compare crystal plane reactive activity in three nano-CeO_2s with varied exposed planes [59]. The overall order of RWGS reactive efficiency of the three studied CeO_2 shapes was ceria nanocube (NC) > ceria-NR > ceria-nanooctahedra (NO) [59]. It is well established that oxygen vacancies formation on ceria (100) or (110) consume less energy than creating them on ceria (111) [60][61]. As a result, the ceria (100) and (110) planes seem to be more attractive choices for catalyzing processes that involve an oxygen cycle with adsorbates [59]. This could be the main reason why the ceria-NC exposed (100) plane had the best CO_2 conversion and selectivity.

Zhang et al. developed self-assembled CeO_2 with 3D hollow nanosphere (hs) (111), nanoparticle (np) (111), and nanocube (nc) (200) morphologies that were employed to support Cu particles [62]. Owing to the large levels of active oxygen vacancy sites, the Cu-CeO_2-hs(111) exhibited the greatest RWGS catalytic activity among the studied catalysts

[62]. Konsolakis et al. looked into the influence of the active phase type and ceria nanoparticle support morphology (NR or NC) on the physicochemical characteristics and CO_2 hydrogenation capability of M-CeO_2 (M = Co or Cu) composites at 1 atm [63]. Regardless of support structure, CO_2 conversion was reported to follow the following order: Co-CeO_2 > Cu-CeO_2 > CeO_2 with the Cu-CeO_2 sample being far more selective toward CO than Co-CeO_2. The Co catalysts supported on NC ceria demonstrated slightly higher catalytic activity than Co supported on rod-like forms, highlighting the importance of support morphology in addition to the choice of metal element; for Cu-based samples and bare CeO_2, the pattern was the opposite [63].

4. Metal–Support Interactions

Activation of catalysts by pretreatment at high-temperature in the presence of hydrogen is often adopted to reduce the oxide nanoparticles and generate oxygen vacancies on the reducible support surface; however, such activation procedures can develop greater interactions between metal nanoparticles and the support, which has been reported to impact catalytic activity in varying ways: positively [64], negatively [65], or in some cases insignificantly [66]. The strong metal–support interaction (SMSI) phenomenon, which typically develops in metals and reducible oxides subjected to high reduction temperature, is one such case [67]. The type of the support [68], metal composition [69], and catalyst synthesis procedure can all influence metal–support interaction (MSI) [70]. According to Goguet et al., the major active site in the RWGS reaction over Pt-CeO_2 catalyst is the interface among Pt and CeO_2 and the reducible site of CeO_2, which is created by the SMSI effect of Pt and CeO_2 [71].

SMSI between Cu species and CeO_2 helps in boosting the reducibility and stability of associated catalysts, which is favorable for catalytic reduction processes [72]. The results of a study by Zhou et al. showed that the H_2 reduction at 400 °C can create oxygen vacancies and active Cu^0 species as active sites in Cu-CeO_2 catalysts [73]. The SMSI phenomenon allows electrons to move from Cu to Ce on its surface, forming the Ce^{3+}-O_v-Cu^0 and Cu^0-$CeO_{2-\delta}$ interface structures that increase the adsorption and activation of the reactant in RWGS reaction. The results suggested that the Cu-CeO_2 catalyst with 8 wt.% Cu had the best CO_2 conversion yield. The full synergistic interaction between the active species via Ce^{3+}-oxygen vacancy-Cu^0 was attributed to its high catalytic activity in the RWGS process [73].

Aitbekova et al. designed the 2.6 nm Ru equally distributed on Al_2O_3, TiO_2, and CeO_2 supports and tested in a CO_2 reduction process [74]. Ru catalysts supported on TiO_2 and CeO_2 were significantly more active than those supported on Al_2O_3, but CH_4 was the predominant product in all cases. Nonetheless, they reported that moderate oxidization of the catalyst at a temperature of 230 °C followed by low temperature reduction (230 °C), named as OX-LTR, leads to the Ru particles' re-dispersion on CeO_2, giving a nearly complete switching of product selectivity from methane to CO, indicating that a weaker adsorption of CO on the single RuO_x site is likely to result in increased selectivity. As they stated in their research, such re-dispersion appears only slightly in Al_2O_3- and TiO_2-supported Ru, probably due to the lower Al_2O_3 and TiO_2 and RuO_x interaction as compared to the CeO_2 support with RuO_x. Moreover, a light oxidation of the catalysts at 230 °C coupled with a high reduction temperature of 500 °C, named as OX-HTR, favored the formation of SMSI in the case of Ru-TiO_2; however, the Ru-CeO_2 catalysts (both OX-LTR and OX-HTR) exhibited fairly similar rates, implying the effect of SMSI is negligible for CeO_2-supported Ru materials under the CO_2 hydrogenation conditions investigated [74]. Similar conclusions were derived by Tauster et al. in a separate study [75].

A capping layer encircling the supported nanoparticles is commonly observed as evidence of the impact [76]. The existence of such an action, on the other hand, could be linked to charge transfer across metallic nanoparticles and the oxide support [77]. For example, Figueiredo et al. synthesized Cu_xNi_{1-x}-CeO_2 (x = 0.25, 0.35 and 60) nanoparticles for use in the RWGS reaction and investigated the SMSI influence on CO_2 dissociation reaction by exploring the nanoparticles' electrical and structural features and discovered the reactivity of nanoparticles was proportional to the Cu content on the surface with Cu-richer ones having a negative impact on the CO_2 dissociation reactivity [78]. According to their experimental results, through the reduction treatment, the SMSI effect does not actually impact nanoparticles synthesized with low Cu amounts. The SMSI situation caused the support's capping layer that surrounds the nanoparticle surface to cover the catalytic active spots on the surface of the nanoparticle, leading to a decrease in the reactivity of CO_2 dissociation [78].

The area of the CO_2 desorption peak and the number of CO_2 adsorption active sites present on the surface of the relevant catalyst are invariably connected. By increasing Cu loading, the peak regions for the ε peak exhibited a volcano pattern, reaching their highest on the 8Cu/$CeO_{2-\delta}$ catalyst. This was explained in their work by the fact that increasing Cu loading (8%) led to a greater number of Cu- $CeO_{2-\delta}$ junctions and encouraged strong MSI. Nonetheless, at larger Cu loadings (>8%), a portion of the surface active sites may be coated by an extreme amount of Cu species [73]. When it comes to the peak φ, the peak regions initially start to increase, up to Cu loading of 10%, and then continue to decrease. This was

explained by the fact that at lower Cu loadings up to 10%, the catalysts' high specific surface areas enable CO_2 molecules to adsorb on their surfaces, whereas at larger Cu loadings (above 10%), the catalysts' active sites are reduced as a result of the evident decrease in specific surface areas [73].

5. Active Metal Loading

The influence of the catalysts' composition has been investigated in many studies. Lloret et al. designed catalysts with two different Cu concentrations and two different quantities of ceria precursor, aiming to have two distinct molar ratios of 20Cu:80Ce and 40Cu:60Ce with two different decomposition methods: pyrolysis (P), and PF [52]. It was revealed that samples with a higher Cu level have weak catalytic activity, whereas catalysts with a lower Cu content have better catalytic behavior in the RWGS process [52]. It is interesting to note that the ceria crystal size is smaller in the catalyst with higher ceria content (lower Cu), and copper dispersion is reduced when there is a large copper loading. According to the TPR results, hydrogen consumption was higher and peaked at lower temperatures in the sample with less Cu. A high Cu content needed the degradation of a greater quantity of HKUST-1, creating a more reducing environment. Therefore, if higher Cu content is there, additional MOFs are needed to break down to adjust to the reducing environment [52]. The impact of metal nanoparticle concentration on CeO_2-supported Pt and Ru catalysts with metal contents of 1, 5, and 10% on CeO_2 has been investigated by Einakchi et al. [79]. Ru and Pt catalysts are likely to have lower metal dispersion at 10 wt.% when compared to metal loadings of 1 wt.%. The high catalytic performance of Pt-CeO_2 was found to be linked with metal loading and particularly sensitive to metal dispersion, with 1 wt.% Pt displaying the optimum catalytic performance. Unlike Pt-CeO_2, no correlation was identified between Ru catalyst RWGS activity and metal loading (Ru dispersion); nonetheless, 5 wt.% Ru metal was proven to be the best loading for Ru-CeO_2 catalysts [79]. In another study, Wang et al. prepared Co-CeO_2 catalysts with different cobalt concentrations (0, 1, 2, 5, 10%) using the CP method employed in the RWGS reaction [80]. The findings revealed that the sample with 2% Co on CeO_2 support showed highly dispersed Co_3O_4 on CeO_2 surface displaying a strong MSI that resulted in an outstanding RWGS catalytic efficiency in terms of activity, CO selectivity, and minimal carbon deposition. Nevertheless, bulk Co_3O_4 with bigger particle size generated in catalysts having high Co content (5% and 10%) lead to considerably higher carbon deposition and enhanced by-product CH_4 generation throughout the process. Their results suggested that for the RWGS reaction, widely dispersed Co which is reduced from highly distributed Co_3O_4 on CeO_2 support, ought to be a major active material, whereas solid Co that has a large particle size could be the main active component for methanation as well as carbon deposition [80]. The same group in another study investigated the effect of the content of cobalt supported on CeO_2 prepared by a colloidal solution combustion technique to form mesoporous catalysts (Co-CeO_2-M) and examined their activity and selectivity toward RWGS reaction and then compared the optimum Co amount sample with the same catalyst prepared by IM and CP [81]. The catalytic analyses revealed that the mesoporous 5% and 10%Co-CeO_2 catalyst had high activity in the RWGS reaction; however, 10%Co-CeO_2 was less selective to CO formation than the 5%Co-CeO_2 one. Nonetheless, both had good stability over a 10-h period at 600 °C. Moreover, the activity and selectivity of 5% Co-CeO_2-M was higher than the 5% Co-CeO_2-IM and 5%Co-CeO_2-CP catalysts. They concluded that the superior catalytic performance of the 5%Co-CeO_2-M catalyst was owing to its unique mesoporous configuration, in which the Co particle is dispersed throughout the pore wall and is in close contact to small CeO_2 particles [81]. When defining the optimal catalyst in terms of activity and selectivity, metal dispersion is not the only factor to consider; the nature of the support also plays an important role. According to research by Jurkovic et al. on various supports for Cu-based catalysts, the supports with the greatest Cu dispersion were Al_2O_3 (77.7%) followed by ZrO_2 (73.6%), CeO_2 (67.6%), TiO_2 (66.3%), and SiO_2 (36.2%) [82]. Nevertheless, the alumina support was found to have the highest reported catalytic activity, followed by ceria, titania, silica, and zirconia. Ceria was ranked by TPR as the second-best support among the studied group, while having the third-best Cu dispersion, most likely because of its reducibility and capacity to hold oxygen [82]. Moreover, according to the literature, there is a direct correlation between the catalysts' activity and acid-base properties [83]. According to Pino et al., the synergistic interaction of Ni and La_2O_3 on a La_2O_3 doped Ni-CeO_2 catalyst boosted catalytic activity because of the creation of a basic site and Ni dispersion improvement [84]. Therefore, it can also be concluded that improving basicity of a catalyst might facilitate CO_2 adsorption [85]. According to the research of Jurkovic et al., Al_2O_3 is a frequently used irreducible support with good performance, where its modest acidity could be a likely contributing factor [82][85].

6. Metal Size Effect

The RWGS reaction is sensitive to the structure of the supported catalysts, and the size of the attached metal active sties that influence the adsorption, intermediate formation and desorption of the products [86]. Reducing the metal particle size may improve MSI by generating a larger metal–support interface, leading to positively increasing the RWGS reaction activity. Indeed, due to the SMSI affect, more oxygen atoms should be attached to the metal surface when the particle size decreases [87]. For example, Li et al. developed a 5% Ir-CeO_2 catalyst including an Ir particle size of around 1 nm,

and a 0.7% Ir-CeO_2 catalyst with atomic dispersion of Ir [88]. Even though the dominant product of CH_4 was produced by an Ir-CeO_2 catalyst with large Ir particles (>2.5 nm), CO was produced mainly by the 5% and 0.7% Ir-CeO_2 catalysts when Ir particle size was less than 1 nm, and the catalytic activity per mole of Ir increased. They also discovered that due of the intense interaction with CeO_2, 1 nm Ir particles and atomically dispersed Ir get partially oxidized, but large Ir particles, more than 2.5 nm, are mostly reduced. As a result, they concluded that the primary active site for a RWGS reaction is partly oxidized Ir that engages extensively with CeO_2 support regardless of Ir particles or atomically dispersed Ir atoms [88]. Metal active sites distributed on an atomic level add more to the CO product than metal clusters at a 3D level [89]. In a study, Zhao et al. produced Pt-CeO_2 catalysts with various Pt sizes to test the influence of size on CO selectivity in the RWGS reaction [90]. Three Pt-CeO_2 catalysts were produced using CeO_2 nanorods, including atomically dispersed Pt species as well as Pt clusters or particles of two different sizes (2.1 and 5.2).

Lu et al. developed mesoporous CeO_2 (surface area = 100 m^2 g^{-1}) as well as NiO-CeO_2 with large surface areas, narrow pore size dispersion, and homogeneous mesopores (intercrystallite voids) [91]. According to the results, with increasing temperature and NiO quantity, the CO_2 conversion rate in RWGS reaction increased. As for CO selectivity, when less than 3 wt.% NiO was used, NiO particles monodispersed in mesoporous CeO_2 resulting in a complete CO_2 conversion to CO which was irrespective of temperature. For more than 3.5 wt.%, due to NiO particle aggregation, 100% CO selectivity was improbable below 700 °C [91]. Wang et al. studied the effect of CeO_2 on RWGS in comparison to In_2O_3 [92]. The surface areas of the In_2O_3–CeO_2 catalysts enhanced compared to pure In_2O_3; as the CeO_2 content increased, the size of the In_2O_3 particles in the In_2O_3–CeO_2 samples reduced and the dispersion of In_2O_3 particles in the In_2O_3–CeO_2 increased. Besides, additional oxygen vacancies were formed, which in turn enhanced the dissociative hydrogen adsorption and increased the quantity of bicarbonate species produced by activated CO_2 adsorption [92].

7. Effect of Adding CeO_2 as a Reducible Transition Metal Oxide Promoter

The inclusion of a cerium oxide as a promoter can affect CO_2 adsorption and activation, as well as the activity and selectivity of the RWGS process [93][94]. Yang et al. showed in their work how adding ceria to alumina support (CeO_2-Al_2O_3) helped in lowering acidity of Ni-based catalysts, which also minimized carbon deposition [95]. The researchers concluded that their findings were mostly due to two aspects occurring together: (1) CeO_2, as a promoter here, reduced the Ni-Al_2O_3 connection, leading to an increase in Ni particle reducibility, owing to the generated Ni-promoter interaction, and (2) because of its intrinsic redox capabilities, CeO_2 offered additional oxygen mobility to the catalysts [96]. In another study by Lee et al., a set of Pt-CeO_2-TiO_2 catalysts were impregnated with different support combinations ranging from 0 to 20% to evaluate the influence of varied CeO_2/TiO_2 ratio on catalytic activity during RWGS reaction [97]. Accordingly, increasing CeO_2 loading improved the catalytic activity of Pt-impregnated catalysts, the Pt-20%CeO_2-TiO_2 sample showing the highest CO_2 conversion. Based on their analysis, by substituting TiO_2 with CeO_2, the lattice and pore configuration changed in favor of more CO_2 conversion in RWGS reaction [97]. With the aim of improving adsorption and activation of CO_2 on Ga_2O_3, Zhao et al. used CeO_2 as a promoter with an optimum Ga:Ce ratio of 99:1 and employed RWGS reaction as a test reaction and indicator for the catalytic performance of the resultant samples [98]. The results showed the positive performance of CeO_2-Ga_2O_3 due to the fact that the inclusion of CeO_2 increases the production of bicarbonate species in CO_2 adsorption, which is thermodynamically more advantageous [98]. The same catalytic system was studied by Dai et al., where the gel sol-gel process was used to create a variety of Ga_2O_3-CeO_2 composite oxide catalysts with various Ga_2O_3 and CeO_2 ratios [99]. When compared to pure Ga_2O_3 and pure CeO_2, the composite oxide catalysts had smaller particles and showed high CO selectivity in the RWGS process. It was discovered that Ga_2O_3 has distinct reaction intermediates from CeO_2 and Ga_2O_3-CeO_2, making it easier to create methane in high H_2 conditions, whereas CeO_2 promotes CO selectivity. In a Ga_2O_3 to CeO_2 ratio of 3:1, composite oxide showed the greatest activity. This is mostly due to the creation of the $Ga_xCe_yO_z$ solid solution phase and the development of additional active sites that result in an increased number of oxygen vacancies, which facilitate CO_2 adsorption and activation. Moreover, it was found that GaCe composite oxides have a more homogeneous mesoporous structure and a greater pore volume, making mass transport in reactions easier [99]. In contrast, there are a few cases in which once ceria was introduced to a catalytic system, CO selectivity improved but CO_2 conversion was slightly decreased [100]. Galvita et al., for example, developed a Fe_2O_3–CeO_2 composite and discovered that incorporating ceria to iron oxide increased solid solution stability but reduced CO production capabilities [101].

On the other hand, when a non-reducible transition metal oxide is used as a promoter for M-CeO_2 catalysts, more oxygen vacancies can emerge during the reduction process [102]. For example, more thermally stable support can be developed by a mixed framework of Al_2O_3-CeO_2 which offers a broad surface for optimum active phase dispersion and enables the development of oxygen vacancies on the surface throughout the catalytic reaction to improve catalytic performance [103].

Zonetti et al. and Wenzel et al. showed that adding Zr to the CeO_2 lattice improved its ability to create oxygen vacancies as well as its thermal stability, which is a desirable feature of catalytic systems [104][105].

8. Bimetallic Effect

Reports indicate that bimetals, where a second metal is introduced along with the primary active metal, can be used to help boost the catalytically active phase [106]. Evidently in many systems, bimetallic compounds have outperformed their individual components [107]. Furthermore, the generation of metal carbide (coke precursor) could be prevented due to the electrical effect caused by metal–metal interactions, resulting in less deactivation [108]. Yang et al. showed how the inclusion of a second element (Cr or Fe) can positively affect the reducibility of monometallic Ni-based catalysts (Ni-CeAl) [95]. The addition of Fe to the Ni-CeAl catalyst system can increase the reducibility of Ni- to 95% compared to 93% for the Ni-CeAl catalyst [95]. Chen et al. synthesized a Cu-Fe bimetallic phase loaded on CeO_2 and evaluated its performance for RWGS reaction at temperatures ranging from 450 to 750 °C at 1 atm. The efficiency of the iron-containing copper-based catalyst was greatly increased over that of the catalyst without iron, and CO_2 conversion nearly approached theoretical levels. The bimetallic CeO_2-supported catalyst was shown to have high selectivity, stability, with no secondary reactions, and no carbon deposition on the catalyst surface after the process [109]. In contrast, Li et al. used CuIn bimetallic catalysts for the RWGS reaction, demonstrating that the promotional impact of In on Cu is support dependent [110]. The CO_2 conversion of the CuIn-ZrO_2 catalyst was higher by far than the Cu-ZrO_2 catalyst; however, the CO_2 conversion of CuIn-CeO_2 was considerably lower than Cu-CeO_2. The cause of the support-sensitivity of RWGS activity was further discovered through systematic analysis. Cu and In combined to form CuIn alloys on the ZrO_2 support, which allowed CO_2 to be activated by oxygen vacancies from partially reduced In_2O_3, whereas, Cu and In were found as metallic Cu and In_2O_3 on the CeO_2 support, respectively. The addition of In prevented Cu dispersion and the development of oxygen vacancies on CeO_2, resulting in lower RWGS activity [110].

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