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Review

Recent Advances in Reverse Water Gas Conversion Reaction

Changjian Zhou [1,†], Jiahao Zhang [1,†], Yuqing Fu [1] and Hui Dai [2,*]

[1] School of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng, Jiangsu Province, 224051, China; zcj@ycit.cn (C.Z.); zjh2794790693@163.com (J.Z.), fuyuqing040115@163.com (Y.F.)
[2] College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China; daihui18@cdut.edu.cn (H.D.)
* Correspondence: daihui18@cdut.edu.cn (H.D.)
† Contributed equally to this work.

Abstract: The increase in carbon dioxide emissions has a significant impact on human society and the global environment. As the most abundant and cheap C1 resource, the conversion and utilization of carbon dioxide has received extensive attention from researchers. In many methods of carbon dioxide conversion and utilization, the reverse water gas conversion reaction is considered to be one of the most effective ways. In this paper, the research progress of reverse water gas conversion reaction in recent years is introduced.

Keywords: CO_2 conversion; CO; reverse water gas conversion reaction

1. Introduction

With the development of industry and human activities, the concentration of carbon dioxide (CO_2) in the global atmosphere is increasing year by year. As the main component of greenhouse gas, CO_2 concentration in the atmosphere continues to rise, causing a series of severe environmental problems such as climate warming, glacier melting and ocean acidification, which seriously threatens the living environment of human beings [1].

At present, fossil fuels are still the main way for human to obtain primary energy, and renewable energy such as solar energy and wind energy are still in the development stage, and it is difficult to fully replace fossil fuels. CO_2 is a kind of abundant, inexpensive, non-toxic, non-flammable and renewable single-carbon structural unit, which can be used as a good carbon source.

In recent years, in order to cope with the negative impact of CO_2, a greenhouse gas on the environment. In addition to developing new energy sources, carbon capture and storage (CCS) and carbon capture and utilization (CCU) technologies have attracted great attention due to their high efficiency and easy application to capture large amounts of CO2 [2]. CCS compresses CO_2 from the source into high-density CO_2, making it suitable for long-term transportation, storage and monitoring, but the potential risk of leakage and continuous on-site monitoring are the main disadvantages of CCS; CCU uses different strategies to convert carbon dioxide into useful chemical products such as fuels (such as methanol) and materials (polymers) [3,4]. CCU is more useful than CCS because value-added products can be obtained using captured CO_2. In addition, CCU also has no possibility of carbon dioxide leakage, which makes it promising in terms of sustainability and environmental friendliness [5]. CO_2 utilization mode mainly includes biological utilization, mineralization utilization, chemical synthesis, etc. In many CO_2 utilization technologies, CO_2 produces a variety of high-value basic chemicals through catalytic conversion, which has been widely concerned by researchers. CO_2 catalytic conversion technology mainly includes thermal catalysis [6-9], photocatalysis [10,11], electrocatalysis [12,13] and so on. The research of CO_2 catalytic conversion mainly focuses on CO_2 catalytic hydrogenation.

CO_2 catalytic conversion research focuses on CO_2 catalytic hydrogenation, a very green and environmentally friendly method for converting carbon dioxide into high-value substances such as

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CO, methanol, olefins, and alkanes [14,15]. According to the reaction pathway, the catalytic hydrogenation of CO_2 mainly generates CO[16,17], methane [18,19], and hydrocarbons [20,21].

In summary, whether from the perspective of protecting the environment or CO_2 utilization, the catalytic hydrogenation of CO_2 is a method with broad application prospects to reduce the greenhouse effect and provide energy resources. However, CO_2 has a very stable C=O bond and is thermodynamically difficult to activate [22]. The researchers tried to reduce the activation energy of CO_2 reduction reaction by adding catalysts to achieve the goal of efficient CO_2 conversion. Therefore, the preparation of simple and easily synthesized high-activity catalyst to convert carbon dioxide into high value-added products is of great significance for improving the natural environment and solving the energy demand.

CO_2 catalytic hydrogenation to CO is known as the reverse water gas conversion (RWGS) reaction. The CO produced by the reaction can be used as syngas, which is often used in the synthesis of methanol, higher alcohols or Fischer-Tropsch fuels. It is expected to be an effective way to achieve carbon neutrality and carbon cycling, and will have a significant impact on the environment and the future energy mix.

RWGS mainly converts the greenhouse gas CO_2 to CO. However, this reaction also produces the byproduct CH_4. Therefore, it is necessary to develop a RWGS reaction catalyst with high CO selectivity to convert CO_2 to CO in the RWGS reaction. RWGS reaction is a typical endothermic reaction. From a thermodynamic point of view, since the RWGS reaction is endothermic, increasing the temperature during the reaction is more conducive to the equilibrium moving in the positive direction of the RWGS reaction. From the kinetic point of view, it has a higher reaction rate at high temperature. Combined with thermodynamics and kinetics, RWGS reaction is a process with high energy consumption [23]. At the same time, high temperature will also lead to the catalyst sintering, carbon deposition and deactivation. Therefore, the development of low temperature, high activity and high selectivity of RWGS reaction catalysts has become the focus of current research.

2. Results and Discussion

2.1. Reaction mechanism of reverse water gas conversion reaction

The RWGS reaction has its unique advantages as one of the ways to utilize CO_2. In order to design a reasonable catalyst, it is important to understand the mechanism of CO formation in the CO_2 hydrogenation reaction in detail. RWGS reaction mechanism has always been a topic of debate among researchers, and existing researchers have proposed two RWGS reaction mechanisms which is redox mechanism and intermediate species decomposition mechanism. Which reaction mechanism to follow depends on the type of catalyst or reaction conditions. The two mechanisms reported in the current literature are still controversial. It is necessary to study the reaction mechanism of various catalyst types clearly for catalyst development.

(1) redox mechanism

This mechanism mainly refers to the continuous oxidation and reduction of the active species in the catalyst in the CO_2 and H_2 atmosphere during the RWGS reaction, so that the catalytic reaction can be sustained. CO_2 first adsorbed on the catalyst, combined with the active site on the catalyst surface after dissociation to produce CO, the generated active oxygen substances exist on the active site of the catalyst, and then continue to reduce the catalyst to generate H_2O, and release the surface active site to continue to participate in the next round of reaction. H_2 is not directly involved in the synthesis of intermediate species. In this process, CO_2 dissociation is the rate-limiting step, and the adsorption and desorption steps of CO and H_2O can be ignored. The basic reactions of the surface REDOX mechanism are as follows

Gines and co-workers prepared two catalysts, $CuO/ZnO/Al_2O_3$ and CuO/Al_2O_3, by co-precipitation method. The mechanism of surface REDOX is proved by the kinetic experiment of RWGS reaction. According to the kinetic experiment results, it can be found that the reaction rate of CO_2 is controlled by dissociation adsorption. The chromatographic analysis showed that only CO was formed when CO_2/N_2 was inserted, which indicated that CO_2 was dissociated from the active site on the catalyst surface to form CO. In the H_2 atmosphere, only H_2O results, indicating that H_2 combines with active oxygen species on the catalyst surface to form H_2O. Wang et al. [25] found that the oxygen vacancy formed on the surface of the pre-reduced Au/CeO_2 catalyst would be oxidized by CO_2 to produce CO. The process accords with the REDOX mechanism of RWGS. The author also loaded Au onto different carriers and found through pulse experiment that the amount of active oxygen on the surface of CeO_2 carrier was significantly higher than that of TiO_2 carrier. This is because CeO_2 has a good oxygen storage and oxygen supply capacity, and can assist Au atoms to complete the removal and production of surface reactive oxygen species.

(2) Decomposition mechanism of intermediate species

Adsorption of intermediate species decomposition mechanism refers to the RWGS reaction, CO_2 and H_2 on the catalyst are first activated to form intermediate species, and then decomposed into CO and H_2O. In recent years, in most of the literature on RWGS reactions, formates, carbonates, and carbonyl groups are the main intermediate species formed, and are considered to be the key steps for further CO generation.

It has been found from many research reports that there are different intermediates in RWGS reactions with different catalysts, and factors such as the properties of catalysts, the different interactions between metals and carriers, and the differences in reaction conditions lead to the complexity of the decomposition mechanism of intermediate species in RWGS reactions.

Liu et al. [26] conducted a CO_2 dissociation experiment to explore the reaction pathway. Combined with the results of the CO_2 dissociation experiment and TPSR, CO_2 activation can be carried out through relevant intermediate pathways. In order to further explore the active intermediate, in situ diffuse infrared Fourier transform spectroscopy (DRIFTS) is performed. After the injection of CO_2 and H_2 on the activated 15CuCe catalyst, the formate signal can be detected in addition to the carbonate signal. In the presence of H_2, the Cu atom captures the H_2 molecule and breaks the H-H bond, then transfers the H atom to the CO_2.

Formate structures are formed with the formation of C-H bonds, and these structures are manifested in the intermediates IMA3, IMA3-I, IMA4, and IMA4-i. Based on the above experimental results and DFT calculation, the authors further concluded that the reaction involved the association mechanism, and the surface formates and carboxylic acid species may be important reaction intermediates. In the reaction process, a large number of surface oxygen vacancies are generated in situ and recycled, forming a synergistic catalytic effect with copper clusters, promoting the activation of CO_2 and the formation of active intermediates. The copper clusters and abundant oxygen vacancies in the 15CuCe catalyst undoubtedly create more oxygen vacancy active interfaces of metal clusters.

Deng et al. [27] explored the mechanism of Cu/SGS catalyst in RWGS reaction, and conducted in-situ DRIFTS experiments to observe intermediates generated during the catalytic process. The characteristic bands of bicarbonate and carbonate appear. The formate band appeared at about 150 °C and then gradually weakened above 200 °C, indicating that formate species formed at low temperatures. SGS is an alkaline carrier with many surface OH groups. With the increase of temperature, the OH band gradually weakened, indicating that the surface OHs participated in the catalytic process. According to DRIFTS experiment results, we observe that gas phase CO band appears above 250 °C, and the band becomes stronger with increasing temperature. However, no formate bands were observed above 250 °C, so it can be inferred that formate species are not intermediates in CO production. Carboxylate bands were found at 1260 cm^{-1} and 1280cm^{1}, so it was determined that the reaction mechanism of Cu/SGS catalyst in the RWGS reaction is similar to the carboxylate pathway, *COOH is the intermediate of CO_2 to CO. Combined with the results of CO_2 TPD, it can be determined that the formation of *COOH comes from the adsorption and activation of CO_2 by the abundant OH groups on the SGS carrier. Species species in which OHs on the surface of SGS react with CO_3^{2-} to form HCO_3^-. H_2 is adsorbed on Cu to form H*, and the HCO_3^- substance reacts with H* on the surface of Cu to form *COOH. In addition, *COOH reacts with H* on the Cu surface to form CO* and OH*, and then CO and H_2O dissociate from the Cu surface.

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2.2. *Overview of catalysts of different systems in reverse water gas conversion reaction*

In industrial production, stable catalysts with high activity and selectivity need to be considered at low temperatures. However, designing a catalyst that meets all these criteria at the same time is a challenge. The current catalysts used for RWGS are mainly divided into precious metal catalysts and non-precious metal catalysts.

Table 1. Summary of RWGS reaction conditions of different catalysts and their CO_2 conversion and CO selectivity.

Catalyst	**Reaction gas ratio H_2 :CO_2 : inert gas**	**temperature ℃**	**Reaction airspeed $mL·gcat^{1}·h^{1}$**	**CO_2 conversion rate%**	**CO selectivity%**
Cu/CeO_2 [25]	3:1:0	600℃	400000	50	100
Cu/SGS [26]	4:1:0	550℃	3600	48	96
Pt/CeO_2 [28]	9:9:2	500℃	30000	30	-
$Pt\text{-}Re/SiO_2$ [29]	4:1:5	400℃	60000	24.3	96.2
Cu/MnO_x [43]	12:3:5	550℃	60000	55.5	100
Ni/ZrO_2 [35]	4:1:4	500℃	13500	27.6	100
Ni/Ga_2O_2 [36]	4:1:5	450℃	60000	40	95
Fe-oxide [37]	1:1:0	600℃	24000	38	>85
Cs/Fe,O [39]	4:1:0	450℃	12000	58	75
$MoO_3/TiAlC_2$ [50]	4:1:0	550℃	15000	30	-
MoO_3/FAU[47]	12.5:12.5:10	500℃	7500	15	100
$Ru@MoO_{3-x}$[49]	9:3:88	250℃	100000	45	>99
$Mo\text{-}P\text{-}Si_2O$[54]	4:1:0	550	12000	18	100
$Cu\text{-}Cs\text{-}Mo_2C$[53]	4:1:0	600	12000	-	100

2.3. *Precious metal catalyst*

Precious metal supported catalysts are the most common catalysts for RWGS. The main active species are Pt, Pd, Au, Ir, Rh, Ru, etc. The main carriers are SiO_2, CeO_2, TiO_2, and Al_2O_3, in which precious metals promote the dissociation of H_2, while oxide carriers facilitate the breakage of the C=O bond in CO_2. Dispersion and chemical state of precious metal nanoparticles are the key factors affecting catalyst performance, and have a great impact on the adsorption behavior of reactants on the catalyst and the subsequent intermediate species transformation [28].

2.3.1. Pt-based catalyst

Supported Pt catalysts are widely used in RWGS reactions due to their excellent H_2 dissociation and hydrogenation activity.

Chen et al. [29] found that the activation energy of CO production on Pt/CeO_2 catalyst was significantly lower than that on pure CeO_2 catalyst. The calculated TOF values were roughly the same across these Pt/CeO_2 catalysts, indicating that the RWGS reaction was insensitive to the size of the anchored Pt particles and the primary crystallinity of the CeO_2 carrier. The results of TPR and XPS showed that with the addition of Pt, the reducibility of CeO_2 carrier was enhanced, oxygen vacancy was more easily generated, and CO_2 activation was accelerated. In addition, through in-situ FT-IR and TPSR-MS experiments, we found that redox-and dissociation mechanisms co-exist in RWGS reactions on Pt/CeO_2 catalysts. CO_2 molecules adsorbed at the Ce^{3}+ active site cannot directly generate CO, which is the same as the previous REDOX mechanism.

Liu et al. [30] prepared $Pt\text{-}Re/SiO_2$ catalysts with different Re contents by co-impregnation and tested the RWGS reaction. The characterization results showed that the oxygenophilic ReOx ($0 \leq x \leq 3.5$) near the Pt particles modified the Pt surface through partial covering and electron interaction, resulting in a decrease in the number of CO adsorption sites and a decrease in adsorption strength.

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At 400℃, the turnover frequency of the optimal PT-Re/SiO_2 catalyst is 3.9 times higher than that of Pt/SiO_2, and the apparent activation energy is reduced. The CO selectivity on Pt-Re/SiO_2 remains above 96.2% compared to Re/SiO_2, which produces large amounts of CH_4. The reaction order analysis showed that Pt promoted H_2 activation, while oxyphilic ReOx enhanced CO_2 adsorption and activation. The peripheral sites of the Pt/ReOx interface have C-O cleavage properties, which can synergistically increase RWGS activity and inhibit the production of CH_4.

To improve the potential of H-doped WOy plasma effects, Ge etal. [31] reported that Mo-doped Pt/WOy (Pt/MoWOy) significantly increases the concentration of dopant (H^+) and oxygen vacancy in Pt/HxMoWOy during H_2 reduction, promoting the photothermal hydrogenation of CO_2 to CO. The developed Pt/HxMoWOy showed excellent catalytic performance (3.1 mmol h^{-1} g^{-1}) in the photothermal RWGS reaction at 140 °C, which was superior to the undoped Pt/ HxWOy (1.02 mmol h^{-1} g^{-1}). The experiment and comprehensive analysis show that the abundant surface free electrons and oxygen vacancy (VO) in Pt/HxMoWOy are the reasons for the effective CO_2 adsorption and transfer. Characterization of catalysts revealed reversible redox of Mo and W atoms during RWGS reactions, confirming that oxygen vacancies between Mo and W atoms in Pt/HxMoWOy act as active sites. Pt nanoparticles activate H_2 to regenerate oxygen vacancies. In addition, density functional theory calculations show that Mo doping significantly reduces the energy barrier of oxygen vacancy formation in WOy during H_2 reduction.

He et al. [32] synthesized a single-atom catalyst Pt1/SiC which the Pt particles are uniformly dispersed on SiC and applied it into the conversion of CO_2 via reverse water gas shift reaction, exhibiting a 100% selectively and 54% CO_2 conversion at 900 oC with a H_2/CO_2 ratio of 1:1. It was found that in the first few hours, the Pt1/SiC catalyst showed excellent stability with negligible decline in activity. However, over time, Pt1/SiC is gradually deactivated. After the reaction for 10 h, the CO_2 conversion rate remained relatively stable at about 50%. The authors attributed the decrease in catalyst activity to two factors: poisoning of Pt1/SiC catalyst caused by CO molecules and reduction of a small amount of Pt1/SiC.

2.3.2. Pd-based catalyst

Nelson et al. [33] dispersed Pd on a TiO_2 carrier. The results show that in RWGS reaction, Pd is mainly dispersed on titanium dioxide in the form of isolated atoms. Achieving atomic dispersion requires artificially increasing the absolute surface area of titanium dioxide by an order of magnitude, which can be achieved by physically mixing the catalyst Pd/TiO_2 with pure titanium dioxide prior to the RWGS reaction. Kinetic analysis, infrared spectroscopy, X-ray absorption spectroscopy and scanning electron microscopy showed that the RWGS activity of Pd/TiO_2-0.01 catalyst was very good within 92 h after in-situ dispersion of Pd atoms. The thermodynamic stability of Pd under high temperature RWGS reaction conditions is related to the PD-Ti coordination, which is related to the formation of oxygen vacancy and the artificial increase of titanium dioxide surface area.

2.3.3. Ru-based catalyst

Tang et al. [34] prepared an efficient RWGS catalyst by encapsulating a Ru cluster with a size of 1nm in a hollow silica shell. The space-confined structure prevents the sintering of Ru clusters, and the permeable silica layer allows diffusion of gaseous reactants and products. This particle size reduction catalyst not only maintains the excellent activity of Ru in CO_2 hydrogenation reaction, but also exhibits close to 100% CO selectivity and excellent stability at 200-500℃.

Abdel-Mageed et al. [35] investigated the effect of carrier particle size on the performance of highly active Ru/TiO_2 catalyst and found that after high-temperature reduction treatment, the selectivity of TiO_2 particle size can be controlled from 100% methanation to 100%CO. The comprehensive characterization of the catalysts shows that while the reaction behavior changes, their structure, chemical and electronic properties also change significantly. The chemical modification of the carrier by oxygen vacancy formation leads to the electronic modification of the Ru centers around the interface, which in turn affects the reaction behavior of these centers in CO_2 reduction reactions, from methanation to RWGS reactions.

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2.3.4. Au-based catalyst

Abdallah et al. [36] loaded titanium dioxide and zirconia support with very low content (<0.1wt%) Au and used it for RWGS reaction, and found that gold-based catalyst showed high catalytic activity for RWGS reaction at low temperature. At 250 °C, the catalytic activity of Au/TiO_2 catalyst is nearly 10 times that of Au/ZrO_2. In situ infrared drift results show that the formate reaction is the main intermediate species on Au/ZrO_2 catalyst, while on Au/TiO_2 catalyst, the reaction is carried out by the formation of hydroxyl carbonyl intermediates. The results of STEM, STEM-EELS, XPS and EPR in situ indicate that AU-O and $-Ti^{3+}$ interface sites are responsible for the excellent activity of Au/TiO_2.

Precious metal catalysts (Pt, Pd, Au, Rh, Ru, etc.), although they have high catalytic activity and stability, are not easy to deactivate, but due to high prices and scarce resources, they are limited in large-scale application in industrialization, and are only suitable for laboratory mechanism research. Therefore, efforts are needed to find some alternative catalysts to precious metals.

2.4. Non-precious metal catalysts

Although the precious metal has excellent CO_2 reduction performance and stability, the high cost limits its large-scale industrial application. Therefore, the exploration of inorganic non-precious metal catalysts has attracted great attention from scientific research staff, and non-precious metal catalysts (Cu, Ni, Fe, Mo, etc.) are often used to replace precious metals because of their low cost and good catalytic activity.

2.4.1. Ni-based catalyst

Nickel-based catalysts have problems of easy sintering and carbon deposition in RWGS reaction, and have low selectivity to CO. Zhang et al. [37] prepared a sulfur-containing Ni/ZrO_2 catalyst to improve the CO_2 conversion and regulate the CO_2 hydrogenation selectivity. The effect of carrier size on the catalytic performance of RWGS was investigated. The results showed that the 80nm Ni/ZrO_2 sample with smaller carrier size had higher Ni dispersion and oxygen vacancy concentration, exposed more active centers, and improved the adsorption and activation ability of CO_2.

Gong et al. [38] proved that the interfacial synergism of Ni/Ga_2O_3 promoted the selective hydrogenation of CO to CO(CO selectivity >95%) in the temperature range of 350-450 °C. Studies show that the synergistic effect of Ni/Ga_2O_3 interface significantly affects the adsorption of H_2 and CO_2, resulting in the formation of different intermediates and products. *HCOO preferently forms on the Ni surface and is further hydrogenated to CH_4 and H_2O. In contrast, the Ni/Ga_2O_3 interface favors the formation of CO with the help of H_2. This study not only provides a highly selective catalyst for RWGS reaction in CO_2 hydrogenation process, but also promotes the surface modification of the catalyst to improve the activity and selectivity.

Our group [8] prepared NiCe-HMS and Ni-HMS limited-structure catalysts by one-pot method, and conducted RWGS tests in the temperature range of 500-750 °C. Compared with Ni/HMS catalysts prepared by traditional impregnation method, Ni-HMS and NiCe-HMS showed higher CO selectivity. This is due to the formation of highly dispersed nickel nanoparticles on the surface of the carrier, which inhibits the formation of CH_4.

2.4.2. Fe based catalyst

Fe-based catalysts, as typical high-temperature catalysts, have also been used in RWGS reaction studies. The carrier-free nano ferric oxide catalyst prepared by Kim et al. has high catalytic activity and stability[39]. Through transmission electron microscope observation, it was found that nano iron oxide was not easy to agglomerate during RWGS reaction. XPS and XRD show that atomic carbon and oxygen formed as a result of dissociative chemisorption of CO or CO_2 appear to diffuse into a large number of nanoparticles to form Fe-oxides and Fe-carbides. CO and CO_2, the products of the reaction between the surface of the iron oxide and the reactants C and O, and RWGS, are diffused into the body of the iron oxide nanocatellist. Therefore, during the RWGS reaction, the structure of the catalytically active surface consisting of metal Fe remains unchanged, so that the catalytic activity remains stable for a long time. For Fe-based catalysts, whether the active phase is metallic iron, iron oxide or iron carbide is still a subject of debate.

They investigated, for the first time, the reduction of CO_2 to CO with hydrogen on alumina-supported CO and Fe catalysts under supercritical conditions with CO or CH_4 as the target product. The selectivity of the Co/Al_2O_3 catalyst for methanation is close to 100%, while the Fe/Al_2O_3 system shows an advantage for Co hydrogenation and significantly forms ethane (up to 15%). Compared with gas phase reaction, the spatio-temporal yield can be increased by one order of magnitude under supercritical conditions. The difference in the crystal phase characteristics of the iron-containing catalyst leads to the reverse water-gas transfer reaction to produce carbon monoxide, while the reduced iron phase leads to the Fischer-Tropsch reaction to produce a mixture of hydrocarbons. Direct methanation occurs selectively on Co catalyst. Methanol formation was not observed on the iron and cobalt catalysts studied [40].

Zhang et al. [41] found that metallic iron was a better RWGS catalyst than Fe_3C. The addition of Cs and Cu can promote the activity of Fe^0, hindering the carburization of iron, while favoring higher conversion rates and higher selectivity. When stability tests were performed, the catalyst aged during the RWGS reaction and a new phase appeared: Fe_5C_2(Hagg carbide). For RWGS reactions, Fe_5C_2 is an excellent catalyst with a higher carbon dioxide conversion rate than samples in which Fe^0 is the active phase. However, Fe_5C_2 has a low CO selectivity compared to Fe^0 based samples. The results showed that the best activity/selectivity was achieved by fine-tuning the Fe/Fe_5C_2 ratio.

2.4.3. Cu-based catalyst

Cu-based catalysts have attracted much attention because of their low price, high activity at relatively low temperatures, and good selectivity to CO. However, since copper is easily sintered or coking, such catalysts are prone to deactivation during the RWGS reaction.

Liu et al. [42] studied the effect of Cu/Ni ratio in Cu-Ni/γ-Al_2O_3 catalysts on the conversion and selectivity of the reaction. Cu facilitated the formation of CO and Ni facilitated the formation of CH_4 in $_3$. Cu-zn catalytic system is also used for RWGS reaction, and has the highest reaction performance when the Cu content is higher (Cu/Zn>3). The RWGS reaction is endothermic, and increasing the reaction temperature is conducive to the formation of CO.

Zhuang etal. [43] added Ru to $Cu/ZnO/Al_2O_3$ catalyst for RWGS reaction. The CO_2 conversion rate is more than two times higher than that of $Cu/ZnO/Al_2O_3$ catalyst. At the same time, the stability of the catalyst has been significantly improved. Through XRD, SEM-EDS, STEM-EDS, and TPR characterization, it is found that this may be due to the formation of Ru-Cu core-shell nanoparticles. In addition, the interaction between Ru and support is also an important factor affecting catalyst selectivity.

Liu et al. [26] constructed stable copper clusters in a Cu/CeO_2 catalyst with a high copper loading capacity of 15wt%. Under very harsh reaction conditions, CeO_2 nanorods partially sintered, forming 2D and 3D copper clusters on their surfaces. This partially sintered catalyst exhibits unparalleled activity and excellent durability at high temperatures. The interaction between copper and CeO_2 ensures that the copper clusters are stably anchored to the CeO_2 surface. A large number of in-situ surface oxygen vacancies form a synergistic effect with adjacent copper clusters, which promotes the reaction.

Deng et al. [27] prepared catalysts with different copper loads by simple impregnation method using NaOH activated slag polymer microspheres (SGSs) as the carrier. The results show that 10% Cu/SGS catalyst has better CO_2 conversion performance. At 550℃, the CO_2 conversion and CO selectivity of 10%Cu/SGS catalyst reached 48% and 96%, respectively. The results show that the high performance of the catalyst is mainly due to the interaction between copper and SGS carrier and the adsorption and activation of CO_2 by the alkaline center on SGS carrier.

Liu et al. [44] loaded Cu onto titanium dioxide nanotubes (TiNT) and titanium dioxide nanoparticles (TiNP), and the RWGS activities of the two catalysts were different. The activity of the nanoparticle carrier is very low, and the content of Cu hardly changes the activity, but the activity of the nanotube carrier is very high, and has three different behaviors as the surface density of copper increases. At low surface density, an active Cu-O-Ti site with low apparent activation energy is formed. At higher surface density, copper nanoparticles are formed on the surface of TiNT and the reaction barrier is reduced. At moderate surface densities, the metal copper clusters are engulfed by a TiOx overlay formed during hydrogen treatment, which is similar to the overlay formed by classical strong metal carrier interactions (SMSI). These reducing layers are significantly more active against RWGS than the initial TiNT surface, but have similar activation barriers, higher than those on exposed copper and TiNP surfaces. SMSI is an important concept in heterogeneous catalysis, but it will inevitably sacrifice catalytic activity due to overcoverage.

González-Arias etal.[45] Prepared series of Cu-MnOx catalysts and found that the improvement of catalyst performance is due to the addition of Mn to enhance the dispersion of Cu and increase the surface alkali concentration. Under standard RWGS conditions, the highest reaction rate of the catalyst is related to the improvement of Cu dispersion and the composition of the highly active Cu-MnOx domains. It is worth noting that the change in the optimal copper-manganese ratio is a function of the RWGS reaction conditions.

Ebrahimi et al. [46] prepared Cu/CeO_2 solid solution by combustion synthesis method, the catalyst exhibits high activity, stability and 100% CO selectivity in the RWGS reaction, and these catalytic activities are attributed to the excess oxygen vacancy on the CeO_2 surface, which can promote CO_2 conversion. The high activity of the catalyst is due to the synergistic effect between the active Cu0 and Ce^{3+} -oxygen vacancy.

Zhang et al. [47] studied a variety of strategies to effectively regulate nanointerfaces from different aspects, such as carrier composition, Cu preparation parameters, pretreatment and reaction conditions, in order to balance the activity and stability of Cu/TiO_2 catalysts in RWGS reactions. The results show that due to the reducibility of TiO_2 and the limited electron transfer from TiO_2 to Cu, only doping Zn in the TiO_2 carrier can inhibit the formation of nanointerfaces during the reduction treatment. Cu coverage on Zn-modified TiO_2 is significantly decreased, but the catalytic activity is increased by 44% and the stability is unchanged.

2.4.4. Mo-based catalyst

Molybdenum is more abundant and cheaper than precious metals, increasing the potential for large-scale industrial applications of molybdenum-based catalysts. Molybdenum-containing catalysts are widely used, including Ni-Mo catalyst [48], molybdenum sulfide catalyst, MoOx catalyst [49], supported MO-based catalyst [50], new Mo_2C and Mo_2N catalysts [51], etc.

Xin et al. [52] found that during the CO_2 hydrogenation reaction, Ru-MoO_3 formed a SMSI state between the metal and the carrier at 250 ^{o}C, which was conducive to CO_2 selective hydrogenation to form CO. During the reaction, Ru nanoparticles promote the reduction of MoO_3 to form an active MoO_{3-x} coating with oxygen vacancy, which migrates to the surface of Ru nanoparticles to form a coating structure (Ru@MoO_{3-x}). The resulting SMSI state changes the catalytic performance of the catalyst from 100% methanation at the Ru site on the exposed surface to 99%CO formation by quasi MVK mechanism in the Moo-X layer. Selective regulation is achieved by different SMSI states in the CO_2 hydrogenation reaction.

Ronda [53] et al. took advantage of the high thermal stability and excellent electrical conductivity of the MAX phase to prepare a MoO_3/Ti_3AlC_2 catalyst to increase its intrinsic RWGS activity. When molybdenum oxide is loaded on the MAX phase of the Ti_3AlC_2, the low surface area of the MAX phase leads to the formation of large MoO_3 rods with blocky characteristics. The presence of electron-rich Ti_3AlC_2 enhanced the redox characteristics of MoO_3 in the RWGS reaction, resulting in a high degree of surface reduction and the formation of a large number of oxygen vacancies. Therefore, the catalyst showed the highest activity in catalytic experiments. When the MAX phase acts as a carrier, the electron-rich Mo site is an ideal activation site for CO_2 via electron transfer to the CO_2 antibond orbital, an interaction that weakens the C-O bond and favors reduction to CO. The catalyst is selective to CO, thus inhibiting the formation of methane and coke.

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Zhang et al. [49] found that the surface modification of Ni by MoOx can regulate RWGS and methanation reaction. The addition of MoOx improves the dispersion of Ni through strong interaction, and the partially reduced MoOx modifies the surface of Ni particles by covering and electron modification, which enhances the desorption of CO on the surface. The addition of a large amount of Mo(Mo/Ni ratio of 1) makes the reaction shift to RWGS, and the CO selectivity is greater than 94%. Kharaji et al. [54] incorporated Mo into the Fe/Al_2O_3 catalyst and found that Mo greatly improved the RWGS catalytic activity and CO selectivity due to the Fe-O-Mo structure formed in the $Fe_2(MoO_4)_3$ phase of the Fe-Mo/Al_2O_3 catalyst. The presence of the Fe-O-Mo structure causes $Fe_2(MoO_4)_3$ to have a lower reducibility, which effectively inhibits the reduction of Fe oxides. On the other hand, the existence of Fe-O-Mo structure promotes the flow of electrons from Fe to Mo, resulting in Fe species being in an electron-deficient state and forming a positive surface charge, which is detrimental to the adsorption of CO and effectively inhibits the further hydrogenation of CO. As an additive and active component, Mo shows good CO selectivity, but its CO_2 conversion needs to be improved.

Zhang et al. [55] reported the preparation of Cu-Cs-MO_2C by using Cu as accelerator and Cs as dopant to improve the conversion and selectivity of the catalyst, respectively. It is found that the increase of CO_2 conversion is due to the addition of copper to provide more active sites for the catalyst, such as Cu+ and Cu°. Cs is due to its significant positive electric properties that create electron perturbations on the catalyst surface, thus enhancing catalytic performance. Its addition can improve CO selectivity, especially at low temperatures. In addition, the carbon-doped catalyst appears to be activated in situ due to the recarburizing phenomenon, which results in the catalyst being fairly stable in continuous operation.

Zhang et al. [56] used silica as the carrier to prepare Mo-P-SiO_2 catalyst, and found that the catalyst was completely oxidized through characterization. Through characterization, it was found that the high selectivity of carbon monoxide was due to the MoP phase generated on the surface of silica carrier, which was more conducive to the direct conversion of carbon dioxide into carbon monoxide through MoP(0001). from the potential energy surface profile thermodynamicall, methane generation on MoP(0001) surface requires higher energy than carbon monoxide. In other words, the MoP(0001) surface is more selective to produce CO than CH_4.

Yuan et al. [57] reported the application of Ni-doped MoS_2 in CO_2 hydrogenation to methanol and prepared series catalysts of MoS_2/NiX. Through DFT calculation, they found that MoS_2/Ni-catalyzed CO_2 hydrogenation tends to the oxidation-reduction pathway, and the optimal adsorption structures and barrier energies of different intermediates are shown in the article. CO_2 and H_2 are directly dissociated to CO*, O*, and 2H* by an energy barrier of 0.63 eV. The large adsorption energy indicates that CO* has a strong interaction with MoS_2 (Eads = -1.27 eV) and is more likely to react further on the carrier without releasing CO.

2.5. Catalysts for other systems

2.5.1. Transition metal carbide catalyst

Transition metal carbide catalyst (TMCs) is also a more promising and attractive catalyst, after the introduction of carbon, the electronic properties of the transition metal change, so that its activity becomes similar to the precious metal catalyst, has a strong H_2 dissociation and CO bond breaking ability, so as to show high activity in the CO_2 hydrogenation to CO reaction. Therefore, it has been reported that catalysts such as vanadium carbide [58], tungsten carbide [59,60] and molybdenum carbide [61,62] have superior catalytic activity and CO selectivity when applied to RWGS reactions.

Juneau et al. [63] found that micellar based silica coating technology could prepare 10 nm tungsten carbide nanoparticle catalyst. The high activity and CO selectivity of nano-WXC carburizing observed at 1000 °C may be due to the fact that the coated silica maintains a particle size of 10nm during carburizing, thus promoting the formation of surface carbides. Compared with the catalyst prepared by impregnation method, the synthesis method affects the formation degree of WxC and the reactivity of RWGS. Reddy [59] synthesized Mo_2C by direct carbonization of Mo precursor. Under

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723K and 1 atmospheric pressure, the CO_2 :H_2 molar ratio of Mo_2C catalyst can reach 57% and the CO selectivity can reach 62%. Marquart etal.[62] prepared four catalysts by using three different synthesis processes have good catalytic activity. The results show that CO_2 forms adsorbed oxygen surface species by dissociating on the carbide surface. Above 850 K, the carbides oxidize into the oxide phase MoO_2 or MoO_3. The different catalysts all exhibit CO_2 conversion rates higher than 30%, and CO selectivity is 99% even at high H_2/CO_2 ratios. Although the new molybdenum carbide catalyst has excellent activity in RWGS reaction, its preparation method is difficult compared with other catalysts.

2.5.2. Perovskite type catalyst

Mixed metal oxides with ABO_3-type perovskite structure acting as carriers of rare earth metals and transition metals are considered to be very promising catalytic ceramic materials [63]. The catalytic properties of perovskites can be modulated by changing the properties of A and B ions or by inserting dopants into the structure. Perovskite oxides have attracted the attention of researchers due to their high mobility of oxygen and ability to stabilize unusual cationic oxidation states, as well as their thermal stability at high temperatures [64]. Alkali metals, alkaline earth metals, and rare earth metals are commonly used as accelerators, which can change the acid-base properties of the catalyst, improve the dispersion of the active species, and increase the strength of the interaction between the active species and the carrier. Kim et al. [65] added Y, Zn and Ce to $BaZrO_3$, and discussed the influence of dopants on the catalytic activity. At 600 °C for 5 h, all catalysts showed stable catalytic properties. Among them, the $BaZr_{0.8}Y_{0.16}Zn_{0.04}O_3$(BZYZ) catalyst showed excellent activity with a CO_2 conversion rate of 37.5% and CO selectivity of 97%. Ce insertion improved the ionic conductivity of BZYZ, but additional Ce did not have any positive effect on the catalytic activity of the RWGS reaction.

In heterogeneous catalysis, the catalytic performance of bifunctional catalysts is often better than that of single-component catalysts. The shape, size and distribution of catalytic particles also have a great influence on the activity of the catalyst. Kopac et al. [66] have theoretically studied the effects of biffunctional groups on RWGS reactions in detail. Density functional theory was used to calculate the energy diagram of RWGS in three surfaces (copper (111), $SrTiO_3$ surface and $Cu/SrTiO_3$ interface between two solids). These three surfaces were combined using mesoscale dynamics Monte Carlo simulations to study the turnover and yield of CO production as a function of particle size. The results show that the reaction speed at the interface is faster. However, in addition to the interface, the binding of copper and carrier sites further accelerates the RWGS reaction, suggesting that the catalyst's bifunction is manifested in more complex interactions between phases rather than just interface effects, such as hydrogen spillover. The authors found three different effects: electronic effect, synergistic effect and geometric effect, and a smaller Cu on the carrier $SrTiO_3$ showed a higher CO formation rate.

2.6. Catalyst deactivation in reverse water gas conversion reaction

Under high temperature conditions, the catalyst used for RWGS reaction has poor thermal stability or weak interaction between the active component and the carrier, which leads to sintering and agglomeration of the catalyst at high temperature and decreases the activity of the catalyst [67]. In addition, carbon deposition is also an important cause of catalyst deactivation. Carbon deposition, as the name suggests, is that the surface of the catalyst is covered by a certain form of carbon, and carbon is mainly formed by carbon-containing substances in the raw material breaking bonds on the surface of the catalyst or first coking and then dehydrogenation. These carbon species cover the active site, thus reducing catalyst activity. Therefore, the stability of the catalyst at high temperatures is extremely important for RWGS reaction.

Yang et al. [67] mixed Fe into Ni/CeO_2-Al_2O_3 and the $NiFe/CeO_2$-Al_2O_3 catalyst showed an excellent CO_2 conversion rate in the stability test at 800000 $mL\cdot g^{1}\cdot h^{-1}$ and 700 °C. FeOx greatly enhances Ni dispersion on the surface, which helps to provide higher activity in the reaction. In addition, FeOx-Ni interaction leads to electron enrichment of Ni surface atoms, and higher electron density is conducive to CO_2 adsorption. The 0.3CuMgAl-LDH-400 catalyst prepared by the hydrothermal method by Chen et al. [68] showed high stability during the RWGS reaction, and the activity remained unchanged for more than 30h, which was due to the fact that the use of LDH as a carrier improved the dispersion of Cu and the presence of more alkaline sites. On the contrary, the catalytic activity of 0.3CuMgAl-IMP-400 prepared by impregnation decreased slightly after 20 h of reaction. The results show that the catalyst prepared with LDH as the support has better stability.

Goguet et al. [69,70] studied the deactivation process of Pt/CeO_2 catalysts. The stability test results show that the initial CO_2 conversion rate is stable at 13.7%, and the CO selectivity is greater than 99%. As the reaction progresses, its catalytic activity begins to gradually decrease, possibly due to carbon deposition of the catalyst, or sintering of the metal. In order to clarify the deactivation principle, the TPO cycle test was performed on Pt/CeO_2 catalyst before and after the reaction. The results show that there is a linear relationship between the degree of deactivation of Pt/CeO_2 catalyst and the amount of carbon deposition. The place where carbon deposition occurs is the active part of the reaction. With the increase of time, the active part is gradually covered by carbon deposition, which leads to catalyst deactivation.

3. Conclusions

Converting carbon dioxide into high value-added chemicals and fuels is a potential path to a carbon neutral future. The reverse water gas conversion reaction converts carbon dioxide to carbon monoxide and produces syngas through Fischer-Tropsch synthesis, methanation and alcohol preparation, which is a promising method of carbon dioxide utilization. However, due to the endothermic reaction, at low temperature, the strong exothermic methanation reaction is competitive with the reverse water gas change reaction. Although high temperature is conducive to the forward reaction, the energy consumption of the reaction is too high. Therefore, the development of catalysts capable of high conversion and selectivity at lower temperatures in the future will be a research focus for scientists. The development of catalysts with high CO_2 conversion rate and high CO selectivity can be started from the following aspects: (1) Improving the preparation method of catalysts to improve the dispersion of active components; (2) Seeking high-activity metal auxiliaries; (3) Modifying the carrier to increase the dispersion metal species and adjust the interaction between the active component and the carrier. In addition, we may be able to promote the development of low-carbon industrial catalysis by using light-driven chemical reactions, and develop and design suitable catalysts to gradually transition RWGS reactions from thermal reactions to photocatalytic processes.

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