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Additional Information

Hydrothermal synthesis of ruthenium nanoparticles with a metallic core and a ruthenium carbide shell for low temperature activation of CO₂ to methane

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▪ **ABSTRACT**

Ruthenium nanoparticles with a core-shell structure formed by a core of metallic ruthenium and a shell of ruthenium carbide have been synthesized by a mild and easy hydrothermal treatment. The dual structure and composition of the nanoparticles have been determined by synchrotron X-ray Photoelectron Spectroscopy (XPS), Near Edge X-ray Absorption Fine Structure (NEXAFS) analysis and Transmission Electron Microscopy (TEM) imaging. According to depth profile synchrotron XPS and X-Ray Diffraction (XRD) analysis, metallic ruthenium species predominate in the inner layers of the material being ruthenium carbide species located on the upper surface layers. The Ruthenium carbon catalysts presented herein are able to activate both CO₂ and H₂, exhibiting exceptional high activity for CO₂ hydrogenation at low temperatures (160-200 °C) with 100% selectivity to methane, surpassing by far the most active Ru catalysts reported up to now. Based on catalytic studies and isotopic ¹³CO/¹²CO₂/H₂ experiments, the active sites responsible for this unprecedented activity can be associated to surface ruthenium carbide (RuC) species, which enable CO₂ activation and transformation to methane *via* direct CO₂ hydrogenation mechanism. Both, the high activity and the absence of CO in the gas effluent confer relevance on these catalysts for the Sabatier reaction, a chemical process with renewed interest for storing surplus renewable energy in the form of methane.

Keywords Ruthenium carbide, CO₂ activation, low temperature Sabatier, NEXAFS, synchrotron XPS, methane, hydrothermal synthesis, isotopic experiments.

▪ INTRODUCTION

The CO₂ concentration in the atmosphere has been growing exponentially in the last decade exceeding the 400 ppm in 2016 and leading to important environmental damages as, for instance, the global warming or sea water acidification.¹ Therefore, the reduction of CO₂ emissions is strongly required. Among the processes reported for CO₂ capture and use, CO₂ methanation reaction (so called Sabatier reaction) has received renewed interest in the last years as a way to store surplus renewable energy in the form of CH₄, which is easily stored, transported and used in the actual industrial infrastructure.² CO₂ methanation is a simple reaction, favoured thermodynamically at low temperatures (CO₂+ 4H₂ ↔ CH₄ + 2H₂O; ΔH = - 252.9 KJ·mol⁻¹), but limited kinetically because of the high CO₂ stability. The catalysts proposed in patents and in the literature for producing CH₄ from CO₂ are based on metals like Ni, Ru, Pd, Rh, mono or multimetallic, with or without promoters (Na, K, Cs, rare-earth elements...) on different supports (TiO₂, SiO₂, Al₂O₃, CeO₂, ZrO₂, CNT doped with N).³⁻⁵ In all cases high temperatures (300-500 °C) are employed which results in large energy input, high operational costs for large-scale production and negative impact on catalyst stability. Ru is a highly active metal for CO₂ methanation at lower temperature, however the highest space time yield to methane reported up to now does not exceed 0.9 μmol_{CH₄}·s⁻¹·g_{cat}⁻¹ at 165 °C and 2.6 μmol_{CH₄}·s⁻¹·g_{cat}⁻¹ at 200 °C and atmospheric pressure, obtained at a 1.6 mL·g⁻¹·s⁻¹ gas feed rate on a Ru/TiO₂ catalyst, still too low for industrial application.^{6,7} Therefore, a breakthrough in the CO₂ methanation reaction will require a highly active and selective catalyst able to operate under mild reaction conditions.

Transition metal carbides appear as appealing catalytic alternatives with interesting properties for many processes, such as isomerization of n-heptane,⁸ steam reforming of methanol,⁹ dry reforming of methane,¹⁰ CO hydrogenation,¹¹⁻¹³ and CO₂ hydrogenation.¹⁴⁻¹⁸ Molybdenum carbide (β-Mo₂C)¹⁴ and metal supported carbides (Me/Mo₂C¹⁷ Me = Ni, Co, Cu; or Me/TiC¹⁶ Me = Cu, Ni, Au) have shown high activity for CO₂ hydrogenation (i.e. 6-8% CO₂ conversion at 200 °C, 20 bar and 2.5 mL·g⁻¹·s⁻¹ gas feed rate),¹⁷ being 3-5 times higher than the corresponding metals supported on conventional oxide supports. However, the selectivity to the target product is relatively low (29% and 42% CH₄ at 200 °C on β-Mo₂C and Ni/Mo₂C respectively)¹⁷ due to CO formation (39% and 37%, respectively). The high activity has been ascribed to the intrinsic activity of metal carbides to adsorb and activate the CO₂ molecule through a net charge transfer from carbide to the CO₂ molecule.^{15,19} The reactivity, i.e. C-O bond cleavage of the CO₂ molecule, strongly depends on the carbon/metal ratio. Thus, CO₂ dissociation occurs spontaneously on a Mo-terminated β-Mo₂C surface yielding CO and O, while

on a carbon rich surface (i.e. δ -MoC) a HOCO intermediate is formed, resulting in different product selectivity.

In an early study, Moreno-Castilla *et al*²⁰ reported the formation of ruthenium carbide (RuC) in a Ru activated carbon catalyst prepared by sublimating Ru₃(CO)₁₂ on a carbon support, followed by thermal decarbonylation in He at 150 °C. Based on CO and H₂ chemisorption data, they argued the formation of a Ru^{IV} active phase, which according to the authors has been assigned to RuC. This result has to be reviewed considering the low tendency of ruthenium to form carbides or solid solution with carbon, usually requiring elevated pressure (5 GPa) and temperatures (1700-2500 °C) for their synthesis.²¹⁻²⁴ Moreover, the reported yield to methane in the CO₂/H₂ reaction was not higher (~1.4-1.0 times) than that of a similar sample without carbide species, which makes the assignation to RuC doubtful.

In the present work, we show the possibility of synthesizing a ruthenium carbide catalyst (labelled as Ru@C) by an easy and mild hydrothermal method instead of using the harsh treatments previously reported. Most importantly, the as synthesized Ru@C catalyst show unprecedented activity for the low temperature (160-200 °C) CO₂ hydrogenation reaction to CH₄. Methane yields up to 3.5 $\mu\text{mol}_{\text{CH}_4}\cdot\text{s}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$ at 160 °C and 13.8 $\mu\text{mol}_{\text{CH}_4}\cdot\text{s}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$ at 200 °C are achieved at atmospheric pressure and at 8.3 mL·g⁻¹·s⁻¹ feed rate, surpassing by far the most active Ru catalyst reported up to now.^{5,6,7,25-26} The catalyst also show good stability under operational conditions with CH₄ selectivity above 99.9%. Finally, we will show that the formation of CH₄ is taken place by direct activation and hydrogenation of CO₂.

▪ EXPERIMENTAL SECTION

Synthesis of Ru@C-EDTA

Samples with different Ru contents were prepared using the same synthetic procedure but modifying the amount of Ru precursor. In general: X (X = 1.5, 3.1, 5.3 and 6.6) g Ru(acac)₃ (Aldrich), 1.77 g Na₂EDTA·2H₂O (Aldrich) and 0.39 g NaOH (Acros) were dissolved in 8 mL of deionized water. Then 4 mL of methanol were added to the mixed aqueous solution under stirring at room temperature, resulting in a red suspension, which was transferred into a 35 mL Teflon-coated stainless steel autoclave followed by static hydrothermal processing at 200 °C for 24 h. After it, the autoclave was taken out of the oven and cooled down to room temperature for 3 h. The generated precipitate was filtered and washed with deionized water and acetone for five times. Samples were labelled as Ru@C-EDTA-X, where X corresponds to the ruthenium loading, determined by ICP (Table S1).

Synthesis of Ru@C-Glucose

120 mg of glucose (Aldrich) dissolved in 7 mL of deionized water were stirred at room temperature for 0.5 h. Then 100 mg of RuO₂ (Aldrich, 99.9%, particle size 32 nm, determined by XRD) were added and mixed under ultra-sonication (Branson 3510 operating at 40 Hz) for 0.5 h, obtaining a black suspension. The so obtained suspension was transferred into a Teflon-coated stainless steel autoclave of 12.5 mL. The autoclave was introduced in an oven placed at 175 °C and kept for 18 h under static conditions. After it, the autoclave was taken out of the oven and cooled down to room temperature for 2 h. The content of the autoclave was then filtrated under vacuum conditions, recovering a black solid. The solid was washed five times first with water and later with acetone. Finally, it was dried in an oven at 60 °C for 12 h. The loading of ruthenium in the sample was 24.3 wt %, according to ICP analysis.

Synthesis of Ru/C-WI

The sample was prepared by a wet impregnation method as follows: 396 mg of Ru(acac)₃ were dissolved in 20 mL toluene for 0.5 h. Then 900 mg of carbon (activated charcoal Norit®, Aldrich) were added and stirred for 15 h at room temperature. The final suspension was evaporated under vacuum resulting in a black solid. The solid was reduced in 50 mL·min⁻¹ H₂ at 250 °C for 3 h with a heating ramp of 10 °C·min⁻¹, followed by cooling down in N₂ to 25 °C. After this, it was oxidized in 50 mL·min⁻¹ O₂ flow at 400 °C for 3 h. The loading of ruthenium in the sample was 3.0 wt %, according to ICP analysis. XRD is shown in Figure S5.

Synthesis of Ru/C-Ar800

58 mg of Ru(acac)₃ were dissolved in 20 mL of acetone and stirred at 50 °C. 1.47 g of Na₂EDTA and 0.12 g NaOH were dissolved in water (20 mL) and the resulting aqueous solution was added to the metal solution and stirred at 50 °C for 0.5 h. Then, 1.6 g of carbon (activated charcoal Norit®, Aldrich) were added and the mixture was refluxed at 50 °C for 24 h. After cooling, the suspension was rotoevaporated, washed with water, filtered and dried at 100 °C overnight. The black solid was pyrolyzed in an Ar flow (10 mL·min⁻¹) at 800 °C for 5 h (5 °C·min⁻¹). XRD is shown in Fig. S5.

Synthesis of Ru@C/NG

The catalyst was synthesized according to Reference 27. Briefly, graphene oxide (GO) support was prepared following the improved Hummers method. GO was doped with nitrogen using formaldehyde (37% in water, Aldrich) and melamine (Acros) and the suspension was transferred into a Teflon-coated stainless steel autoclave (12.5 mL) and kept at 180 °C for 12 h. The gel obtained was submitted to pyrolysis in a N₂ flow at 750 °C for 5 h. NG support was dispersed in a phosphate buffered solution with the metal precursor (RuCl₃·3H₂O, Johnson Matthey), dopamine hydrochloride (Aldrich) and CTAB (Acros) and hydrothermally treated at 140 °C for 6

h. The resulting suspension was centrifuged and the solid was washed with water and dried. The catalyst was obtained after a high temperature treatment in argon (800 °C, 10 mL·min⁻¹) for 3 h.

Ruthenium references

Commercial Ru on carbon, **Ru/C-com** (Acros Organics, 5 wt % Ru) and **Ru-Black** (Aldrich, >98%) were used as reference samples in catalytic and spectroscopic studies. XRD are shown in Figure S5.

Catalysts characterization

The Ru content was analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using a Varian 715-ES spectrometer. The samples were dissolved in aqua regia at 60 °C for 20 h. X-Ray powder diffraction (XRD) was recorded with a Philips X'Pert diffractometer using a monochromatic Cu K α radiation ($\lambda=0.15406$ nm). Average particle size was calculated from the main peaks (38.4, 42.2, 44.0, 58.3, 69.4, 78.4; 2θ) of Ru⁰ (JCPDS: 00-006-0663) using the Scherrer equation and assuming a shape factor $k=0.9$. Transmission Electron Microscopy (TEM) measurements were performed in a JEOL-JEM 2100F operating at 200 kV. Samples were prepared by dropping the suspension of the powder catalyst using ethanol as the solvent directly onto holey-carbon coated Cu grids. The amount of surface ruthenium metal sites was measured by CO chemisorption at 25 °C in a Quantachrome Autosorb-1C instrument by extrapolating the total gas uptakes in the adsorption isotherms at zero pressure and assuming an adsorption stoichiometry of 1:1 (Ru:CO).²⁰ Before measurements, about 300 mg of catalyst were activated in a helium flow at 100 °C (2 h) and in vacuum at the same temperature (1 h). Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra at Ru L_3/L_2 edge were collected by the total fluorescence yield *via* Lytle detector at beamline 16A1 at Taiwan Light Source. The spot size was 0.5 x 0.5 (HxV) mm², where probed at the Ru powder sample by incident 45° angle. X-ray energy from Si (111) monochromator was calibrated using the energy jump of standard Mo foil at L_3 edge. Synchrotron X-ray Photoelectron Spectroscopy (XPS) experiments were performed at beamline BL24-CIRCE (NAPP branch) at ALBA Synchrotron Light Source (Cerdanyola del Vallès, Barcelona). CIRCE is an undulator beamline with a photon energy range of 100-2000 eV. Data acquisition was performed using a PHOIBOS 150NAP electron energy analyser (SPECS GmbH). The spectra were acquired with exit slit of 20 μ m and pass energy of 20 eV. The X-ray spot size was 100 μ m x 65 μ m (HxV). Incident photon energies of 500 and 1150 eV for Ru 3d and C 1s were used to record the XPS spectra. Binding energies (BE) were calibrated with respect to C 1s signal settled at 284.5 eV. The sample (50 mg) was pelletized, mounted onto the sample holder and measured at room temperature at a 10⁻⁹ mbar pressure without previous activation. Shirley type background and Lorentzian type curves have been used in the spectra fitting. Laboratory X-ray Photoelectron Spectroscopy (XPS) experiments were performed on a SPECS equipment

with a Phoibos 150 MCD-9 detector and using non-monochromatic AlK α (1486.6 eV) X-ray radiation. The pass energy was 20 eV and the X-ray power was 100 W. Raman studies were performed using a Renishaw "In via" spectrometer connected to an Olympia Microscope. The instrument is equipped with a He-Ne green laser (514 nm), a diode laser (785 nm) and a CCD detector. Temperature Programmed Reduction with H₂ (TPR-H₂) studies were performed using a quartz reactor, connected online to a mass spectrometer Balzer (QMG 220M1). 120 mg of catalyst were flushed with Argon at 25 °C for 30 min, and then switched to a 70 vol % H₂ in Ar flow (14 mL·min⁻¹). The reaction was carried out at increasing temperatures (160, 180, 200, 220, 260 and 280 °C, at a rate of 10 °C·min⁻¹). The m/z values used to monitor each product were 44 (CO₂), 28 (CO and CO₂), 2 (H₂), 15 (CH₄), 16 (CH₄) and 18 (H₂O).

Isotopic ¹³CO/¹²CO₂/H₂ experiments

Catalytic tests with carbon labelled species were performed in a home-made stainless steel cell connected online with a mass spectrometer (Balzer QMG 220M1). The catalysts (15 mg) were pelletized and kept in vacuum at 120 °C for 0.5 h. In case of Ru/C-com, the sample was additionally reduced *in situ* with a H₂ flow (280 °C, 1 h, 10 mL·min⁻¹) before reaction. After activation, a mixture of ¹³CO/¹²CO₂/H₂ (1:1:6 vol %) was fed continuously at 15 mbar total pressure. Then, the temperature was increased to 160 °C and finally the pressure was set at 25 mbar. The reaction evolution was monitored by Mass Spectrometry (MS) with m/z values: 44 (¹²CO₂), 45 (¹³CO₂), 28 (¹²CO), 29 (¹³CO), 15 (¹²CH₄), 17 (¹³CH₄), 18 (H₂O) and 2 (H₂).

CO₂ hydrogenation catalysis

CO₂ hydrogenation was performed in a stainless steel fixed bed reactor with an inner diameter of 11 mm and 240 mm length. Typically, 210 mg of catalyst (particle size 400-600 μ m) were diluted in SiC in a weight ratio 0.14 (Cat/SiC). Ru@C-EDTA and Ru@C-Glucose were not activated before reaction, while the other samples were *in situ* reduced prior to catalytic tests (25 mL·min⁻¹ H₂, 280 °C, 1 h, 10 °C·min⁻¹). The reaction took place at atmospheric pressure and the reaction temperatures were 160, 180 and 200 °C. Each temperature was maintained for at least 1.5 h. The reaction was carried out at 21428 h⁻¹ GHSV under concentrated (23.8 vol % CO₂, 71.3 vol % H₂, 5 vol % N₂) or diluted (5 vol % CO₂, 20 vol % H₂, 75 % vol N₂) conditions. Direct analysis of the reaction products was done by online gas chromatography (GC), using a SCION-456-GC equipment with TCD (MS-13X column) and FID (BR-Q Plot column) detectors. Blank experiments (in the presence of SiC) shown the absence of homogeneous contribution to the reaction. Turnover frequency values (TOFs) were obtained from CO chemisorption data.

CO hydrogenation catalysis

CO hydrogenation was performed in the CO₂ hydrogenation reactor setup described before. In this case, the inlet gas mixture was 30 % vol CO, 60 % vol H₂ and 10 % vol Ar with identical

total flow ($100 \text{ mL}\cdot\text{min}^{-1}$). The process took place at atmospheric pressure and in a temperature range of $160\text{-}240 \text{ }^\circ\text{C}$, using 210 mg of catalyst.

▪ RESULTS AND DISCUSSION

The Ru@C-EDTA samples are prepared under hydrothermal conditions (details in Experimental Section), modifying the amount of Ruthenium(III) acetylacetonate ($\text{Ru}(\text{acac})_3$) in the synthesis gel, while keeping constant the ethylenediaminetetraacetic acid disodium salt dihydrate ($\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$). The synthesis takes place at autogenous pressure at $200 \text{ }^\circ\text{C}$ for 24 h. The ruthenium loading in the as prepared samples, determined from ICP analysis, takes values between 6 wt % and 28 wt % (Table S1). Representative TEM images obtained from the Ru@C-EDTA samples are presented in Figure 1 and Fig.S1-S4, which show the presence of Ru^0 NP embedded in a carbon matrix. An homogeneous distribution of small Ru NP with average particle sizes of 2-5 nm are observed in the Ru@C-EDTA-6, Ru@C-EDTA-12 and Ru@C-EDTA-20 samples. However, a more heterogeneous size distribution of small (2-5 nm) and bigger (10-15 nm) Ru nanoparticles can be detected in the Ru@C-EDTA-28 sample (Fig.S4).

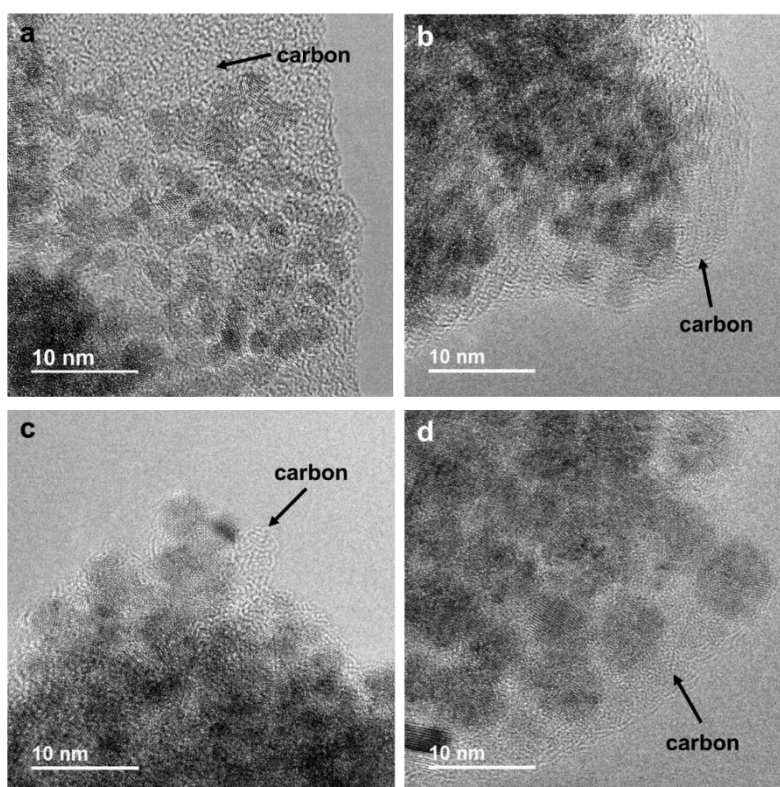


Figure 1. TEM images of Ru@C-EDTA samples prepared by hydrothermal synthesis with different ratios of Ru/EDTA. (a) Ru@C-EDTA-6, (b) Ru@C-EDTA-12, (c) Ru@C-EDTA-20 and (d) Ru@C-EDTA-28.

This is in accordance with the bulk information extracted from X-ray diffractograms (Fig.S5) where the peak broadening observed in samples Ru@C-EDTA-6, Ru@C-EDTA-12 and Ru@C-EDTA-20 samples corresponds to a small crystallite size, whereas some sharp peaks are visualized in the Ru@C-EDTA-28 sample, corresponding to crystalline Ru⁰ (hexagonal, JCPDS: 00-006-0663). The nature of the carbon matrix studied by Raman spectroscopy shows a graphitic structure (1600 cm⁻¹) with defects (1371 cm⁻¹) and some amorphous carbon (1506 cm⁻¹)²⁹ (Fig.S6). In addition, concerning to the nature of ruthenium species, XPS studies performed in a laboratory scale spectrometer using AlK α (1486.6 eV) X-ray energy (Fig.S7) displays the presence of Ru⁰ (279.3 eV) and RuO₂ (281.0 eV). However, high-resolution XPS spectroscopy using synchrotron radiation allowed us to obtain surface sensitive information of the Ru@C-EDTA samples working at variable X-Ray excitation energy. In fact, at low X-ray excitation energy (500 eV) with a probing depth of around 2.2 nm,³⁰ an additional ruthenium specie at 279.6 eV, together with Ru⁰ (at 279.1 eV) and RuO₂ (281.0-280.4 eV) are clearly observed (Fig.2a). The surface concentration of this new specie slightly increases from ~56% to ~70% at decreasing the Ru content in the samples (Fig.2b).

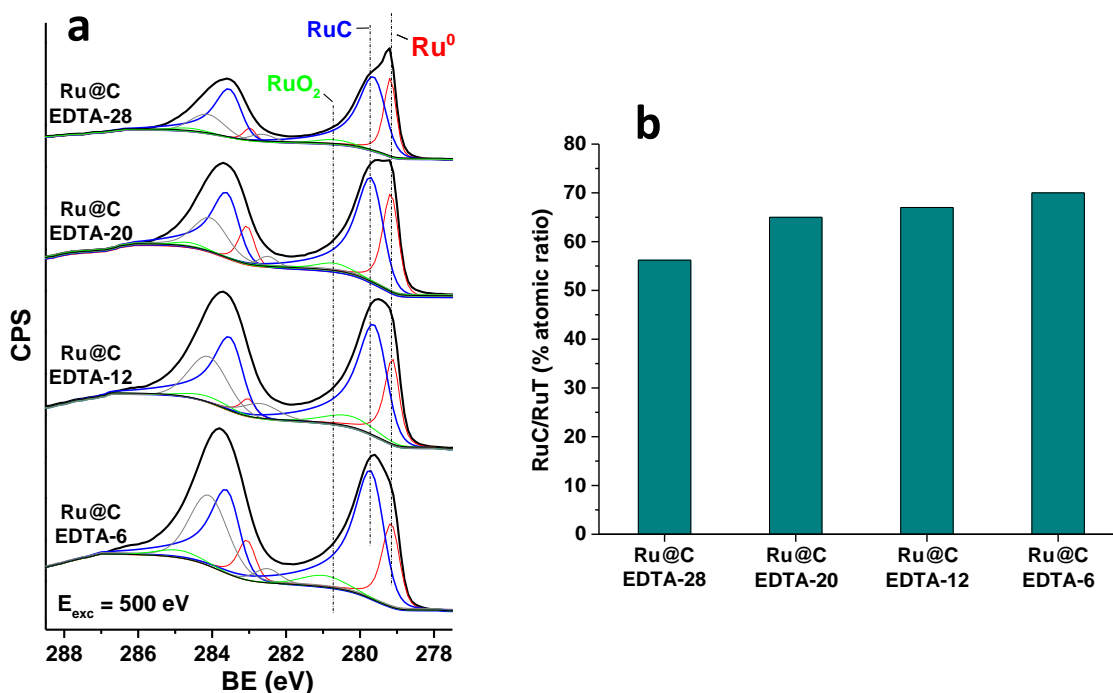


Figure 2. a) Synchrotron XPS of the C 1s and Ru 3d_{5/2} core levels at 500 eV X-ray excitation energy on fresh Ru@C-EDTA samples. Colour code for components: Ru⁰ (red), RuC (blue) RuO₂ (green), C (grey). b) Surface concentration of the RuC phase relative to the total Ru (RuT).

Based on XPS depth profile analysis at a sample depth of 4.4 nm, the contribution of the new component at 279.6 eV to the total Ru peak intensity decreases ~ 30-40% in all samples at the

expense of the component of Ru⁰ (Fig.S8), meaning that the new Ru specie identified by synchrotron XPS is preferentially located on the upper surface layers of the catalyst. This new component is ascribed in our work to ruthenium carbide (RuC) species. However, their assignation is not straightforward, due to the lack of reference data associated with RuC and uncertainties that exist in the literature regarding to the assignation of ruthenium chemical states.³¹ Our assignation has been made based on previous studies where a +0.5 eV shift respect to the metal was related to carbide species,³² and is also supported by HRTEM analysis (Fig.3a and Fig.S9), in where lattice fringes at 0.21 and 0.31 nm, corresponding to Ru⁰ and RuO_x respectively, and 0.28 nm, due to RuC (PDF number 01-089-3016) are detected. In addition to XPS and HRTEM analysis, the assignation of the new detected specie to RuC is supported by Near-Edge X-ray Absorption Fine Structure (NEXAFS) technique performed on the Ru@C-EDTA-20 sample at the Ru L_{2,3}-edge, which is compared with RuO₂ and Ru⁰ references (Fig.3b). The spectra reflect the electronic structure of surface Ru species and their local environment, which don't correspond to RuO₂ nor Ru⁰. Indeed, the Ru L_{2,3}-edge white lines of Ru@C-EDTA-20 (located around 2840 and 2969 eV for the L₃ and L₂, respectively) are shifted to higher photon energy compared to that of Ru metal, and to lower energy respect to that of RuO₂, while are compatible with the RuC phase.³⁴ Moreover, the global spectral shapes characteristic of Ru⁰ and RuO₂ result incompatible with the spectra collected on the Ru@C-EDTA-20 sample, where both the double peak structure around 2850 (L₃) / 2980 (L₂) eV (characteristic of the metal phase) and the one broadened peak structure of the white line (characteristic of the RuO₂ phase) are absent (details in Fig.S10(a),(b)). **Curve fitting simulation from the NEXAFS spectra at L₃ and L₂ edge is shown in Figure 3c, representing two peaks corresponding to the electronic transition 2p->4d-t_{2g} (A) and 4d-e_g (B) state. The A/B ratios in RuO₂ and Ru metal at L₃ edge (L₂) are 0.024 (0.17) and 2.61 (2.92) respectively, which are the opposite cases by their electronic configurations (4d⁴ and 4d⁸ electrons). In the Ru@C-EDTA-20 sample, the A/B ratios result at L₃ edge (1.19) and L₂ edge (2.00), which is between RuO₂ and Ru metal, reflecting a different feature symmetry and ligand environment in the Ru@C-EDTA sample.** This agrees with the previous results and indicates that the upper surface of our catalysts is most likely ascribed to RuC. To our knowledge, this is the first time that a ruthenium carbide phase is formed under mild conditions (hydrothermal synthesis at 200 °C) in opposite to the harsh conditions (5 GPa and 1000-2500 °C) usually required for its synthesis.²¹⁻²⁴

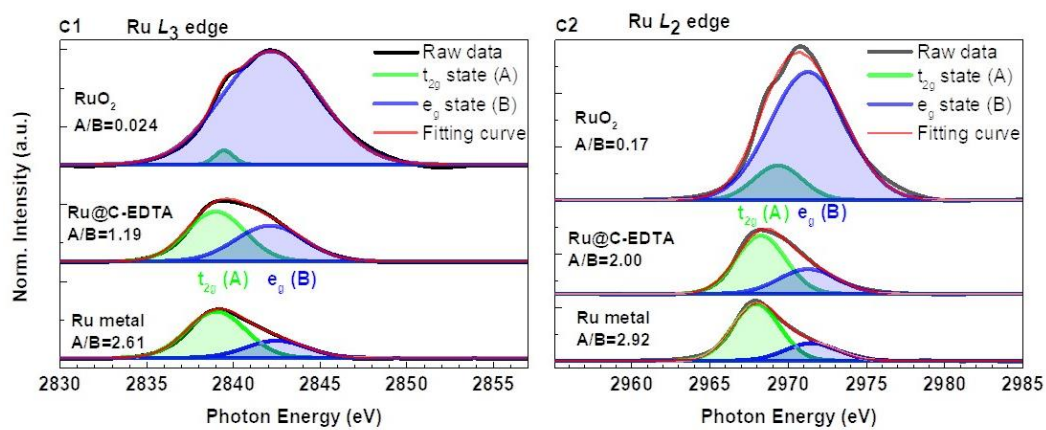
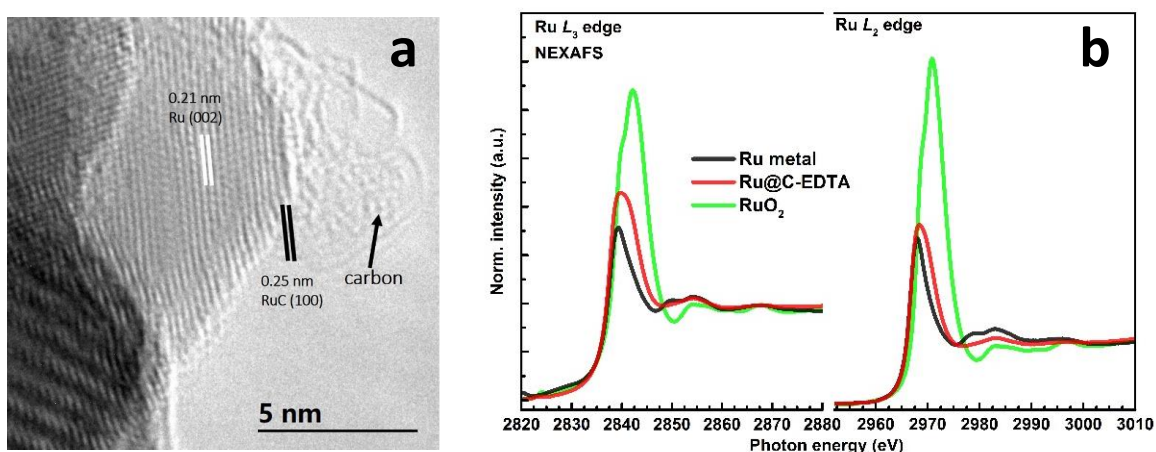


Figure 3. (a) HRTEM image of the Ru@C-EDTA-20 sample. (b) L_3 -edge spectra (left panel) and L_2 -edge spectra (right panel) of Ru^0 , Ru@C-EDTA-20, and RuO_2 . (c) **Curve fitting simulation from the NEXAFS spectra at L_3 and L_2 edge on RuO_2 , Ru@C-EDTA-20 and Ru^0 .**

From the point of view of their application in the CO_2 hydrogenation reaction, an important issue to deal with is the thermal stability of the Ru@C-EDTA catalytic systems under H_2 rich conditions, which is proved by a TPR- H_2 study. In this experiment, performed in H_2 flow at atmospheric pressure, the CH_4 formation (due to carbide and/or carbon hydrogenation) is followed by online Mass Spectrometry (MS). Under these conditions, CH_4 MS signal ($m/z=15$) clearly evolves above 240°C (Fig.S11), limiting the catalytic studies to this temperature.

The herein reported Ru@C-EDTA catalysts show markedly high activity at low temperature ($160\text{-}200^\circ\text{C}$) and atmospheric pressure for the CO_2 hydrogenation reaction, with 99.9% selectivity to methane, operating at 21428 h^{-1} GHSV (details in Experimental Section). The CO_2 conversion and the methane space time yield (STY_{CH_4}) in the $160\text{-}180^\circ\text{C}$ temperature range at concentrated reaction conditions is summarized in Table 1a, where an increase in the catalytic activity is observed at increasing Ru loading in the samples. The catalyst stability of Ru@C-EDTA-

20 sample tested over a period of ~15 h reaction time at 160 °C is plotted in Figure 4. A decrease in activity (~8%) is observed in the first 12 h of reaction, while it remains stable in the last 3 h. The observed loss of activity corresponds to a partial removal of surface ruthenium carbide species under reaction conditions, as evidenced from XPS studies using synchrotron radiation performed on the spent catalysts (Fig.S12a) **while maintaining the carbonaceous matrix where the Ru NPs are embedded (see Raman spectra of the spent catalysts in Fig.S6)**. In fact, a loss of RuC species is observed in all samples according to the XPS spectra acquired at 500 eV X-ray excitation energy, being in the order of 31-23% on the Ru@C-EDTA-6, Ru@C-EDTA-12 and Ru@C-EDTA-20 samples and of 5% on the Ru@C-EDTA-28 sample (Fig.S12b). Based on this data, a fairly good correlation between the amount of surface RuC of the spent Ru@C-EDTA catalysts and the STY_{CH_4} at 160 °C (Table 1a) is found, as displayed in Figure 5. These results suggest that the RuC species should play a key role in the catalytic activity of the Ru@C-EDTA samples, as discussed later.

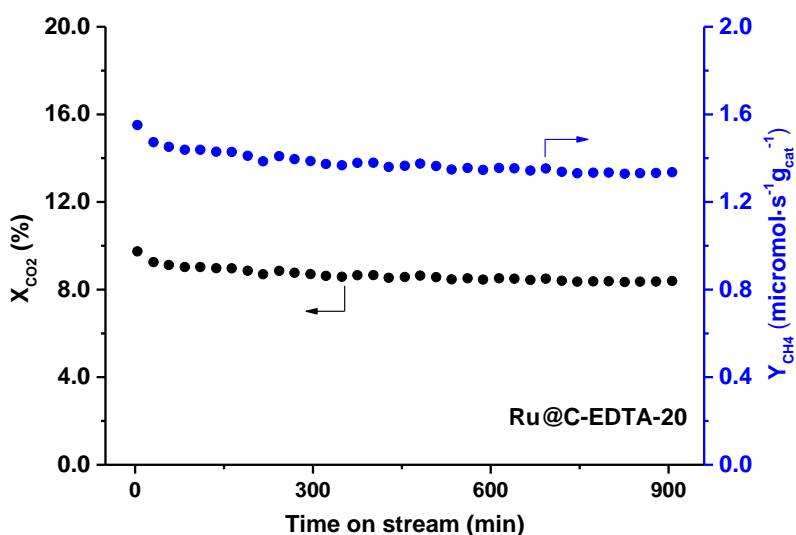


Figure 4. CO_2 conversion (left axe, black) and methane STY (right axe, blue) on the Ru@C-EDTA-20 catalyst at 160 °C, 21428 h^{-1} GHSV and 5% CO_2 , 20% H_2 and 75% N_2 (% vol).

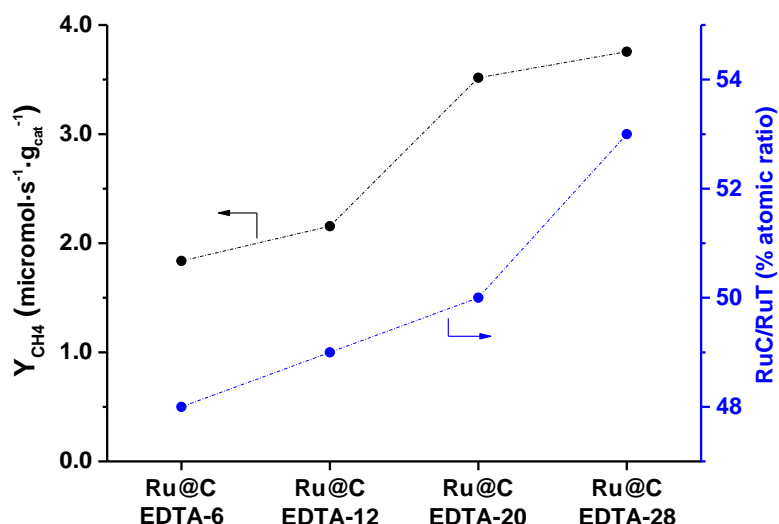


Figure 5. Methane STY (left axe, black) at 160 °C, 21428 h⁻¹ GHSV and 23.8% CO₂, 71.3% H₂, 5% N₂ (% vol). On the right axe (blue), RuC/RuT atomic ratio obtained from XPS analysis on the spent Ru@C-EDTA catalysts at 500 eV X-ray excitation energy (Fig.S12).

The activity of the Ru@C-EDTA samples surpasses by far that of other synthesized ruthenium carbon catalysts as shown in Table 1b and is markedly higher than that of most active ruthenium catalysts we found in the literature (Table S2). Being aware that the CO₂ methanation on Ru catalysts has been reported to be size dependent, where large particles were found to be more active than smaller ones,³⁵ reference catalysts with different particle sizes have been considered. All catalysts prepared by different synthesis strategies, some of them reproducing those of the literature,^{20,27,36} and the commercial type catalysts (such as Ru/C-com and Ru-Black) show negligible activity at the mild operation conditions considered in this work. Moreover, the selectivity to methane is almost 100 % on the Ru@C-EDTA samples, while other by-products like CO or C_xH_y are formed on the other samples (Fig.S13). Altogether endows in a very promising catalyst for the Sabatier reaction. In addition, the synthesis of this type of catalyst can be also achieved starting from other precursors like RuO₂ and glucose, using water as solvent (see Experimental Section and Fig.S14). The similar catalytic activity achieved in the Ru@C-Glucose catalyst, (see Table S3) allows to discard the enhanced catalytic activity of the Ru@C-EDTA catalysts due to the presence of nitrogen or Na⁺ additives coming from the Na₂EDTA precursor.

Regarding to the ruthenium surface speciation in the samples, Ru⁰ is the only specie present in all reference catalysts (Table 1b). However, in Ru@C-EDTA materials, it exists a combination of Ru⁰ and RuC (that predominates in upper layers), together with carbon coating, which could explain their much superior performance. In fact, if the RuC phase in Ru@C-EDTA-20 is removed by treating the catalyst in H₂ at 280 °C, the catalytic activity strongly decreases (Fig.S15). This

result reinforces our previous assumption of RuC species as a key component responsible for the high catalytic reactivity obtained in the CO₂ methanation reaction at low temperature.

Table 1. a) Catalytic activity in the CO₂ hydrogenation reaction at concentrated reaction conditions^a on the Ru@C-EDTA samples; b) Catalytic activity at 160 °C of the Ru@C-EDTA-20 sample compared to other reference ruthenium carbon samples.

a)

Sample	160 °C		180 °C	
	X _{CO2} (%)	STY _{CH4} ($\mu\text{mol}_{\text{CH}_4}\cdot\text{s}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$)	X _{CO2} (%)	STY _{CH4} ($\mu\text{mol}_{\text{CH}_4}\cdot\text{s}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$)
Ru@EDTA-28	4.9	3.76	13.2	10.07
Ru@EDTA-20	4.6	3.52	9.8	7.56
Ru@EDTA-12	2.7	2.16	6.5	5.26
Ru@EDTA-6	1.3	1.84	2.5	3.48

b)

Sample	wt% Ru (Part. size) ^f	X _{CO2} ^a (%)	STY _{CH4} ($\mu\text{mol}_{\text{CH}_4}\cdot\text{s}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$)	(%) Selectivity CH ₄ / CO / C ₂ H ₆
Ru@C-EDTA-20	20.2% (--)	4.6	3.52	99.9 / 0 / 0.1
Ru/C-WI ^b	3.0% (17 nm)	<0.1	0.04	38.3 / 61.5 / 0.2
Ru/C-com	5.0% (2 nm) ^g	<0.1	0.07	92.7 / 6.8 / 0.5
Ru/C-Ar800 ^c	4.0% -	0.1	<0.01	73.4 / 25.6 / 1.0
Ru@C/NG ^d	13.0% ²⁷ -	0	-	-
Ru ₃ (CO) ₁₂ /C ^e	2.5% (1.2 nm) ²⁰	<0.1	0	0 / 100 / 0
Ru-Black Aldrich	100% (20 nm)	0.3	0.23	99.9 / 0 / 0.1

^a1 bar, GHSV 21428 h⁻¹, reactant feed composed of 23.8 vol % CO₂, 71.2 vol % H₂, 5 vol % N₂; ^bPrepared by wet impregnation of Ru(acac)₃ on a carbon support; ^cPrepared by pyrolysis of the metal precursors according to ref. 36; ^dPrepared through thermal annealing of polydopamine (PDA) coated Ru NP supported on a three-dimensional N-doped graphene layer as in ref. 27; ^ePrepared from Ru₃(CO)₁₂ precursor as described in ref. 20; ^fCalculated by XRD; ^gCalculated by HRTEM.

The reaction mechanism (direct CO₂ hydrogenation or *via* reverse water gas-shift (RWGS)) of the Ru@C-EDTA samples have been studied combining catalytic studies using a CO/H₂ feed, with isotopic studies using a ¹³CO/¹²CO₂/H₂ (1:1:6) reactant feed. For this purpose, the Ru@C-EDTA-20 catalyst is selected as the reference sample that presents surface RuC species, and its behaviour compared to a sample containing only Ru⁰ (i.e. commercial Ru/C-com). Catalytic studies show negligible CO conversion (~0.01-0.05%) on the Ru@C-EDTA-20 sample in the 180-240 °C temperature range, while CO reacts in the commercial Ru/C sample (Table S4). Isotopic studies in the presence of both ¹³CO/¹²CO₂ show a very high preferential ¹²CO₂ hydrogenation versus ¹³CO on the Ru@C-EDTA-20 sample, since only ¹²CH₄ is detected (Fig.S16a). Meanwhile, ¹³CO is preferentially hydrogenated versus ¹²CO₂ on the Ru/C sample, resulting in ¹³CH₄ formation (Fig.S16b). Combining both results, and taking into account the different selectivity to CO obtained during the CO₂ hydrogenation, (CO is not detected in the Ru@C-EDTA-20 sample, while it is formed as the major by-product in the Ru/C sample, Fig.S13), we can conclude that a direct CO₂ hydrogenation path to CH₄ takes place on the Ru@C-EDTA-20 sample, while contribution of a RWGS reaction mechanism occurs on the Ru/C sample in the presence of Ru⁰, in agreement to previous studies.^{35,37-42} Moreover, the fact that ¹³CH₄ is not observed in the isotopic studies of the Ru@C-EDTA-20 sample allows to discard the co-existence of Ru⁰ species on the catalyst surface or, if present, they should be in a very low amount, being the activity ascribed predominately to the presence of RuC species. Based on it, a core-shell structure containing a metallic core and an upper shell of ruthenium carbide and carbon species can be proposed in our catalysts. The RuC phase has been proven to be the active specie in the CO₂ hydrogenation, which in accordance with the literature,^{15,19} favors CO₂ binding and activation.

▪ CONCLUSION

We have described an easy hydrothermal synthesis method that allows the stabilization of surface ruthenium carbide species on a metallic ruthenium core. Advanced surface-sensitive characterization techniques such as synchrotron XPS, NEXAFS and HRTEM were required to elucidate the presence of these carbidic species, which are not present in other catalysts previously reported. Surface RuC enables CO₂ activation, which is hydrogenated to methane in

a direct reaction path, yielding 100% selectivity to CH₄. The high activity at low temperature (160-200 °C) and the absence of CO in the gas effluent makes the herein synthesized Ru@C-EDTA and Ru@C-Glucose samples very promising candidates for the Sabatier reaction.

▪ ASSOCIATED CONTENT

Supporting Information includes XRD diffractograms of tested materials; Raman spectra of Ru@C-EDTA-20 sample; Laboratory XPS; C 1s and Ru 3d Synchrotron XPS core levels of the Ru@C-EDTA samples; HRTEM images of Ru@C-EDTA samples; NEXAFS experiments; TPR-H₂ profile of Ru@C-EDTA-20; Catalytic results on Sabatier reaction at atmospheric pressure of Ru@C-EDTA-20, RU@C-glucose and other reference samples; State of art in Sabatier reaction; Catalysis with Syngas; Isotopic ¹³CO/¹²CO₂ experiments.

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Notes

The authors declare no competing financial interest.

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▪ ABBREVIATIONS

CNT, carbon nanotube; acac, acetylacetonate; EDTA, ethylenediaminetetraacetic acid derived salt; CTAB, Cetyl Trimethyl Ammonium Bromide; NP, nanoparticle; wt, weight; vol, volume.

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▪ GRAPHICAL ABSTRACT (“For Table of Contents Only”)

