Origin of the Excellent Performance of Ru on Nitrogen-doped Carbon Nanofibers for CO₂ Hydrogenation to CH₄

Laura Roldán, Yanila Marco, Enrique García-Bordejé*

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza,
Spain,

Abstract: Carbon materials have rarely been used as support for CO₂ methanation, which is usually carried out using catalysts supported on metal oxides. Here, it is shown that Ru nanoparticles supported on nitrogen-doped carbon nanofibers (NCNF) provides CH₄ production rate and stability competitive to those of alumina supported catalyst. Contrary to the general belief about the inert nature of carbon support, it is demonstrated that NCNF is a non-innocent spectator in CO₂ methanation due to its ability to store a high amount of CO_{ad} reaction intermediates. This explains the excellent catalytic behaviour afforded by this unconventional catalyst support.

Introduction

The reaction between CO₂ and H₂ to produce CH₄ is known since a century ago under the name of Sabatier reaction.^[1] Recently, It has gained a renewed interest for the coupling of CO₂ conversion and storage of renewable H₂ in the form of Synthetic Natural Gas (CH₄).^[2] CH₄ is a convenient way to capture chemically the intermittently-generated energy from sun and wind because the current gas infrastructures can be used for its storage and transport. Another niche application for this reaction is in astronautics. NASA has demonstrated interest in this reaction as an integral part of mission architectures for future long-duration human space exploration to the Moon and Mars as a way to recycle metabolically-generated CO₂ into CH₄ and H₂O.^[3, 4]

Electrocatalysis,^[5] photocatalysis^[6] and thermal homogeneous^[5, 7] and heterogeneous catalysis have been employed for CO₂ methanation. State-of-the-art photocatalysts used in artificial photosynthesis yield low CO₂ conversions, rendering the process inefficient thus far.^[6] Homogeneous catalysts show satisfactory activity and selectivity, but the recovery and regeneration are troublesome. Alternatively, heterogeneous catalysts are preferable in terms of stability, handling, separation and reactor design, reducing the costs for large-scale productions. Moreover, reactor design to optimise heat management is a very important issue for this exothermic reaction. Isothermal conditions should be maintained during reaction to avoid hot-spots that decrease CH₄ selectivity. Therefore, the reactor should be designed to dissipate quickly the heat produced.^[8-11]

* Corresponding author: Tel.: + 34 976733977; fax.: +34 976733318 *E-mail address:* jegarcia@icb.csic.es

As supported active phase, both transition metals such as Co^[12, 13] and Ni^[14-17] and noble metals including Ru,^[18-20] Rh,^[21-24] Pd,^[24] and Pt,^[24, 25] have demonstrated to be active for this reaction. Concerning the support, several materials have been used in CO₂ hydrogenation such as alumina,^[10, 26-28] titania,^[29-31] titanium carbide,^[32] silica,^[13] ceria,^[16, 20, 33] zeolite,^[34] or carbon materials such as activated carbon^[35] or carbon nanotubes.^[36, 37] In heterogeneous catalysis, the support can play different roles in the catalytic reaction. For instance, it may interact with the reactant(s), products or reaction intermediates increasing its local concentration.^[38] At the interphase between metal and support, special interfacial sites can be created where reactions can proceed readily.^[29, 39, 40]

CO₂ reduction is reported to require a bifunctional catalyst, *i.e.* one function to activate CO₂ and another to activate H₂, and the support is not just an innocent spectator.^[19, 27, 35, 41, 42] Park and MacFarland^[42] observed a selectivity shift from CO to CH₄ by modifying Pd on SiO₂ with MgO, while MgO/SiO₂ showed no measurable activity. They rationalized their results suggesting a bifunctional mechanism in which CO₂ first strongly adsorbs onto MgO inhibiting CO desorption, while Pd dissociates H₂. There are also strong indications that CO₂ interacts with hydroxyl groups of metal oxide support such as Al₂O₃ to produce carbonates/bicarbonates.^[28, 43-45] Therefore, metal oxide supports participate actively in the reaction mechanism. On the other hand, carbon nanotubes are usually considered as an inert support material. In fact, when using carbon nanotubes as noble metal catalyst support for CO₂ hydrogenation, the activity was negligible, which was attributed to the lack of the function to activate CO₂.^[46]

It was reported some time ago that the incorporation of basic nitrogen groups into the carbon framework ensures an improved adsorption/absorption for acidic gases.^[47] More recently, the enhanced capture of CO₂ when using N-doped carbons has been extensively reported.^[48-58] The Lewis basic sites of N-doped CNT are assigned to pyridinic like nitrogen (N_p), located at the edges of the graphene layers.^[59, 60] Hao et al. proposed that the Lewis basic nitrogen atoms such as pyridinic N-6 and pyrrolic N-5 atoms might play a key role for stronger interactions with CO₂ molecules.^[51] Additionally, Sevilla et al. pointed out that the pyridonic N content as well as high total N content of porous carbon materials might be important factors for an efficient CO₂ capture.^[56] The Lewis basicity stems from the electronic structure of pyridine groups. The pyridine-like N-atom is sp²-hybridized and it has the ion-pair electrons in the sp² hybrid orbital that does not participate in π -system while contribute to the π system with one p-electron.^[61] On the other hand, Pyrrole and pyridone functionalities donate two p-electrons to the π -system. The basicity of N-CNF is expected to increase CO₂ adsorption and thus promoting subsequent catalytic reduction.

In a previous paper,^[62] we studied the effect of metal loading for Ru supported on both CNF and NCNF. It was found that the selectivity to CH₄ increases dramatically as the metal loading increases from 2 to 5 wt%. The catalyst with the highest Ru loading (5% Ru/NCNF) provided the highest selectivity to CH₄, *i.e.* in the range 90-97 % for all the studied temperatures (up to 670 K). In contrast, the selectivity to CH₄ is below 20% for the low metal content catalysts. We tentatively explained the difference in selectivities by the different interparticle space depending on the loadings which is in agreement with recent literature reports.^[44] The mentioned article put forward that small interparticle distances are required to allow the readsorption and subsequent reduction of the CO intermediate to hydrocarbon.

Herein, we used CNF, NCNF and carbon nanotubes (CNT) as support for 5 wt% Ru metal nanoparticles and benchmarked its catalytic performance against that of a commercial Ru on alumina catalyst with the same metal loading. The catalysts have been characterised by TEM, N₂ physisorption and transient response techniques such as temperature programmed desorption of preadsorbed CO₂ (CO₂-TPD), temperature programmed surface reaction (TPSR) and transient response to the step removal of CO₂ from reaction feed. This characterisation led to unravel the reasons of the excellent performance of NCNF supported catalyst.

Figure 1 displays the performance at steady state of 5 wt% Ru on the different supports. At temperatures below 550 K, where the CO₂ conversion is far from equilibrium, the alumina-supported catalysts provided slightly higher CH₄ formation rate than the carbon supported catalysts. However, for reaction temperatures providing CO₂

conversion close to equilibrium, the performance of catalyst supported on NCNF is boosted, supplying similar conversions as alumina-supported one. CNT-supported catalyst exhibited also an excellent performance, only slightly below that of alumina and NCNF-supported catalysts, contrasting with the inactivity of other CNT-supported catalyst reported elsewhere.^[46] The poorest performance in all the temperature range corresponded to CNF-supported catalyst. The selectivity to CH₄ was above 95% at conversions close to equilibrium for all the catalysts except for CNF supported one which showed lower selectivity. The catalysts were characterised by HAADF-STEM and the metal particle size distribution of each catalyst and average size is show in Figure S1 of supporting information and Table 1, respectively. The average metal particle size was very similar for all catalysts except for that supported on CNT, which consisted of slightly larger particles. The textural characterisation by N₂ physisorption (Table S1) showed that the porosity of all the catalysts is in the range of mesoporosity with negligible microporosity.

Figure 1. CO₂ conversion (a) and CH₄ selectivity (b) of 5%Ru on different supports.

The excellent performance of NCNF supported catalyst prompt us to study the mechanism of reaction in more detail using transient techniques such as temperature programmed CO₂ desorption (CO₂-TPD) and temperature programmed surface reaction (TPSR). CO₂-TPD after CO₂ pre-adsorption at several temperatures supplies information about the interaction of CO₂ with the different catalysts. The CO₂ adsorption was carried out at several temperatures varying from 298 K to 573 K. Figure 2 shows the CO₂-TPD curves for 5% Ru/Al₂O₃, 5% Ru/NCNF, 5% Ru/CNT and 5% Ru/CNF, respectively. In CO₂-TPD curves of Ru/Al₂O₃ (Figure 2a), two peaks are distinguished one at ~370 K and other at higher temperatures. The 370 K peak appears at all the temperatures and also for the bare support without metal and its intensity decays as the temperature of CO₂ adsorption increases. Thus, this peak is attributed to physisorbed CO₂. The high-temperature peak takes place at ~50 K higher temperature than the temperature of CO₂ adsorption. This desorption peak corresponds to chemisorbed CO₂. The CO₂ chemisorption is a process activated by the metal catalyst since this peak was absent in CO₂-TPD of the support without metal. Since desorption is an endothermic process, it occurs at higher temperature than that of CO₂ adsorption which is exothermic. The CO₂-TPD curves of carbon supported catalyst are very similar between them and somehow different from that of 5%Ru/Al₂O₃. The amount of physisorbed CO₂ is less for carbon supported catalyst than for alumina-supported ones. For carbon materials, chemisorbed CO₂ evolves in a broader temperature range, although a CO₂ chemisorption peak can be also spotted at around ~50 K above the temperature of CO₂ adsorption, as for alumina-supported catalyst. The main difference compared to alumina-supported catalyst is that carbon supported catalysts exhibited a pronounced CO₂ desorption at temperatures higher than 600 K for all the temperatures of CO₂ adsorption.

Table 1. Average Ru particle size and comparison of parameters of CO₂-TPD, TPSR and steady state reaction

	Average Ru particle size (nm)	Desorbed CO ₂ in TPD after pre- adsorption at 573 K (mmol g ⁻¹)	Tempera- ture of first CH ₄ peak in TPSR (K)	CH ₄ productivity at 600 K steady state (mmol g ⁻¹ h ⁻¹)
5%Ru/Al ₂ O ₃	1.7±0.1	2.5	460	75
5% Ru/NCNF	1.7±0.1	9.2	490	77
5% Ru/CNT	2.3±0.2	6.4	463	68
5% Ru/CNF	1.6±0.1	4.4	508	37

Figure 2. Temperature programmed desorption of CO_2 pre-adsorbed at different temperatures for 5% Ru/ Al_2O_3 (a), 5% Ru/NCNF (b), 5% Ru/CNT (c), and 5% Ru/CNF (d).

For the sake of comparison between different supports, Figure 3 compiles the CO₂-TPD curves after CO₂ adsorption at 573 K and Table 1 listed the quantification of chemisorbed CO₂ for the different catalysts. We considered as chemisorbed CO₂ that desorbed at temperatures above 450 K. It is clearly observed that Ru supported on carbon materials desorb significantly more chemisorbed CO₂ than 5% Ru/Al₂O₃. Particularly, 5% Ru/NCNF provided the highest amount of chemisorbed CO₂ (9.2 mmol g⁻¹) while 5% Ru/CNF furnished the least amount of chemisorbed CO₂ among the carbon-based catalysts.

Figure 3. Comparison of CO₂-TPD for the different catalyst after CO₂ pre-adsorption at 573 K.

Additionally, temperature programmed surface reaction (TPSR) experiments were performed after CO₂ adsorption at temperatures from 298 K to 573 K (Figure 4). In TPSR experiments, the temperature of CH₄ peak ($m/z=16$) occurs at the same temperature independently of the temperature of CO₂ adsorption (Figure 4) in contrast to CO₂ peak in CO₂-TPD experiments (Figure 2). The CH₄ peak temperature is characteristic for each catalyst and it is related to its intrinsic activity. The lower the temperature of CH₄ evolution peak, the higher the intrinsic activity of the catalyst. According to the CH₄ peak (Table 1 and Figure 4), the intrinsic activity of the catalysts follows this order: 5% Ru/Al₂O₃ = 5% Ru/CNT > 5% Ru/NCNF > 5% Ru/CNF. It is worthy to note that 5% Ru/NCNF showed lower intrinsic activity than 5% Ru/CNT and Ru/Al₂O₃. Nevertheless, its performance at steady state (Figure 1 and Table 1) was superior to the former and comparable to the latter. This may be explained by the remarkable ability of 5%Ru/NCNF to store CO_{ad} species as observed by CO₂-TPD, underlining that the catalytic performance at steady state is not only governed by the intrinsic activity of the catalyst but also by the ability of the support to store and supply CO_{ad} intermediate species. To assess the stability in long-term operation, the catalyst 5 wt%Ru/NCNF was tested at 623 K, during 20 hours (Figure S2), exhibiting very stable performance. The conversion and selectivity even increased slightly with time-on-stream resulting in selectivity at steady state of 99 % to CH₄ and conversion of 66%.

Figure 4. Temperature programmed surface reaction (TPSR) of CO_2 pre-adsorbed at different temperatures 5%Ru/ Al_2O_3 (a), 5% Ru/NCNF (b), 5% Ru/CNT (c), 5% Ru/CNF (d).

In summary, Ru nanoparticles supported on NCNF exhibited remarkable CH₄ productivity and stability in CO₂ hydrogenation, which are competitive to those of commercial alumina-supported catalyst. The reasons of the excellent catalytic performance were elucidated by using transient response techniques. It was revealed that the NCNF support cooperate actively in reaction by storing the highest amount of CO_{ad} reaction intermediates among the tested catalysts, which lends NCNF supported catalyst its superior performance. Moreover, an improvement of the performance of NCNF supported catalyst is envisaged by increasing the intrinsic activity of the catalytic sites, which is still amenable to optimization.

Experimental Section

CNFs and N-CNF were grown as described in previous work.^[62] Subsequently, they were purified leaving less than 0.5 wt% residual growth catalysts. The used CNTs were NC7000™ from nanocyl. 5% Ru/Al₂O₃ catalyst was supplied by Sigma-Aldrich. The preparation of ruthenium catalysts was performed by incipient wetness impregnation from Ru nitrosyl nitrate (Ru(NO)(NO₃)) in an ethanol:water mixture (4:1). 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 actual metal loading was analysed by inductive coupled plasma-optical spectrometry (ICP-OES).

Catalytic testing was carried out in a continuous-flow 6 mm o.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 698 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 698 K for 1 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.

Temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) experiments were conducted in the same set-up according the procedure that is schematized in Figure S3. In brief, 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 1 h. Subsequently, the temperature was set at a certain temperature between 298-573 K and CO₂ was flushed for 1 h. The gas was switched to 100 ml/min Ar and the reactor was allowed to cool down to room temperature. Ar flow was kept overnight to remove all weakly physisorbed CO₂. Then the gas was adjusted to 60 ml/min of Ar for CO₂-TPD experiments or to 60 ml/min 15% H₂ in Ar for TPSR experiments. When the signal in mass spectrometer was stabilised, the temperature was raised until 698 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. Surface areas were determined by N₂ adsorption at 77 K (BET) using a Micromeritics ASAP 2020 apparatus, after outgassing for 4 h at 423 K.

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Keywords: CO₂ methanation • Ru catalyst • carbon nanofibers • nitrogen-doped carbon • carbon nanotubes

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