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Ultra-low temperature carbon (di)oxide hydrogenation catalysed by hybrid ruthenium-nickel nanocatalysts: towards sustainable methane production

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Abstract: It is a paradox that the excess of carbon dioxide in our atmosphere can endanger lives and even the civilisation that has been founded on carbon. Human addiction to carbon is persistent and therefore we need novel chemistry for the efficient conversion of CO₂ to harmless or useful products. Accordingly, catalytic CO₂ hydrogenation has been widely studied as a potential method for fuel engineering, and methane production in particular. Syngas, a blend of CO with H₂ has been observed as an incomplete product of this reaction. Here we report a surprising discovery that syngas to methane conversion can be attained in flow at temperatures starting from -7 °C with a hybrid bimetallic Ru/Ni catalyst. In turn, the ultra-low temperature effect cannot be observed for the Re/Ni and Pd/Ni combinations. To our knowledge, this is the first report showing that such a process can be performed at a temperature lower than the freezing point of water. These ultra-low temperature conditions could potentially lead to sustainable methane production.

Introduction

Our life has been founded on carbon. Our civilization has relied and continues to rely on the use of fossil carbon sources such as oil, coal, and natural gas. Their high potential energy is easily released and used upon combustion, thereby resulting in carbon (di)oxide evolution. In particular, the fragile environmental carbon dioxide balance has been attracting attention because of increasing concerns about its involvement in anthropogenic impacts on climate change. On the one hand, the production of carbon dioxide endangers the safety of our energy supply because of the urgent requirement for reductions in energetic flue gas emissions. On another hand, however, a carbon footprint is an unavoidable consequence of human activity. Therefore, our increasing awareness of the environmental role of carbon dioxide has posed a challenge to contemporary chemistry but also an opportunity for the development of new sustainable technologies if carbon dioxide can be seen as a raw material and not only a waste product. In particular, sustainable carbon (di)oxide chemistry currently focuses on a relative improvement in the carbon balance, for example, in CO₂ conversion

to syngas or methane, rather than on the absolute reduction of CO₂ emission by means of a single technology¹. Accordingly, CO₂ could be an attractive, renewable, safe, cheap and sustainable C₁ building block for both organic chemistry and fuel engineering and, therefore, CO₂ hydrogenation is currently a major topic of research²⁻¹⁰. Hydrocarbons of fossil origin have been depleted: They have been widely used for centuries because of their abundance, high potential energy and physico-chemical properties which make them energetic materials that are easy-to-handle and distribute. Methane, which is the main component of natural gas, should constitute the most environmentally friendly energy source from the many carbon-based fuels because it has the highest hydrogen to carbon proportion^{11,12}. Methane could be directly produced by hydrogenation (methanation) from carbon oxide or dioxide in a sustainable process inspired by the circular economy concept, thus avoiding the environmentally questionable extraction from soils, for example in the case of shale gas. In turn, the catalytic photothermal version of CO₂ methanation can be potentially used in solar fuel production¹³. Specifically, this would use a blend of CO and H₂ known as syngas. In a recent development, water/carbon dioxide splitting was shown to yield solar syngas (H₂ + CO)¹⁴. The different approaches for this include CO₂ dissociation combined with H₂O splitting¹¹ or CO₂ to CO conversion using thermochemical cycles involving solar energy^{2,12}. In turn, the methanation of solar CO or syngas could produce a synthetic replacement for natural gas. However, the potential for CO or CO₂ methanation is considerably hindered by unfavorable economics. Accordingly, generation of the hydrogen that is needed as the CO₂ or CO co-educt for methane production allows us to exploit an energy surplus from other processes. In turn, the combustion of methane would provide an energy-recovering step. It is worth mentioning that cyclic CH₄ oxidation coupled with CO₂ reduction theoretically presents an environmentally benign chemistry enabling the complete reduction of CO₂ emission. As the world probably cannot cope without carbon fuels in the near future,

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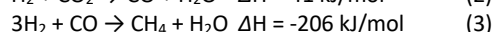
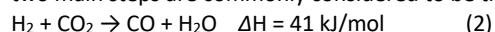
the potential of carbon di(oxide) to CH₄ inter-conversion deserves special attention. The challenge for designing such viable processes is the energetic balance. Ideally the energy would be supplied by solar light, an extraterrestrial source of energy, through natural or artificial photosynthetic systems or through catalysis, thus lowering the activation energy of the processes^{3,4}. Electrochemical reduction of CO₂ is also a current field of research in this context⁷⁻⁹. Furthermore, these processes must be economically viable and cost-effective.

Overall, CO₂ methanation can be expressed by the following equation¹⁵:



Interestingly, the overall methanation of carbon dioxide is thermodynamically favorable ($\Delta G = -165 \text{ kJ mol}^{-1}$); however, the reduction of oxidised carbon to methane brings significant kinetic limitations, which require a suitable catalyst to achieve acceptable rates and selectivity. Processes occurring at a catalyst surface and involving adsorption of the educts and desorption of water and methane as the products can be highly specific. For example, it has recently been shown that adsorption of CO₂ on the surface of a Ru catalyst, which blocks catalyst reactivity, can be overcome by photoexcitation of the adsorbed CO₂; however, the conversion achieved at 200 °C was relatively low¹⁶. On the other hand, photocatalysis on graphene-supported NiO/Ni nanoparticles indicated that H₂O desorption was a limiting step at 200 °C while the reaction could proceed with a quantum yield of 1.98%¹⁷.

Notably, CO₂ methanation is actually a multistep process^{18,19}, and two main steps are commonly considered to be the following¹⁶:



Reactions 2 and 3 are not synchronised according to their thermal effects. Endothermic CO₂ to CO conversion is followed by exothermic CO hydrogenation. The latter reaction is used extensively in industry to remove trace amounts of CO from the hydrogen streams produced by steam reforming of hydrocarbons¹⁹⁻²⁰.

Lowering the reaction temperature could help to attain economic viability and to improve the net energetic profit of methanation²¹. In this context, low temperature processing of crude carbon oil could be used for economically sustainable fuel engineering²². Interestingly, thermodynamic equilibrium constants for reversible reactions of CO₂/CO hydrogenation become higher and higher as the temperature gets lower¹⁹, which also makes low temperatures attractive in terms of process thermodynamics.

Currently, existing low temperature CO, CO₂ or syngas methanation studies typically exceed 200 °C for CO methanation and 300 °C for CO₂ methanation^{23,24}. The reactions are often performed at elevated pressures as well, thereby incurring an additional cost for safety and installations. For example, the kinetics of such reactions have been widely investigated^{25,26}, and the lowest temperature reported for CO methanation was 170 °C (SiO₂/Ni/AlVOx catalyst)²⁷. In turn, under high pressure (50 bar), this could be reduced to 120-150 °C. Catalytic CO methanation approaches have been reviewed by Snytnikov et al.²⁸. Recently, homogeneous catalytic systems were reported independently for the conversion of CO to MeOH via the intermediate formation of a formamide at temperatures of 145-150 °C at 50-70 bars in batch reactors^{5,29}.

A variety of systems were described for CO methanation. The usual temperature range needed to operate these systems is 270-400 °C (for the extensive literature survey see Supporting Information). Can methanation be made more sustainable and how efficient could this process be at ambient temperature and pressure? Chemically,

methanation is a reduction reaction. Accordingly, can we profit from the expected availability of solar syngas that provides CO as the intermediate reduced form of CO₂? Examining the performance and limiting factors of individual processes under such conditions would provide important insights into low temperature processing.³⁰ To address these questions, we have focused on syngas (CO + H₂) conversion to CH₄ by CO methanation, which decouples CO₂ methanation into two steps. Surprisingly, we discovered that this process could be observed in flow at temperatures starting from -7 °C with a hybrid bimetallic Ru/Ni catalyst. To the best of our knowledge, this is the first report to show that the process could be performed at temperatures lower than the freezing point of water. The method for our Ru/Ni catalyst preparation included the formation of Ru/SiO₂, from which silica was digested in the presence of Ni. In this system, unalloyed nanometallic Ru/Ni conjugates were formed at the surface³¹. In the above-mentioned catalytic system, the reaction could proceed as long as catalytically active sites were not getting blocked. Unblocking the access to the catalytic sites would require the removal of adsorbed surface species blocking catalyst active sites. The catalyst could thus be regenerated *in situ* by the removal of adsorbates. Freeze drying (reducing pressure at temperatures below the freezing point of water) is an option for catalyst regeneration; however, inductive heating appeared to be the most efficient method to supply energy directly to the Ru/Ni surface which activates the catalyst. Accordingly, the catalyst could then work by oscillating between active and inactive forms. The heat pulse initiates exothermic methanation, which increases the temperature at the catalyst surface providing the energy needed for the desorption of surface species and enhancing the progress of the reaction. This process could be further enhanced by in-situ water sorption. The selective conversion of syngas to CH₄ in such a system is 100 % at 156 °C.

Results

Ultralow temperature carbon (di)oxide methanation

Ru, Pd or Re nanoparticles were deposited on Ni following a previously reported method to obtain hybrid catalysts for which comprehensive characterisation (HRTEM, SEM, chemical analyses)^{31,32} was additionally supported by EDXRF, XRD, TOF-SIMS, Raman analyses and the TEM images of the catalysts (**Supporting Information**). The powder catalysts (200 mg) were loaded in a quartz microreactor and methanation was performed under atmospheric pressure in a quartz flow microreactor with a fixed catalyst bed and a diameter of 7.5 mm. The feeding gas mixture was continuously injected at a flow rate of 3 L/h. The conversion was determined by analyzing the composition of the tail gas effusing from the microreactor using a thermal conductivity detector-equipped SRI gas chromatograph (1/8 inch diameter, 3 m long column; micropacked with active carbon 80-100 mesh; column temperature of 80 °C with Ar as the carrier gas, 10 L/h) or in site gas analyser GX-6000 (RIKEN). The limit of detection for methane is 1ppm for the GX-6000 and 10 ppm for GC SRI 3100C.

Syngas was obtained by catalytic hydrogenation of CO₂. The CO ratio was tuned to obtain a blend with H₂ to CO ratio of v/v 3:1. Syngas methanation was tested on Ru/Ni, Re/Ni, Pd/Ni catalysts in our custom designed reactor. The effluent gases were analysed by gas chromatography and in line gas analyser that provided fast, real-time measurements. A representative set of syngas methanation data for

Ru/Ni system is presented in **Fig. 1** in which we illustrate both the temperature of syngas hydrogenation and the associated conversion percentages. The details are additionally specified in Supplementary **Tables S3-S5** and **S7-S9**. The process can be performed at room temperature (without heating); however, the reaction stops after a short period. To proceed further, the reaction needs an external energy supply to reactivate the catalyst. Heating fully activates the catalyst to the level observed for a virgin catalytic system. Accordingly, what we observed is that the process sequentially oscillates between activity and inactivity. In the reactive phase, the conversion gradually decreases to a final stop. In turn, during the re-activation phase, the conversion gradually increases to reach the maximal level depending on the temperature (**Fig. 1**). Surprisingly, the Ru/Ni system appeared to be sufficiently active to yield methane even if the reactants and catalyst were cooled to a temperature below the freezing point water, as low as -7 °C. The conversion of CO ranges from 1.2% at -7 °C to 16.7% at 25 °C, i.e., at ambient temperature, maximal conversion reached a value of ca. 17%.

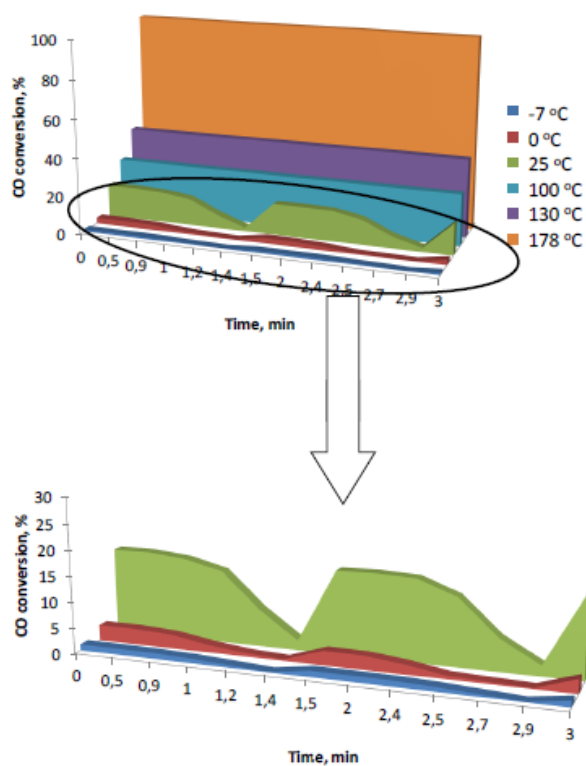


Figure 1. CO conversion into CH₄ at the Ru/Ni catalyst. The conversion proceeds cyclically at temperatures lower than 100 °C, while a temperature of 178 °C was required to achieve 100% conversion. The legend indicates the color codes for each temperature tested. Upper panel: full range of temperatures; lower panel: lower temperatures only, which feature cyclic behavior

The temperature rise is observed directly after the titration of reactants in the CO stream (**Table S3; entries 2-3**). For the CO stream at ambient temperature (25 °C) the temperature gain was 2 °C to reach 27 °C (**Table S3; entry 2**). At -7 °C the measured temperature of effluent gases remained ca. -7 °C (**Table S3; entry 1**).

The conversion indicates two phases within the reactivity phase. Accordingly, in the first phase the conversion percentage is nearly

constant, but then decreases rapidly to a complete stop in the next phase (**Fig. 1**). The lifetime of the catalyst depends on the temperature of the process, ranging from 1.4 to 2.5 minutes, at -7 °C and 25 °C, respectively (**Fig. 1**). After this time, the reaction stops. The reactivation of the catalyst could be achieved in situ by various methods. Heating of the catalyst, e.g., by increasing of the temperature of the flowing reactant gases, is one of few options. Alternatively, another option for catalyst reactivation would be freeze drying at low temperature and low pressure, which also proceeded efficiently when tested. The regeneration fully renewed the original catalyst activity (data not shown).

The reaction was fully selective toward methane and no methanol or higher-order hydrocarbons were detected. In particular, to prove selectivity, the reaction system was chromatographically calibrated by flowing CO, CO₂, H₂ and C₁ to C₄ hydrocarbons to simulate the potential reactants and products that could be present in the effluent gases. This proved that the reaction proceeds selectively to form methane, and that C₂ to C₄ hydrocarbons (retention time ca. 4 to 12 min) were not detected among the products using gas chromatography.

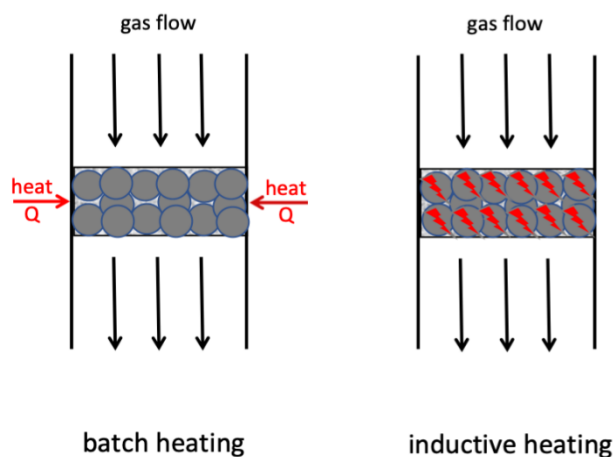


Figure 2. Inductive catalyst heating. The catalyst is deactivated as the active sites are enveloped with surface species (left). Inductive heating supplies energy directly to the metal-envelope interphase, thus efficiently removing the deactivating envelope (right)

Thus far we have addressed syngas reactivity at ambient or lower temperatures for which the reacting syngas needed to be cooled. Subsequently, in **Fig. 1** (upper panel) and **Table S3, entries 1-3** and **5-7** we present data in which the reacting syngas had been heated. Two modes of heating were used, namely, batch heating of the gaseous reactants and direct inductive heating of the bimetallic Ru/Ni catalyst. The latter version was designed to focus directly at the catalyst surface to desorb chemical species blocking its active sites (**Fig. 2**). The comparison clearly indicates the superiority of inductive heating (for example, full conversion can be achieved at 152 °C with inductive heating, vs. 206 °C with batch heating for the Ru/Ni catalyst system).

In **Fig. 1** (brown profile) we illustrate an experiment that was designed to determine what temperature is needed at the catalyst surface to achieve 100% CO conversion for a flow of syngas introduced at ambient temperature (**Table 3, entry 7**). We observed that a temperature of 178 °C was sufficient to observe this effect while the temperature of the efflux gases was 177 °C. Once more,

the reaction proceeded with 100% selectively to methane, as confirmed by gas chromatography and gas analyser. Finally, to evaluate the catalyst durability, we tested the performance of CO methanation at 206 °C for 50 h steady state. The conversion and selectivity remained unchanged. The temperature of the durability test was well above the lowest temperature needed for the catalyst steady state operation (178 °C).

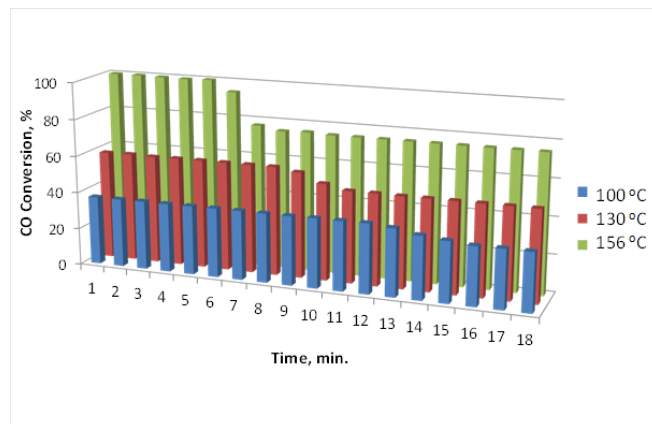


Figure 3. CO conversion over time at different temperatures for the Ru/Ni DFM system. Upon water sorption, the drying agent is deactivated

The CO conversion at 178 °C is 100% (selectivity 100%) which compares advantageously to the CO conv. 80.2% and methane selectivity of 90.3% at 275 °C. TOF for our Ru/Ni system is 9.89 h⁻¹ at 100% CO conversion and 100% methane selectivity at 178 °C (WHSV = 15 L.g⁻¹.h⁻¹).

The concept of dual functional materials (DFM) has attracted interest recently³³. For example, as applied to methanation reactions, a DFM system was designed in which in a first cycle CO₂ was absorbed to the catalyst to be subsequently hydrogenated in the next cycle³⁴. Here, we report a DFM-type system that can enhance CO/CO₂ hydrogenation in its reactive phase by combining water sorption with hydrogenation. Accordingly, in a series of experiments, the catalytic material was combined with 4Å molecular sieves to test the influence of water removal. The results were reported in **Fig. 3 (Table S4, entries 5-7)**. Interestingly, at ambient or higher temperatures, this increases conversion (**Table S4, entry 3-7**). For example, a catalyst temperature of 156 °C was sufficient to yield 100% conversion by combining inductive heating and water sorption (**Table S4, entry 7**). In turn, the addition of a sorption agent slightly decreased CO conversion at low temperature (**Table S4, entries 1-2**). In another series of experiments, we screened other bimetallic systems for potential catalysts of the reaction. Interestingly, the low-temperature effect was not observed for the Re/Ni or the Pd/Ni system, (**Fig. 4, Tables S3, S5 and S8**).

Low temperature CO₂ methanation

If the educts were CO₂ and H₂ instead of syngas, ultralow temperature reaction on the Ru/Ni catalyst was no longer observed. When tested, a continuous process of CO₂ methanation proceeded when the catalyst surface temperature was fine-tuned to a temperature of 133 °C (minimal temperature to achieve a conversion) or 197 °C (temperature needed to achieve 100% conversion) (**Table S3, entry 13**). Once again, the reaction proceeded selectively to methane, as tested chromatographically.

Sorption enhanced CO₂ conversion to 100% CH₄ at 178 °C vs. 197 °C without water sorption (**Table S3, entry 13 vs. Table S4, entry 13**).

These results, however, remained highly competitive when compared to existing methodologies.

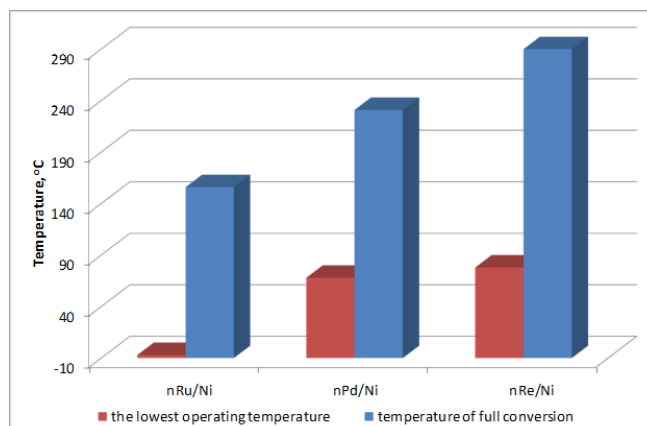


Figure 4. Comparison of Ru/Ni, Pd/Ni and Re/Ni DFM catalyst performance. Ru/Ni is the only system that shows the ultralow temperature effect at -7 °C. Ru/Ni also fully converts syngas at 156 °C, while 220 °C and 280 °C were needed for Pd/Ni and Re/Ni, respectively

Mechanism of ultralow syngas methanation

XPS and Raman spectra for the three different catalytic systems, namely, Ru/Ni, Pd/Ni, Re/Ni (**Fig S1**) were recorded before and after the reaction. The analysis of the Ru 3d doublet and C 1s photoemission lines, which are situated in a partly overlapping range of energy is presented in **Fig. S1a**. Before the reaction, the dominating Ru component is the highly oxidised RuO₃, which is revealed by the main doublet at 281.8 (Ru 3d_{5/2}) and 286.0 (Ru 3d_{3/2}) eV. The origin of the second doublet of a higher binding energy with the Ru 3d_{5/2} peak at 283.1 eV is not clear. It is likely that it comes from a complex oxide or hydroxide structure where Ru has a valence of +6 or +7. In turn, the lines originating from carbon can be assigned to various chemical states. Carbon species could also be identified at the sample surface before the reaction. Interestingly, C-H (or C-C, because C-C and C-H forms cannot be differentiated by XPS) is a common state for both series of samples. This means that the system is active enough to bind the atmospheric CO₂ that is further reduced during catalyst preparation involving a hydrogenation step. Raman spectra recorded on the catalysts were hardly modified, thus supporting this hypothesis (**Fig. S2**).

Methanation obviously changes the relative ruthenium to carbon ratio, which can be derived from the fitted XPS spectra attributed to Ru and C. The Ru/C ratio decreased from 2.7 to 0.7 after the reaction. The reaction also changed the structure of carbon bonds observed by XPS. Namely, a contribution from carbon bonding to oxygen was significantly increased and a relatively high intensity peak at 290.0 eV, corresponding to a C=O, was observed in the sample after methanation.

In the Re/Ni system the Re 4f doublet had a complex structure showing the peaks that can be attributed to Re_xNi_y alloys and to oxides (**Fig. S1be**). The lowest energy doublet of the metallic Re was shifted by about 1 eV vs the metallic Re and, as observed in our studies of the Re/SiO₂ system,³² this indicates the presence of a Re_xNi_y alloy. The catalytic methanation does not affect the position of that doublet. The next doublets are related to Re oxides: Before the process they were assigned to ReO₂ and ReO₃. After the process, the oxidation state increases, as revealed by the presence of a high

intensity doublet with the $4f_{7/2}$ line placed at about 47 eV, which was assigned to Re_2O_7 . The increased intensity of the satellites at energies above 50 eV is difficult to explain. One of the possibilities is excitation within the valence band that often accompanies unstable valence. While the main line at about 284.8 eV (C-C and C-H bonds, **Fig. S1c**) and the line at 284.8 eV (C-O) are stable, the intensity of the highest energy line above 290 eV is significantly intensified indicating a formation of the double C=O bond. The energy above 291 eV indicates the presence of surface CO_2 species³⁵.

The reaction with syngas also leads to changes in the chemical structure of the Pd/Ni system, which can be determined from the XPS data. Namely, the reduction of Pd could be observed (**Fig. S1d, S1e**). The main components before and after the reaction are Pd or Pd_xNi_y alloy and PdO. After the reaction, the fraction of the higher oxidised PdO structures decreased. In turn, the Ni 2p doublet did not show any significant changes, the Pd/C ratio was hardly affected and the variation of the C 1s photoemission line structure was not strong. A slightly increased contribution from the Pd/Ni carbides was observed. The dominating chemical state was attributed to single C-C or C-H bonds.

TOF-SIMS analysis of the Ru/Ni catalyst after syngas methanation indicated the presence of the Ru bounded carbon species RuCO_2H^- ($m/z=147$) and CORu^- ($m/z=130$). In turn, NiH^- ions ($m/z=59$) indicated the presence of hydrogen. Among several possible hydrocarbon products in the C_1 - C_4 range, ions CH_4^+ and CH_3^+ , markers of C_1 product methane, were the highest signals observed in terms of intensity. Water presence was determined upon observation of OH^- ions. Since the same ions were observed in virgin and used Ru/Ni catalyst, we additionally tested the Ru/Ni catalyst undergoing a flow of H_2 or CO_2 separately. Interestingly, TOF-SIMS of all samples indicated the presence of the above-mentioned ions. Finally, Si^+ ($m/z=28$) indicated vestigial traces of the porous silica used in the preparation of the catalyst (**Fig. S3ad**). The analysis of chemical states of Ni before and after methanation is shown and discussed in Supporting Information (Fig S1a).

Discussion

Catalytic carbon (di)oxide methanation is a complex process involving both a variety of chemical reactions and physicochemical processes at the catalyst surface. In particular, they involve CO and H_2 , known as syngas, which is often used for synthetic fuel engineering. Solar syngas production is an emerging concept, and the potential availability of such CO/H_2 mixtures holds promise as a sustainable energy source. The relevant question, in this regard, is how efficiently CO/H_2 mixtures could be converted to methane at low temperatures to become energetically viable, and therefore economically viable as well. This could entail a core process of syngas processing towards C_1 and higher order building blocks. Or, alternatively, it could equally involve carbon dioxide methanation. In addressing this question, we discovered that syngas methanation could proceed in flow at temperatures as low as -7°C at an unalloyed Ru/Ni conjugate surface. To our knowledge, this is the first report of CO methanation at temperatures below the freezing point of water. In other words, this study redefines what we mean by low temperature methanation, opening a path towards more sustainable access to methane.

Recently, the stoichiometry of syngas methanation has been thoroughly studied at temperatures above 200°C for CO and H_2

mixtures forming 1:1; 1:3 and 1:5 v/v blends³⁶. For our study, we used the intermediate CO to H_2 blend of 1:3 v/v and observed the ultralow temperature syngas hydrogenation that is illustrated in **Fig. 1**. Firstly, CO hydrogenation can proceed without heating at temperatures lower than ambient temperature (25°C). Under such conditions, the process proceeds as long as the catalyst surface is not blocked by the reactants/products up to a point where the reaction stops. The superposition of the chemical reaction and the catalytic effects can be observed in a form of the sequential activity/inactivity phases (**Fig. 1** enlarged profile in the lower panel). Accordingly, in the first phase, the conversion at a certain temperature is practically constant, e.g. ca. 17% at 25°C . This suggests that, in this phase, the reaction is limited by the kinetics of CO hydrogenation, depending only on temperature. In turn, in the second phase at 25°C , we observed a steady decrease of conversion from 17% to 0%. The catalyst is increasingly covered by surface species that envelop the active sites which makes surface desorption/absorption the kinetically limiting processes. As a result, a sharp decrease in conversion is typical in this phase. Moreover, the gradual decrease of the available catalyst surface also decreases the progress of the exothermal reaction. Therefore, the energy needed to desorb the inactivating species blocking the surface becomes less and less available. The temperature of the catalyst further decreases the direct contact with the incoming flow of low temperature reactants up to a point at which the temperature at the catalyst surface is lower than that required to desorb the adsorbates. The catalyst is thus blocked until those species are removed from the surface. This negative feedback loop rapidly stops the reaction.

The above-mentioned experiments prove that, for low temperature methanation in this Ru/Ni system, the removal of blocking surface species at the catalyst's active sites is an essential limiting factor. Accordingly, energy supply to the catalyst surface can remove blocking species, thereby recovering active catalyst sites and allowing the reaction to progress. At the same time, the direct transmission of energy to the catalyst surface is the most efficient approach for this rejuvenation. One way to direct an energy supply to the catalyst would be inductive heating since both Ru and Ni are ferromagnetics. The efficiency of inductive heating has been previously demonstrated in organic synthesis³⁷. Here, inductive heating allowed us to release the blocking species from the catalyst by employing an internally occurring mode of heating rather than conventional heating that is applied externally with a high concomitant energy loss. In particular, the catalyst heated to 177°C is able to make CO hydrogenation a continuous process with 100% conversion. This temperature is lower than that required for 100% conversion with batch heating of the flowing gas (206°C). This finding clearly indicates that the catalyst surface is the site where heat should be supplied for optimal efficiency. Basically, for both heating modes, the catalyst surface is in an equilibrium between adsorption/desorption states; however, the mass and heat transfer between the dynamic gas stream and the stationary surface species at the catalyst needed higher temperatures to proceed efficiently. Inductive heating provides energy just-in-time-and-place where it is needed, i.e. directly to the metal surface. The temperature difference for the processes with inductive heating vs. the batch gas heating in this particular example is as high as 30°C . It is worth noticing that we did not observe a similar ultralow temperature effect with cyclic behavior for CO_2 methanation at the Ru/Ni catalyst. Instead, a temperature of ca. 130°C was needed to start the conversion of the reacting CO_2 and H_2 to methane³¹.

Water sorption has previously been studied as a potential enhancement factor for CO₂ methanation reactions at standard (higher) temperatures^{38,39}. Accordingly, in the first cycle of hydrogenation, water is transferred from the catalyst surface to the sorption agent through equilibrium in the gas phase, which frees the catalytic active sites. The temperature of CO conversion could thus be further decreased in our reaction by implementing a dual functional material (DFM) system consisting of our catalyst coupled with 4A molecular sieve as the water sorption agent to achieve 100% CO conversion at 156 °C, in contrast to 178 °C without the water sorption agent (Table S4, entry 7 vs. Table S3, entry 7). Water sorption performs in cycles, which means that an active sorbent performs up to its maximal sorption capability. After this, water removal is needed to reactivate the DFM system. Accordingly, with the increasing water loading on the surface, the water sorption agent is deactivated, and water can no longer be moved from the Ru/Ni catalyst to molecular sieves. Water desorption from the molecular sieves is thus needed to reactivate the DFM for further activity. The DFM with water sorption agent can also enhance CO₂ methanation and 100% CO₂ conversion was observed at 178 °C vs. 197 °C without water sorption (Table S3, entry 13 vs. Table S4, entry 13). Not surprisingly, considering the gas phase equilibrium, at low temperatures (-7 °C or 0 °C) the DFM system did not improve the temperature performance of the system with CO conversion at -7 °C with ca. 0.8% (DFM) vs. 1.2% without the water sorption agent (Table S3, entry 1 vs. Table S4, entry 1).

To test how generally applicable the low temperature effect can be, we also tested the Re/Ni and Pd/Ni systems. Ru, Re and Pd usually produce a volcano curve when the adsorption energy of the reactants on catalysts are compared, where the reactivity is the highest for the element with medium adsorption energy. The reactants can then come into contact with the surface that is not blocked (poisoning effect). The sequence of the CO dissociation energy for the tested triad is Re<Ru<Pd^{40,41}. Accordingly, Ru is at the top of the volcano plot (showing CO dissociation energy) which is consistent with our results, and explains why Ru/Ni is the only system among the tested catalysts that showed such a marked low temperature effect. XPS analyses of the catalytic surface indicated a possible reason for the unique reactivity of the Ru/Ni catalytic system. Specifically, the presence of non-stoichiometric oxides, RuO_x/Ru, is worth mentioning as nonstoichiometric oxides and defects were indicated as an important issue promoting catalytic activity in carbon dioxide hydrogenation⁴². The role of metal/oxide interfaces for oxide reducibility has also been highlighted recently⁴³. The Raman spectra registered in the current investigations resemble these that have been previously registered for the nano-Ru/TiO₂ catalyst under CO/CO₂ at various temperatures.⁴⁴ Mechanism of low temperature (below 200 °C) Ru and/or Ni or similar (Rh, Ni) catalysis in carbon (di)oxide methanation has been widely investigated recently.⁴⁵ In particular, for the latter system, this involves such effects as CO₂ to CO and O dissociation at the catalyst surface and enhancing hydrogen stocking by the Ni catalyst moiety. Interestingly, CO₂ to CO dissociation has been determined to be the rate-limiting step.⁴⁶ Our XPS, Raman and TOF-SIMS analyses indicate similar effects. The XPS comparison of the catalyst system before and after reaction clearly reveals carbon species on the surface structure of Ru/Ni after the reaction. First, methanation results in a significant extent of the reduction of Ru oxidation state. The dominating state can be attributed to RuO₂, but higher oxidation states are still present. Although reduction suggests hydrogen accumulation at Ru nanoparticles, we should keep in mind that CO binding to Ru oxides

also means reduction of the Ru species. The Ru/C ratio decreased from 2.7 (before reaction) to 0.7 (after reaction). Both carbonyl (Ru-CO) and carboxyl (Ru-COOH) forms of ruthenium were recorded by TOF-SIMS analysis. As could be expected in the samples after flowing pure H₂, the intensity of the carbonyl form Ru-CO evidently increases. Signals of ions derived from methane were of highest intensity illustrating the selectivity of the process against putative higher hydrocarbon products formation.⁴⁶ Hydrogen stocking function of Ni species within the catalyst was clearly revealed by Ni-H ions observed by TOF-SIMS analysis⁴⁷. Finally, the presence of silica reliefs can be important for the catalyst activity as previously suggested.³¹ Additionally, a comparison of the Ru/Ni catalyst action vs. atmospheric air (virgin catalyst) with the catalyst undergoing a flow of H₂ or CO₂ or used in CO methanation by TOF-SIMS analysis indicated atmospheric CO₂ already adsorbed at the catalyst surface. Since CO₂ to CO dissociation is the rate limiting process⁴⁶, attempts to perform ultralow temperature CO₂ methanation appeared unsuccessful. Fig. 5 is a brief illustration of the mechanism.

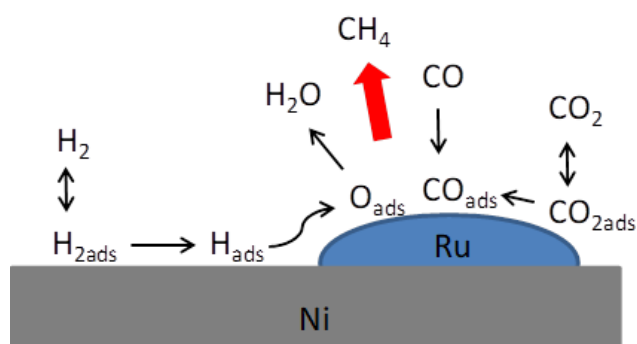


Figure 5. Carbon species formed on the catalyst surface during syngas processing. Adsorption of both CO and H₂ leads to reduction of the surface Ru oxides as demonstrated by XPS of Ru/Ni catalyst samples before and after reaction. The adsorption of H₂ proceeds mostly on Ni, and CO on Ru oxide, where CH₄ is then formed

Conclusion

In conclusion, ultra-low temperature CO hydrogenation on unalloyed Ru/Ni conjugate was demonstrated. This process can proceed cyclically, even at temperatures below 0 °C. Moreover, we designed an inductive heating scheme that allowed for the efficient minimisation of the energy required for a continuous catalyst operation and additionally improved the process with the design of a DFM by combining the Ru/Ni catalyst with molecular sieves. Under optimised conditions, 100% CO conversion was observed at 156 °C. This investigation provides new insights into carbon di(oxide) hydrogenation redefining low temperature option which can significantly lower energy consumption, thus improving the feasibility and economic efficiency of the process.

Conflicts of interest

There are no conflicts to declare.

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