Understanding the function of support and metal loading on catalytic CO₂ reduction using Ru nanoparticles supported on carbon nanofibers

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Abstract

Catalytic CO₂ reduction has been performed using carbon nanofibers or nitrogen doped carbon nanofibers as novel support for several Ru contents. The catalyst consisting of 5 wt% Ru on nitrogen doped carbon nanofiber exhibited the highest conversion at relatively low temperature, complete selectivity to CH₄ and stable catalytic performance. The catalytic performance was substantially superior to catalysts supported on carbon nanotubes and akin to the best metal oxide supported catalyst in the literature. The characterisation of the prepared catalyst by transient experiments (CO₂-TPD, TPSR and transient response to CO₂ removal) revealed that the catalyst support participates actively in the reaction. The Ru content governed the selectivity, either favouring CO formation for lower Ru contents (0.5-2 wt%) or CH₄ formation for 5 wt% Ru loading. The mean Ru particle size determined by TEM was similar for the several metal loadings. Therefore, the substantially different selectivity patterns cannot

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be attributed to structure sensitivity. The higher selectivity to CH$_4$ can be explained by the enhanced supply of 4 H$_{ad}$ to the activated CO$_{ad}$ intermediate, which was demonstrated to be the rate determining step.

*Keywords: carbon nanofibers, nitrogen doping, catalyst support, ruthenium nanoparticles, CO$_2$ hydrogenation, reaction mechanism.*

1. **Introduction**

The perceived risk of running out of conventional fossil fuels and the pollution risks associated with burning fuels led the boom in programs for developing renewable energy. The efficient utilization of renewable energy sources from wind turbines and solar panels is still an ongoing challenge. Naturally, power generated by renewable energies (wind, photovoltaics) are intermittent, highly volatile and not in line with the demand of electricity. Electricity from wind and sun is generated at irregular intervals and the energy is produced at locations where it is not directly consumed. Only the large-scale storage of energy can reliably secure an economic supply from renewable sources. Thus, solutions for long-range transportation and storage of renewable energies are currently of great interest.$^{[1]}$

Recently, much interest has been devoted to energy conversion based on the hydrogen cycle ("hydrogen economy") such as water splitting. It is easy and affordable to convert electricity to hydrogen via electrolysis, a proven technology in the chemical industry.$^{[2]}$ The main unsolved problem of H$_2$ as energy carrier is its storage. Hydrogen can be stored and used in the existing gas infrastructure but the discharge time is typically lower than 100 hours, depending on technical regulations. Research is being undertaken to widen the use of hydrogen in the existing gas infrastructure. When it is a need of long temporary storage it is possible to convert H$_2$ with CO$_2$ into Synthetic Natural Gas
Synthetic Natural Gas can be stored and used in the existing gas infrastructure without limitation. This fact has the additional advantage that the gas infrastructure (transport, storage and distribution) is immediately available and there is no investment needed. This will allow also the transportation of energy from areas with high renewable power (sun or wind rich) to remote areas with less renewable energy. A cost estimation study of a CO₂ recycling system producing CH₄ using photovoltaic energy in Middle East and transporting it to Japan found that the cost of energy input of CO₂ recycling is similar to the obtaining of LNG from wells (mining, liquefaction and purification). Moreover, 79% of CO₂ emissions from a 1 GW CH₄-combustion power plant can be reduced by CO₂ conversion to CH₄ when CO₂ is recovered at the power plant. The conversion of CO₂ into fuels and useful chemicals using renewable H₂ will permit that the carbon-cycle, which has generally an open end due to burning of fossil fuels and release as CO₂ into atmosphere, can be closed by capturing CO₂ in the power station and recycling it to fuel. Thus, this approach allows killing two birds with a stone, the storage of renewable H₂ and the reduction of CO₂ emissions. Several projects are currently run worldwide exploiting this concept of green natural gas such as the “e-gas” by Audi or “Power2gas” by E.ON.

The reaction of CO₂ and H₂ was first reported a century ago and it is known as the Sabatier reaction. It has been more intensively investigated recently, due to fundamental and practical significance in the context of catalysis, surface science, biology, nanotechnology and environmental science. Photocatalysis, electrocatalyst and thermal homogeneous and heterogeneous catalysts have been used to hydrogenate CO₂. State of the art photocatalysts used in artificial photosynthesis produce low CO₂ conversions rendering the process inefficient thus far. Homogeneous catalysts show satisfactory activity and selectivity, but the recovery and
regeneration are problematic. Alternatively, heterogeneous catalysts are preferable in terms of stability, separation, handling, reuse and reactor design, reducing the costs for large-scale productions. Regarding heterogeneous catalysis, supported transition metals Ni\textsuperscript{[10-13]} and Co\textsuperscript{[14, 15]} and noble metals including Ru,\textsuperscript{[16-18]} Pd,\textsuperscript{[19]} Pt,\textsuperscript{[19, 20]} and Rh,\textsuperscript{[19, 21-23]} are active for this reaction. The support plays an important role in the catalytic reaction as it may interact with the reactant(s), stabilize intermediates or reaction products or create special interfacial sites where reactions can proceed. Support can have electronic effects on the catalytic nanoparticle\textsuperscript{[24]} or it can adsorb some of the reactants increasing the local concentration of the reactant.\textsuperscript{[25]} Accordingly, some reactions have been reported to take place in the interphase between metal and support.\textsuperscript{[26, 27]} Several support materials have been used in CO\textsubscript{2} hydrogenation such as alumina,\textsuperscript{[28-31]} titania,\textsuperscript{[27, 32, 33]} titanium carbide,\textsuperscript{[34]} silica,\textsuperscript{[15]} ceria,\textsuperscript{[12, 18, 35]} zeolite,\textsuperscript{[24]} or carbon materials such as activated carbon\textsuperscript{[36]} or carbon nanotubes.\textsuperscript{[37, 38]}

CO\textsubscript{2} reduction is reported to require a bifunctional catalyst, \textit{i.e.} one function to activate CO\textsubscript{2} and another to activate H\textsubscript{2}. Park and MacFarland\textsuperscript{[19]} observed a selectivity shift from CO to CH\textsubscript{4} by modifying Pd on SiO\textsubscript{2} with MgO, while MgO/SiO\textsubscript{2} showed no measurable activity. They rationalized their results suggesting a bifunctional mechanism in which CO\textsubscript{2} first strongly adsorbs onto MgO inhibiting CO desorption, while Pd dissociates H\textsubscript{2}. There are also clear evidences that CO\textsubscript{2} interacts with Al\textsubscript{2}O\textsubscript{3} support to produce alumina-bound carbonates/bicarbonates.\textsuperscript{[31, 39]} Therefore, metal oxide supports are clearly not innocent in this reaction. On the other hand, CNT is usually considered as an inert support material. In fact, when using CNT as Ru support for CO\textsubscript{2} hydrogenation, the activity was negligible, which was attributed to the lack of the function to activate CO\textsubscript{2}.\textsuperscript{[40]} To the best of our knowledge, Ru on carbon nanofibers (CNF) has not been studied for CO\textsubscript{2} methanation.
Herein, we used CNF and nitrogen doped CNF (N-CNF) as support for several Ru loadings. The catalyst showed remarkable activity in CO$_2$ hydrogenation, in contrast to previous reports using CNT as support. This prompted us to study the mechanism of reaction. Since in-situ spectroscopic characterisation is not usually performed using carbon-based catalysts because it is hampered by high absorbance of carbon, the mechanism of reaction was studied here by catalytic transient response. This characterisation enabled to explain the effect of support and metal loading on the excellent selectivity to CH$_4$. It was revealed that the support played an active role in the reaction, which lends the catalyst an outstanding performance compared to metal oxide supported ones.

2. Experimental

2.1. Catalyst preparation

CNFs were grown on a 20 wt% Ni on alumina catalyst prepared by incipient wetness impregnation of nickel nitrate on alumina (Pural, Sasol) and calcined at 873 K in N$_2$ flow. The powder catalyst was placed on a porous frit of a vertical reactor. After reducing the catalyst at 823 K using 100 ml/min of H$_2$:N$_2$ mixture during 1 h, the CNFs growth was carried out at 873 K using 100 ml/min of a C$_2$H$_6$:H$_2$ mixture (50:50). N-CNF were grown on a 20 wt% Fe on alumina catalyst prepared by incipient wetness impregnation of iron nitrate on alumina (Pural, Sasol) and calcined at 873 K in N$_2$ flow. The catalyst was reduced at 823 K using 100 ml/min of a H$_2$:N$_2$ (50:50) mixture during 1 hour. Subsequently, the reactor was heated to the growth temperature (1023 K) under Ar. After reaching the temperature, the reaction mixture was admitted. The reaction mixture consisted of 100 ml/min Ar mixed with 0.15 ml/min of ethylenediamine (10 ml
in total) fed using a syringe. The ethylenediamine in argon mixture passed through an evaporator at 473 K and a heated line to the reactor containing the growth catalyst.

Both CNFs and N-CNFs supports were purified from the growth catalyst under reflux of NaOH (5M) for 4 h at 353 K and later under reflux of HCl at 373 K for another 4 h. After HCl treatment, thorough rinsing with distilled water was carried out until neutrality of the filtrate. After this purification process, the residual catalyst was less than 1 wt% as determined by oxidation in thermobalance and no HCl traces were detected by XPS.

The preparation of ruthenium catalysts was performed by incipient wetness impregnation. The CNF or N-CNCF supports were crushed to powders of particle size smaller than 200 µm. The desired amount of Ru nytrosil nitrate (Ru(NO)(NO₃)) was dissolved in an ethanol:water mixture (4:1) and impregnated in the catalysts to achieve different Ru loadings (0.5, 2, 5 wt%) with respect to the total sample. After drying, the catalyst was first calcined in N₂ at 723 K using a heating rate of 1 K/min and subsequently reduced in H₂ at the same temperature and heating rate. The reduced catalysts have been denoted as loading%Ru/support. The actual Ru content on the catalyst was analysed by ICP-OES.

2.2. Catalytic tests and characterisation

Catalytic testing was carried out in a continuous-flow 6 mm i.d. quartz reactor inside vertical furnace with a temperature controller (Eurotherm). 50 mg of catalyst diluted in SiC were placed on quartz wool inside the reactor. Prior to catalytic test, the catalyst was heated to 723 K in N₂ flow using a heating ramp of 10 K/min and it was reduced with 100 ml/min of H₂:N₂ (50:50) at 723 K for 0.5 h. The reaction temperature was controlled with a thermocouple inside the catalytic bed. The reaction conversion and
selectivities were recorded at steady state using 60 ml/min of a reaction mixture consisting of 5 % CO₂, 15 % H₂ and Ar to balance. This flow rate gives rise to a space velocity of 19000 h⁻¹. Gas analysis was performed with a Pfeiffer vacuum mass spectrometer. The following m/z signals were recorded in mass spectrometer: 2, 16, 18, 28, 40, 44. The signals of the gases were calibrated taking into account the baseline of Ar and the fragmentation pattern of each mass. The main m/z signals used for each gas were m/z= 2 (H₂), m/z= 16 (CH₄), m/z= 18 (H₂O), m/z= 28 (CO), m/z= 40 (Ar), m/z= 44 (CO₂). The concentration of CO was calculated subtracting the contribution of CO₂ to m/z=28. The concentration of CH₄ was calculated subtracting the contribution of CO₂ and CO to m/z=16. The correct calibration of the mass spectrometer was double-checked analysing the gases by calibrated Agilent Micro GC 3000A. Stability tests were conducted in the same conditions but leaving the reaction overnight.

The transient response behaviour of reactant and products to the sudden removal of CO₂ from reactant gas under isothermal reaction conditions was studied. To this end, after recording reaction at steady state using a feed gas consisting of 5% CO₂, 15% H₂, Ar to balance, CO₂ was suddenly removed from the reaction mixture and the total flow rate was kept constant by completing the balance with Ar. The dead volume at the outlet line to the mass spectrometer was determined to be negligible. Therefore, all the changes in the mass spectrometer signals reflected accurately the changes of the gases in contact with the catalyst.

Temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) experiments were conducted as follows. The catalyst was heated to 723 K at a heating rate of 10 K/min in inert gas. At this temperature, it was reduced with 100 ml/min of H₂:N₂ mixture for 0.5 h. The reactor was allowed to cool down until 298 K and CO₂ was flushed for 0.5 h. The gas was switched to 100 ml/min Ar and it was
kept during 1 h to remove weakly physisorbed CO\textsubscript{2}. Then the gas was adjusted to 60 ml/min of Ar for TPD experiments or to 60 ml/min 15\% H\textsubscript{2} in Ar for TPSR experiments. When the signal in mass spectrometer was stabilised, the temperature was raised until 723 K at a rate of 10 K per minute while monitoring the desorbed gases.

Ru metal nanoparticle size on carbon nanofibers was measured by scanning transmission electron microscopy (STEM) using a FEI TECNAI F30 electron microscope equipped with Gatan Energy Filter and cold field emission gun (FEG) operated at 300 kV with 1.5 Å lattice resolution. TEM specimens were prepared by ultrasonic dispersion in ethanol of powder catalyst. A drop of the suspension was applied to a holey carbon support grid. The particle size distribution was calculated by statistical analysis of 400 particles in ~20 images on CNFs. Mean Ru particle size evaluated as the Surface area weighted diameter ($\bar{d}_{Ru}$) was computed according to the following equation:

$$\bar{d}_{Ru} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

Where $n_i$ represents the number of particles with diameter $d_i$ ($\sum n_i \geq 400$)

3. Results

3.1. Catalytic testing

Figures 1 A-C show the CO\textsubscript{2} conversion, CH\textsubscript{4} and CO yields, respectively, for three different Ru loadings on CNF and N-CNFS. There are very significant differences in terms of conversion and selectivity as a function of the loading, irrespective of the support either CNFs or N-CNFS. Comparing the performance of 0.5 wt\% and 2 wt\% Ru loaded catalysts, the differences in CO\textsubscript{2} conversions are very modest or even inexistent for CNF and N-CNFS supported catalyst, respectively. The CO\textsubscript{2} conversion increases
significantly as loading does from 2 to 5 wt% Ru. The catalysts containing 5 wt% Ru achieve thermodynamic equilibrium at around 620 K. Comparing the two supports, the 5%Ru/N-CNF provided larger conversion than 5%Ru/CNF. The rise of conversion as metal loading increases can be easily rationalized on the basis of a larger number of sites to activate CO$_2$. However, the effect of loading on selectivity is still more noticeable and not that straightforward to explain. The selectivity to CH$_4$ increases substantially as the metal loading increases (Figure 1B). The highest selectivity to CH$_4$ corresponds to 5%Ru/N-CNF, which exhibited selectivity to CH$_4$ between 90-97 % in all the range of studied temperatures (up to 670 K). The onset of CO occurs at around the same temperature (~520 K) for all catalysts (Figure 1C). The CO yield increases as the temperature rises and it is observed a peak maximum at temperatures around that of the onset of CH$_4$ evolution (Figure 1B). For temperatures above the onset of CH$_4$, the CO yield decreases or remains stable. For this reason, the catalyst for which the onset in CH$_4$ evolution occurs at the lowest temperature, i.e. 5%Ru/N-CNF, the CO yield remains at negligible values in all the range of temperatures. For the highest tested temperatures, some catalysts exhibited a slight increase of CO and a decrease of CH$_4$, which may be attributed to the thermodynamic equilibrium. Since the hydrogenation of CO$_2$ is highly exothermic ($\Delta H=-164$ KJ/mol), at higher temperatures, the thermodynamic equilibrium favours steam reforming of CH$_4$ and reverse water gas shift, which are endothermic processes and lead to the production of CO.$^{[29]}$ Thus, these reactions are responsible for the small rise of the CO yield at the highest temperatures. We decided to keep reaction temperatures below 673 K to avoid these undesired reactions and also the gasification of the support that was found for temperatures > 650 K as revealed in TPSR experiment shown below.
Table 1. Turnover rates at two temperatures and space time yield at 673 K

<table>
<thead>
<tr>
<th>Temperature/ K</th>
<th>Turnover rate</th>
<th>CH₄ productivity</th>
<th>Space time yield</th>
</tr>
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<tbody>
<tr>
<td>500</td>
<td>500</td>
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<tr>
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</tr>
</tbody>
</table>
To get some insight into the reaction mechanism, transient experiments were performed. First, we performed temperature programmed desorption (TPD) in Ar flow after adsorption of CO\(_2\) at room temperature on the catalyst prereduced at 723 K and flushed with Ar at room temperature to remove weakly physisorbed species. All the catalysts showed similar TPD profiles. Representative TPD profiles corresponding to 5\%Ru/N-CNF are shown in Figure 2. The formation of H\(_2\)O peaked at 400 K indicates that there was hydrogen and oxygen adsorbed on the catalyst surface. H\(_2\) should come from dissociative adsorption of H\(_2\) on metal surface during reduction step that was not removed during flushing with Ar. Oxygen should come from the dissociative adsorption of CO\(_2\) into O\(_{\text{ad}}\) and CO\(_{\text{ad}}\) on the catalyst surface. Some very small amount of CH\(_4\) seems to be formed from reaction of chemisorbed H\(_{\text{ad}}\) and CO\(_{\text{ad}}\) species. The CO\(_2\) profile shows desorption peaks at around 350 K and at 700 K, which may be attributed to physisorbed CO\(_2\) and some CO\(_2\)-desorbing oxygenated groups, respectively, formed in CO\(_2\) adsorption stage. There is no CO desorption in all the range of temperatures, indicating that CO\(_{\text{ad}}\) species formed by CO\(_2\) dissociation are very strongly adsorbed on the catalyst/support.

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>mol(<em>{\text{Conv}}) (mol(</em>{\text{Ru}}))(^{-1}) s(^{-1})</th>
<th>mol(_{\text{CH}<em>4}) (mol(</em>{\text{Ru}}))(^{-1}) s(^{-1})</th>
<th>Kg(_{\text{CH}_4}) (Kg cat)(^{-1}) h(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Ru/CNF</td>
<td>0.30</td>
<td>0.04</td>
<td>0.13</td>
</tr>
<tr>
<td>2%Ru/CNF</td>
<td>0.07</td>
<td>0.03</td>
<td>0.37</td>
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<tr>
<td>5%Ru/CNF</td>
<td>0.05</td>
<td>0.05</td>
<td>1.42</td>
</tr>
<tr>
<td>0.5% Ru/N-CNF</td>
<td>0.26</td>
<td>0.06</td>
<td>0.20</td>
</tr>
<tr>
<td>2%Ru/N-CNF</td>
<td>0.06</td>
<td>0.02</td>
<td>0.23</td>
</tr>
<tr>
<td>5%Ru/N-CNF</td>
<td>0.05</td>
<td>0.05</td>
<td>1.54</td>
</tr>
</tbody>
</table>
Figure 2. TPD of pre-adsorbed CO$_2$ at 298 K on 5% Ru/N-CNF.

To shed more light into the CO$_2$ reduction mechanism we performed temperature programmed surface reaction (TPSR) experiments (Figure 3). The formation of H$_2$O at low temperatures (peak around 370 K in Figures 3B and D) indicates that CO$_2$ flushed previously to TPSR dissociated as O$_{ad}$ and a CO$_{ad}$ species on Ru nanoparticle surface in agreement with TPD. In TPSR, O$_{ad}$ species generates H$_2$O readily by reaction with H$_{ad}$ species coming from the dissociation of H$_2$ present in gas phase.
Figure 3. Signals of CH\(_4\) (A, C) and H\(_2\)O (B, D) in temperature programmed surface reaction (TPSR) experiments using Ru on CNF (A, B) and Ru on N-CNF (C, D) containing different metal loadings.
In Figures 3 A and C, the peak corresponding to CH$_4$ formation is observed. The calibration of the CH$_4$ signal and the integration of the peak after subtracting baseline enabled the quantification of desorbed CH$_4$, which is compiled in Table 2. The moles of desorbed CH$_4$ give an indication of the CO$_2$ that has been dissociated and retained on the catalyst surface during CO$_2$ saturation at room temperature previous to TPSR. For catalysts evolving CH$_4$ at lower temperatures, i.e. those with higher Ru loadings, the quantified CH$_4$ can be unambiguously ascribed to the hydrogenation of CO$_{ad}$ species, which were adsorbed previously. For catalysts containing the lowest loading (0.5 wt%), since the CH$_4$ peak occurs at high temperatures, it cannot be completely ruled out that part of quantified CH$_4$ stems from gasification of the support. Comparing the CH$_4$ produced in TPSR with the moles of Ru present on the catalyst (Table 2), it is apparent that the moles of CO$_2$ retained on the catalyst surface are almost one order of magnitude higher than the moles of Ru, suggesting that the support participates also on the storage of CO$_{ad}$ coming from CO$_2$ dissociation. TPSR of the pristine supports after CO$_2$ pre-adsorption did not show desorption of any gas at temperatures below 673 K (Figure S1 of supplementary information), pointing out that the support needs the participation of ruthenium nanoparticles to dissociate CO$_2$ to species that are subsequently transferred to the support.

The peak of CH$_4$ formation in TPSR (Table 2 and Figures 3 A and C) occurs at decreasing temperatures as the Ru loading increases which is in agreement with the rising selectivity to CH$_4$. Moreover, the CH$_4$ peak is concomitant with a H$_2$O desorption peak indicating that the formation of at least part of CH$_4$ occurs via an oxygenated intermediate such as CO$_{ad}$.

Table 2. Quantification of TPSR and catalytic parameters

16
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature of CH₄ peak K</th>
<th>Molar Ru loading mmol/g</th>
<th>CH₄ per catalyst weight in TPSR mmol/g</th>
<th>Molar CH₄/Ru ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%Ru/CNF</td>
<td>606</td>
<td>0.049</td>
<td>3.75</td>
<td>76</td>
</tr>
<tr>
<td>2%Ru/CNF</td>
<td>557</td>
<td>0.20</td>
<td>2.37</td>
<td>12</td>
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<tr>
<td>5%Ru/CNF</td>
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<td>0.50</td>
<td>4.08</td>
<td>8.2</td>
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<tr>
<td>0.5%Ru/N-CNF</td>
<td>575</td>
<td>0.05</td>
<td>1.93</td>
<td>39</td>
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<tr>
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<td>0.19</td>
<td>1.16</td>
<td>5.8</td>
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<tr>
<td>5%Ru/N-CNF</td>
<td>481</td>
<td>0.49</td>
<td>3.14</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Figure 4 shows the transient behaviour after the sudden removal of CO₂ from gas feed at three reaction temperatures for some selected catalysts. Similar experiments for the rest of catalysts are provided in Figures S2 and S3 of supporting material. It is a general behaviour of the catalysts that both CO₂ and CO signals decay as soon as CO₂ is removed from the gas feed. This suggests that the produced CO is released to gas phase directly by decomposition of CO₂ on the metal catalyst surface. On the other hand, CH₄ desorption shows a tail indicating that it is formed following a multistep process in which adsorbed intermediates are further hydrogenated until releasing CH₄. It is also noteworthy, that the CH₄ concentration in gas phase increases just when CO and CO₂ concentrations decay. CH₄ concentration reaches a maximum and then it declines because adsorbed CH₄-generating intermediates are depleted from catalyst surface. The CH₄ peak is less intense for higher reaction temperatures. For the same reaction temperatures, the maximum is more pronounced for 5%Ru/CNF (Figure 4 B) than for 5%Ru/N-CNF (Figure 4 A) and for a lower loading (2wt% Ru, Figure 4 C) more intense than for the higher loading (5 wt% Ru, Figure 4 B). The appearance of CH₄
peak seems to indicate that the rate determining step for CH$_4$ formation is the activation of H$_2$ and supply of 4 H$_{\text{ad}}$ species to reduce the CO$_{\text{ad}}$ intermediate. When CO$_2$ is removed from feed gas more Ru adsorption sites become available for the dissociative adsorption of H$_2$. This favours the supply of H$_{\text{ad}}$ chemisorbed species to the CO$_{\text{ad}}$ intermediate, enhancing CH$_4$ formation. This is consistent with the fact that the intensity of CH$_4$ peak exhibited an inverse relationship with the conversion at steady state, i.e. the peak is less intense for 5%Ru/N-CNF than for 5%Ru/CNF, for the higher loadings and for higher reaction temperatures. This later is consistent with the fact that the coverage of the metal by adsorbed species is lower at higher reaction temperatures, leaving more sites for H$_2$ chemisorption.

The H$_2$O signal (dashed line) in Figure 4 continues at the same concentration long time after removal of CO$_2$ from gas feed. Afterwards, the H$_2$O concentration decays to zero as observed in Figure 4 C and supplementary Figures S3 A and B. The holding up of H$_2$O formation after CO$_2$ removal should be due to the reaction of accumulated O$_{\text{ad}}$ species with continuously fed H$_{\text{ad}}$ species. The duration of H$_2$O formation thus has a direct relationship with the amount of reactive O$_{\text{ad}}$ species on catalyst/support surface generated during previous CO$_2$ reduction reaction. The duration of H$_2$O formation increases as reaction temperature and Ru loading increase. These two factors favour higher CO$_2$ conversions and hence the building up of higher amount of O$_{\text{ad}}$ species. The duration is also longer for CNF-supported catalyst than for N-CNF supported one (Figure S2 and S3 of supplementary information) which may suggest that CNF can lodge more adsorbed O$_{\text{ad}}$ species than N-CNF. A reaction pathway is suggested in the discussion consistent with the results gathered during the transient experiments.
Figure 4. Experiments of transient response to CO\(_2\) removal from the reaction mixture at three reaction temperatures for three selected catalysts: (A) 5%Ru/N-CNF catalyst, (B) 5%Ru/CNF catalyst, (C) 2%Ru/CNF catalyst. CO\(_2\) concentration, thin solid line; CH\(_4\) concentration, thick solid line; CO concentration, dotted line; H\(_2\)O concentration, dashed line. Feed gas composition: 5% CO\(_2\), 15% H\(_2\), Ar to balance.

To assess the stability, the catalyst with the highest activity, \textit{i.e.} 5%Ru/N-CNF, was tested at the temperature of maximum CH\(_4\) productivity, \textit{i.e.} 623 K, during 20 hours reaction (Figure 5). The conversion even increased slightly with time on stream and the selectivity to CH\(_4\) remained at constant values (>95 %). Additionally, long-term test was performed using a catalyst with the lowest Ru content, namely 0.5%Ru/N-CNF. This catalyst exhibited also an increase of conversion and the initial high selectivity to CO even increased further. Therefore, the catalysts are highly stable and the difference between their selectivities was even more accentuated after long-term testing.
Figure 5. Long-term reaction stability tests with two catalysts containing different Ru loadings (0.5 and 5wt% Ru on N-CNF) and different selectivities at 623 K reaction temperature. (■) CH$_4$ yield (%), (△) CO yield (%).

3.2. TEM characterisation

We characterised the Ru particle size by STEM for the several prepared catalysts after reduction step at 723 K (Figure 6). For all the catalysts, more than 90% of the observed Ru particles had diameters smaller than 1.5 nm and no particles larger than 3.5 nm were found. Metal particles of sizes ranging from 2 to 3.5 nm were absent in catalysts containing 0.5 wt% Ru and were only between 4-9 % of total number of particles in catalysts containing 2 and 5 wt% Ru loadings. These two later catalysts showed very different selectivities to CH$_4$, despite their very similar particle size distribution. What is different between these two catalysts is the spatial distribution of the nanoparticles as observed in STEM images. For 2 wt% Ru loading, the nanoparticles are sparsely...
distributed while the Ru nanoparticles are closer to each other for 5 wt% Ru loading, leaving less support space between them.

Catalysts after stability test during 20 hours shown in Figure 5 were also characterized by STEM (Figure S4 supplementary information). The particle size distribution did not show significant change after long-term operation at 623 K, which is in line with the stable catalytic performance.
Figure 6. STEM images and particle size distribution of the different catalyst after reduction step at 723 K. (A) 0.5%Ru/CNF, (B) 0.5%Ru/N-CNF, (C) 2%Ru/CNF, (D) 2%Ru/N-CNF, (E) 5%Ru/CNF, (F) 5%Ru/N-CNF.

4. Discussion
The mechanism of CO\textsubscript{2} reduction to CH\textsubscript{4} on oxide-supported metal catalysts has been debated largely in the literature. Some authors propose that CO\textsubscript{ad} is a key intermediate in the CO\textsubscript{2} methanation reaction and it is subsequently hydrogenated \textit{via} the mechanism suggested for CO methanation. CO\textsubscript{ad} can be formed \textit{via} the reverse water gas shift through formate intermediate\cite{17} or via dissociative CO\textsubscript{2} adsorption in a redox center\cite{41-43}.

Subsequently, the formation of CH\textsubscript{4} from CO\textsubscript{ad} was proposed to proceed either by the initial C-O bond breaking\cite{44-47} or with association of H\textsubscript{2} with CO\textsubscript{ad} to form an intermediate and subsequent bond breaking\cite{48, 49}.

On the basis of the results of transient experiments conducted here, the following reaction mechanism could be proposed. CO\textsubscript{2} is dissociated on reduced Ru nanoparticles even at room temperature and O\textsubscript{ad} species and CO\textsubscript{ad} species spilt over to the CNF support close to the interphase of metal nanoparticles. The dissociative chemisorption energies calculated in reference \cite{50} for CO, CO\textsubscript{2} and H\textsubscript{2} on ruthenium are -1.62, -1.09 and -0.77 eV, respectively, with respect to molecules in vacuum. Therefore, CO is chemisorbed less strongly than CO\textsubscript{2} and H\textsubscript{2} on Ru nanoparticles and it can be displaced by the reactants towards the metal-support interphase, favouring the proposed spill over mechanism. The CO\textsubscript{ad} species might be stored on the support due to some interaction with the edges of graphitic basal planes of CNF. The accumulation of O\textsubscript{ad} species on support is evidenced by the formation of water at around 370 K in TPSR (Figure 3) and by the sustained formation of H\textsubscript{2}O in transient response experiments after CO\textsubscript{2} removal from gas feed (Figure 4). The quantified moles of CH\textsubscript{4} produced in TPSR, which is one order of magnitude larger than moles of Ru, indicates that CO\textsubscript{ad} intermediate species accumulated on the carbon support as well. The presence of Ru nanoparticles is necessary to dissociate CO\textsubscript{2} since no species were desorbed in TPSR using pristine supports \cite{Figure S1 supplementary material}. Some of the CH\textsubscript{4}-generating intermediates
are partially oxidised as inferred from the synchronous evolution of CH₄ and H₂O in TPSR. The nature of this CH₄-generating intermediate species is not clarified yet. Some authors have proposed the formation of reversible bicarbonates by reaction of CO₂ with the OH- groups of Al₂O₃ support.³¹,³⁹ Similarly, bicarbonate species may be formed on OH- groups present on the edges of CNF basal planes. Contrarily, the mechanism of bicarbonate formation would hardly occur in the case of CNT support because exposed basal planes of CNT have fewer defects for CO_ads chemisorption. This would explain the negligible activity when CNTs are used as Pd catalyst support in the literature.⁴⁰

The catalytic results showed that the selectivity pattern depends strongly on the metal loading. The selectivity is steered either towards CO for low Ru loadings or towards CH₄ for larger Ru loadings. Several authors found similar selectivity patterns as a function of the metal loading for different catalysts such as Ru on alumina,³⁰ Pd on alumina⁴⁰ or Ni on MCM-41.¹⁰ Some of these authors attributed it to the different metal particle size, nano–sized metal clusters (2–5 nm) in 10% Pd on Al₂O₃ and atomically dispersed for 0.5 % Pd on Al₂O₃.³⁰,⁴⁰ In the other case,¹⁰ sub-nanometer Ni cluster were reported irrespective of the metal loading and the size did not change after reaction. On the contrary, other authors observed an increase of CH₄ selectivity for smaller particles using Pd nanoparticles embedded in porous silica and ascribed this behaviour to the increased amount of corner and edge atoms.⁵¹ Using nanoparticle model Co catalyst on silica, it was not observed any effect of particle size on selectivity to CH₄.⁵² Therefore, it seems that there is not a particle size effect generalizable to all catalytic systems. In our case, we cannot attribute the different selectivity pattern to different Ru particle sizes because the differences in particle size distribution measured by STEM are inappreciable, especially between 2 wt% and 5 wt% Ru loaded catalysts. The main difference between those catalysts observed by STEM is that the Ru
nanoparticles are closer for the highest Ru loading. Since the apparent particle size is very similar for all samples, those with higher Ru loading have also longer perimeter of interphase with the support. From the catalyst dispersion, the concentration of Ru on the perimeter was estimated (Table S1 supplementary material). Figure 7 shows that CH$_4$ yield exhibits a quasi-linear relationship with the concentration of Ru on the perimeter, especially for the catalyst supported on CNF. Similar importance of the metal catalyst perimeter has been previously reported for CO$_2$/CH$_4$ reforming to syngas using Pt/ZrO$_2$ catalyst.$^{[26]}$ It is claimed that CO$_2$ is activated via carbonate species on the support which must be in the proximity of the Pt particles to react with the methane activated on the metal.

![Figure 7: CH$_4$ yield at 673 K as a function of the concentration of Ru on the perimeter for the different Ru loadings supported either on CNF (■) or N-CNF (□).](image_url)

According to the reaction mechanism proposed on the basis of transient experiments, the support would play a crucial role in the reaction. Therefore, a longer interphase
perimeter between metal nanoparticles and support can be the reason of the different CH₄ selectivities. Since the supply of H_ads to the adsorbed CO_ads intermediate was found to be the rate determining step in transient response experiments (Figure 4), the closer proximity of Ru nanoparticles and larger interphase perimeter may also favour the supply of H_ads to the CO_ads intermediate and hence boosting the formation of CH₄. In fact, the CH₄ peak upon CO₂ removal in transient experiments almost vanished for catalyst exhibiting the highest activity at steady state, indicating that H₂ activation and H_ads supply is not that rate limiting in those cases. The overall reaction is governed by a subtle balance of adsorbed molecules, dissociated species and the reaction between them. Therefore, it is not straightforward to gather in one picture the whole process. For clarity, the simplified scheme of Figure 8 illustrates how different Ru loadings can affect the selectivity pattern. For the lower loadings (A), the metal particles are more separated and the supply of four H_ads to the activated CO_ads intermediate on the support is hindered. In contrast, for the highest loading the separation between nanoparticles is shorter and the supply of four H_ads atoms is enhanced.

The 5 wt% Ru catalyst supported on N-CNF outperforms its counterpart supported on CNF. Due to the several factors involved in this reaction, further research would be needed to unravel the exact reason of the enhanced performance of N-CNF supported catalyst. Transient response experiments (Figure 4 A and B) seem to indicate that the supply of H_ads active species is favoured for N-CNF supported catalyst. Additionally, the CH₄ desorption peak in TPSR of 5%Ru/N-CNF occurs at about 20 K lower temperature than that of 5%Ru/CNF which can be a result of the enhanced supply of H_ads or also to the formation of more reactive CO_ads intermediates upon CO₂ dissociation.
Figure 8. Scheme of different selectivity pattern depending on the different spatial separation of the Ru nanoparticles for the several Ru loadings. (A) hindered supply of \( \text{H}_\text{ad} \) for 0.5 and 2 wt% loaded catalyst. (B) Enhanced supply of \( \text{H}_\text{ad} \) to 5 wt% loaded catalyst.

The 5 wt% Ru on N-CNFe catalyst showed activity comparable to catalyst supported on metal oxide supports reaching thermodynamic equilibrium conversion at 623 K and complete selectivity to \( \text{CH}_4 \) at a high space velocity (19000 h\(^{-1}\)). The catalyst is stable during long term operation, and the Ru particle size distribution remains constant after long term testing due to the strong attachment of Ru nanoparticles to the carbon support.
It has been recently reported that Ru nanoparticles on CNT are thermally stable keeping a high dispersion due to their anchoring via acetate ligands which are reconstructed after thermal treatment in the presence of oxygen.\cite{53} Not all the metals supported on carbon nanotubes showed stability in CO\textsubscript{2} methanation. For instance, Ni supported on CNT catalyst tested in CO\textsubscript{2} methanation at 623 K during 6 hours showed a decrease of yield from 75\% to 62\% which was attributed to Ni sintering.\cite{37}

Not only the catalyst here prepared outperforms other catalysts supported on carbon materials but it exhibits either superior CH\textsubscript{4} productivity than some of the best metal oxide supported catalysts tested in the literature under similar conditions (Table 3).

Table 3. Comparison of CH\textsubscript{4} productivity of this catalyst with some of the best catalysts in the literature tested under similar conditions.

<table>
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<th>Reaction temperature (K)</th>
<th>CH\textsubscript{4} productivity (mol h\textsuperscript{-1}g\textsubscript{metal}\textsuperscript{-1})</th>
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<td>[30]</td>
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<td>643</td>
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</table>
5. Conclusions

Ru supported on CNF or N-CNF showed remarkable activity and stability in the CO₂ reduction to CH₄, contrasting with the poor activity and selectivity reported for carbon nanotube supported catalysts. Moreover, the catalyst 5%Ru/N-CNF showed CH₄ productivity comparable to the best catalysts supported on metal oxides in the literature. Thus, the catalyst can be efficiently used in a CO₂ recycling process situated close to a place where renewable or by-product H₂ can be utilized.

To get insights about the reasons of this outstanding performance, catalytic transient response experiments were carried out. Transient experiments underscore the active participation of CNF and N-CNF support on the reaction as storage for reaction intermediate species. Thus the reaction occurs likely close to the interphase between Ru metal nanoparticles and support. The former assists the dissociation of H₂ to H_ad and of CO₂ to O_ad and a reduced intermediate CO_ad species. The dissociated species spilt over to the carbon support that functions as storage for O_ad and CO_ad species. Transient experiments revealed that CH₄ formation rate is controlled by the supply of 4 H_ad to the CO_ad intermediate. The selectivity depends strongly on the metal loading. For 0.5 and 2 wt% Ru loadings, the reduction is steered mainly to CO formation while for 5 wt% Ru loading the selectivity to CH₄ is 97 %. Since the Ru particle sizes did not differ significantly for catalysts containing different loadings, the different selectivity pattern cannot be ascribed to structure sensitivity. The higher selectivity to CH₄ is most likely explained by the enhanced supply of 4 H_ad to the activated CO_ad intermediate, which is
favoured by the proximity between nanoparticles or to the longer interphase perimeter between metal nanoparticles and support.

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**Supporting information statement**

Temperature Programmed Surface Reaction (TPSR) experiments of the supports CNF and N-CNФ. Experiments of transient response to CO₂ removal from gas feed for all catalysts. Representative STEM images and particle size distribution of catalysts 0.5 after testing for 20 hours at 623 K.

**Reference List**


N-doped carbon nanofibers demonstrated to be an effective support of Ru nanoparticles for the reduction of CO\textsubscript{2} to CH\textsubscript{4}. Higher loadings favoured the selectivity to CH\textsubscript{4}. The catalyst support not only helps to stabilise Ru nanoparticles but also participates actively in reaction mechanism.