Bimetallic Ni-Based Catalysts CO2 Methanation

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CO_2 methanation has recently emerged as a process that targets the reduction in anthropogenic CO_2 emissions, via the conversion of CO_2 captured from point and mobile sources, as well as H_2 produced from renewables into CH_4. Ni, among the early transition metals, as well as Ru and Rh, among the noble metals, have been known to be among the most active methanation catalysts, with Ni being favoured due to its low cost and high natural abundance. However, insufficient low-temperature activity, low dispersion and reducibility, as well as nanoparticle sintering are some of the main drawbacks when using Ni-based catalysts. Such problems can be partly overcome via the introduction of a second transition metal (e.g., Fe, Co) or a noble metal (e.g., Ru, Rh, Pt, Pd and Re) in Ni-based catalysts. Through Ni-M alloy formation, or the intricate synergy between two adjacent metallic phases, new high-performing and low-cost methanation catalysts can be obtained.

CO2 methanation | bimetallic catalysts | Ni-based catalysts | promoters | alloy nanoparticles | bimetallic synergy

1. Introduction

During the last hundred years, rapid industrialization and the high energy demands of our society have disrupted the carbon cycle through ever increasing greenhouse gas emissions, and the ramp-up of renewable energy production has yet to offset the negative effects on our planet's climate and ecosystems [1][2]. However, progress made in hydrogen production technologies through water electrolysis has raised hopes for the utilization of this green fuel that produces no CO_2 emissions upon its combustion [3], despite the fact that its storage and transportation remain challenging when compared to other traditional energy carriers, such as natural gas [4]. In the last decade, research efforts have been focused on the development of catalysts that can utilize this excess renewable hydrogen in order to hydrogenate CO_2 released from industrial flue gases. This way, H_2 can be transformed into a reliable energy carrier, that is, CH_4 or synthetic natural gas (SNG), with a significantly higher energy density, all the while creating a closed carbon cycle [5]. The complete hydrogenation of CO_2 into CH_4, or CO_2 methanation, is also known as the Sabatier reaction and is an exothermic reaction with the following equation:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H_{298\ K} = -165\ \text{kJ/mol} \qquad (1)$$

Ni has become a favourite active metal for this reaction, since its high methanation activity, low cost and natural abundance render it attractive for industrial-scale applications [6]. Since CH_4 yield peaks at a relatively low temperature (300–400 °C, depending on the reaction conditions) [7], structural degradation of Ni-based catalysts, though not completely avoided, plays a minor role compared to other reactions (e.g., methane dry reforming) [8]. The choice of the metal oxide support also appears to be of great importance in the performance of Ni-based catalysts [9][10][11]. Ni/CeO_2 catalysts, for example, are much more active compared to Ni/Al_2O_3 or Ni/SiO_2 catalysts. This is mainly attributed to ceria's intricate redox and O^{2-}-defect chemistry, with it being able to transport oxygen species and oxygen ion vacancies throughout its lattice, having higher basicity compared to other metal oxides that favours CO_2 chemisorption and activation, as well as exhibiting a strong metal–support interaction that favours a higher Ni dispersion [12].

The activity of Ni-based catalysts can be further improved via modification of the metal oxide supports. For example, alkali and alkaline earth metals [13], transition metals and rare-earth metals [14] can be used as promoters that modify the physicochemical properties of metal oxide supports. In some cases, these ions can enter the lattice of the metal oxide supports (e.g., Ca^{2+} ions in CeO_2 and ZrO_2 lattices) [15], or form segregated metal oxide phases supported on the support surface (e.g., La_2O_3, CeO_2 and MnO_x in Al_2O_3) [16]. Such modifications can lead to an increase in support basicity, so that the initial step of CO_2 chemisorption step is accelerated, or to an increase in the active metal dispersion [17]. In most cases, the low-temperature activity and stability of Ni-based catalysts is enhanced following modification of the metal oxide supports.

Besides Ni, Ru and Rh noble metals have been extensively studied as active metallic phases in CO_2 methanation and they usually achieve a much higher activity at low temperatures [18][19]. Since CH_4 is thermodynamically favoured over other CO_2 hydrogenation products such as CO, at low temperatures, CH_4 selectivity can be significantly higher when using noble metal catalysts. Among the two noble metals, Ru can achieve higher activity and its price is considerably lower compared to Rh, while it can also provide significant methanation activity when supported on cheap supports (e.g., Al_2O_3 or TiO_2) at a metal loading as low as 1% or even 0.5% [20]. Ru is also preferable to Ni for application in the combined capture and methanation of CO_2 derived from industrial flue-gases since the high reducibility of RuO_x oxides allows for isothermal operation at low temperatures [21][22].

A popular method to counter some of the drawbacks of Ni-based catalysts is to use a second metal (e.g., Fe, Co or Ru) as a dopant, in order to create appropriate bimetallic CO_2 methanation catalysts. Such an approach has been successfully employed in other reactions. For example, NiFe alloys are active and stable catalysts for dry reforming of methane, since Fe can promote carbon gasification and significantly reduce coking through an intricate dealloying and realloying mechanism [23]. The combination of Ni with other metals can either lead to the formation of Ni-M alloys, or monometallic heterostructures with closely located active metallic Ni-M phases [24]. There are two types of metals that are used in such Ni-M bimetallic catalysts, the one an early transition metal such as Fe and Co and the other a noble metal, namely Ru, Rh, Pt, Pd and Re.

Fe and Co can easily dissolve into the Ni lattice due to the similar crystallographic properties of the corresponding metallic phases. In the example of Fe, the dissolution of Fe atoms into the Ni lattice leads to the formation of NiFe alloys, with Ni_3Fe being the most thermodynamically stable [25][26]. The introduction of Fe causes an expansion of the Ni fcc lattice up to a specific Fe amount and a shift of the (111) Ni reflection in XRD towards lower 2θ values. At higher Fe contents, the lattice becomes Fe rich and switches to the more compact bcc structure of pure Fe [27]. The introduction of the dopant metal can be used to tailor the electronic properties of Ni, so that the new alloy phase can achieve superior activity compared to monometallic Ni. This can also lead to a higher dispersion, stability and/or resistance towards deactivation. The application of computational methods has shown that specific alloys can lower the M-CO binding energy and lead to higher CO methanation activities [28].

Noble metals Ru, Rh, Pt, Pd and Re can increase the reaction activity by enhancing the reducibility of the primary Ni phase, by increasing the Ni dispersion, or by changing the reaction pathway [29]. Ru and Ni mostly form monometallic heterostructures that rely on the synergistic effect between the two separate metallic phases, while Pt and Pd mostly lead to the creation of NiPt and NiPd alloys [30][31][32]. It has been shown that an addition of only a miniscule amount of noble metal (e.g., 0.5% or 1%) can greatly enhance the reducibility and low-temperature activity of Ni-based catalysts without the need to use high loadings of precious metals [33].

2. Promotion with Transition Metals and Noble Metals

The race for the development of low-cost and high-performing CO_2 methanation catalysts thus stems from the need to efficiently convert excess electricity and H_2 generated from renewables, as well as CO_2 captured from flue gases, into a reliable energy carrier. Ni is the standard option to be used in CO_2 methanation catalysts, due to its high activity and low cost. However, insufficient low-temperature activity and the degradation of Ni catalysts over time due to oxidation and sintering creates the need for the employment of specific metal additives to counter such drawbacks. These additives can fall in two generalized categories: other transition metals (including Fe and Co) and noble metals (including Ru, Rh, Pt, Pd and Re).

The transition metals Fe and Co offer the obvious advantage of being cheap like Ni and their similar size and electronic properties allow for their intricate interaction with the Ni primary phase and their easy dissolution into the Ni lattice, forming NiFe and NiCo alloys, respectively. The composition of the formed alloy is of great importance, since only specific bimetallic combinations can lead to an optimal CO_2 methanation performance, especially in the case of NiFe alloys. The combined bimetallic catalysts can also offer additional advantages, such as higher stability, as well as resistance towards oxidation and sulphur poisoning.

Noble metals generally increase the reducibility and dispersion of the Ni primary phase and they can also participate in the reaction as active CO_2 methanation phases. Stand-alone Ru catalysts are highly active for low-temperature CO_2 methanation and the presence of Ru in bimetallic Ni catalysts as a separate monometallic phase also boosts catalytic activity. Additionally, the cost-effectiveness of Ru compared to other noble metals renders the bimetallic NiRu combinations quite popular in the field of heterogeneous catalysis. Rh and Pt can also greatly enhance the catalytic activity for CO_2 methanation when dissolved or deposited upon Ni in small quantities. Lastly, Pd and Re have been also tested as potential promoters in Ni-based catalysts.

The assumed trade-off between cost and catalytic activity for CO_2 methanation catalysts can be potentially overcome via the development of bimetallic Ni-containing catalysts with an optimised Ni–dopant metal synergy.

Recent advances in operando spectroscopic techniques can shed light on how the reaction mechanism differs between Ni-based alloys or Ni–dopant metal interfaces and monometallic Ni, allowing for the development of catalysts with the lowest possible cost and highest possible performance.

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